Buffer solution

Ionic Equilibrium

Basic terms

Electrolytes ; Can ionize in fused condition or aqueous system & pass electric current

Types; 1. Strong electrolyte, eg HCl, NaCl, KOH (almost completely ionized)

2. Weak electrolyte, eg CH_3COOH, NH_4OH (feebly ionized)

$NaOH \longrightarrow Na^+ + OH^-$ (completely ionization)

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ (feebly ionized)

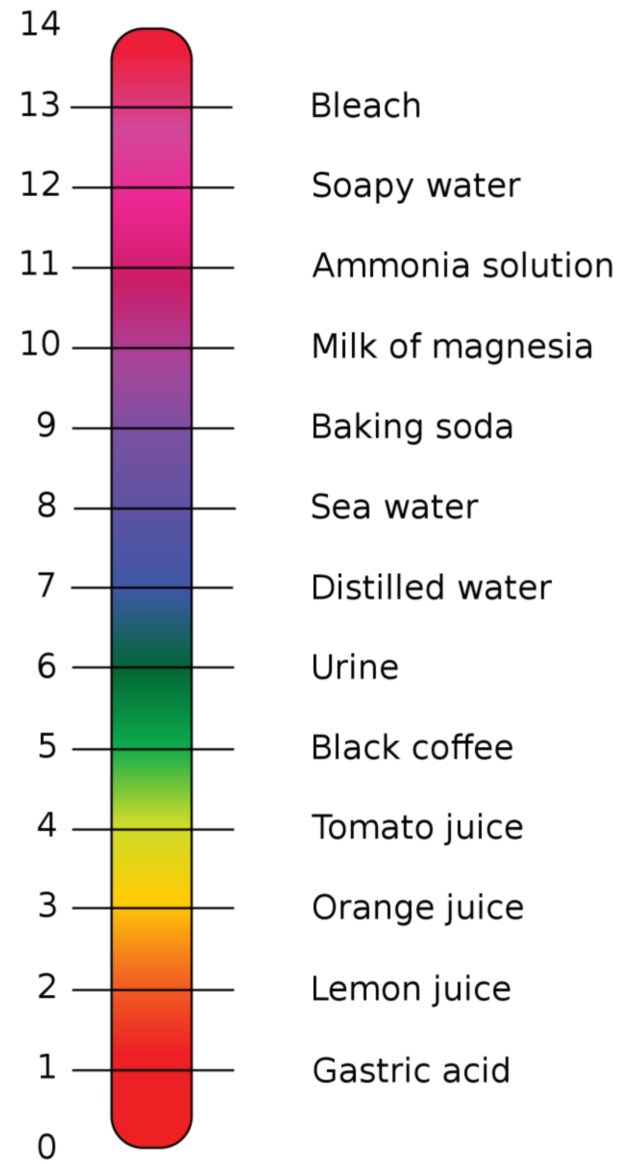
pH and pH scale

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

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

$pH + pOH = 14$

pH scale



Common ion effect and Le-chateliers principle

Ionization of weak electrolyte is highly suppressed in presence of strong electrolyte which gives common ion. Eg ionization of ammonia in presence of ammonium chloride

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

(Equilibrium shifts toward left)

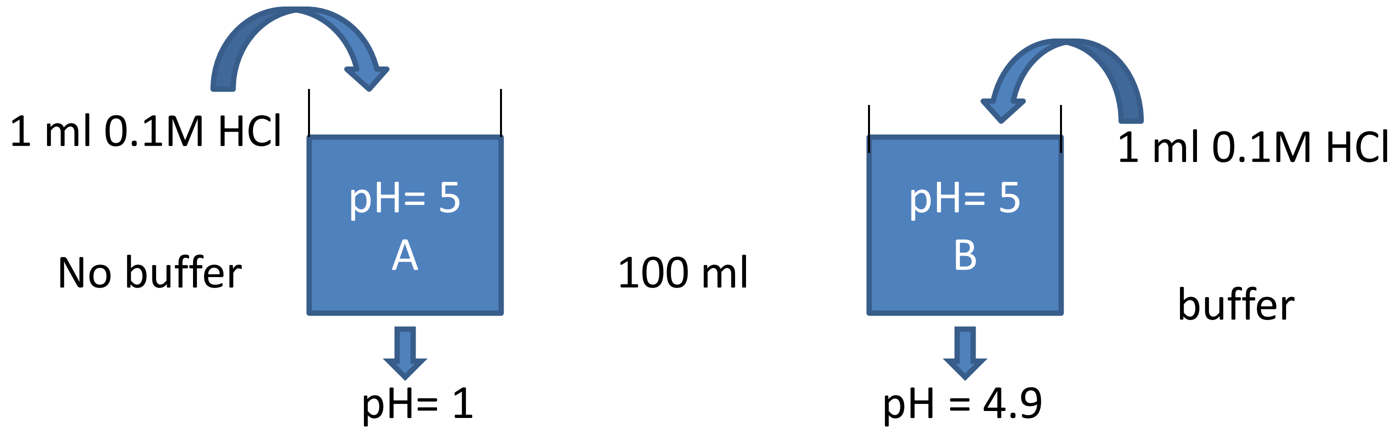
$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

