UNIT-V pH, buffers and Isotonic solutions

Sorensen's pH scale :-

pH is a unit → measures the degree of acidity or basicity of a solution.

→ In 1909 → a Danish Biochemist

⇓

Soren Peber Lauritz Sorensen

⇓

defined the pH as

" Negative logarithm of hydrogen ion (H^+) concentration."

S,

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

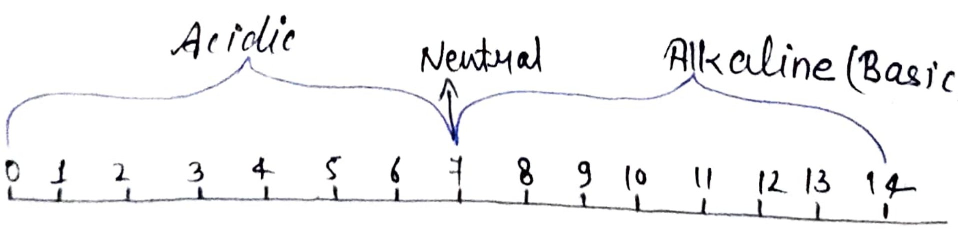
$$pH = \log \frac{1}{[H^+]}$$

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

pH value range from 0 to 14.

→ Acidic solution ⇒ $[H^+] > [OH^-]$, $pH < 7$.

Basic Solution ⇒ $[H^+] < [OH^-]$, $pH > 7$.



Determination of pH :-

The method of measuring pH are -

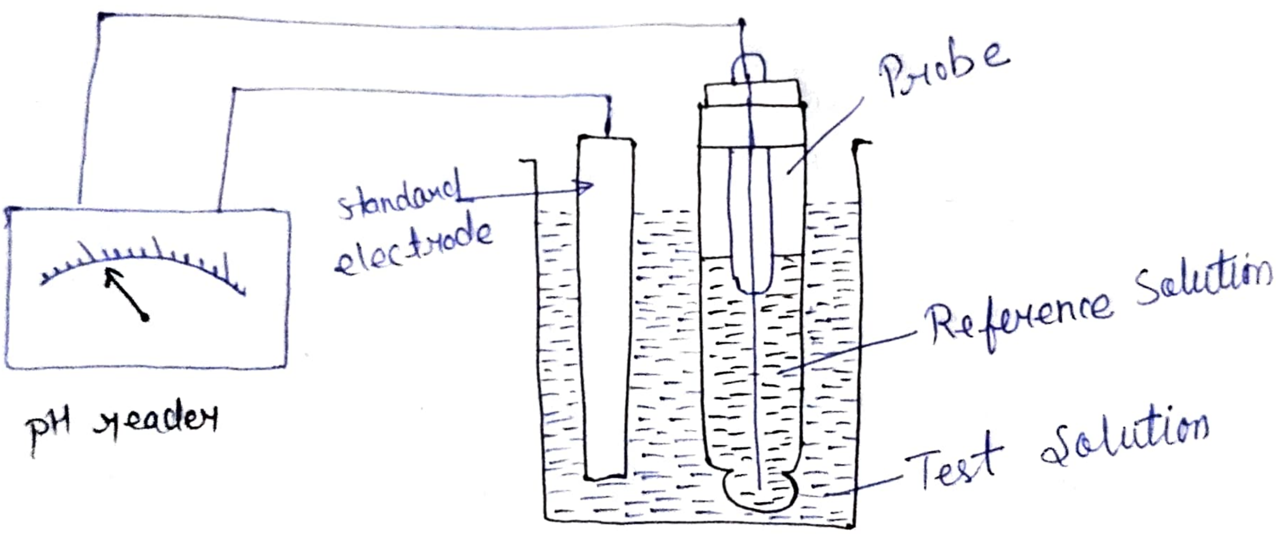
① Electrometric Method

② Calorimetric Method

Determination of pH by Electrometric Method :-

Apparatus is called → pH meter.
⇓
consists of a valtameter connected to 2 electrodes

(a) Standard electrode → known as potential
(b) Special electrode → known as probe.
↓
enclosed in a glass membrane that allow migration of H^+ ions
(contain reference solution of dilute HCl)



- Two electrodes are clipped in the solution to be tested.

If solution pH differ from probe solution pH electrical potential results
⇓
this potential is recorded by an inbuilt potentiometer
⇓
potential reading is automatically converted electrically to a direct reading of pH.

(4) Determination by Calorimetric Method

Take the calorimetric paper
↓
dip in water sample
↓
obtained colour is computed from the standard table
↓
respective pH value recorded.

