

## Acid and Bases

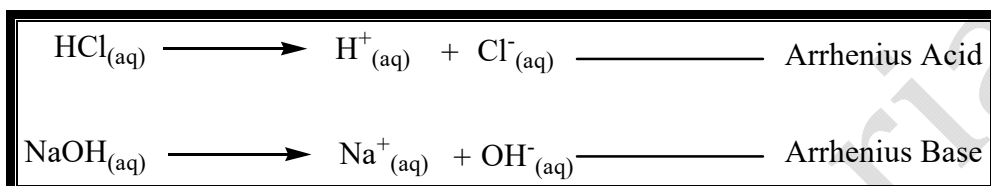
By Dr. Vipul B. Kataria

- We have been seeing the phenomenon of acid and bases from time of our childhood. The tile cleaner and vinegar in food stuffs are kind of acids, whereas bicarbonate for cooking, and carbonate for washing clothes are kind of base.
- When electrolyte dissolves in water, it produces  $H^+$  and  $OH^-$  ions.
- The solution becomes acid, base or neutral that depends upon concentration of the respective ions.
- If there is higher concentration of  $H^+$  ions, it will be acid and pH will be lower than 7.
- If there is higher concentration of  $OH^-$  ions, it will be base and pH will be higher than 7 and lower than 14.
- If the concentration of both the ions is same than the solution will be neutral and pH will be 7.
- The phenomenon of acid and base can be explained by three theories.



**(A) Arrhenius concept:**

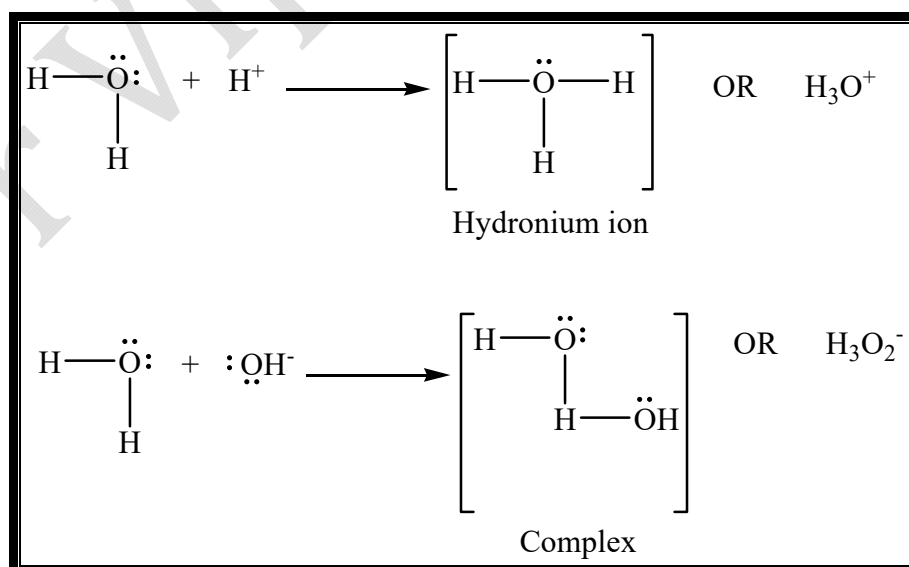
- Savante Arrhenius gave concept of acid and bases based upon the tendency of solution to release ions ( $H^+$  and  $OH^-$ ).
- If the compound releases  $H^+$  ions in water it is acid.
- If the compound releases  $OH^-$  ions in water it is base.
- For example, HCl is Arrhenius acid and NaOH is Arrhenius base.



- In HCl,  $H^+$  ions are responsible for acidic properties whereas in NaOH,  $OH^-$  ions are responsible for basic properties.

**Limitations:**

- **Free  $H^+$  and  $OH^-$  ions do not exist in free state in water:** The  $H^+$  and  $OH^-$  ions produced by acids and bases do not exist in water in free state. They react with water molecules forming hydrogen bond to give different products. The  $H^+$  ions will form hydronium ion ( $H_3O^+$ ) while  $OH^-$  will form complex ( $H_3O_2^-$ ).

