

pH

It is defined as the negative logarithm(log) of the hydrogen ion concentration. It can be expressed as,

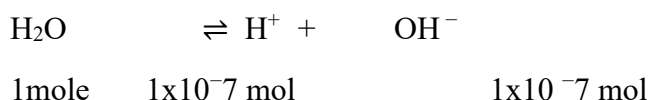
$$\text{pH} = -\log [\text{H}^+]$$

where $[\text{H}^+]$ is the hydrogen ion concentration/moles per liter.

Similarly, the concentration of OH^- ions in aqueous solution of a base is given as,

$$\text{pOH} = -\log [\text{OH}^-]$$

Now to define the pH, let's take an example of autoionization of Pure water at 25° C,



Here, very small concentrations of water is ionized relative to that of non-ionized water.

So, $\text{H}^+ = 1 \times 10^{-7}$

Taking $-\log$ on both sides,

$$\begin{aligned} -\log [\text{H}^+] &= -\log(1 \times 10^{-7}) \\ &= -[\log(1) + \{-7(\log 10)\}] \\ &= -[-7 \times 1] \\ &= 7 \end{aligned}$$

Therefore, $\text{pH} = 7$

Similarly, $\text{OH}^- = 1 \times 10^{-7}$

Taking $-\log$ on both sides,

$$\begin{aligned} -\log [\text{OH}^-] &= -\log(1 \times 10^{-7}) \\ &= -[\log(1) + \{-7(\log 10)\}] \\ &= -[-7 \times 1] \\ &= 7 \end{aligned}$$

Therefore, $\text{pOH} = 7$

Now $\text{pH} + \text{pOH} = 7 + 7 = 14$

$$\text{and } \text{pH} = 14 - \text{pOH}$$

Now, pH in terms of dissociation constant,

Again, dissociation constant (ionization constant/autoionization constant) of water, is expressed as,

$$K_w = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = [\text{H}^+][\text{OH}^-], \text{ where } K_w = \text{dissociation constant of water}$$

(\therefore when one of the component in reaction have excess of concentration as compared to others, its concentration is considered as unity, so $[\text{H}_2\text{O}] = 1$)

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

$$= 10^{-14} \text{ at } 25^\circ\text{C}$$

Taking Log on both sides,

$$-\log K_w = -(\log[\text{H}^+] + \log[\text{OH}^-])$$

$$\text{p}K_w = \text{pH} + \text{pOH} = 14$$

Where p is just a p -factor represents $-\log$, whereas, [] is activity represents concentration in mol/l

Question = what will be the pH of the solution when the concentration of $[\text{H}^+]$

is 10^{-2}

Ans: $\text{pH} = 2$ (Power of concentration is equal to pH)

Notes to remember

$$1. \text{pH} = -\log [\text{H}^+]$$

$$2. \text{pOH} = -\log[\text{OH}^-]$$

$$3. \text{pH} + \text{pOH} = 7 + 7 = 14$$

$$\text{and } \text{pH} = 14 - \text{pOH}$$

4. Ionization/dissociation constant of Water,

$$K_w = \frac{[H^+][OH^-]}{[H_2O]} = [H^+][OH^-]$$
$$= 10^{-14} \text{ at } 25^\circ\text{C}$$

5. $pK_w = pH + pOH = 14$

6. Ionization constant of water = K_w

$$pK_w = -\log K_w$$

Ionization Constant of acid = K_a ,

$$pK_w = -\log K_w$$

Ionization constant of base = K_b

$$pK_w = -\log K_w$$

7. The equilibrium constant (K_w , K_a and K_b) measures the degree of dissociation of a water or acid or base in specified condition.

