

Chapter-8

ACIDS, BASES AND SALTS

Acids were originally identified by their sour taste while bases by their bitter taste and slippery touch. Now acids and bases are identified by the colour changes of dyes called indicator.

Science Society relationship:

Hyperacidity (Stomach acidity) is a common problem. Most of the people in third world experience bouts of acidity attacks. Stomach secretes gastric juice which contains HCl to liquefy your sumptuous meal. However, due to certain pathological conditions (some disease process) and physiological conditions (stress, emotions, smoking and dietary factors like chilies, alcohol excessive tea or coffee) excess of HCl is secreted by stomach cells. This condition is known as hyperacidity. A person suffering from hyperacidity feels a burning sensation just above the stomach, or right below your breast bone. This is the most classic sign of acidity. Other people experience acid bad mouth. This happens when you are lying horizontal on your bed. You may have a sour taste in your mouth, which resembles the taste of an orange that had gone stale.

Acidic, Basic and Amphoteric Substances:

There are three theories or concepts about acids and bases namely Arrhenius concept, Bronsted-Lowery concept and Lewis concept.

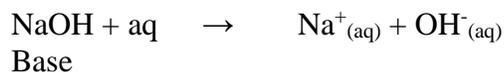
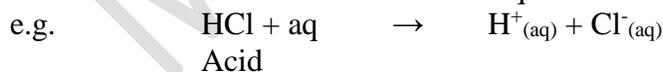
(i) Arrhenius Concept of Acids and Bases:

According to Arrhenius concept,

“A substance that furnish H^+ ions in aqueous solutions is called acid”

and

“A substance that furnish OH^- ions in aqueous solutions is called base”

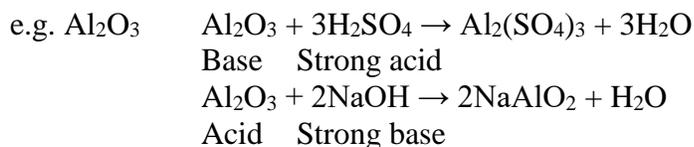


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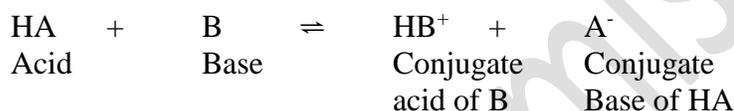
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“A substance which act both as acid as well as a base is called amphoteric substance”

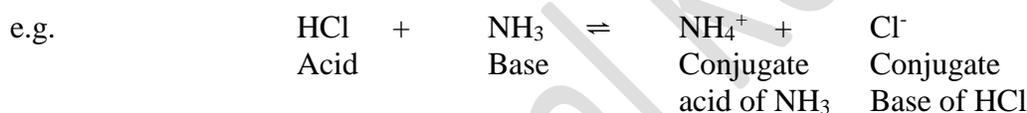


(ii) Bronsted-Lowery Concept of Acids and Bases:

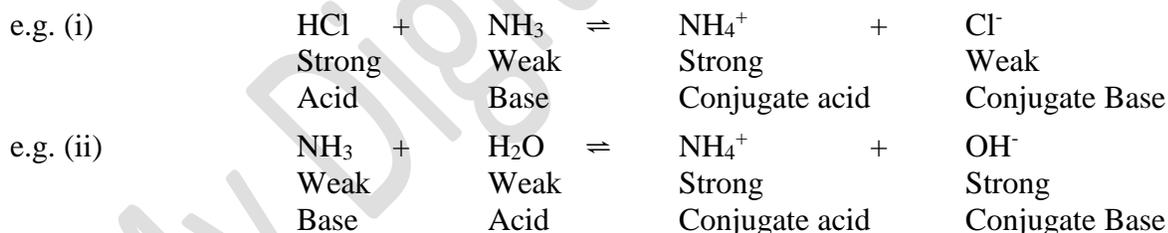
According to Lowry-Bronsted concept, acid is proton donor while base is proton acceptor. It further states that an acid after donating proton becomes a base and is known as conjugate base, similarly a base after accepting proton becomes an acid and is known as conjugate acid.