common ion

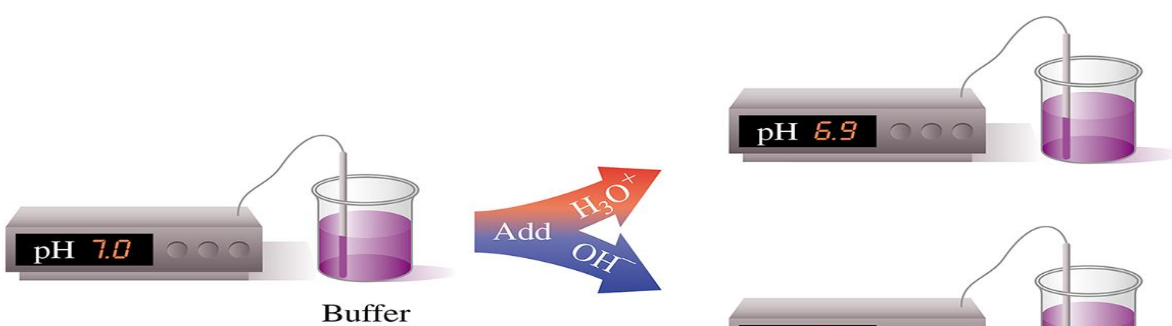
$$k_B = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

(At equilibrium)

Buffer solution



A buffer solution is a solution that resists changes in pH (or maintain pH almost constant) either when diluted or when limited amounts of strong acid or base are added to it. Such a solution can be generally prepared by combining a weak acid and its salt with a strong base (conjugated base) or, analogously, a weak base and its salt with a strong acid (conjugated acid).



Important of buffer

1. In biosystem (METABOLISM)

2. In industry (pharmaceuticals)

3. In laboratory (different titration)

Types of Buffer solution

Acidic buffer (pH<7); it is a mixture of weak acid & its salt with strong base

$$\underset{WA}{CH_3COOH} + \underset{SB}{NaOH} \longrightarrow \underset{\text{salt of WA with SB}}{CH_3COONa} + H_2O$$

Ie mixture of CH_3COOH & CH_3COONa is acidic buffer

2. Basic buffer (pH>7); it is a mixture of weak base & its salt with strong acid

$$\underset{WB}{NH_4OH} + \underset{SA}{HCl} \longrightarrow \underset{\text{salt of WB with SA}}{NH_4Cl} + H_2O$$

Ie mixture of NH_4OH and NH_4Cl is basic buffer

Some examples

- Acidic buffer;
  1. $CH_3COOH + CH_3COONa$
  2. $HCOOH + HCOONa$
  3. Oxalic acid + sodium oxalate
- Basic Buffer;
  1. $NH_3 + NH_4Cl$
  2. $NH_4OH + NH_4NO_3$
  3. Methylamine+Methyl ammonium chloride