* The pH value indicate wether the sample is acidic or alkaline.

Buffer Solution :

A buffer solution is one which maintain its pH constant even upon addition of small amount of acid or base.

⇒ The solution that are able to resist the change in pH value termed as buffer solution.

Types -

① **Acidic buffer** :- a weak acid together its salt of same acid with a strong base.
e.g. $CH_3COOH + CH_3COONa$.

② **Basic Buffer** :- a weak base and its salt with a strong acid.
e.g. $NH_4OH + NH_4Cl$.

Buffer Action

→ Operation of Acid Buffer :-

The pH ~~a~~ of buffer is governed by-

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

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

(i) Addition of HCl :-

Addition of HCl increase H^+ ions

↓

~~concent~~ Counteracted by association with excess of acetate ions to form unionised CH_3COOH.

↓

Thus added H^+ ions neutralised and pH of buffer remain ~~co~~ unchanged.

Addition of OH^- → H_2O

$$CH_3COOH \rightleftharpoons \boxed{H^+} + CH_3COO^-$$

$$CH_3COONa \longrightarrow Na^+ + \boxed{CH_3COO^-}$$

Addition of H^+ → CH_3COOH

(ii) Addition of NaOH :-

⇒ Addition of NaOH increase OH^- ions

↓

additional OH^- ions combined with H^+ ions to form water molecule

↓

Thus added OH^- ions neutralised and pH of buffer remain unchanged.

Operation of basic buffer :-

1) ~~Additi~~ $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

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

ii) Addition of HCl and NaOH →

Addition of H^+ → H_2O

$$NH_4OH \rightleftharpoons NH_4^+ + \boxed{OH^-}$$

$$NH_4Cl \longrightarrow \boxed{NH_4^+} + Cl^-$$

Addition of OH^- → NH_4OH

→ Applications of Buffer :-

- The process of fermentation uses buffer solutions.
- Chemical analysis and calibration of pH meters are also using buffer solution.
- The pH for the enzymes, required to perform different functions in many organisms is maintained by the buffer solutions.
- Maintainance of life → most of biochemical process work within a relatively small pH range. The body move its own buffer solution which maintain a constant pH.

e.g. Blood contain a bicarbonate buffer that keep the pH close to 7.4 (blood pH).

- Buffers are used in food industry to maintain the acidity of food, and also for microbiological stability of food.

⇒ Buffer solution also used in textile industry e.g. Many dyeing processes use buffer to maintain the correct pH for various dyes

Buffer Equation

It is used to calculate the pH of a buffer solution and the change in pH with the addition of an acid/base.

Buffer equation for Acidic buffer :-

The dissociation of weak acid HA expressed as -

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

Applying law of ~~active~~ mass active,

So,

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

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

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

Taking negative log both side -

$$-\log[H^+] = -\log ka - \log \frac{[acid]}{[Salt]}$$

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

and $-\log ka = pka$

So, $pH = pKa - \log \frac{[acid]}{[salt]}$

or $\boxed{pH = pKa + \log \frac{[salt]}{[acid]}}$

This relationship is called Henderson-Hasselbalch Equation.

⇒ In similar way Henderson-Hasselbalch Equation for a basic buffer can be written as -

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

Buffer Capacity

Buffer capacity also referred as → Buffer Index
→ Buffer Efficiency
→ Buffer Coefficient
→ Buffer value

⇒ Buffer capacity of a solution is a measure of its magnitude of resistance to change in pH on addition of an acid or a base.

⇒ Buffer Capacity β has been defined as

ratio of → increasement of strong acid or base to small change in pH brought about by this addition.

So,

$$\boxed{\beta = \frac{\Delta A \text{ or } \Delta B}{\Delta pH}}$$

Where, ΔA or ΔB = Small increment in gram equivalent per litre of strong acid or base.

ΔpH = change in pH.

Buffer in pharmaceutical System :-

Buffers are added in pharmaceutical products
↓
to maintain the required stability and pharmacological effect.

① In Parentral Preparations – pH should be 7.4 (pH of blood)
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If pH deviates serious consequence may occur.

→ The most commonly used buffer in parentral product
↓
acetate, citrate, phthalate, glutamate.

② In ophthalmic preparations := pH should be 7 - 8 (pH of Lachrymal fluid)

→ The most commonly used buffer in ophthalmic product
↓
borate, carbonate & phosphate buffer.