The process is reversible and establishes equilibrium. There is difference of one proton between an acid and its conjugate base, similarly there is difference of one proton between a base and its conjugate acid.



If acid is strong its conjugate base will be a weak base and vice versa. Similarly when base is strong its conjugate acid will be a weak acid and vice versa.



Advantages of Bronsted-Lowery Concept:

- (i) Arrhenius concept of acids and bases is restricted to only aqueous solutions, while Bronsted-Lowery concept is applicable non-aqueous solutions, which can also gain or lose proton.
- (ii) Bronsted-Lowery concept can also be extended to gases
 e.g. $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$
 Base Acid

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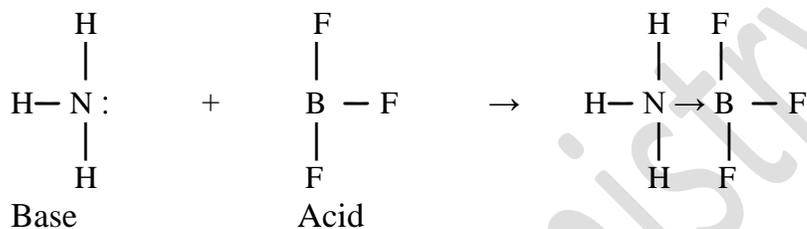
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Limitation:

Bronsted-Lowery concept is restricted to reaction involving proton transfer.

(iii) Lewis Concept of Acids and Bases:

According to Lewis concept, acid is electron pair acceptor while base is electron pair donor.

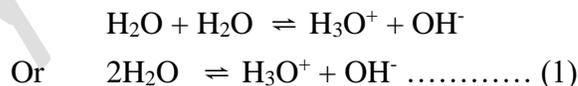
**Expressing the strength of Acid and Base:**

The acids and bases that dissociates completely in ions are called strong acids and bases, while weak acids and bases dissociates only partially.

The strength of acids and bases is expressed in terms of $[\text{H}^+]$, $[\text{OH}^-]$, pH, pOH, K_a , K_b , $\text{p}K_a$ & $\text{p}K_b$.

Self Ionization of Water:

Pure water is very poor conductor of electricity which shows that it dissociates into ions to small extent. Water undergoes self ionization. Water is amphoteric i.e. it act as proton donor as well as proton acceptor. In self ionization one water molecule donates proton while other accepts proton.



H_3O^+ is strong acid than H_2O while OH^- is strong base than H_2O therefore the reverse reaction is favoured and equilibrium lies to the left or in other words water dissociates to a very small extent. The dissociation of water can also be written as



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Its equilibrium expression can be written as

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

$$K_c [\text{H}_2\text{O}] = [\text{H}_3\text{O}^+][\text{OH}^-] \quad \text{or} \quad [\text{H}^+][\text{OH}^-]$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}^+][\text{OH}^-]$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14} \dots\dots\dots (3)$$

K_w is ionic product of water.

According eq-1 or 2 there are equal number of H^+ and OH^- ions so

$$[\text{H}_3\text{O}^+] \text{ or } [\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7}$$

The ionic product of aqueous Solution of acids as well as bases is also same as is for water i.e 10^{-14}

So we can write

$$K_w \text{ for acid, base and neutral solutions} = [\text{H}^+][\text{OH}^-] = 10^{-14}$$