8. K_a and K_b are related to each other through the ion constant for water, K_w ;

$$K_w = K_a \times K_b$$

pKa and pKb of common weak acid and bases

Name	Formula	K_a	K_b	pK_a	pK_b
acetic	CH ₃ COOH	1.8×10^{-5}		4.74	
Ammonia/ Ammonia solution	NH ₄ OH		1.8×10^{-5}		4.75

Problem : 1

What is the pH of a solution of

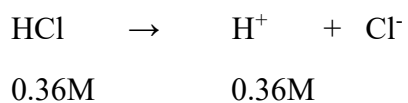
a) 0.36 M HCl

b) 0.62 M NaOH,

solution,

Now for a) 0.36HCl

Here HCl is strong acid, so it completely dissociates

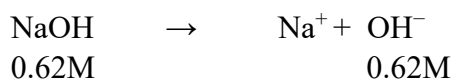


We know,

$$\begin{aligned} \text{pH} &= -\log[\text{H}^+] \\ &= -\log[0.36] \\ &= 0.4 \end{aligned}$$

\therefore pH of the 0.36 M HCl is 0.4

b) 0.62 M NaOH



We know,

$$\begin{aligned} \text{pOH} &= -\log[\text{OH}^-] \\ &= -\log[0.62] \\ &= 0.20 \end{aligned}$$

Now for pH;

$$\begin{aligned} \text{pH} &= 14 - \text{pOH} \\ &= 14 - 0.20 \\ &= 13.8 \end{aligned}$$

\therefore pH of 0.62M NaOH is 13.8

Problem- weak acid/base

Problem 1. Hydrofluoric acid has a K_a value of 7.2×10^{-4} . What is the pH of a 0.04M solution of hydrofluoric acid?

Solution;

Hydrofluoric acid is a weak acid, The balanced reaction for hydrofluoric acid in water is:

\therefore pH of a 1.5M ammonia solution is ---?

Problem3. A sample of gastric juice has a pH of 2.5. What is the hydrogen ion concentration in this secretion?

Problem 4. what is the pH of 0.05M aqueous solution of NaCN? pKb of CN⁻ is 4.74. Ans=pH-11.5

Solution,

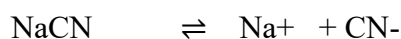
Given,

$$[\text{NaCN}] = 0.05\text{M}$$

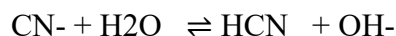
$$\text{pKb of CN}^- = 4.74$$

$$\text{Kb} = ?$$

Here NaCN completely dissociates in water to give Na⁺ and CN⁻. CN⁻ get hydrolyzed to give HCN and OH⁻.



$$0.05\text{M} \qquad 0.05\text{M} \qquad 0.05\text{M}$$



$$0.05-x \qquad x \qquad x$$

Now apply dissociation constant of CN⁻ is given as;

$$\text{Kb} = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}$$

..... Do yourself

Problem 5. Calculate the pH of a 0.1M acetic acid when it is half neutralized. (K_a=1.7 x 10⁻⁵).
Ans- 3.03

Solution:

Dissociation of acetic acid takes place as,



Here concentration of CH₃COOH is 0.1, but it is half neutralized, so its concentration now becomes 0.05M

----- Try it to do.

Buffer solution

A buffer solution resists a change in pH when small amounts of acid or base are added.

Example. A solution of acetic acid and sodium acetate($\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$), ammonium chloride and ammonium hydroxide($\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$) etc.

Types of buffer solution:- there are two types of buffer solution;

- a) Acidic buffer
- b) Basic buffer

Acidic buffer :

The buffer solution whose pH is less than 7 is called acidic buffer. Generally, it contains the mixture of weak acid and its salt with strong base.

Eg. $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ - Acetate Buffer

$\text{HCOONa} + \text{HCOOH}$ –formate buffer

$\text{Na}_2\text{HPO}_4 + \text{NaH}_2\text{PO}_4$ –phosphate buffer etc.

Basic buffer:-

The buffer solution whose pH is greater than 7 is called basic buffer. Generally it contains the mixture of weak base and its salt with strong acid.

Eg. $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ = ammonia buffer

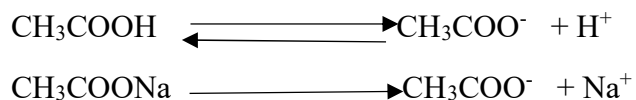
$\text{H}_2\text{CO}_3 + \text{HCO}_3^-$ = Carbonate buffer etc

Mechanism of buffer action:-

In order to explain the mechanism of buffer action let us consider acidic and basic buffer separately

- a) Mechanism of acidic buffer: -

Let us consider an acidic buffer solution containing acetic acid and sodium acetate. They ionize as;



Here, CH_3COOH is weak acid, so it ionises weakly and give rise to few H^+ ions and unionised CH_3COOH ; whereas, CH_3COONa is strong electrolyte, which give excess of CH_3COO^- ions. Because of large amount of CH_3COO^- ions, common ion effect comes into action and ionisation of CH_3COOH is suppressed.