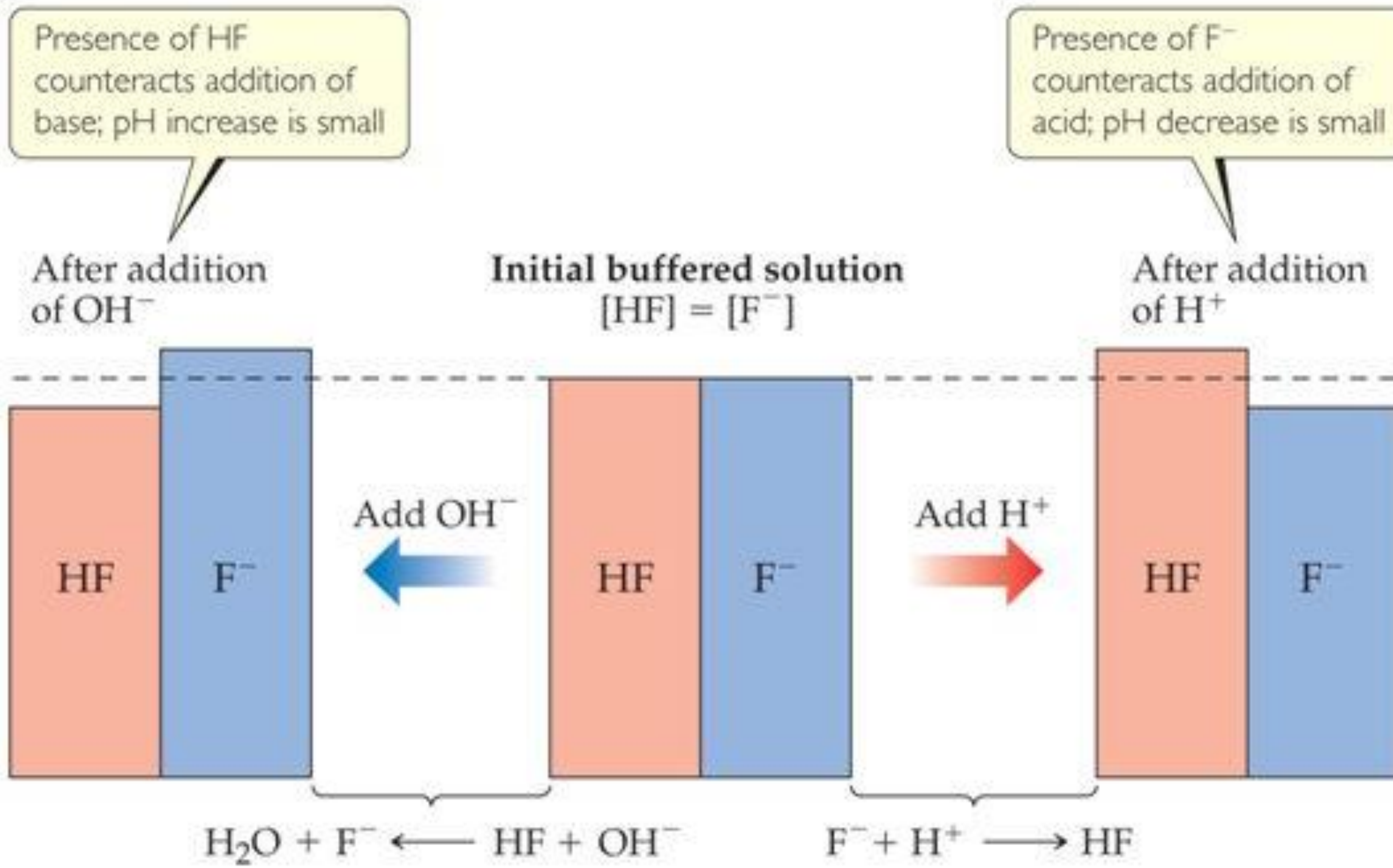
A **buffer solution**

- contains a combination of acid–base conjugate pairs, a weak acid and a salt of its conjugate base, such as

$$CH_3COOH(aq) \text{ and } CH_3COO^-(aq)$$

$$\underset{\text{weak acid}}{CH_3COOH} \longrightarrow \underset{\text{its conjugate base}}{CH_3COO^-}$$

- Should have equal concentration of a weak acid and its salt.