However for water

$$[\text{H}_3\text{O}^+] \text{ or } [\text{H}^+] = 10^{-7} \quad \text{and} \quad [\text{OH}^-] = 10^{-7}$$

for acid

$$[\text{H}_3\text{O}^+] \text{ or } [\text{H}^+] > 10^{-7} \quad \text{and} \quad [\text{OH}^-] < 10^{-7}$$

for base

$$[\text{H}_3\text{O}^+] \text{ or } [\text{H}^+] < 10^{-7} \quad \text{and} \quad [\text{OH}^-] > 10^{-7}$$

e.g. For 0.00015M HCl if we calculate H^+ ion and OH^- ion concentrations



It shows that $[\text{H}^+] = [\text{HCl}] = 0.00015 = 1.5 \times 10^{-4}$ which is greater than 10^{-7}

But

$$[\text{H}^+][\text{OH}^-] = 10^{-14}$$

Therefore

$$[\text{OH}^-] = \frac{10^{-14}}{[\text{H}^+]}$$

Or

$$[\text{OH}^-] = \frac{10^{-14}}{1.5 \times 10^{-4}} = 6.7 \times 10^{-11} \text{ which is less than } 10^{-7}$$

So we find that for acid

$$[\text{H}^+] > 10^{-7} \quad \text{and} \quad [\text{OH}^-] < 10^{-7}$$

pH and pOH:

Although strength of an acid or base could be measured in terms of its H^+ ion or OH^- ion concentrations but the values are not convenient to memorize. Therefore in 1909 Sorenson developed a logarithmic scale to measure these concentrations known as pH and pOH scales.

pH i.e. power of hydrogen or hydronium ion is defined as “*Log of reciprocal of hydrogen ion or hydronium ion concentration or negative log of hydrogen or hydronium ion concentration*”.

$$\text{pH} = \log \frac{1}{[\text{H}_3\text{O}^+]} = \log \frac{1}{[\text{H}^+]}$$

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Or
$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log[\text{H}^+] \dots\dots\dots (4)$$

It means a solution having higher hydrogen ion concentration will have low pH and vice versa. pH scale varies from 0 to 14.

For water	pH = 7
For acid	pH < 7
For base	pH > 7

pOH i.e. power of hydroxyl ion is defined as “Log of reciprocal of hydroxyl ion concentration or negative log of hydroxyl ion concentration”.

$$\text{pOH} = \log \frac{1}{[\text{OH}^-]}$$

Or
$$\text{pOH} = -\log [\text{OH}^-] \dots\dots\dots (5)$$

It means a solution having higher hydroxyl ion concentration will have low pOH and vice versa. pOH scale varies from 0 to 14.

For water (neutral)	pOH = 7
For acid	pOH > 7
For base	pOH < 7

Relationship between pH and pOH:

Consider eq-3 i.e. $K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] \text{ or } [\text{H}^+] [\text{OH}^-] = 1 \times 10^{-14}$

Or $[\text{H}_3\text{O}^+] [\text{OH}^-] \text{ or } [\text{H}^+] [\text{OH}^-] = 10^{-14}$

Taking log of both sides $\log [\text{H}_3\text{O}^+] [\text{OH}^-] \text{ or } \log [\text{H}^+] [\text{OH}^-] = \log 10^{-14}$

Using log properties $\log [\text{H}_3\text{O}^+] + \log [\text{OH}^-] \text{ or } \log [\text{H}^+] + \log [\text{OH}^-] = -14 \log 10$

Or $\log [\text{H}_3\text{O}^+] + \log [\text{OH}^-] \text{ or } \log [\text{H}^+] + \log [\text{OH}^-] = -14 \times 1$

Multiplying both sides by negative $-\log [\text{H}_3\text{O}^+] - \log [\text{OH}^-] \text{ or } -\log [\text{H}^+] - \log [\text{OH}^-] = 14$

Or $\{-\log [\text{H}_3\text{O}^+]\} - \log \{[\text{OH}^-]\} \text{ or } \{-\log [\text{H}^+]\} + \{-\log [\text{OH}^-]\} = 14$

