UNIT: 01

pH and BUFFERS

INTRODUCTION:

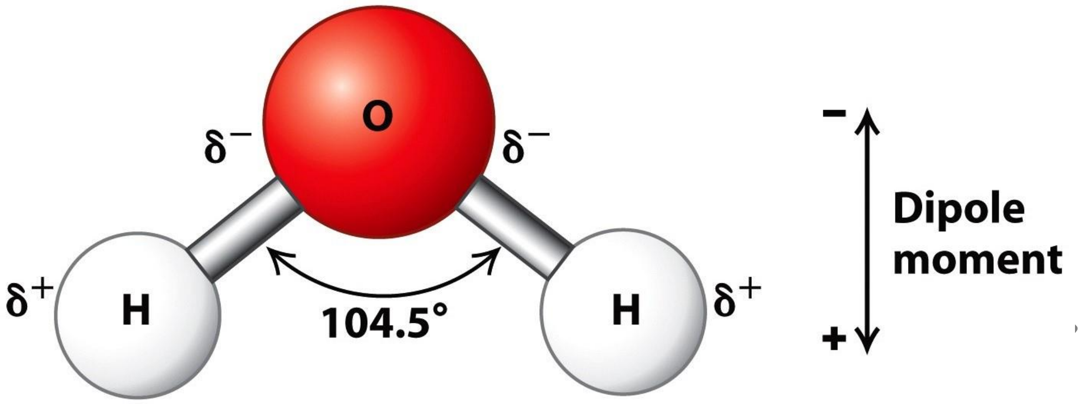
Water is one of the basic needs and is required by all life on earth. It dominates a majority of the space on our planet, covering about 71% of the total surface area of Earth. Hydrology is the study of the distribution, availability, consumption, and movement of ground water. Water exists in all three of its states, namely, solid (ice), liquid, and gas (stream). It is a transparent colourless chemical substance with one oxygen atom covalently bonded to two hydrogen atoms. Water is cycled continuously on Earth through evaporation, transpiration, condensation, precipitation, and other means.

Water has the important ability to dissolve many other substances. Indeed, the versatility of water as a solvent is essential to living organisms. **Life is believed to have originated in the aqueous solutions of the world's oceans, and living organisms depend on aqueous solutions, such as blood and digestive juices, for biological processes.** In small quantities water appears colourless, but water actually has an intrinsic blue colour caused by slight absorption of light at red wavelengths.

PHYSICO-CHEMICAL PROPERTIES OF WATER:

- Water is the most abundant substance in the living system, making up to 70% or more of the weight of most of the organisms.
- Hydrogen bonds between water molecules provide the cohesive forces that make water a liquid at room temperature.
- Water is called a universal solvent as most of the molecules are soluble in it. The molecules that are soluble in water are called polar molecules.
- Polar biomolecules dissolve readily in water because they can replace water-water interactions with more energetically favourable water-solute interactions.
- In contrast, the non-polar molecules are unable to break water-water interaction and are unable to form water-solute molecule. Hence, non-polar molecules are poorly soluble in water.
- Water has higher melting, boiling and heat of vaporization than most of the other common solvents.
- Each hydrogen atom of a water molecule shares an electron pair with the central oxygen atom.
- The geometry of the molecule is dictated by the shapes of the outer electron orbitals of the oxygen atom, which is similar to the SP^3 bonding orbitals of carbon.

- These orbitals describe a rough tetrahedron with a hydrogen atom at each of two corners and unshared electron pairs at the other two corners.



DIPOLE NATURE OF WATER MOLECULE

- The H-O-H bond angle is **104.5°**, slightly less than **109.5°** of a perfect tetrahedron because of crowding by the non-bonding orbitals of the oxygen atom.

Properties	
Molecular formula	H_2O
Molar mass	18.01528(33) g/mol
Appearance	white solid or almost colorless, transparent, with a slight hint of blue, crystalline solid or liquid
Density	1000 kg/m^3, liquid (4 °C) (62.4 lb/cu. ft) 917 kg/m^3, solid
Melting point	0 °C, 32 °F, (273.15 K)
Boiling point	99.98 °C, 211.97 °F (373.13 K)
Acidity (pK_a)	15.74 ~35–36
Basicity (pK_b)	15.74
Refractive index (n_D)	1.3330
Viscosity	0.001 Pa s at 20 °C
Structure	
Crystal structure	Hexagonal
Molecular shape	Bent
Dipole moment	1.85 D

- During electrolysis, water molecules naturally dissociate into H^+ and OH^- ions which are attracted towards the cathode and anode respectively.
- At the cathode, $2H^+$ ions pick up electrons and form H_2 gas and at the anode, $4OH^-$ ions combine and release O_2 gas, molecular water and 4 electrons.
- The standard potential of the water electrolysis cell is a minimum of 1.23V at 25°C.
- An important property of water is its polar nature. **Oxygen has higher electronegativity than hydrogen,** the side of the molecule with the oxygen atom has a partial negative charge. Also, the presence of the lone pair tends to push the oxygen away.
- The oxygen end is partially negative and the hydrogen end is partially positive, because of this, the direction of the dipole moment points from the oxygen towards the centre of the hydrogens.
- The charge difference of the oxygen and hydrogen of the water molecule to be attracted to each other and to other polar molecules. This attraction contributes to **hydrogen bonding.**
- A water molecule can form a maximum of 4-Hydrogen bonds because it can accept 2 and donate 2 hydrogen atoms.
- **CONDUCTIVITY:** Pure water containing no exogenous ions is an excellent insulator, but not even "deionized" water is completely free of ions.
- Water undergoes auto-ionization in the liquid state i.e., 2 water molecules form 1 hydroxide anion (OH^-) and 1 hydronium cation (H_3O^+).
- Maximum electrical resistivity for water is approximately **182KΩm at 25ºC.**
- Electrical conductivity of pure water is 0.055 Siemens per meter (S/m) at 25°C.
- The density of water is approximately $1 g/cm^3$.
- When cooled from room temperature, liquid water becomes increasingly dense as with other substances, but at approximately 4°C (39°F), pure water reaches its maximum density.
- Percentage of elements in water by mass contains nearly 11.1% of hydrogen and 88.9% oxygen.
- When ice melts or water evaporates, heat is taken up by the system i.e.,

$$H_2O\ (\text{solid}) \rightarrow H_2O\ (\text{liquid}) \quad \Delta H = +5.9\ \text{KJ/mol}$$
$$H_2O\ (\text{liquid}) \rightarrow H_2O\ (\text{gas}) \quad \Delta H = +44.0\ \text{KJ/mol}$$

- Water is a polar solvent. It readily dissolves most of biomolecules which are generally charged or polar compounds.
- Compounds that dissolve easily in water are hydrophilic (water loving). In contrast, non-polar solvents such as chloroform and benzene are poor solvents for biomolecules but easily dissolve those compounds that are hydrophobic non-polar, such as lipids and waxes.

- Water has a high dielectric constant, a physical property that reflects the number of dipoles in a solvent.
- For water, dielectric constant at 25°C is 78.5.

LAW OF MASS ACTION:

The law was formulated over the period 1864–79 by the Norwegian scientists **Cato M. Guldberg** and **Peter Waage** but is now of only historical interest. Law of mass actions helps to derive the relation between the velocity of the chemical reaction, molar concentration of the reactants at particular time and temperature. This law was useful for obtaining the correct equilibrium equation for a reaction, but the rate expressions it provides are now known to apply only to elementary reactions.

The law states that "the rate of a chemical reaction at a given point of time is directly proportional to the mass of reacting substances present at that time".

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

(Reactants) (Products)

$V \alpha [A] [B]$----- Eq_1

According to law of mass action,

$V_r = K_1 [A] [B]$ (forward reaction)

$V_p \alpha [C] [D]$----- Eq_2

$V_p = K_2 [C] [D]$

At equilibrium, $V_r = V_p$

$K1 [A] [B] = K2 [C] [D]$

$$\frac{K1}{K2} = \frac{[C][D]}{[A][B]} = \text{K equilibrium}$$

$$\textbf{K equilibrium} = \frac{\underline{\textbf{Molar concentration of products}}}{\textbf{Molar concentration of reactants}}$$

- Equilibrium constants are dimensionless
- The equilibrium constant is fixed and characteristic for any chemical reaction at a specified temperature.
- It defines the composition of the final equilibrium mixture, regardless of the starting amounts of reactants and products.

pH (Hydrogen Potentials):

- pH is the quantitative measure of the acidity or basicity of aqueous or other liquid solutions.
- The term, widely used in chemistry, biology, and agronomy, translates the values of the concentration of the hydrogen ion—which ordinarily ranges between about 1 and 10^{-14} gram-equivalents per litre—into numbers between 0 and 14.
- The measurement was originally used by the **Danish biochemist S.P.L. Sorensen to represent the hydrogen ion concentration,** expressed in equivalents per litre of an aqueous solution.
- **pH of a solution is defined as negative logarithm to the base ten of molar concentration of hydrogen ions in the solution.**
- A pH scale is a tool for measuring acids and bases.
- The scale ranges from 0-14.
- The pH scale is logarithmic and shows the solution's concentration of hydrogen ions inversely. This is because the formula used to measure pH approximates the molar concentration of hydrogen ions in the solution to the negative of the base 10 logarithms. More specifically, pH is the negative of the activity of the H^+ ion from the base 10 logarithms.