③ In Ointments and Creams – pH should be 5.5 (pH of skin)

→ It is fairly acidic → helps to avoid effect of harmful bacteria and fungi

→ Buffer used are → citric acid and sodium citrate or phosphoric acid / Sodium phosphate

④ One of the special applications of buffer is to reduce the gastric irritation caused by acidic drug. ~~For~~
ex- Sodium bicarbonate, magnesium carbonate

and sodium citrate antacids are used for purpose of reducing toxicity as a solid dosage form.

⇒ Buffers in Biological System

① Blood :-

⇒ The pH of blood is maintained about 7.4 by two buffer systems :-

ⓐ Primary buffer - In plasma, compound like

↓

carbonic acid / carbonate and acid / alkali sodium salt of phosphoric acid

⇓

which maintain the pH.

ⓑ Secondary System - The erythrocytes

⇓

oxy- haemoglobin / haemoglobin and acid / alkali potassium salts of phosphoric acid.

② Lacrimal fluids :-

Lacrimal fluids (tears) have been found to have a great degree of buffer capacity, allowing dilution of 1:15 with neutral distilled water. The pH range of tear about 7 to 8.

Buffered Isotonic Solution

Pharmaceutical solutions that are meant for applications to delicate membrane of the body should also be adjusted to approximately the same osmotic pressure as that of the body fluids.

⇒ Isotonic salutions cause no swelling or contraction of the tissue with which they come in contact and produce no discomfort when instilled in the eyes, nasal tract, blood or other body tissue .

Eg. Blood → 0.9% w/v NaCl Salution.

- Their are three types of salutions :-

ⓐ Isotonic Salution :-
A buffer salution have same osmotic pressure as body fluid. (0.9% w/v NaCl).

ⓑ Hypertonic :- A buffer salution have high concentration of saluto (osmotic pressure) than 0.9% NaCl.

⇒ If red blood cells are suspended in paratonic salution, the water in RBCs pass out to dilute surrounding salt salution than cause to shrink the cell.

ⓒ Hypotonic :- A buffer salution have less conc. of salute (osmotic pressure) than 0.9% w/v NaCl.

⇒ If RBCs mixed with paratonic salution, the salt (water) pass into RBCs causes swelling and finally bursting cell called haemolysis.

Measurement of Tonicity

① Haemolytic Method :-

In this method → RBC are suspended into solution to be tested

if causes shrinkage of cells → said hypertonic

If causes swelling and haemolysis → said hypotonic.

② Colligative Methods :-

The solution have same tonicity → have similar colligative properties such as

- Same → Iso-tonic
- > 0.9% → Hypertonic
- < 0.9% → Hypotonic

→ Lowering of vapour pressure
→ depression of freezing point
→ Boiling point

Methods of Adjusting Tonicity :-

① Freezing point Depression Method or Cryoscopic Method :-

⇒ Body fluids → Blood plasma, Lacrimal secretion } have a freezing point of −0.52°C.

So all solutions which have freezing point −0.52°C → will be isotonic with these fluids.

⇒ Following formula is used for calculation of the quantity of a substance required to make solution isotonic with physiological fluids -

% w/v of adjusting substances = $\frac{0.52 - a}{b}$

Where,

a = Freezing point of the unadjusted Solution.

b = Freezing point of 1% w/v Solution of adjusting substance.

② Molecular Concentration Method:-

Percentage w/v of adjusting substance required = $\frac{0.03\ M}{N}$

Where, M = Gram molecular weight of the Substance.

N = Number of ions which the substance is ionized.

③ Sodium Chloride equivalent Method:-

★ Developed by Mellen and Seltzer

consider tonic effect drug equivalent of sodium chloride.

Called E value of the drug.

⇒ The E-value of drug represents the amount of sodium chloride which will exert toncie effect equal to one gram of the drug

$$\boxed{E = 17 \times \frac{L_{iso}}{M}}$$

Where,

L_{iso} = Specific value of L

M - Molecular weight of drug

E = sodium chloride equivalent or amount of NaCl required.

④ White-Vincent Method:-

→ This method involves → addition of sufficient quantity of water to a drug to prepare a isotonic solution.

So,

$$\boxed{V = W \times E \times 111.1}$$

Where,

V = volume of water added in solution to make it isotonic.

W = weight of drug in gram.

E = Equivalent weight of drug (Sodium Chloride Equivalent)

⑤ The Sprowls Method:-

→ It is modification of White-Vincent Method

↓

weight of drug (W) was fixed that is 0.3 g.

∴ $V = 0.3 \times E \times 111.1 \Rightarrow \boxed{V = 33.33\,E}$