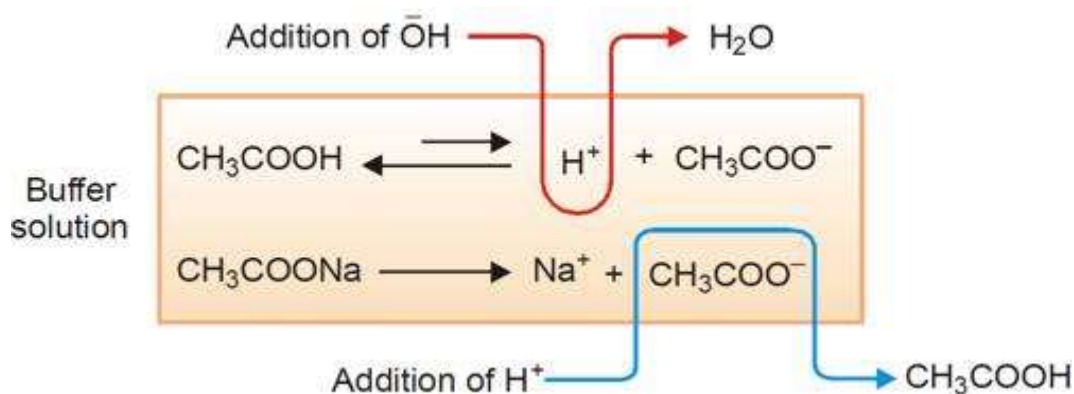
Adding acid:

When small amount of acid ie. HCl is added to the buffer solution, the H^+ ions combine with CH_3COO^- ions of buffer to form unionizing CH_3COOH so its pH value does not change.



Adding base:

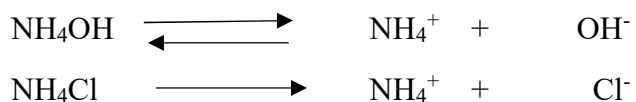
Similarly, when small amount of base ie NaOH is added to the buffer solution, the OH^- ions combines with H^+ ions of buffer to give H_2O . On the other hand, to maintain it constant H^+ ions the ionization of CH_3COOH takes place to some extent. So its pH value does not change.



In this way an acidic buffer maintains its constant pH value on addition of small amount of acid and base But after the equilibrium its pH value may change.

b) Mechanism of basic buffer: -

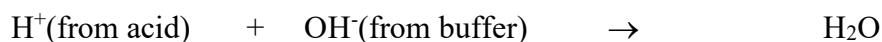
Let us consider a basic buffer solution containing ammonium hydroxide and ammonium chloride. They ionize as;



Here due to common ion effect ionization of NH_4OH is suppressed so the buffer solution contains large amount of NH_4^+ , Unionized NH_4OH and few OH^- ions.

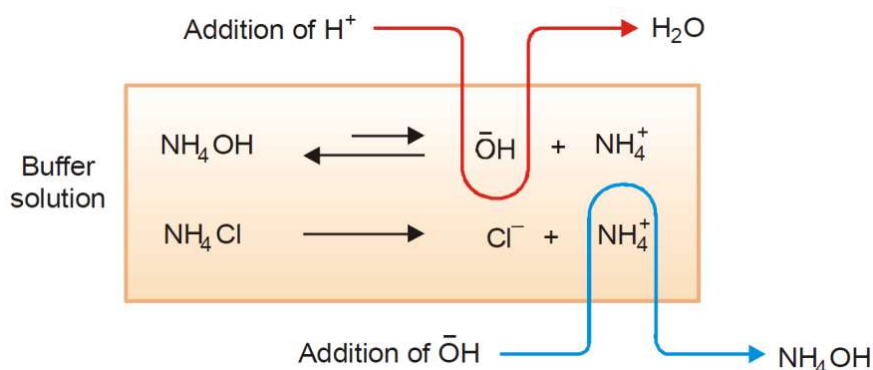
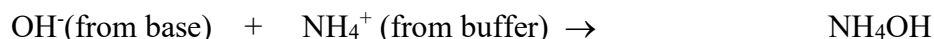
Adding acid:

when small amount of acid i.e. HCl is added to the buffer solution, the H^+ ions from acid combines with OH^- ions of buffer to give H_2O . But to maintain constant value of OH^- ions the ionization of NH_4OH takes place to some extent So its pH value does not change.



Adding base:

Similarly, when small amount of base i.e. NaOH is added to the buffer solution it provides OH^- ions to the buffer but it combines with NH_4^+ ions of buffer to form unionizing NH_4OH . so, its pH value does not change.



In this way a basic buffer maintains its constant pH value on addition of small amount of acid and base.

Que. Define buffer solution. Also explain the mechanism of acidic buffer containing acetic acid and sodium acetate.

Que . Mention the types of buffer. Explain the mechanism of basic buffer

pH of Buffer solution(how to calculate pH of buffer solution): -

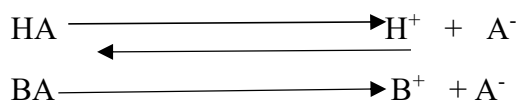
pH of buffer solution depends upon;

- ionization constant of weak acid or base;
- concentration of buffer components.

It is determined by Henderson's equation

Henderson's equation for acidic buffer: -

Let us consider an acidic buffer containing weak acid HA and its highly ionizing salt with strong base BA. They ionize as:



The ionization constant of weak acid is given by

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

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

Taking common -log on both sides

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

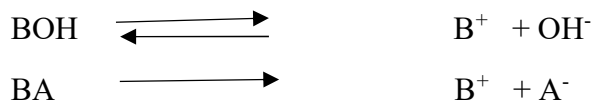
$$\text{Or, pH} = \text{p}K_a - \log \frac{[\text{acid}]}{[\text{salt}]}$$

$$\therefore \text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

This is the required Henderson's equation for acidic buffer.

Henderson's equation for basic buffer: -

Let us consider a basic buffer containing weak base BOH and its highly ionizing salt with strong acid BA. They ionize as



The ionization constant of weak base is given by

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

$$\text{Or, } [OH^-] = K_b \frac{[BOH]}{[B^+]}$$

Taking common -log on both sides

$$-\log [OH^-] = -\log(K_b) + (-\log \frac{[BOH]}{[B^+]})$$

$$\text{Or, } pOH = pK_b - \log \frac{[Base]}{[salt]}$$

$$\therefore pOH = pK_b + \log \frac{[salt]}{[Base]}$$

This is the required Henderson's equation for basic buffer.

Application of Buffer

Buffers have many applications. Some of which are

1. In biochemical process inside the body: uses buffer solution to maintain a constant pH. For example, blood contains a carbonate/bicarbonate buffer to keep the pH close to 7.4
2. In shampoos and soaps: uses buffer to maintain slightly acidic pH balance
3. In brewing industry: buffer solutions are added before fermentation to prevent the solution becoming too acidic
4. In textile industry: during dyeing, bleaching and finishing process buffer is used to maintain the correct pH

Numericals Related to Buffer

For acidic buffer; $pH = pK_a + \log \frac{[salt]}{[acid]}$

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \text{ for acids}$$

For basic buffer; $pOH = pK_b + \log \frac{[salt]}{[Base]}$

$$pOH = pK_b + \log \frac{[BH^+]}{[B]} \text{ for bases}$$

Example 1

Calculate the pH of a buffer solution containing 0.20 mol/L CH_3COOH and 0.50 mol/L CH_3COONa . K_a for CH_3COOH is 1.8×10^{-5} .