Presence of HF counteracts addition of base; pH increase is small
Presence of F^- counteracts addition of acid; pH decrease is small
After addition of OH^-
Initial buffered solution
$[HF] = [F^-]$
After addition of H^+
HF
F^-
Add OH^-
HF
F^-
Add H^+
HF
F^-
$H_2O + F^- \longleftarrow HF + OH^-$
$F^- + H^+ \longrightarrow HF$

In the buffer with acetic acid (CH_3COOH) and sodium acetate (CH_3COONa),

- **the salt produces acetate ions and sodium ions.**

$$CH_3COONa(aq) = CH_3COO^-(aq) + Na^+(aq)$$

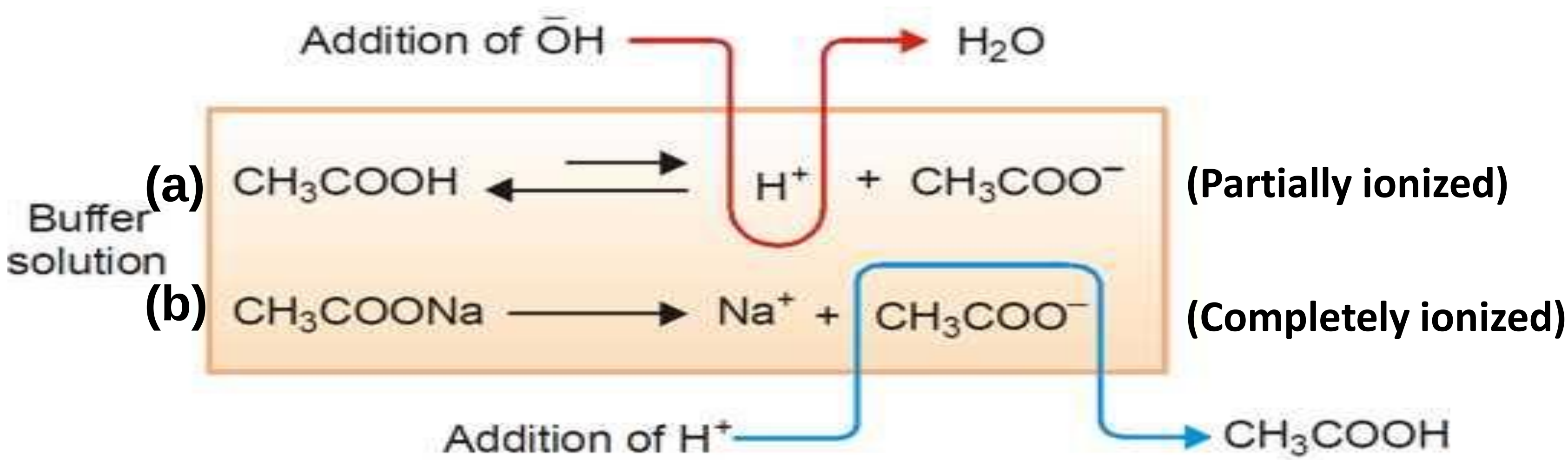
- **the salt is added to provide a higher concentration of the conjugate base CH_3COO^- than from the weak acid alone.**

$$\underset{\text{Large amount}}{CH_3COOH(aq)} + H_2O(l) \rightleftharpoons \underset{\text{Large amount}}{CH_3COO^-(aq)} + H_3O^+(aq)$$