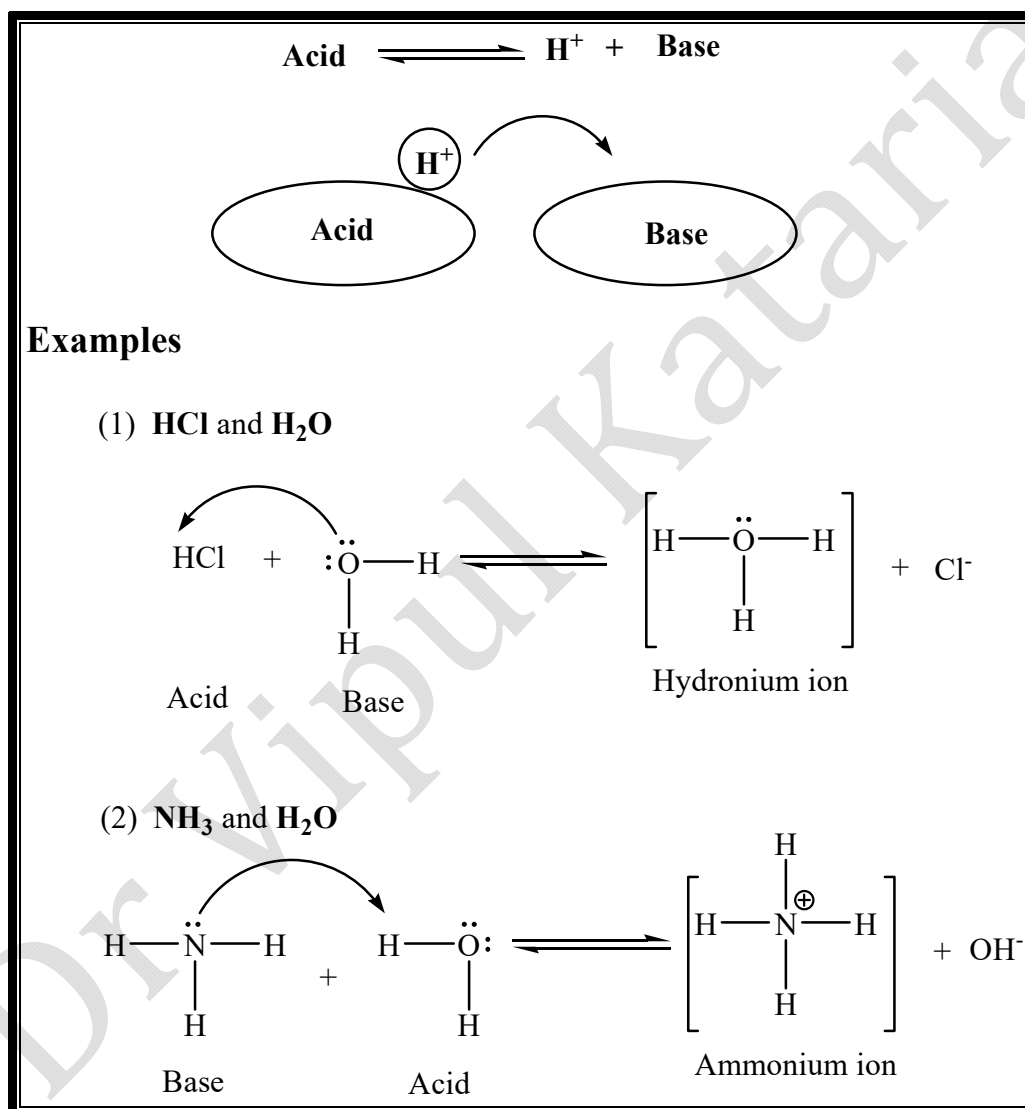


- **Limited to water only:** Arrhenius defined acid and base depending upon its tendency producing  $H^+$  and  $OH^-$  ions in water only. It fails to give an idea of acid and base in other solvents.
- **Some bases do not contain  $OH^-$ :** There are several compounds having basic properties but are not base according to Arrhenius concept. The concept fails to describe such bases like ammonia ( $NH_3$ ), calcium oxide ( $CaO$ ).