Solution;

Given,

$$[\text{CH}_3\text{COOH}] = 0.20 \text{ mol/L}$$

$$[\text{CH}_3\text{COONa}] = 0.50 \text{ mol/L}$$

$$\text{Ionization constant } K_a = 1.8 \times 10^{-5}$$

We know,

the Henderson-Hasselbalch for acidic buffer,

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{pH} = -\log (1.8 \times 10^{-5}) + \log \frac{0.50}{0.20}$$

$$\text{Or, pH} = -\log (1.8 \times 10^{-5}) + \log (2.5)$$

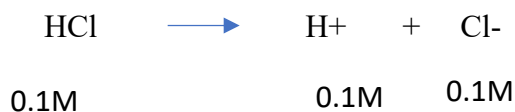
$$\text{Or, pH} = 4.74 + 0.40$$

$$\therefore \text{pH} = 5.14$$

Problem 3

The pH of a buffer solution containing 0.5 mol/l of CH_3COOH and 0.5 mol/l of CH_3COONa is 4.76. What will be the pH of the solution after addition of 0.1 mol/l HCl is added to buffer, assuming volume is unchanged. $K_a = 1.75 \times 10^{-5}$.

Solution;



Given,

$$[\text{CH}_3\text{COOH}] = 0.5\text{M} + 0.1\text{M} = 0.6\text{M}$$

$$[\text{CH}_3\text{COONa}] = 0.5\text{M} - 0.1\text{M} = 0.4\text{M}$$

$$\text{pH} = 4.76$$

Dissociation constant, $K_a = 1.75 \times 10^{-5}$

Again, $pK_a = -(\log K_a)$

$$= -(\log 1.75 \times 10^{-5})$$

$$= -4.75$$

Now, For Acidic Buffer

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

$$pH = 4.58$$

problem 4

A liter of buffer solution contains 0.1M CH_3COOH and 0.1M CH_3COONa with pH 4.74. what will be the pH of buffer solution after adding 5mL of 0.02M NaOH. K_a of acetic acid is 1.8×10^{-5} .

Solution,

Given;

$$[CH_3COOH] = 0.5M + 0.1M = 0.6M$$

$$[CH_3COONa] = 0.5M - 0.1M = 0.4M$$

$$pH = 4.76$$

Dissociation constant, $K_a = 1.75 \times 10^{-5}$

Problem 5

How many moles of sodium acetate and acetic acid must you use to prepare 1L of a 0.100 mol/L buffer with pH 5.00.

Solution

Given;

$$[CH_3COOH] + [CH_3COONa] = 0.1 \text{ mol/L}$$

$$\text{Ionization constant } K_a = 1.8 \times 10^{-5}$$

Let us consider, X moles of acid and

Y moles of salt is needed

we know, for acidic buffer ;

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{Or, } 5.00 = 4.74 + \log \frac{[\text{Y}]}{[\text{X}]}$$

$$\text{Or, } \log \frac{[\text{Y}]}{[\text{X}]} = 0.26$$

$$\text{or, } \frac{[\text{Y}]}{[\text{X}]} = 10^{0.26} = 1.82 \quad \text{or, } [\text{Y}] = 1.82[\text{X}]$$

We know, $[\text{X}] + [\text{Y}] = 0.1$ moles

$$\text{or, } [\text{X}] + 1.82 [\text{X}] = 0.1 \text{ moles}$$

$$\text{or, } 2.82[\text{X}] = 0.1 \text{ moles}$$

$$\text{or, } [\text{X}] = 0.0355 \text{ moles}$$

$$\therefore [\text{Y}] = (0.100 - 0.0355) \text{ moles}$$

$$= 0.0645 \text{ mol/L}$$

\therefore 0.0355 mol of acetic acid and 0.0645 mol of sodium acetate to prepare 1 L of the buffer.

Problem 6

A buffer solution contains 0.4 mole/lit NH_4OH and 0.6 mol/lit NH_4Cl . What will be the pH of the solution after adding 0.075 M HCl solution to the buffer? Assume that volume is unchanged. K_b of $\text{NH}_4\text{OH}(\text{NH}_3 \text{ solution})$ is 1.8×10^{-5} .

Problem 7

Calculate the pH of a solution obtained by mixing 0.083 moles of acetic acid and 0.091 moles of potassium acetate and making the volume 500ml. K_a of acetic acid is 1.75×10^{-5} .