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

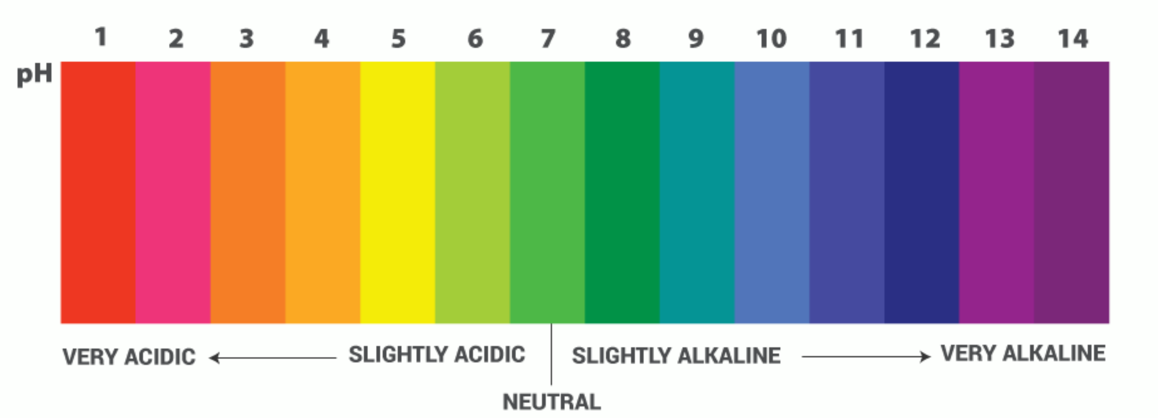
pH of Acids and Bases:

1. The pH of a solution varies from 0 to 14.
2. Solutions having a value of pH ranging 0 to 7 on pH scale are termed as **acidic** and for the value of pH ranging 7 to 14 on pH scale are known as **basic** solutions.
3. Solutions having the value of pH equal to 7 on pH scale are known as **neutral** solutions.
4. Solutions having the value of pH equal to 1 are known to be strongly acidic solutions. Further, the acidity decreases as the value of pH increases from 1 to 7 whereas, solutions with the value of pH equal to 14 are termed as strongly basic solutions.
5. The basicity decreases as the value of pH decreases from 14 to 7.
6. The strength of acids and bases depends on the number of H^+ and OH^- ions produced.
7. Acids furnishing a greater number of H^+ ions are known to be strong acids and vice versa.
8. The degree of ionisation of acids and bases differ for different acids and bases.
9. It helps in the determination of the strength of acids and bases.

10. The strength of an acid depends on the concentration of hydronium ion (H_3O^+) too.
11. With the help of the comparison between the concentration of hydronium ion and the hydroxyl ion, we can distinguish between acids and bases.

i. For acidic solution: **$[H_3O^+] > [OH^-]$**
ii. For neutral solution: **$[H_3O^+] = [OH^-]$**
iii. For basic solution: **$[H_3O^+] < [OH^-]$**

pH Scale:



pH Scale

Examples: (CALCULATION OF pH)

.01: pH of 0.01M HCl

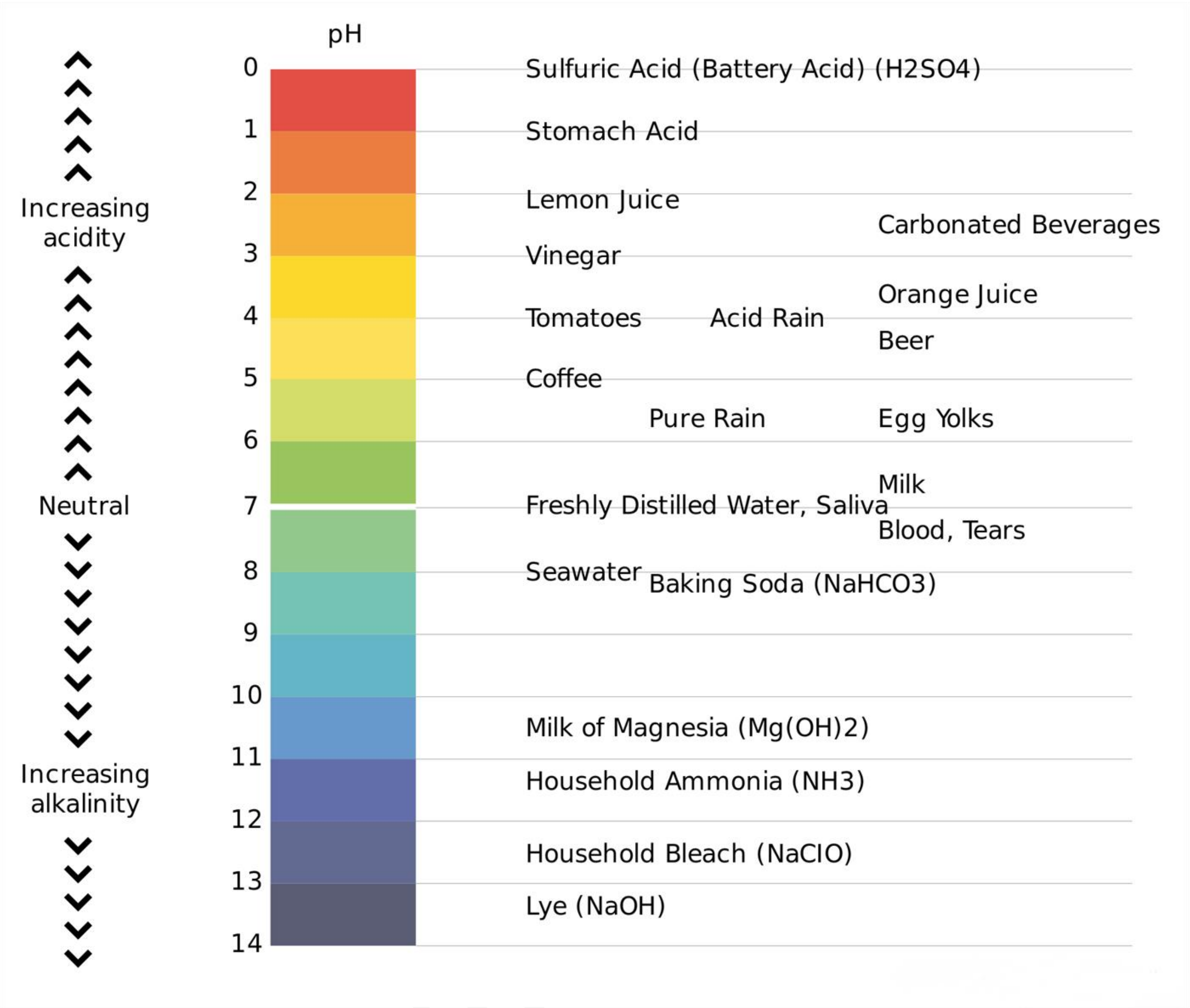
$$HCl \rightarrow H^+ + Cl^-$$

$[H+] = 0.01M = 10^{-2}M$
$pH = -\log [H^+]$
$= -\log [10^{-2}]$ **log Mn = n log M and log to base 10 = 1 (log 10=1)**
$= -(-2) = 2.$

.02: pH of 0.01M HCl

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

$[H+] = 10^{-7}M$
$pH = -\log [H^+]$
$= -\log [10^{-7}]$ **log Mn = n log M and log to base 10 = 1 (log 10=1)**
$= -(-7) = 7.$



GENERAL pH SCALE

pOH:

pOH of a solution is defined as negative logarithm to the base ten of molar concentration of hydroxyl ions in a solution.

pOH gives the hydroxyl ion concentration in the given solution. It can’t be measured directly. The measurement is done by calculating the pH of the solution and pOH is found using the relation:

$$\mathbf{pH + pOH = 14.}$$

pOH indicates the alkalinity of the solution. In the pH scale, the compounds falling in the range between 7-14 are called bases and their measurement is called basicity.

pOH is used during the calculation of pH of the substances which lack hydrogen ions in them. Using the indirect relation, the pH could be calculated.