As $-\log [\text{H}_3\text{O}^+] \text{ or } -\log [\text{H}^+]$ is pH and $-\log [\text{OH}^-]$ is pOH so above expression becomes

$$\text{pH} + \text{pOH} = 14 \dots\dots\dots (6)$$

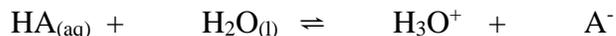
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Acid Dissociation Constant, K_a :

When a weak acid is dissolved in water it dissociates to a little extent and establishes equilibrium



Its equilibrium expression can be given as

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

Since concentration of water (being solvent) is constant so we can write

$$K_c[\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

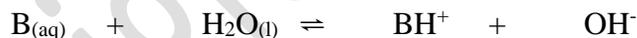
$$\text{Or } K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

Where, K_a is dissociation constant for weak acids. It represents the extent to which an acid dissociates in aqueous solution. It also shows the strength of an acid.

e.g. K_a for Acetic acid (CH_3COOH) is 1.8×10^{-5} so it is a weak acid and it dissociates only 1.3%.

Base Dissociation Constant, K_b :

When a weak base is dissolved in water it dissociates to a little extent and establishes equilibrium.



Its equilibrium expression can be given as

$$K_c = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}][\text{H}_2\text{O}]}$$

Since concentration of water (being solvent) is constant so we can write

$$K_c[\text{H}_2\text{O}] = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

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

Where as K_b is dissociation constant for weak bases. It represents the extent to which a base dissociates in aqueous solution. It also shows the strength of a base.

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e.g. K_b for Ammonium hydroxide (NH_4OH) is 1.81×10^{-5} so it is a weak base and it dissociates very little.

pK_a and pK_b :

These are logarithmic forms of K_a and K_b respectively. They have convenient values to memorize than that of K_a and K_b .

pK_a is defined as “Log of reciprocal of K_a or negative log of K_a ”.

$$pK_a = \log \frac{1}{K_a} = -\log K_a$$

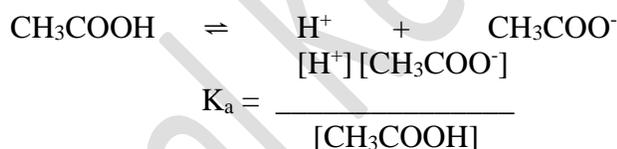
pK_b is defined as “Log of reciprocal of K_b or negative log of K_b ”.

$$pK_b = \log \frac{1}{K_b} = -\log K_b$$

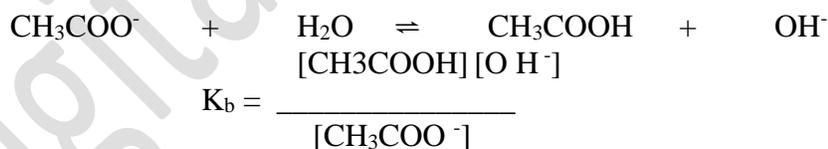
Larger is pK_a low will be K_a and weaker will be the acid and vice versa. Similarly larger is pK_b low will be K_b and weaker will be the base and vice versa.

Relationship between K_a and K_b also between pK_a and pK_b :

To establish relationship between K_a and K_b consider following case



CH_3COO^- is a strong conjugate base, it reacts with water according to following



Product of K_a and K_b can given as

$$K_a \times K_b = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \times \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

Or $K_a \times K_b = [\text{H}^+][\text{OH}^-]$

Or $K_a \times K_b = K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$
 $K_a \times K_b = 10^{-14}$

Taking log of above relation

$$\begin{aligned} \log (K_a \times K_b) &= \log K_w = \log 1 \times 10^{-14} \\ \log K_a + \log K_b &= \log K_w = -14 \log 10 \\ \log K_a + \log K_b &= \log K_w = -14 \times 1 && \text{as } \log 10 = 1 \\ \log K_a + \log K_b &= \log K_w = -14 \end{aligned}$$

Multiplying both sides by negative

$$[-\log K_a] + [-\log K_b] = -\log K_w = -(-14)$$

Or $\boxed{pK_a + pK_b = pK_w = 14}$

- Conjugate base of a weak acid is a strong base and vice versa.
- Conjugate acid of a weak base is a strong acid and vice versa
- Stronger is the acidic strength of an acid weaker will be its basic strength. So $K_a \propto 1/K_b$

Leveling Effect:

The strong acids having close pKa values dissociates completely in water and show leveling effect.