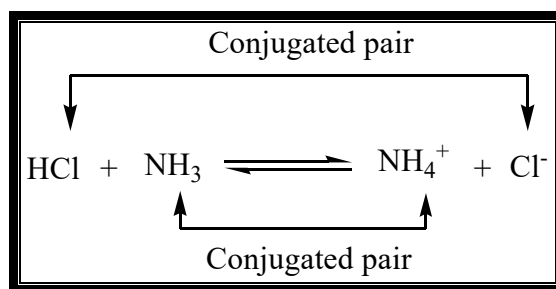
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**(B) Lowry-Bronsted Theory**

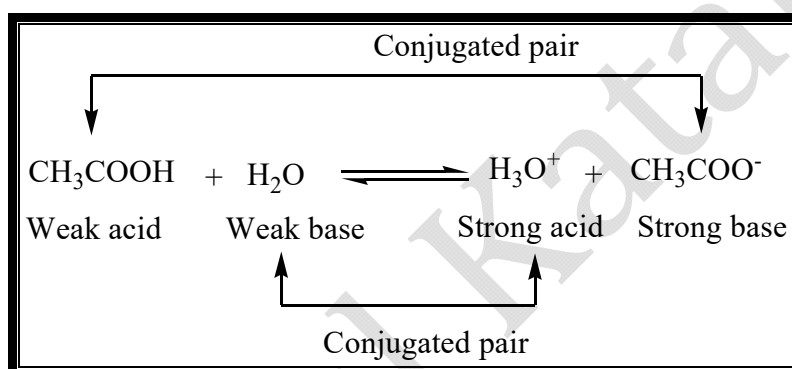
- Lowry and Bronsted suggested a principle for acid and base based upon proton transfer in 1923.
- An acid is a compound which has a tendency to donate a proton ( $\text{H}^+$ ).
- A base is a compound which has a tendency to accept a proton ( $\text{H}^+$ ).
- In simple word, acid is proton donor while a base is proton acceptor.



- Water acts as acid in presence of ammonia while as base in presence of HCl. Such compounds are said to be amphiprotic or amphoteric.
- As we can see that, the reaction is reversible which give rise a new phenomenon of conjugate pair.



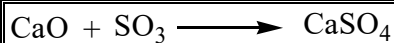
- Acid donates a proton and produces a base that is known as conjugated base.
- Base accepts a proton and produces an acid that is known as conjugated acid.
- It is important to know the relative strength of acid-base conjugated pairs. For sake of understanding, consider the below example.



- Acetic acid is a weak acid that less ionizes in water.
- Weak acid has stronger conjugated base.
- Weak base has stronger conjugated acid.

### Limitations

- The theory does not explain the acid-base behaviour in aprotic solvents like benzene or dioxane.
- Some substance like  $\text{BF}_3$ ,  $\text{AlCl}_3$  do not have proton still they act as an acid. It cannot be explained by Lowry-Bronsted theory.
- There are some reactions which occur in absence of any solvent. It is not possible to explain them by Lowry-Bronsted theory.



# Bronsted-Lowry Theory: Acids and Bases

Hello! My name is Alfie. I'm an acid. I like to receive protons! This is my friend Billy ...

... I'm a base and I like to give protons to Alfie!!!

Everytime I get a proton, ..... something funny happens to me. I become a conjugate base!

... and I become a conjugate acid!!!

Some acids are really strong .... like me!!!

Some acids can give more than one proton!

I am confused ... I can give protons ... I can receive protons ... I am amphoteric!!!

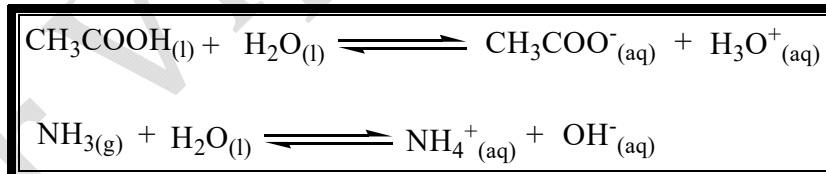
**PROTONS!!**

**(C) Lewis Concept**

- Lewis in 1930, proposed a much improved theory to describe acid and base.
- According to Lewis, an acid is a substance that accepts the pair of electron and a base is a substance that donates the pair of electron.
- In simple words, acid is electron pair acceptor, and base is electron pair donor.
- It can be said that all the cations (having positive charge) or molecules deficient of electron pair act as acid, and all the anions (having negative charge) or molecules having electron pair act as base.
- The theory is enough competent to rule out the limitations of Arrhenius and Lowry-Bronsted theory.
- The concept is applicable to the reactions which do not involve proton transfer.