Example: pH of 0.001M NaOH

$NaOH \rightarrow Na^+ + OH^-$

[OH-] = 0.001M = 10-3
pOH = -log [OH$^-$]
= -log [10^{-3}] **log Mn = n log M and log to base 10 = 1 (log 10=1)**
= -(-3) = 3.

pH + pOH = 14
pH + 3 = 14
pH = 14-3
pH = 11.

The Relationship Between pH and pOH:

pH	pOH	[H$^+$] mol/L	[OH$^-$] mol/L
0	14	1.0	10^{-14}
2	12	0.01	10^{-12}
4	10	0.0001	10^{-10}
6	8	10^{-6}	10^{-8}
8	6	10^{-8}	10^{-6}
10	4	10^{-10}	0.0001
12	2	10^{-12}	0.01
14	0	10^{-14}	1.0

NOTE:

There are four following math logarithm formulas:

1. **Product Rule Law:**

$\log (MN) = \log M + \log N$

2. **Quotient Rule Law:**

$\log (M/N) = \log M - \log N$

3. **Power Rule Law:**

$\log M^n = n \log M$

4. **Change of base Rule Law:**

$\log_a M = \log_b M \times \log_a b$

DISSOCIATION OF WATER:

Dissociation is a process of splitting up of the molecule into its constituent atoms or ions. Water being polar molecule dissociates into its constituent ions and water acts ac both acid and base.

When water dissociates, one of the hydrogen nuclei leaves its electron behind with the oxygen atom to become a hydrogen ion, while the oxygen and other hydrogen atoms become a hydroxide ion.

Since the hydrogen ion has no electron to neutralize the positive charge on its proton, it has a full unit of positive charge and is symbolized as H+.

The hydroxide ion retains the electron left behind and thus has a full unit of negative charge, symbolized by OH-.

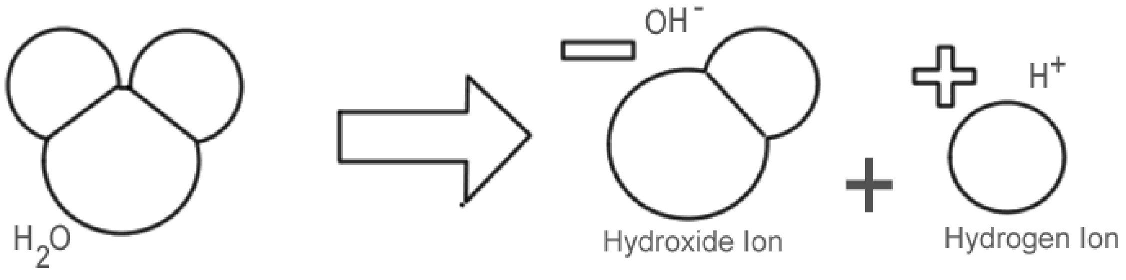
The hydrogen ion (proton) does not wander long by itself before it attaches to the oxygen atom of a second un-ionized water molecule to form a hydronium ion (H_3O^+).

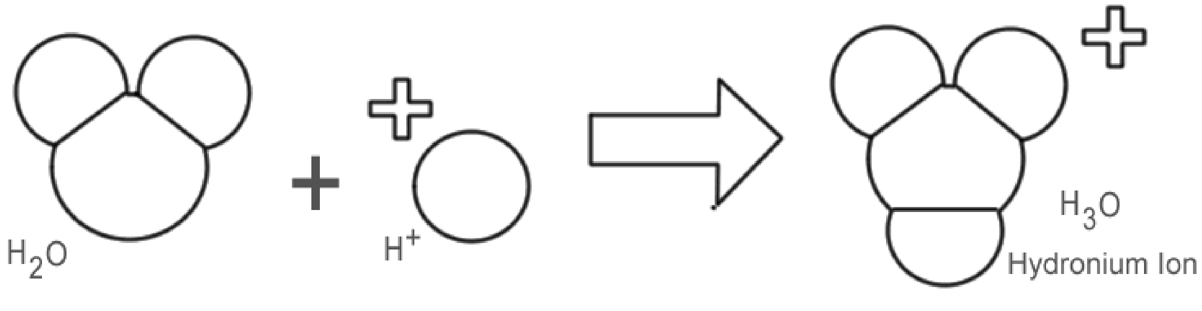
H_2O can act as both a proton donor and acceptor for itself. A proton can be transferred from one water molecule to another, resulting in the formation of one hydroxide ion (OH-) and one hydronium ion (H_3O^+).

$$2H_2O\ (liq) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

This is called the **autoionization** or **dissociation** of water. This equilibrium can also be expressed as:

$$H_2O\ (liq) \rightleftharpoons H^+(aq) + OH^-(aq)$$





In the above equilibrium, water acts as both an acid and a base. The ability of a species to act as either an acid or a base is known as amphoterism.

The concentrations of H_3O+ and OH- produced by the dissociation of water are equal.

IONIC PRODUCT OF WATER:

In water, the product or concentration of its constituent ions i.e., H+ and OH- will remain constant at a given temperature. This is termed as ionic product of water.

The degree of ionization of water at equilibrium is small, at 25 °C only about two of every 10^9 molecules of pure water undergo ionization at any instant.

Water undergoes self-ionization to very small extent as;

$$\mathbf{H_2O \rightleftharpoons H^+ + OH^-}$$

Equilibrium constant for the reversible ionization reaction of water is

$$\mathbf{K\ eq = \frac{[H+]\ [OH-]}{[H_2O]}\text{----- eq 1}}$$

In pure water, at 25 °C, the concentration of water is 55.5 M grams per litre and is essentially constant in relation to the very low concentration of H+ and OH- i.e., $1x10^{-7}$ M.

Substituting the value of in eq 1, we get

$$\mathbf{K\ eq = \frac{[H+]\ [OH-]}{[55.5\ M]}}$$

On rearranging,

$$\mathbf{(55.5M)\ (K.\ eq) = [H+]\ [OH-]\text{ ----- eq 2}}$$

Where, K eq can be written as Kw as it designates he ionic product of water at 25 °C.

The value of K eq is determined by electrical conductivity of pure water and it found to be $1.8x10^{-16}$ M. Substituting this value in eq 2, which gives

$$\mathbf{(55.5M)\ (1.8x10^{-16}\ M) = [H+]\ [OH-] = Kw}$$

$$\mathbf{1.0x10^{-14}\ M^2 = [H+]\ [OH-] = Kw}$$

Thus, the product H+ and OH- in aqueous solution at 25 °C always equals $1.0x10^{-14}$ M^2, when there are exactly equal concentrations of H+ and OH- as in pure water, the solution is said to be at neutral pH.

At this pH, the concentration of H+ and OH- can be calculated from the ionic product of water, i.e.,

$$\mathbf{Kw = [H+]\,[OH-]}$$

Considering, H+ and OH- ions are equal, therefore OH- can be written as H+ or vice versa.

$$\mathbf{Kw = [H+]\,[OH-] = [H+]^2 = [OH-]^2}$$

Solving for H+,

$Kw = [H+]\,[OH-] = [H+]^2$
$Kw = [H+]^2$
$[H+]^2 = Kw$
$[H+] = \sqrt{Kw}$
$[H+] = \sqrt{1.0 \times 10^{-14}\ M^2}$
$\mathbf{[H+] = 10^{-7}\ M = [OH-]}$

Therefore, the ionic product of water is constant and whenever the H+ ion concentration is greater than 1×10^{-7} M, OH- ion concentration must be less than 1×10^{-7} M and vice versa.

When H+ is very high, as in case of HCl, OH- will be very low. From the ionic product of water, its possible to calculate the H+ if OH- is known and vice versa.

ELECTROLYTES:

Electrolyte, is a substance that conducts electric current as a result of a dissociation into positively and negatively charged particles called ions, which migrate toward and ordinarily are discharged at the negative and positive terminals (cathode and anode) of an electric circuit, respectively.

OR

An electrolyte is a substance that dissociates in water into charged particles called ions. Positively charged ions are called cations. Negatively charged ions are called anions. Simply, an electrolyte is a substance that can conduct an electric current when melted or dissolved in water.

The most familiar electrolytes are acids, bases, and salts, which ionize when dissolved in such solvents as water or alcohol. Many salts, such as sodium chloride, behave as electrolytes when melted in the absence of any solvent; and some, such as silver iodide, are electrolytes even in the solid state.