“Acids having very close pKa values, dissociate to same extent in water. This dissociation of acids to same extent is called leveling effect.”

Water is called leveling solvent as it levels all strong acids to same strength.

It is not possible to find the order of increasing strengths of these acids because they dissociates completely in water. However, significant difference in their strengths is observed when they are dissolved in anhydrous acetic acid.

Acid	pKa	Acid	pKa
HClO ₄	-10	(COOH) ₂	1.3
HI	-10	H ₂ SO ₃	1.8
HBr	-9	CH ₃ COOH	4.7
HCl	-7	H ₂ CO ₃	6.4
H ₂ SO ₄	-3	H ₂ S	7.0
HNO ₃	-3	NH ₄ ⁺	9.3
HClO ₃	-1	HCN	9.4

This shows $\text{HClO}_4 > \text{HCl} > \text{H}_2\text{SO}_4$

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Buffer Solutions:

Normally if acidic or basic solutions are stored for longer time, they change their pH. Acids react with base component of glass container and are neutralized so their pH changes while bases react with carbon dioxide of air and are neutralized so their pH changes. On other hand there are solutions which maintain their pH, they are called Buffers.

“The solutions which maintain their pH even on addition of small amount of acid or base, are called buffers”

- pH of buffer solutions also changes but very slightly that can be neglected.

A buffer could be:

- Solution of a weak acid and its highly ionizable salt
e.g. $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$, $\text{H}_2\text{CO}_3/\text{NaHCO}_3$ or
- Solution of a weak base and its highly ionizable salt
e.g. $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$, $\text{NH}_3/\text{NH}_4\text{Cl}$ or
- Solution of salt of a weak acid and a weak base
e.g. $\text{CH}_3\text{COONH}_4$

Buffer Action:

“The technique or mechanism by which a buffer acts to maintain its pH is called buffer action.”

OR

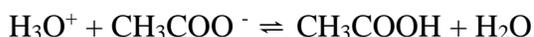
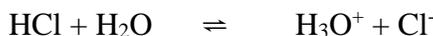
“The resistance offered by a buffer solution to change in pH on addition of acid or base” is called buffer action.

- Buffer containing a weak acid and its highly ionizable salt e.g. Solution of CH_3COOH and CH_3COONa .



Due to common ion effect the dissociation of acetic acid will be suppressed in presence of common acetate ions, so acetic acid will almost remain un-ionized.

When an acid such as HCl is added to this solution, the hydronium ions produced by HCl will combine with acetate ions to form un-ionized acetic acid.



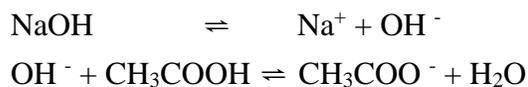
As hydronium ions produced by HCl are removed so pH remains same. Equilibrium of rxn-2 will shift to the right to produce acetate ions that are consumed by hydronium ions.

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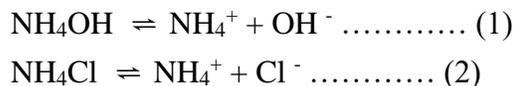
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When a base such as NaOH is added to this solution, the hydroxyl ions produced by NaOH will combine with acetic acid.



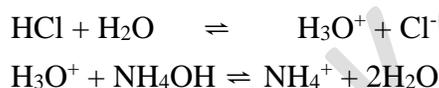
As hydroxyl ions produced by NaOH are removed so pH remains same. Equilibrium of rtn-2 will shift to the left to consume the increased acetate ions.