**Acid-Base Dissociation and Equilibrium**

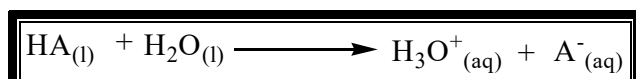
- The dissociation constant of an acid (acidity constant or acid ionization constant) is a quantitative measure of strength of acid in solution.
- The strong acids (HCl, HNO<sub>3</sub>) and strong base (KOH, NaOH) dissociate completely in aqueous solution while weak acid or base ionizes partially.
- Weak acid like CH<sub>3</sub>COOH and weak base like NH<sub>3</sub> ionizes in water at less extent hence there will be equilibrium between ionized and unionized molecules. The ionization process is reversible that can be written as follows.



- The dissociation constant for acid is known as K<sub>a</sub> while for base is known as K<sub>b</sub>.

**Derivation of K<sub>a</sub> and K<sub>b</sub>****For weak acid**

- Consider the following reaction to get an idea about dissociation constant.



- In the above reaction, HA is monobasic acid, and dissociates at less extent in water, and equilibrium will be between undissociated HA and the dissociated  $H_3O^+$ .
- Now the equilibrium constant  $K_c$  can be given on the basis of chemical equilibrium, and can be given as follows.

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \dots \dots \dots (1)$$

Where, [] represents the concentration of compound or ions in mole/litre.

Now, the solution is very dilute hence the concentration of water will be very high so we can take its concentration as constant K.

$$K_c = \frac{[H_3O^+][A^-]}{[HA]K} \dots \dots \dots (2)$$

$$K \cdot K_c = \frac{[H_3O^+][A^-]}{[HA]} \dots \dots \dots (3) \quad \text{Now, } K \cdot K_c = K_a$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \dots \dots \dots (4)$$

Now, the concentration of weak acid will be almost same to its original concentration as weak acid ionize into water to very less extent. So,  $[HA] = C_o$

$$K_a = \frac{[H_3O^+][A^-]}{C_o} \dots \dots \dots (5)$$

The concentration of  $H_3O^+$  ions will be same to  $A^-$  ions hence we can take  $[H_3O^+]$  in place of  $A^-$ .

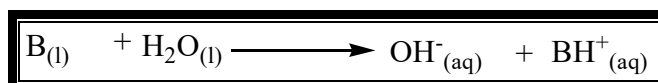
$$K_a = \frac{[H_3O^+]^2}{C_o} \dots \dots \dots (6)$$



$$[H_3O^+] = \sqrt{K_a C_o} \dots \dots \dots (7)$$

### For Weak bases

- Consider the following reaction to get an idea about dissociation constant.



- In the above reaction, B is weak base, and dissociates at less extent in water, and equilibrium will be between undissociated B and the dissociated OH<sup>-</sup>.
- Now the equilibrium constant  $K_c$  can be given on the basis of chemical equilibrium, and can be given as follows.

$$K_c = \frac{[BH^+][OH^-]}{[B][H_2O]} \dots \dots \dots (1)$$

Where, [] represents the concentration of compound or ions in mole/litre.

Now, the solution is very dilute hence the concentration of water will be very high so we can take its concentration as constant K.

$$K_c = \frac{[BH^+][OH^-]}{[B]K} \dots \dots \dots (2)$$

$$K \cdot K_c = \frac{[BH^+][OH^-]}{[B]} \dots \dots \dots (3) \quad \text{Now, } K \cdot K_c = K_b$$

$$K_b = \frac{[BH^+][OH^-]}{[B]} \dots \dots \dots (4)$$

Now, the concentration of weak base will be almost same to its original concentration as weak acid ionize into water to very less extent. So, [B] =  $C_o$

$$K_b = \frac{[BH^+][OH^-]}{C_o} \dots\dots\dots(5)$$

The concentration of  $BH^+$  ions will be same to  $OH^-$  ions hence we can take  $[OH^-]$  in place of  $[BH^+]$ .

$$K_b = \frac{[OH^-]^2}{C_o} \dots\dots\dots(6)$$

$$[OH^-] = \sqrt{K_b C_o} \dots\dots\dots(7)$$

The value for  $K_a$  and  $K_b$  are relative. Higher the value for constant, higher the strength of acid or base.

### Dissociation of water

Water dissociates to a less extent in  $H^+$  and  $OH^-$  ions.