TYPES OF ELECTROLYTE:

- **Strong Electrolytes** – Electrolytes are chemical species that conduct electricity when dissolved in solution.
- **Weak electrolytes** – An electrolyte that ionises to a small extent in solution is called weak electrolyte.

THE DIFFERENCE BETWEEN STRONG AND WEAK ELECTROLYTES:

Strong electrolyte:	Weak electrolyte:
The electrolytes which are completely ionised, called strong electrolytes.	The electrolytes which are partially ionised called weak electrolytes.
The extension of ionisation is more.	The extension of ionisation is less.
They have high electrical conductivity.	They have low electrical conductivity.
Ostwald's dilution law is not applicable.	Ostwald's dilution law is applicable.

STRONG ELECTROLYTES:

- The substances, in aqueous which ionize almost completely into ions are known as strong electrolytes.
- The unionized molecules are present to such a small extent that it is not of any significance to study the ionization constant of strong electrolytes.
- For example: HCl, H_2SO_4, HNO_3, NaOH, KOH, NaCl etc. are strong electrolytes.

The equation which involves the ionization of strong electrolytes is represented with only single headed arrow directed to the right. For example,

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

WEAK ELECTROLYTES:

- The substances, in aqueous which ionize to a small extent into ions are known as weak electrolytes.
- For example: CH_3COOH, NH_4OH, HCN etc. are weak electrolytes.

In this case, the molecules are in equilibrium with their ions. The equation which involves the ionization of weak electrolytes is represented with double headed arrows.

For example,

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO–$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH–$$

DISSOCIATION OR IONISATION OF STRONG ELECTROLYTES:

In order to explain the dissociation and other properties of electrolytes in a solution, Arrhenius proposed the ionic theory, which states that,

When an electrolyte is dissolved in water, its molecules spontaneously split into positively and negatively charged particles called ions. This process is called **dissociation or ionisation.** The postulates of Arrhenius theory are;

- General example (electrolyte) i.e.,

$$BA \rightleftharpoons \underset{\text{Cation}}{B^+} + \underset{\text{Anion}}{A^-}$$

- In a solution, the total positive charge and negative charge are exactly equal. Hence, the whole solution is electrically neutral.
- Ions are responsible for the passage of electric current through the electrolytes.
- Ionisation is a reversible process. A state of equilibrium exists between ions and the undissociated molecules in the solution i.e.,

$$BA \rightleftharpoons B^+ + A^-$$

$$K = \frac{[B^+]\,[A^-]}{[BA]}$$

- Degree of ionisation of an electrolyte increases with dilution.
- The properties of electrolytes are the properties of the ions present in them i.e., chemical reactions between electrolytes in the solution takes place between the ions instead of the molecules.

Strong electrolytes are the substances that readily dissociates into its constituent ions when dissolved in water. The strong electrolytes dissociate completely and readily cations and ions are formed which helps in electrical conductivity. Examples of strong electrolytes include HCl, NaOH, KCl etc.

$$HCl \rightarrow H^+ + Cl^-$$

$$\underline{H2O \rightarrow H^+ + OH^-}$$

$$HCl + H_2O \rightarrow \underset{\text{Cation}}{H_3O^+} + \underset{\text{Anion}}{Cl^-}$$

HCl, dissociates completely into its constituent ionic form when dissolved in water. This is the reason that HCl is called a strong electrolyte.

Strong electrolyte might be an acid or even a base. But the dissociation property remains same.

MERITS OF ARRHENIUS THEORY:

- Experimental observation shows that the conductance of a solution increases upon dilution. This is agreement with the theory as more ions are formed during dilution.
- The solutions of copper sulphate, cupric sulphate, cupric chloride is all blue coloured because they all contain Cu^{2+} ions. This confirms that properties of electrolytes are properties of ions present in them.
- Ionic theory explains the constancy in enthalpy of neutralization of any strong acid and strong base.
- Silver Nitrate solution reacts with solutions of sodium chloride, potassium chloride and barium chloride etc to develop a curdy white precipitate. This is possible because these solutions contain chloride ions in common which combines with Ag+ ions of silver nitrate.

DEMERITS/LIMITATIONS OF ARRHENIUS THEORY:

- The x-ray analysis of crystals like sodium chloride shows the existence of ions even in the solid state. Ions are even present in the molten state. However, according to the theory, ions are formed only in solution i.e., when they are dissolved in water.
- The theory does not explain the reason for ionisation when the salt or acid (electrolyte) is dissolved in water.
- The theory fails to explain the source of energy for ionisation.
- Certain electrolytes like HCL (strong electrolyte) ionise completely when dissolved in water whereas other electrolytes like acetic acid (weak electrolyte) ionise partially.

IONISATION/DISSOCIATION OF WEAK ELECTROLYTES (ACIDS & BASES):

Weak electrolyte is a substance when dissolved in water dissociates partially but not completely. The acid that ionises partially is called weak acid and the base that ionises partially is called weak base. Examples: Acetic acid etc.

A weak acid ionises partially as:

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

Applying the law of mass action to the above equation,

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

Where, Ka is called the dissociation constant of weak acid.

Therefore**, dissociation constant of a weak acid is the ratio of the product of molar concentration of the products that are ionised to the molar concentration of the unionised acid at equilibrium.** Larger the value of Ka, stronger is the acid.

Similarly, a weak base (BOH) partially ionises as:

$$BOH \rightleftharpoons B^+ + OH-$$

The dissociation constant for the weak base is given by;

$$Kb = \frac{[B^+]\,[OH^-]}{[BOH]}$$

Therefore, **the dissociation constant of a weak base is the ratio of the product of molar concentrations of the products ionised to the molar concentration of the unionised base at equilibrium.** Larger the value of Kb, stronger is the base.

HENDERSON-HASSELBALCH EQUATION:

The Henderson-Hasselbalch equation is an approximate equation that shows the **relationship between the pH or pOH of a solution and the pKa or pKb and the ratio of the concentrations of the dissociated chemical species.**

An equation to calculate the pH of a buffer solution was derived by **Lawrence Joseph Henderson in 1908. Karl Albert Hasselbalch** rewrote this formula in logarithmic terms in **1917.**

The pH of a buffer solution can be estimated with the help of this equation when the concentration of the acid and its conjugate base, or the base and the corresponding conjugate acid, are known.

The Henderson-Hasselbalch equation can be written as:

$$\mathbf{pH = pK_a + \log_{10} \frac{[A^-]}{[HA]}}$$

Where $[A^-]$ denotes the molar concentration of the conjugate base (of the acid) and [HA] denotes the molar concentration of the weak acid. Therefore, the Henderson-Hasselbalch equation can also be written as:

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

DERIVATION OF THE HENDERSON-HASSELBALCH EQUATION:

- The ionization constants of strong acids and strong bases can be easily calculated with the help of direct methods.
- However, the same methods cannot be used with weak acids and bases since the extent of ionization of these acids and bases are very low (weak acids and bases hardly ionize).
- Therefore, in order to approximate the pH of these types of solutions, the Henderson-Hasselbalch Equation is used.

A. LET US TAKE AN EXAMPLE OF IONIZATION OF WEAK ACID "HA":

$$\mathbf{HA + H_2O \leftrightharpoons H^+ + A^-}$$

Acid dissociation constant, K_a can be given as:

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

Taking, negative log of RHS and LHS:

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

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

As we know, $\mathbf{-\log [H^+] = pH}$ **and** $\mathbf{-\log Ka = pKa}$**,**

The equation above can also be written as,

$$\mathbf{pKa = pH - \log \frac{[A^-]}{[HA]}}$$

Rearranging the equation,

$$\Rightarrow \mathbf{pH = pKa + log \frac{[A-]}{[HA]}}$$

The above equation is known as **Henderson-Hasselbalch equation,** popularly known as Henderson equation. It is very useful for estimating the pH of a buffer solution and finding the equilibrium pH in acid-base reactions.

This equation fits the titration curve of all weak acids and enables to decide some quantitative relationships. Ex: It shows that pKa of a weak acid is equal to the pH of the solution at mid-point of its titration.