(ii) Buffer containing a weak base and its highly ionizable salt e.g. Solution of NH_4OH and NH_4Cl .



Due to common ion effect the dissociation of ammonium hydroxide will be suppressed in presence of common ammonium, so ammonium hydroxide will almost remain un-ionized.

When an acid such as HCl is added to this solution, the hydronium ions produced by HCl will combine with ammonium hydroxide.



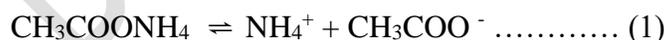
As hydronium ions produced by HCl are removed so pH remains same. Equilibrium of rtn-2 will shift to the left to consume the increased ammonium ions.

When a base such as NaOH is added to this solution, the hydroxyl ions produced by NaOH will combine with ammonium ions to produce un-ionized ammonium hydroxide.

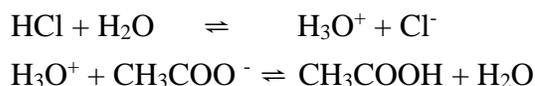


As hydroxyl ions produced by NaOH are removed so pH remains same. Equilibrium of rtn-2 will shift to the right to produce ammonium ions which are consumed in above reaction.

(iii) Buffer containing salt of a weak acid and a weak base e.g. Solution of $\text{CH}_3\text{COONH}_4$.



When an acid such as HCl is added to this solution, the hydronium ions produced by HCl will combine with acetate ion to produce un-ionized acetic acid.



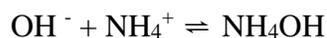
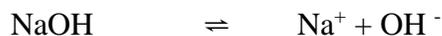
As hydronium ions produced by HCl are removed so pH remains same. Equilibrium of rtn-1 will shift to the right to produce acetate ions which are consumed in above reaction.

When a base such as NaOH is added to this solution, the hydroxyl ions produced by it will combine with ammonium ions to produce un-ionized ammonium hydroxide.

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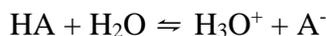
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As hydroxyl ions produced by NaOH are removed so pH remains same. Equilibrium of rtn-1 will shift to the right to produce ammonium ions which are consumed in above reaction.

Calculations of pH of Buffer Solution:

For a weak acid we can write



Expression for dissociation of acid can be written as

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

Or

$$[\text{H}_3\text{O}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]}$$

Taking log of both sides

$$\log [\text{H}_3\text{O}^+] = \log \left[K_a \times \frac{[\text{HA}]}{[\text{A}^-]} \right]$$

Using log property we can write

$$\log [\text{H}_3\text{O}^+] = \log K_a + \log \frac{[\text{HA}]}{[\text{A}^-]}$$

Multiplying both sides by negative

$$-\log [\text{H}_3\text{O}^+] = -\log K_a - \log \frac{[\text{HA}]}{[\text{A}^-]}$$

But $-\log [\text{H}_3\text{O}^+] = \text{pH}$ and $-\log K_a = \text{p}K_a$ so above expression can be written as

$$\text{pH} = \text{p}K_a - \log \frac{[\text{HA}]}{[\text{A}^-]}$$

Or

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Since A^- is ion from salt and its concentration is equal to that of salt, furthermore A^- is anion of weak acid so it is a strong conjugate base. While HA is an acid so we can write

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Base}]}{[\text{Acid}]}$$

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For buffer consisting of weak acid and its ionizable salt, the equation can be written as

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

For buffer consisting of weak base and its ionizable salt, the equation can be written as

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Base}]}{[\text{Salt}]}$$

This relation is called Henderson – Hasselbalch equation, used for calculating pH of buffer solutions.