The equilibrium constant according to law of chemical equilibrium can be given by

$$K_c = \frac{[H^+][OH^-]}{[H_2O]} \dots\dots\dots(1)$$

Now, the solution is very dilute hence the concentration of water will be very high so we can take its concentration as constant  $K$ .

$$K_c = \frac{[H^+][OH^-]}{K} \dots\dots\dots(2)$$

Now  $K \cdot K_c$  is  $K_w$  where  $K_w$  is dissociation

constant for water.

$$K_w = [H^+][OH^-] \dots\dots\dots(3)$$

The value for dissociation constant for water at  $25^\circ C$  is  $1 \times 10^{-14} \text{ mol}^2/\text{litre}^2$

As in pure water concentration for both ions ( $[H^+][OH^-]$ ) will be same hence

$$[H^+] = [OH^-] = \sqrt{K_w} = \sqrt{1 \times 10^{-14}} = 1 \times 10^{-7} \text{ mol/litre}$$

### The pH of solutions

The term pH was given by Danish chemist Søren Peder Lauritz Sørensen in 1909. It is a scale to express concentration of  $H^+$  ions in aqueous solution. It is a measure of the acidity or basicity of an aqueous solution.

‘It is negative logarithm of hydrogen ion concentration in solution.’

$$pH = -\text{Log}_{10}[H_3O^+]$$

pOH is used to indicate concentration of hydroxyl ion ( $OH^-$ ).

$$pOH = -\text{Log}_{10}[OH^-]$$

At 25 ° C the concentration of  $H^+$  and  $OH^-$  ions is  $1 \times 10^{-7} \text{ M}$

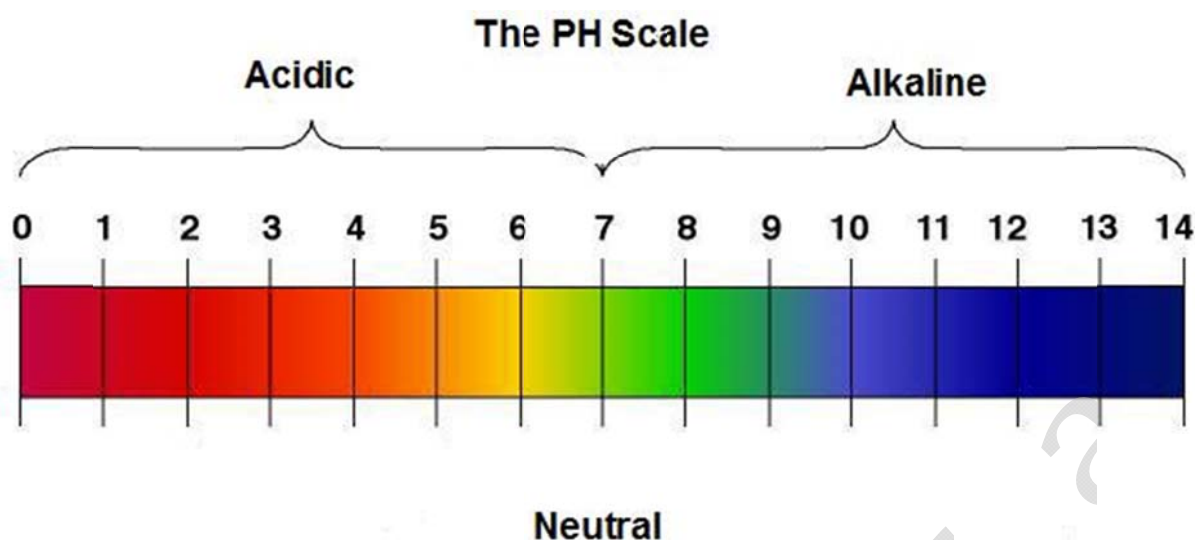
Hence  $H^+ = OH^- = 1 \times 10^{-7} \text{ M}$ .

$$pH + pOH = 14$$

If the concentration of  $H_3O^+$  ions increases the pH will decrease and if the concentration of  $OH^-$  ions increases pH will increase.

If the pH of solution is lower than 7 solution is acidic.

If the pH of solution is higher than 7 solution is basic.



The pH of strong acid or base can be calculated by using the concentration of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions respectively. However for weak acid or base the dissociation constant need to be considered.

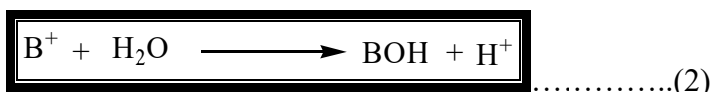
The pH can be calculated roughly by pH paper however for exact calculation of pH, pH meters are used.

### Hydrolysis of salts

When the salt of weak acid and strong base dissolves in water,  $\text{A}^-$  anions tend to react with water by accepting a proton ( $\text{H}^+$ ), and convert into unionized molecules ( $\text{HA}$ ).