At the mid-point of, [HA] = [A-]

$$\mathbf{pH = pKa + log \frac{[A-]}{[HA]}}$$

$$\mathbf{pH = pKa + log\ 1}$$

$$\mathbf{pH = pKa + 0}$$

$$\mathbf{pH = pKa}$$

B. SIMILARLY, FOR A WEAK BASE “B”:

$$\mathbf{B + H_2O \leftrightharpoons OH^- + HB^+}$$

Base dissociation constant, Kb, of the base can be given as,

$$\mathbf{Kb = \frac{[BH+]}{[OH-][B]}}$$

Taking negative log of RHS and LHS

$$\mathbf{-log\ Kb = -log \frac{[BH+]}{[OH-][B]}}$$

$$\mathbf{\Rightarrow -log\ Kb = -log\ [OH-] - log \frac{[BH+]}{[B]}}$$

As we know, **−log [OH−] = pOH and −log Kb = pKb,**

Above equation can be written as,

$$pKb = pOH - \log \frac{[BH+]}{[B]}$$

Rearranging the equation,

$$\Rightarrow pOH = pKb + \log \frac{[BH^+]}{[B]}$$

HENDERSON-HASSELBALCH EQUATION ALSO ALLOWS US TO;

- Calculate pKa if pH and the molar ratio of proton donor and acceptor are given.
- Calculate pH, given pKa and the molar ratio of proton donor and acceptor.
- Calculate the molar ratio of proton donor and acceptor, given pH and pKa.

EXAMPLES OF H-H EQUATION:

1. **pH OF AN ACIDIC BUFFER:**
   In solute, a weak acid like acetic acid partially dissociates as

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

Applying the law of mass action to the above equation,

$$Ka = \frac{[H^+]\,[A^-]}{[HA]} \quad \text{----eq 1}$$

Ka is constant at constant temperature. If a little salt of the acid BA is added to it, the added salt ionises completely as

$$BA \rightarrow B^+ + A-$$

Due to common ion effect, the dissociation of HA gets suppressed. Under this condition, it can be assumed that [HA] = acid and [A-] = salt.

Substituting these in eq 1;

$$Ka = \frac{[H^+]\,[Salt]}{[Acid]}$$

OR

$$[H^+] = Ka \frac{[Acid]}{[Salt]}$$

Taking -log on both sides,

$$-\log [H^+] = -\log Ka - \log \frac{[Acid]}{[Salt]}$$

$$pH = pKa + \log \frac{[Salt]}{[Acid]}$$

2. **pOH OF A BASIC BUFFER:**

A weak base BOH like NH4OH ionises partially in solution as

$$BOH \rightleftharpoons B^+ + OH-$$

The dissociation constant for the weak base is given by;

$$Kb = \frac{[B^+]\,[OH^-]}{[BOH]} \quad \text{eq 1}$$

Kb is constant at constant temperature. If little salt of the base BA is added to it, the added salt ionises completely as;

$$BA \rightarrow B^+ + A-$$

Due to common ion effect, the dissociation of BOH gets suppressed. Under this condition, it can be assumed that [BOH] = base and [B+] = salt. Substituting these in eq 1;

$$Kb = \frac{[Salt]\,[OH^-]}{[Base]}$$

OR

$$[OH^-] = Kb \frac{[Base]}{[Salt]}$$

Taking -log on both sides;

$$-\log [OH^-] = -\log Kb - \log \frac{[Base]}{[Salt]}$$

$$pOH = pKb + \log \frac{[Salt]}{[Base]}$$

TITRATION CURVES:

- Titration curves are used to determine the amount of acid in a given solution.
- A measured volume of the acid is titrated with a solution of a strong base usually NaOH of known concentration.
- The NaOH is added in small increments until the acid is consumed or neutralized as determined with an indicator or dye or a pH meter.
- The concentration of the acid in the original solution can be calculated from the volume and concentration of NaOH added.
- A plot of pH against the amount of NaOH added {titration curve} reveals the pKa of the weak acid.

Consider the titration of 0.1M solution of acetic acid with 0.1M NaOH at 25°C. two reversible equilibria are involved in the process (for the simplification of equation, acetic acid is denoted as HAc)

$$H_2O \rightleftharpoons H^+ + OH^- \quad \text{----eq1}$$

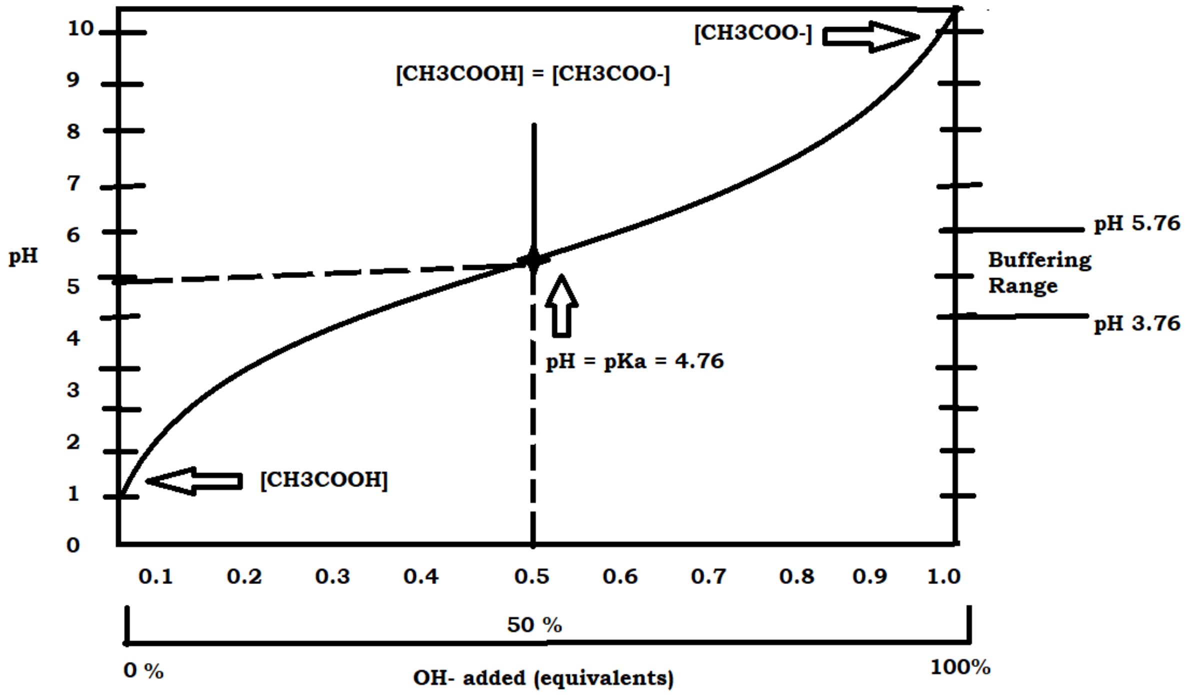
$$HAc \rightleftharpoons H^+ + Ac^- \quad \text{----eq2}$$

The equilibria must simultaneously conform to their characteristic equilibrium constants, which are

$$Kw = [H^+]\,[OH^-] = 1\times10^{-14}\ M^2 \text{ ----eq1}$$

$$Ka = \frac{[H^+]\,[Ac^-]}{[HAc]} \text{ ----eq2}$$

At the beginning of the titration, before any NaOH is added, the acetic acid is slightly ionized to an extent that can be calculated from its ionization constant (eq 2).



THE TITRATION CURVE OF ACETIC ACID

As NaOH is gradually introduced, the added OH- combines with the free H+ in the solution to form water to an extent that satisfies the equilibrium relationship in equation 1.

As free H+ is removed, HAc dissociates further to satisfy its own equilibrium constant equation 2. The net result as the titration proceeds that more HAc ionizes forming AC- as the NaOH is added further.

At the midpoint of the titration, at which exactly 0.5 equivalent of NaOH has been added, one-half of the original acetic acid has undergone dissociation, so that the concentration of the proton donor (HAc) now equals that of the proton acceptor (Ac-). At this midpoint, a very important relationship holds, i.e., the pH of the equimolar solution of acetic acid and acetate is exactly equal to the pKa of the acetic acid (pKa=4.76).

As the titrations continued by adding further increments of NaOH, the remaining non-dissolved acetic acid is gradually converted into acetate. The end point of the reaction is when the pH is around 7.0 and all the acetic acid has lost its proton to NaOH, to form water and acetate. Throughout the titration, both the equilibria (equation 1 and 2) co-exist, always confirming ti its equilibrium constant.

BUFFERS:

A solution which has the capacity to resist the change in its pH value upon adding a small amount of acid or base to it is called a buffer solution.

OR

Buffer Solution is a water solvent-based solution which consists of a mixture containing a weak acid and the conjugate base of the weak acid, or a weak base and the conjugate acid of the weak base. They resist a change in pH upon dilution or upon the addition of small amounts of acid/alkali to them.