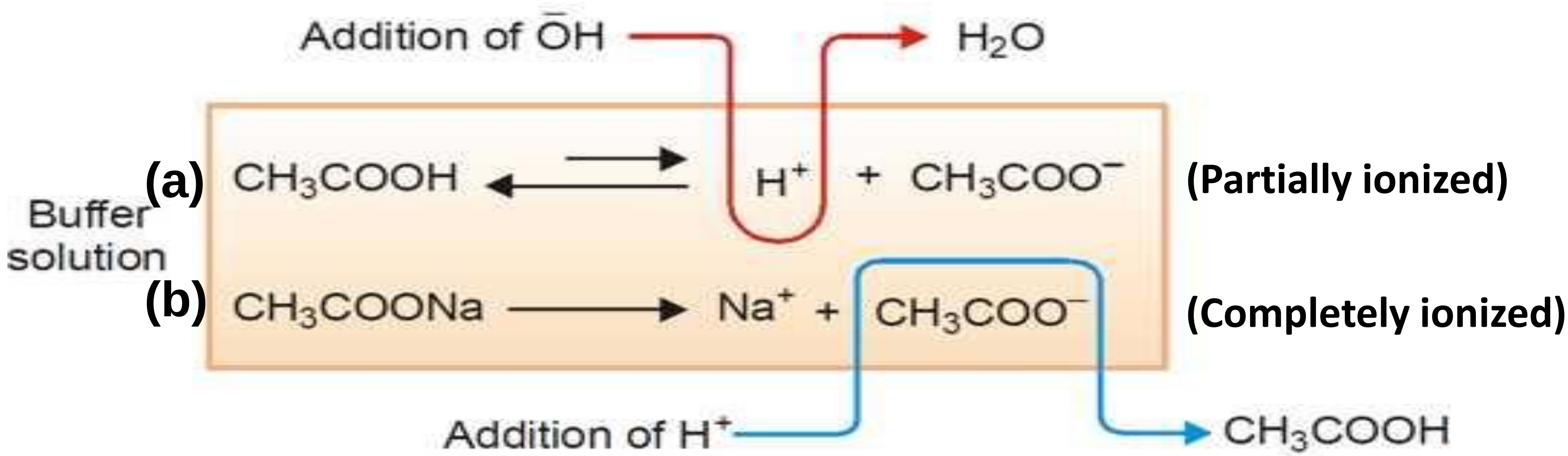
Mechanism of buffer action (VI)

The mechanism of buffer action can be explained with the help of common Ion effect and Le-chateliers principle. Let us take acidic buffer of acetic acid & sodium acetate where acetic acid being a weak electrolyte is partially Ionized where as salt is completely ionized as given in equation (a) and (b), respectively.

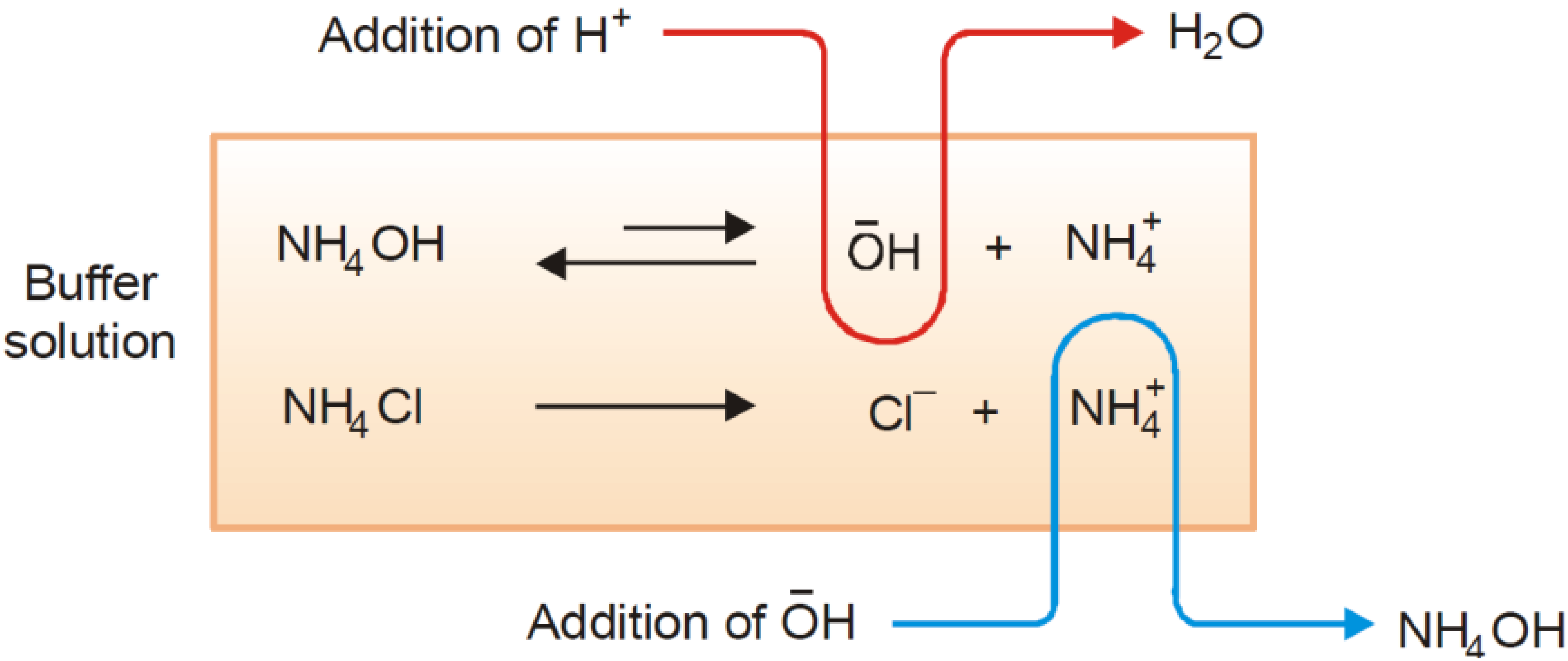
When small amount of strong base (eg NaOH) is added , OH^- ion of base combines with $H^+$of buffer system and decreases the amount of H^+ in system which makes the disturbance of equilibrium state of eq (a). But according to Le-chateliers principle, this disturbance is minimized by shifting the equilibrium state of eq (a) towards right side (to fulfill the decresed amount of H^+ ion), ie,. amount of H^+ remains constant and therefore, there is no change in pH of buffer solution