Similarly, the salt of weak base and strong acid dissolves in water,  $\text{B}^+$  cations react with water by accepting a hydroxyl ion ( $\text{OH}^-$ ), and convert into unionized molecules ( $\text{BOH}$ ).



‘Hydrolysis usually means the cleavage of chemical bonds by the addition of water.’

In anionic hydrolysis solution becomes slightly basic. In cationic hydrolysis solution becomes slightly acidic.

Four types of salts are possible in order to understand the hydrolysis.

- (a) Salts of strong acid and strong bases: NaCl, KCl, NaNO<sub>3</sub>
- (b) Salts of weak acid and strong bases: KCN, NaCN, CH<sub>3</sub>COONa
- (c) Salts of strong acid and weak bases: NH<sub>4</sub>Cl, FeCl<sub>3</sub>, CuSO<sub>4</sub>
- (d) Salts of weak acids and weak bases: CH<sub>3</sub>COONH<sub>4</sub>, NH<sub>4</sub>CN

**(a) Salts of strong acid and strong bases**

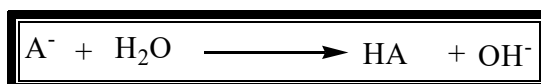
Salts of strong acid and strong bases do not hydrolyse. For example NaCl; when NaCl dissolved in water, Na<sup>+</sup> and Cl<sup>-</sup> ions do not react with H<sup>+</sup> and OH<sup>-</sup> ions hence there will not be any change in pH.

**(b) Salts of weak acid and strong bases**

Hydrolysis is reversible reaction. The equilibrium constant for this is denoted by K<sub>h</sub>, and derived by application law of mass to hydrolysis reaction.

The degree of the hydrolysis is the fraction of salt which has been hydrolysed at the time of equilibrium. It is denoted by x.

The general hydrolysis reaction for weak acid and strong base is can be exemplified by following.



Applying law of chemical equilibrium and taking concentration of water as constant

$$K_h = \frac{[H^+][OH^-]}{A^-} \dots \dots \dots (1)$$

**Relation between  $K_h$ ,  $K_a$ , and  $K_w$** 

The dissociation constant for water is

$$K_w = [H^+][OH^-] \dots \dots \dots (2)$$

And the dissociation constant for weak acid is

$$K_a = \frac{[H^+][A^-]}{[HA]} \dots \dots \dots (3)$$

Divide equation 2 by 3

$$\frac{K_w}{K_a} = \frac{[OH^-][HA]}{A^-} \dots \dots \dots (4)$$

Comparing equation 1 and 4

$$K_w/K_a = K_h$$

The hydrolysis constant is inversely proportional to the dissociation constant of acid. Therefore weaker the acid higher the hydrolysis constant.

**Relation between hydrolysis constant ( $K_h$ ) and degree of hydrolysis (x)**

If the C is the initial concentration and x is the degree of hydrolysis at the time of equilibrium then

	$A^- + H_2O \longrightarrow$	$HA + OH^-$
Initial concentration	C	0      0
At equilibrium	$C(1-x)$	$Cx$ $Cx$

Now hydrolysis constant will be

$$K_h = \frac{[HA][OH^-]}{A^-} \dots \dots \dots (1)$$

$$K_h = \frac{cx \times cx}{c(1-x)} = \frac{cx^2}{1-x}$$

Now if x is too small than we can ignore it and (1-x) will be 1

$$K_h = Cx^2$$

Therefore  $x = \sqrt{K_h/c}$  but  $K_h = K_w/K_a$

$$x = \sqrt{\frac{K_w}{K_a C}}$$

If we know the value of  $K_w$ ,  $K_a$  and C we can have the value of x.

The degree of hydrolysis is inversely proportional to the concentration. It increases with decrease in concentration.