Ability of the buffer solution to resist a change in its pH value upon adding a little acid or base to it is called **buffer capacity.** This phenomenon is called **Buffer action.**

Since the pH of a buffer solution does not change by adding little acid or base, buffer solutions are called **solutions of reserve acidity or reserve alkalinity.**

The buffer solution is a solution able to maintain its Hydrogen ion concentration (pH) with only minor changes on the dilution or addition of a small amount of either acid or base. **Buffer Solutions are used in fermentation, food preservatives, drug delivery, electroplating, printing, the activity of enzymes, blood oxygen carrying capacity need specific hydrogen ion concentration (pH).**

Solutions of a weak acid and its conjugate base or weak base and its conjugate acid are able to maintain pH and are buffer solutions.

TYPES OF BUFFER SOLUTION:

The two primary types into which buffer solutions are broadly classified into are

1. Acidic buffers and
2. alkaline buffers.

Generally, good buffer solutions are of two types:

1. A solution containing a mixture of a weak acid and its salt with a strong base. These are called acidic buffers. Ex: a mixture of CH_3COOH and CH_3COONa solutions.
2. A solution containing a mixture of a weak base and its salt with a strong acid. These are called basic buffers. Ex: a mixture of NH_4OH and NH_4Cl solutions.

Note: Ammonium acetate solution is a neutral buffer.

ACIDIC BUFFERS:

- As the name suggests, these solutions are used to maintain acidic environments.
- Acid buffer has acidic pH and is prepared by mixing a weak acid and its salt with a strong base.
- An aqueous solution of an equal concentration of acetic acid and sodium acetate has a pH of 4.74.
- pH of these solutions is below seven.
- These solutions consist of a weak acid and a salt of a weak acid.
- An example of an acidic buffer solution is a mixture of sodium acetate and acetic acid (pH = 4.75).

ALKALINE BUFFERS:

- These buffer solutions are used to maintain basic conditions.
- Basic buffer has a basic pH and is prepared by mixing a weak base and its salt with strong acid.
- The aqueous solution of an equal concentration of ammonium hydroxide and ammonium chloride has a pH of 9.25.

- The pH of these solutions is above seven
- They contain a weak base and a salt of the weak base.
- An example of an alkaline buffer solution is a mixture of ammonium hydroxide and ammonium chloride (pH = 9.25).

FORMULATION/PREPARATION OF BUFFERS:

1. PREPARATION OR FORMULATION OF ACID BUFFER:

Consider an acid buffer solution, containing a weak acid (HA) and its salt (KA) with a strong base (KOH). Weak acid HA ionizes, and the equilibrium can be written as-

$$HA + H_2O \leftrightharpoons H^+ + A^-$$

Acid dissociation constant = $\mathbf{Ka = \frac{[H^+]\,[A^-]}{[HA]}}$

Taking, negative log of RHS and LHS:

$$-\log Ka = -\log [H+] - \log \left(\frac{[A^{-}]}{[HA]} \right)$$

$$pKa = pH - \log \left(\frac{[salt]}{[acid]} \right)$$

$$\textbf{pH of acid buffer} = \textbf{pKa} + \frac{\textbf{[salt]}}{\textbf{[acid]}}$$

The equation is the Henderson-Hasselbalch equation, popularly known as the Henderson equation.

Example: **CH_3COOH and CH_3COONa (Acetic acid and Sodium acetate) buffer system.**

A mixture of acetic acid and sodium acetate solutions contains a large number of CH_3COOH molecules, because acetic acid being weak acid it remains largely in the molecular form. It also contains plenty of CH_3COO- ions produced by the ionisation of sodium acetate.

$$CH_3COONa \rightarrow CH_3COO^{-} + Na^{+}$$

If a little amount of strong acid like HCl is added, H+ ions of the added substance combine with CH_3COO- ions of the solution to form CH_3COOH molecules.

$$H^{+} + CH_3COO^{-} \leftrightharpoons CH_3COOH$$

Hence, H+ ion concentration of the solution does not increase i.e., pH does not change.

If a little amount of strong base like NaOH is added, OH- ions of the added base reacts with CH_3COOH molecules as;

$$OH^{-} + CH_3COOH \leftrightharpoons CH_3COO^{-} + H_2O$$

Hence, OH- ion concentration does not increase even after the addition of strong base i.e., the pH does not increase.

2. PREPARATION OR FORMULATION OF BASIC BUFFER:

Consider base buffer solution, containing a weak base (B) and its salt (BA) with strong acid. pOH, can be derived as above,

pOH of a basic buffer = $$\mathbf{pKb + \log \frac{[salt]}{[acid]}}$$

pH of a basic buffer = $$\mathbf{pKa - \log \frac{[salt]}{[acid]}}$$

Example: **NH_4OH and NH_4Cl (ammonium hydroxide and ammonium chloride) buffer system:**

A mixture of NH_4OH and NH_4Cl solutions contains a large number of NH_4OH molecules because ammonium hydroxide being a weak base remains largely in the molecular form. It also contains plenty of NH_4^+ ions produced by the ionization of ammonium chloride.

$$\mathbf{NH_4Cl \rightarrow NH_4^+ + H_2O}$$

If a little strong acid like HCl is added, H+ ions of the added acid react with NH_4OH molecules of the solution.

$$\mathbf{H^+ + NH_4OH \leftrightharpoons NH_4^+ + H_2O}$$

Hence, H+ ion concentration of the solution does not increase even after addition of little acid i.e., pH does not decrease.

If a little strong base like NaOH is added, OH- ions of the added base combine with NH_4+ ions of the solution to form NH_4OH molecules.

$$\mathbf{OH^- + NH_4^+ \leftrightharpoons NH_4OH}$$

Hence, OH- ion concentration of the solution does not increase even after adding a little base i.e., pH does not increase.

SIGNIFICANCE OF BUFFER AND BUFFER SYSTEM:

- Buffer solutions are needed to determine the unknown pH of a solution by colorimetric method.
- Certain bio-chemical reactions require media of a definite pH, because the efficiency of enzymes would be optimum at certain definite pH. In such cases, buffer solutions are used.

- pH of intercellular fluids in living bodies is controlled by buffer action.
- There exist a few alternate names that are used to refer buffer solutions, such as pH buffers or hydrogen ion buffers.
- An example of the use of buffers in pH regulation is the use of bicarbonate and carbonic acid buffer system in order to regulate the pH of animal blood.
- Buffer solutions are also used to maintain an optimum pH for enzyme activity in many organisms.
- The absence of these buffers may lead to the slowing of the enzyme action, loss in enzyme properties, or even denature of the enzymes. This denaturation process can even permanently deactivate the catalytic action of the enzymes.
- Buffer formulation is highly useful while performing the experiments at laboratory conditions to maintain a constant pH.

BIOLOGICAL BUFFERS:

Biological buffers are substances that are synthesised in the body which help to maintain constant pH at desired organ level to have proper metabolic activities throughout.

The three major buffer systems of our body are;

1. carbonic acid bicarbonate buffer system,
2. phosphate buffer system and
3. protein buffer system.

Carbonic acid bicarbonate buffer system:

- The carbonic acid-bicarbonate buffer system plays an extremely important role in maintaining pH homeostasis of the blood.
- Carbonic acid-bicarbonate buffer system converts strong bases to a weak base (bicarbonate ion), and strong acids to a weak acid (carbonic acid)

Phosphate buffer system:

- The phosphate buffer consists of phosphoric acid (H_3PO_4) in equilibrium with dihydrogen phosphate ion ($H_2PO_4^-$) and $H+$.
- The pK for the phosphate buffer is 6.8, which allows this buffer to function within its optimal buffering range at physiological pH.
- It plays a very minute role in the blood.

Protein buffer system:

- Protein buffer helps to maintain acidity in and around the cells.
- Proteins containing amino acid histidine are also good at buffering.

BUFFER SYSTEMS IN THE BODY:

The buffer systems in the human body are extremely efficient, and different systems work at different rates. It takes only seconds for the chemical buffers in the blood to make adjustments to pH.

The respiratory tract can adjust the blood pH upward in minutes by exhaling CO_2 from the body.

The renal system can also adjust blood pH through the excretion of hydrogen ions (H+) and the conservation of bicarbonate, but this process takes hours to days to have an effect.

The buffer systems functioning in blood plasma include plasma proteins, phosphate, and bicarbonate and carbonic acid buffers.

The kidneys help control acid-base balance by excreting hydrogen ions and generating bicarbonate that helps maintain blood plasma pH within a normal range. Protein buffer systems work predominantly inside cells.

I. BUFFERING SYSTEM OF BLOOD (Carbonic acid bicarbonate buffer system)

Maintaining a constant blood pH is critical for the proper functioning of our body. The buffer that maintains the pH of human blood involves a carbonic acid and bi-carbonate buffer system.