Similarly, when small amount of strong acid (eg HCl) is added , H^+ concentration In buffer system is increased which makes the disturbance of equilibrium state of eq (a). But according to Le-chateliers principle, this disturbance is minimized by shifting the equilibrium state of eq (a) towards left side, ie,.H^+ of HCl combines with CH_3COO^- of sodium acetate to give CH_3COOH. In this way we are adding strong acid but there is formation of unionized weak acid and therefore, there is no change in H^+ concentration which maintain pH almost constant.



For basic buffer action mechanism explain yourselves



Buffer capacity

<u>**Buffer capacity (β) is defined as the amount of a strong acid or a strong base that has to be added to 1 litre of a buffer to cause pH change of 1 pH unit: ie.,**</u>

$$\beta = \frac{\Delta c_b}{\Delta pH} = -\frac{\Delta c_{ac}}{\Delta pH}$$

The buffer capacity depends on the amounts of substance of the weak acid and its conjugated base (or weak base and its conjugate acid) in the buffer. The buffer capacity is maximum with 1:1 ratio of conjugate acid base pair. Moreover, its value decreases with increasing dilution

Question; which has highest buffer capacity

a. 0.1 M HF and 0.1M NaF
b. 1M HF and 1M NaF
c. 0.001M HF and 0.001M NaF
d. 1M HF anf 0.1M NaF

Calculation of pH of buffer solution
Henderson Equation

Derivation;

Let us take acidic buffer of acetic acid (HA) and sodium acetate (NaA)

(a) HA + H2O $\rightleftharpoons$ A + H3O$^+$ (feebly ionized)
(b) NaA $\longrightarrow$ A$^-$ + Na$^+$ (completely ionized)

By applying law of mass action at equilibrium state of eq (a)

$$Keq = \frac{[H_3O^+]\,[A^-]}{[HA\,[H_2O]]} \quad ....(1)$$

$$\text{Or, } Keq \times [H_2O] = \frac{[H_3O^+]\,[A^-]}{[HA\,]}$$

$$\text{Or, } K_a = \frac{[H_3O^+]\,[A^-]}{[HA\,]}$$

$$\text{Or, } [H_3O^+] = K_a \frac{[HA]}{[A^-\,]} \quad ....(2)$$

Taking log of this equation (2)

$$\text{Or, } \log_{10} [H_3O^+] = \log_{10} K_a + \log \frac{[HA]}{[A^-]}$$

$$\text{Or, } -\log_{10} [H_3O^+] = -\log_{10} K_a - \log \frac{[HA]}{[A^-]}$$

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

$$pH = pKa + \log_{10} \frac{[Salt]}{[Acid]} \quad ....(3)$$

For basic buffer solution

$$pOH = pKb + \log_{10} \frac{[Salt]}{[Base]} \quad ....(4)$$

Equation (3) and (4) are Henderson equation

Q1. Calculate the pH mixture containing 100 ml of 0.5M NH_4OH and 400 ml of 0.1M NH4Cl (Kb of NH_4Cl = 1.8 x 10-5).