Applications of Buffers:

- (i) They are used in industrial processes, where these processes are interrupted by large pH changes e.g. electroplating, leather, photographic materials, dyes etc.
- (ii) They are used in bacteriological research culture media, because a constant pH is required for the growth of bacteria being studied.
- (iii) Biochemical reactions in both animals and plants are very sensitive to pH changes, so buffer are needed to maintain pH in animals and plants e.g. pH of Human blood is 7.4 and is maintained by bicarbonates, phosphates and complex protein system.
- (iv) Buffers are used during study of proteins because the magnitude and kind of electrical charge carried by protein molecules depend on the pH.
- (v) Buffers are used in analytical chemistry research.
- (vi) Buffers are used in the form of fertilizer in soil to maintain pH of soil for getting good crops.
- (vi) Buffers are used for pH calibration.

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Hydrolysis of Salts:

Reaction of water with salt to produce acid and base is called hydrolysis. It is opposite of neutralization. In hydrolysis reaction H-OH bond breaks. A salt consists of cations or basic radicals and anions or acidic radicals. Salts are of four types

(i) Salts of strong acid and strong base:

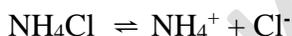
When salts of strong acid and strong base are dissolved in water they dissociate into ions e.g. NaCl, KBr, SrCl₂.



Na⁺ ion is from strong base so it is weak conjugate acid and it will not show hydrolysis reaction with water similarly Cl⁻ ion is from strong acid so it is weak conjugate base and it will also not show hydrolysis reaction with water. Thus the solution will be neutral having pH = 7.

(ii) Salts of strong acid and weak base:

When salts of strong acid and weak base are dissolved in water they dissociate into ions e.g. NH₄Cl, CuSO₄.



NH₄⁺ ion is from weak base so it is strong conjugate acid and it will show hydrolysis reaction with water and produces H₃O⁺ ion.



while Cl⁻ ion is from strong acid so it is weak conjugate base and it will not show hydrolysis reaction with water. Thus the solution will be acidic due to increased H₃O⁺. pH of solution < 7
Similarly



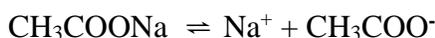
Cu²⁺ ion is from weak base so it is strong conjugate acid and it will show hydrolysis reaction with water and produces H₃O⁺



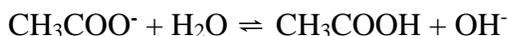
while SO₄²⁻ ion is from strong acid so it is weak conjugate base and it will not show hydrolysis reaction with water. Thus the solution will be acidic due to increased H₃O⁺. pH of solution < 7

(iii) Salt of Weak acid and strong base:

When salts of weak acid and strong base are dissolved in water they dissociate into ions e.g. CH₃COONa, NaHCO₃.



Na⁺ ion is from strong base so it is weak conjugate acid and it will not show hydrolysis reaction with water while CH₃COO⁻ ion is from weak acid so it is strong conjugate base and it will show hydrolysis reaction with water and produces OH⁻ ions.



Thus the solution will be basic due to increased OH⁻. pH of solution > 7.

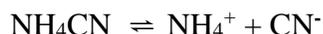
(iv) Salts of weak acid and weak base:

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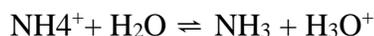
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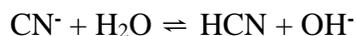
When salts of weak acid and weak base are dissolved in water they dissociate into ions e.g. NH_4CN , $\text{CH}_3\text{COONH}_4$, $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ (Ammonium acetate $\text{CH}_3\text{COONH}_4$)



NH_4^+ ion is from weak base so it is strong conjugate acid and it will show hydrolysis reaction with water and produces H_3O^+



Similarly CN^- ion is from weak acid so it is strong conjugate base and it will also show hydrolysis reaction with water and produces OH^- ions.



Thus the solution may be very slightly acidic or very slightly basic or neutral depending upon K_a and K_b values of acid and base respectively. e.g. In case of NH_4CN the K_b of CN^- is greater than K_a of NH_4^+ so CN^- hydrolyses to more extent than NH_4^+ so solution is slightly basic having $\text{pH} > 7$.

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