- Blood forms the basis of circulatory system in the body.
- Transport of vital components across the body is via blood.
- Hence, any addition or removal of substance from the blood cause change in pH.
- Blood can become both acidic and basic because of which the mechanism of transportation could be hampered.
- Therefore, maintaining constant pH of about 7.45-7.65 is very essential.

- This process is undertaken by carbonic acid and bi-carbonate system of buffer action.

$$\underset{\text{weak acid}}{H_2CO_3 + H_2O} \rightleftharpoons \underset{\text{conjugate base}}{HCO_3^- + H_3O^+}$$

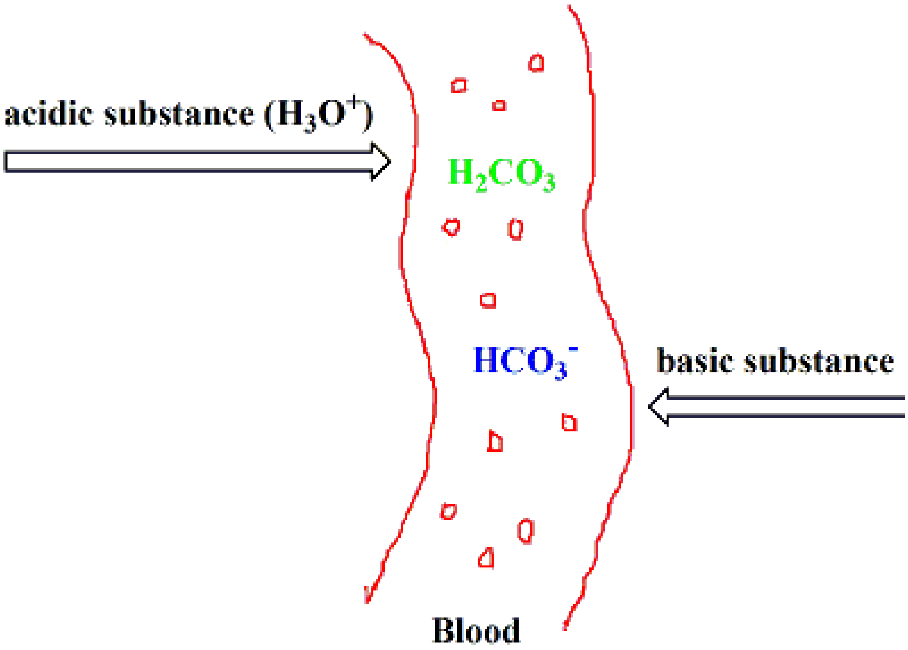


Diagram carbonic acid - bicarbonate ion system in human blood

When any acidic substance enters the bloodstream, the bicarbonate ions neutralize the hydronium ions forming carbonic acid and water. Carbonic acid is already a component of the buffering system of blood. Thus, hydronium ions are removed, preventing the pH of blood from becoming acidic.

$$HCO_3^- + H_3O^+ \longrightarrow H_2CO_3 + H_2O$$

Chemical reaction diagram of bicarbonate ions neutralizing hydronium ions forming carbonic acid and water

On the other hand, when a basic substance enters the bloodstream, carbonic acid reacts with the hydroxide ions producing bicarbonate ions and water. Bicarbonate ions are already a component of the buffer. In this manner, the hydroxide ions are removed from blood, preventing the pH of blood from becoming basic.

$$H_2CO_3 + OH^- \longrightarrow HCO_3^- + H_2O$$

Chemical diagram of carbonic acid reacting with hydroxide ions producing bicarbonate ions and water

As depicted below, in the process of neutralizing hydronium ions or hydroxide ions, the relative concentrations of carbonic acid and bicarbonate ions fluctuate in the blood stream. But this slight change in the concentrations of the two components of the buffering system doesn't have any adverse effect; the critical thing is that this buffering mechanism prevents the blood from becoming acidic or basic, which can be detrimental.

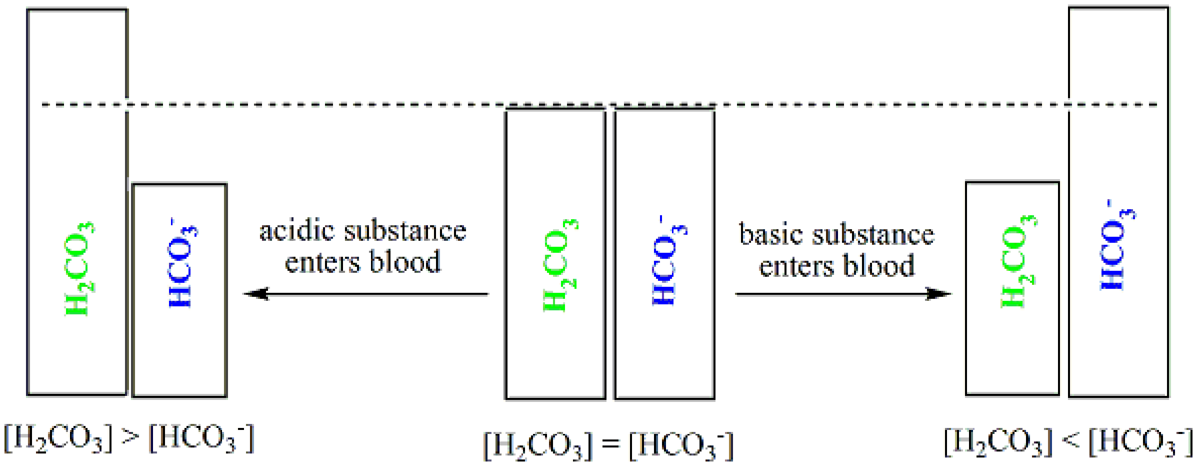


Diagram of blood pH maintained at approx. 7.4 by the carbonic acid – bicarbonate ion buffering system

The pH of blood is maintained at ~ 7.4 by the carbonic acid – bicarbonate ion buffering system.

II. PHOSPHATE BUFFER

Phosphates are found in the blood in two forms: sodium dihydrogen phosphate ($Na_2H_2PO_4$–), which is a weak acid, and sodium monohydrogen phosphate ($Na_2HPO_4^{2}$-), which is a weak base.

When $Na_2HPO_4^{2}$- comes into contact with a strong acid, such as HCl, the base picks up a second hydrogen ion to form the weak acid $Na_2H_2PO_4$– and sodium chloride, NaCl. When $Na_2HPO_4^{2-}$ (the weak acid) comes into contact with a strong base, such as sodium hydroxide (NaOH), the weak acid reverts back to the weak base and produces water. Acids and bases are still present, but they hold onto the ions.

$$\mathbf{HCl + Na_2HPO_4 \rightarrow NaH_2PO_4 + NaCl}$$

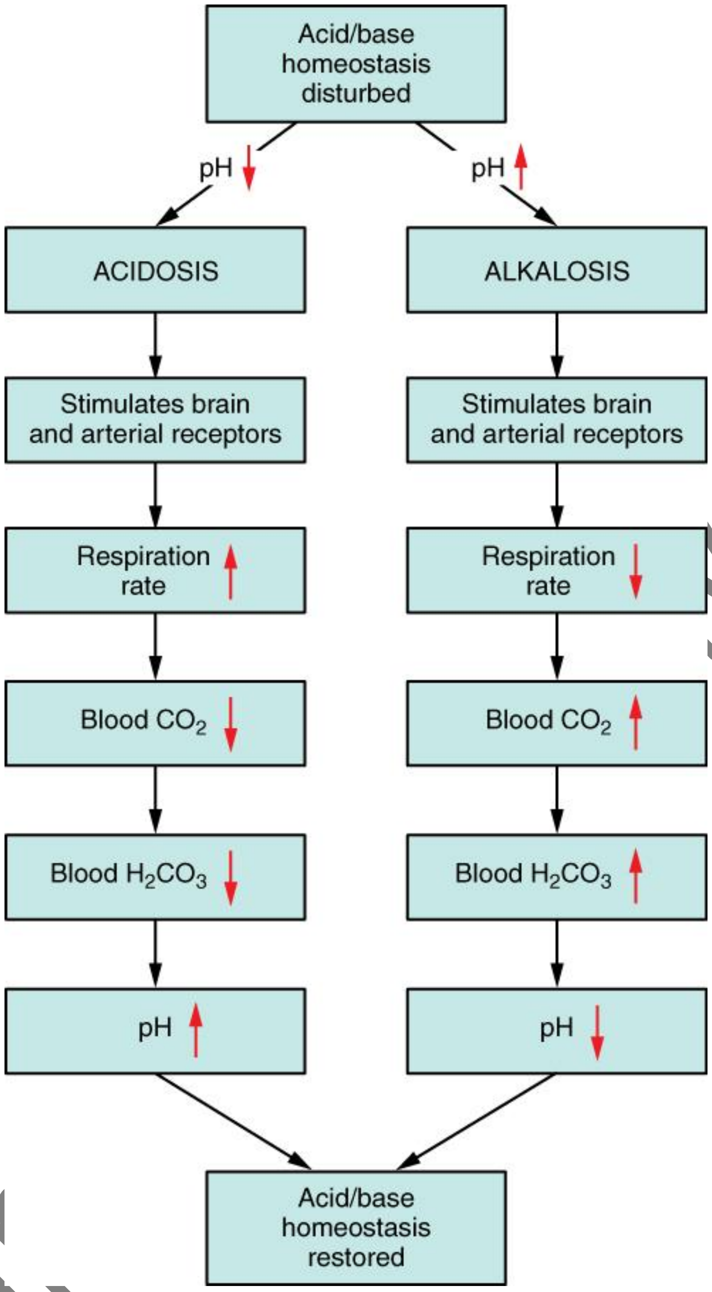
(strong acid) + (weak base) → (weak acid) + (salt)

