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BUFFER EQUATION / HENDERSON HASELBALCH EQN

This is also referred to as Henderson Haselbalch equation. This equation is used to calculate the pH of the solution or to find out the concentration of H^+ ion.

Consider an acidic buffer containing weak acid, HA and its salt BA .

Dissociation of acid is given by:-



Dissociation of HA is at lesser extent in comparison to its salt. Salt completely dissociates increasing the value of A^- . Using Law of Mass Action

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

$[HA]$ - initial concentration

$[H^+]$ - conc of weak acid

$[A^-]$ - " " salt.

Rearranging the equation, we get:-

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

$$H^+ = K_a \times \frac{\text{acid}}{\text{salt}}$$

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Taking log

$$-\log [H^+] = -\log K_a - \log \left[\frac{\text{acid}}{\text{salt}} \right]$$

Thus $\boxed{pH = pK_a + \log \left[\frac{\text{salt}}{\text{acid}} \right]}$ \rightarrow (Weak Acid)

pK_a - dissociation exponent (negative logarithm of K_a)

$$\boxed{pH = pK_a + \log \left[\frac{\text{salt}}{\text{base}} \right]}$$
 \rightarrow (Weak Base)

The buffer equation is important in preparation of buffered pharmaceutical solutions. It is satisfactory for calculations with pH range 4 to 10.

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

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

$$H^+ = K_a \frac{\text{acid}}{\text{salt}}$$

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BUFFER CAPACITY.

- Buffer Capacity is defined as the resistance offered by the buffer in the change in pH on addition of small amount of acid / base. It is denoted by β .
- Buffer Capacity is also known as Buffer index / Buffer efficiency / Buffer value.
- Buffer Capacity is also defined as the ratio of small increment caused by strong acids or strong bases causing small change in the pH on its addition.

$$\beta = \frac{\Delta B}{\Delta pH}$$

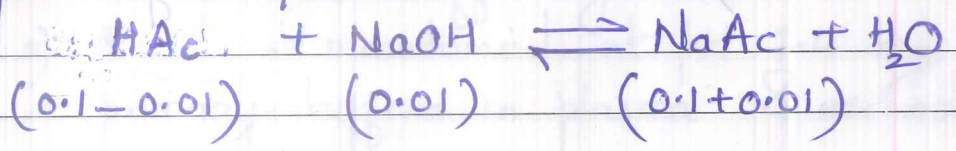
ΔB is the small increment in gram equivalents / liter of strong base added to the buffer solution to produce a pH change of ΔpH .

Calculation of Buffer Capacity

1) Consider acetate buffer containing 0.1 mole of acetic acid and 0.1 mole of sodium acetate, in 1 litre of solution.

2) Add 0.01 mole of NaOH.

3) When 0.01 mole of NaOH is added, the concentration of sodium acetate (salt) \uparrow ses by 0.01 moles/litre, whereas acetic acid (acid) \downarrow ses by 0.01 moles/litre.



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HAc - Acetic acid. (Acid)

NaAc - Sodium acetate (Salt)

4) These changes in the concentration of salt & acid are represented by buffer equation

$$pH = pK_a + \log \frac{[\text{salt}] + [\text{Base}]}{[\text{Acid}] - [\text{Base}]}$$

5) Before adding NaOH, pH of the buffer solution is

$$pH = 4.76 + \log \frac{0.1 + 0}{0.1 + 0}$$

$$= 4.76$$

Thus $pH = pK_a$.

6) Buffer capacity decreases rapidly as we add base and is greatest before adding base, where $[\text{salt}] / [\text{Acid}] = 1$.

7) The more exact equation for calculating Buffer Capacity is.

$$\beta = 2.3 C \frac{K_a [H_3O^+]}{(K_a + [H_3O^+])^2}$$

C - total buffer concentration,

K_a - Dissociation constant

$[H_3O^+]$ - hydrogen ion concentration.

* Buffer capacity depends on 2 parameters:-

a) Concentration of salt & acid present

b) Concentration ratio of salt to that of acid

BUFFERS IN PHARMACEUTICAL & BIOLOGICAL SYSTEMS

A) Buffers in Pharmaceutical Systems :-

→ Salicylic acid stored in soft glass bottles :- Sodium ion leaches out combining with Salicylic acid to form Sodium Salicylate & forming a buffer system. i.e. Salicylic acid & Sodium Salicylate. This serves as a buffer maintaining the pH & product remains stable.

→ Ephedrine & Ephedrine HCl :- When HCl is added to Ephedrine fraction of it gets converted to Ephedrine HCl. Mixture HCl & Ephedrine HCl acts as buffer resisting the change in pH of the solution.

→ Buffer system consisting of boric acid, sodium borate and sufficient sodium chloride to make the mixture isotonic & used for ophthalmic solutions in pH range of 7 to 9.

→ Mixture of salts of sodium phosphate with pH 6 to 8. Sodium chloride is added to make it isotonic with body fluids.

B) Buffers in Biological Systems :-

→ In-vivo Biologic Buffer Systems.

a) Blood - maintained at pH 7.4 by primary buffers in plasma & secondary

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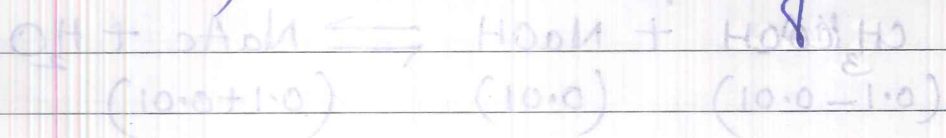
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buffers in erythrocytes

- Plasma → Carbonic acid / Bicarbonate & sodium salts of phosphoric acid.
- Erythrocytes → Hemoglobin / Oxyhemoglobin & potassium salts of phosphoric acid.

b) lacrimal fluid / Tears have pH of about 7.4

→ Urine

Normal adult urine has pH of about 6. It may be as low as 4.5 or as high as 7.8.

When pH of urine is below normal values, hydrogen ions are excreted by kidneys and when pH is above 7.4, hydrogen ions are retained by kidneys.