Solution; Total volume = 100 + 400 = 500 ml

New concentration of NH4OH ; $N_1V_1 = N_2V_2$

$$0.5 \times 100 = N_2 \times 500$$

$$N2 = 0.5 \times 100/500 = 0.1M$$

New concentration of NH4Cl; $N_1V_1 = N_2V_2$

$$0.1 \times 400 = N_2 \times 500$$

$$N_2 = 0.1 \times 400/500 = 0.08M$$

Click to add text

$$pOH = pKb + \log_{10} \frac{[Salt]}{[Base]}$$

$$pOH = 4.74 + \log_{10} \frac{(0.08)}{(0.1)}$$

$$pOH = 4.74 + (-0.0967)$$

$$= 4.64$$

Q2. Calculate the weight in gram of CH_3COONa required to make acidic buffer having pH= 5.2 with acetic acid having 1.2 L of 0.1 M CH_3COOH (PKa = 4.74).

Solution;

$$pH = pKa + \log_{10} \frac{[Salt]}{[Acid]}$$

$$5.2 = 4.74 + \log_{10} \frac{(Salt)}{(0.1)}$$

$$\log \frac{(Salt)}{(0.1)} = 0.46$$

$$\frac{[Salt]}{0.1} = 10\ 0.46$$

$$= 0.2884$$

[Salt] = 0.2884M

M = wt in gm/molecular weight x vol. in ltr

0.2884 = x / 82x1.2

X = 28.37 g

Q3. 4 millimole of NaOH is added to 200 ml of a buffer which is 0.1 M acetic acid and 0.1 M in sodium acetate. Calculate the change in pH of the solution.

Solution;

Before the addition of NaOH

$$pH = pKa + \log_{10} \frac{[Salt]}{[Acid]}$$

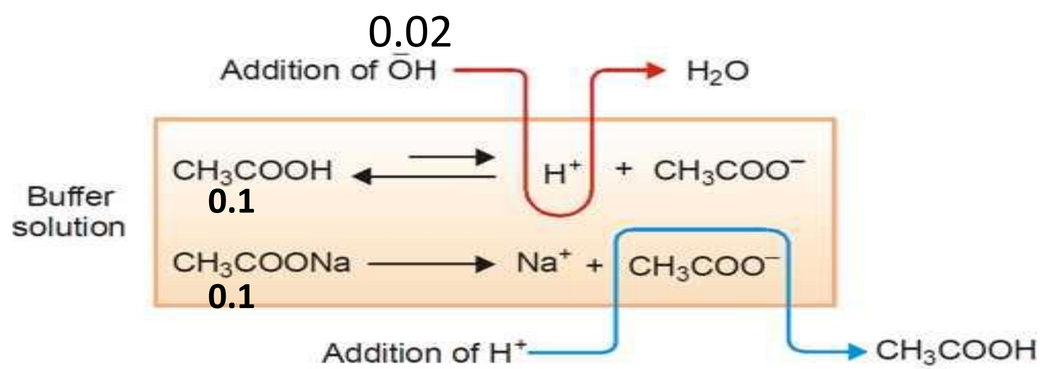
$$pH = 4.74 + \log_{10} \frac{(0.1)}{(0.1)}$$

$$pH = 4.74$$

After the addition of NaOH

Molarity of NaOH = no of millimole/vol in ml

= 4/200 = 0.02M



Now, concentration of acid = 0.1- 0.02

Concentration of salt = 0.1 + 0.02

$$pH = 4.74 + \log_{10} \frac{(0.12)}{(0.08)}$$

$$pH = 4.74 + 0.176$$

$$pH = 4.91$$

Change of pH = 4.91-4.74

= 0.17

Question for examination

1 . What is buffer solution?

2. Give the mechanism of buffer action.

3. What do you mean by buffer capacity?

4. Write down five example of basic buffer.

5. Is our blood a buffer system? If yes, what are the components for this buffer?

Project work

1. Is there any acidic buffer having pH > 7? Find out the answer and explain with suitable example.

2. List out the product applied in health care technology (BIOMEDICAL ENGINEERING) using buffer system for their industrial production.

Submission date of Tutorial

2078/3/15

Next time corrosion