$$\mathbf{NaOH + NaH_2PO_4 \rightarrow Na_2HPO_4 + H_2O}$$

(strong base) + (weak acid) → (weak base) + (water)

RESPIRATORY REGULATION OF ACID-BASE BALANCE:

- The respiratory system contributes to the balance of acids and bases in the body by regulating the blood levels of carbonic acid.
- CO_2 in the blood readily reacts with water to form carbonic acid, and the levels of CO_2 and carbonic acid in the blood are in equilibrium.
- When the CO_2 level in the blood, the excess CO_2 reacts with water to form additional carbonic acid, lowering blood pH.
- Increasing the rate and/or depth of respiration allows to exhale more CO_2.
- The loss of CO_2 from the body reduces blood levels of carbonic acid and thereby adjusts the pH upward, toward normal levels.
- Excessive deep and rapid breathing rids the blood of CO_2 and reduces the level of carbonic acid, making the blood too alkaline.
- This brief alkalosis can be remedied by rebreathing air. Rebreathing exhaled air will rapidly bring blood pH down toward normal.



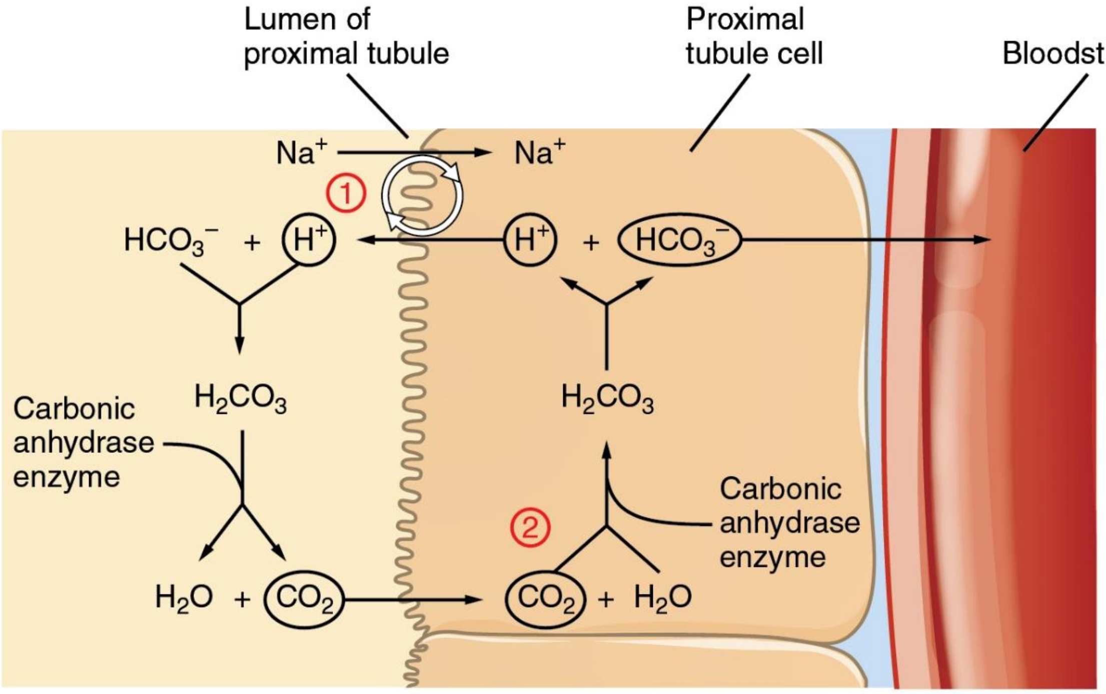
- The chemical reactions that regulate the levels of CO_2 and carbonic acid occur in the lungs when blood travels through the lung's pulmonary capillaries.
- Minor adjustments in breathing are usually sufficient to adjust the pH of the blood by changing how much CO_2 is exhaled.
- The body regulates the respiratory rate by the use of chemoreceptors, which primarily use CO_2 as a signal.
- Peripheral blood sensors are found in the walls of the aorta and carotid arteries. These sensors signal the brain to provide immediate adjustments to the respiratory rate if CO_2 levels rise or fall. Yet other sensors are found in the brain itself. Changes in the pH of CSF affect

the respiratory centre in the medulla oblongata, which can directly modulate breathing rate to bring the pH back into the normal range.

- Hypercapnia, or abnormally elevated blood levels of CO_2, occurs in any situation that impairs respiratory functions, including pneumonia and congestive heart failure.

RENAL REGULATION OF ACID-BASE BALANCE:

- The renal regulation of the body's acid-base balance addresses the metabolic component of the buffering system.
- Whereas the respiratory system controls the blood levels of carbonic acid by controlling the exhalation of CO_2, the renal system controls the blood levels of bicarbonate.



REGULATION OF ACID-BASE BY KIDNEY

- The kidneys have two main ways to maintain acid-base balance - their cells reabsorb bicarbonate HCO_3^- from the urine back to the blood and they secrete hydrogen H^+ ions into the urine.
- By adjusting the amounts reabsorbed and secreted, they balance the bloodstream's pH.
- Our kidneys filter blood continuously by distributing the blood that comes into the kidney to millions of tiny functional units called nephrons.
- Each nephron is made up of the glomerulus, or a tiny clump of capillaries, where blood filtration begins.

- When blood passes through a glomerulus, about one-fifth of the plasma leaves the glomerular capillaries and goes into the renal tubule.
- Reabsorption of the good stuff---water and electrolytes---and leaving behind the bad stuff---waste products and acid--- is the job of the renal tubular system.
- The renal tubule is a structure with several segments: the proximal convoluted tubule, the U- shaped loop of Henle with a thin descending and a thick ascending limb, and the distal convoluted tubule, which winds and twists back up again, before emptying into the collecting duct, which collects the final urine.
- Each of these tubules is lined by brush border cells which have two surfaces.
- One is the apical surface that faces the tubular lumen and is lined with microvilli, which are tiny little projections that increase the cell’s surface area to help with solute reabsorption.
- The other is the basolateral surface, which faces the peritubular capillaries, which run alongside the nephron.
- So with bicarbonate reabsorption, as the filtrate leaves the glomerulus, it first goes through the proximal convoluted tubule.
- Now at first, this filtrate contains the same concentration of electrolytes as the plasma it came from. But when a molecule of bicarbonate approaches the apical surface of the brush border cell it binds to hydrogen H+ secreted by the brush border cell in exchange for a sodium ion from the tubule to form carbonic acid.
- At that point, an enzyme called carbonic anhydrase type 4 which lurks in the tubule in the microvilli like a shark, swims along and splits the carbonic acid into water and carbon dioxide.
- Unlike charged bicarbonate anions, which are stuck in the tubule, the water and carbon dioxide happily diffuse across the membrane into the cells where carbonic anhydrase type 2 facilitates the reverse reaction - combining them to form carbonic acid, which dissolves into bicarbonate and hydrogen.
- A sodium bicarbonate co-transporter on the basolateral surface snatches up the bicarbonate and a nearby sodium, and shuttles both into the blood.
- Alternatively, a bicarbonate chloride exchanger exchanges bicarbonate HCO_3^- with chloride Cl- leaving the bloodstream to enter the cells.
- All this chemical trickery effectively moves 99.9% of the filtered bicarbonate that’s in the tubule back into the bloodstream.
- Hydrogen H+ ions, with their positive charge don’t naturally want to pass through cell membranes out into the urine. They need to be pushed out.