### pH of hydrolysed salt solution

We know that  $[OH^-] = Cx$

$$\text{Now } x = \sqrt{\frac{K_w}{K_a C}}$$

$$[OH^-] = C \sqrt{\frac{K_w}{K_a C}} = C \left( \frac{K_w}{K_a C} \right)^{1/2} = \left( \frac{K_w C}{K_a} \right)^{1/2}$$

$$[OH^-] = \sqrt{\frac{K_w C}{K_a}}$$

Taking negative logarithm at both the side

$$-\text{Log} [\text{OH}^-] = -\frac{1}{2} \text{Log} K_w - \frac{1}{2} \text{Log} C + \frac{1}{2} \text{Log} K_b$$

$$\text{pOH} = \frac{1}{2} \text{PK}_w - \frac{1}{2} \text{Log} C - \frac{1}{2} \text{PK}_b$$

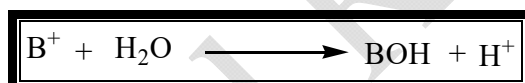
$$\text{POH} = 7 - \frac{1}{2} \text{Log} C - \frac{1}{2} \text{PK}_b$$

Now the pOH will be less than 7 hence pH will be higher than 7 so the solution will be basic.

The solution of weak acid and strong base will always be basic.

### (c) Salt of weak base and strong acid

The general hydrolysis reaction for salt of weak acid and strong acid is can be exemplified by following.



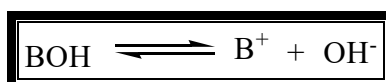
Applying law of chemical equilibrium and taking concentration of water as constant

$$K_h = \frac{[\text{H}^+][\text{BOH}]}{[\text{B}^+]} \dots \dots \dots (1)$$

### Relation between $K_h$ , $K_b$ , and $K_w$

The dissociation constant for water is

$$K_w = [\text{H}^+][\text{OH}^-] \dots \dots \dots (2)$$



And the dissociation constant for weak base is

$$K_b = \frac{[\text{B}^+][\text{OH}^-]}{[\text{BOH}]} \dots \dots \dots (3)$$



Divide equation 2 by 3

$$\frac{K_w}{K_b} = \frac{[H^+][BOH]}{[B^+]} \dots\dots\dots(4)$$

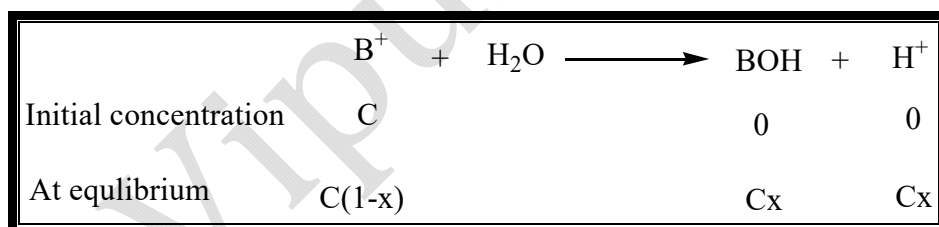
Comparing equation 1 and 4

$$K_w/K_b = K_h$$

The hydrolysis constant is inversely proportional to the dissociation constant of base. Therefore weaker the base higher the hydrolysis constant.

#### Relation between hydrolysis constant ( $K_h$ ) and degree of hydrolysis ( $x$ )

If the C is the initial concentration and x is the degree of hydrolysis at the time of equilibrium then



Now hydrolysis constant will be

$$K_h = \frac{[H^+][BOH]}{[B^+]} \dots\dots\dots(1)$$

$$K_h = \frac{cx \times cx}{c(1-x)} = \frac{cx^2}{1-x}$$

Now if x is too small than we can ignore it and (1-x) will be 1

$$K_h = Cx^2$$

Therefore  $x = \sqrt{K_h/c}$  but  $K_h = K_w/K_b$

$$x = \sqrt{\frac{K_w}{K_b C}}$$

If we know the value of  $K_w$ ,  $K_b$  and  $C$  we can have the value of  $x$ .

The degree of hydrolysis is inversely proportional to the concentration. It increases with decrease in concentration.

### Derivation of pH

From the above discussion  $[H^+] = Cx$

Now put value of  $x$

$$[H^+] = C\sqrt{\frac{K_w}{K_b C}} = C\left(\frac{K_w}{K_b C}\right)^{1/2} = \left(\frac{K_w C}{K_b}\right)^{1/2}$$

$$[H^+] = \sqrt{\frac{K_w C}{K_b}}$$

Now take negative logarithm at both sides

$$-\text{Log } [H^+] = -\frac{1}{2} \text{Log } K_w - \frac{1}{2} \text{Log } C + \frac{1}{2} \text{Log } K_b$$

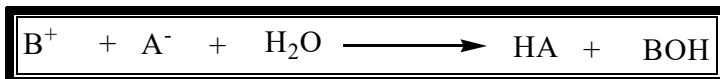
$$\text{pH} = \frac{1}{2} \text{PK}_w - \frac{1}{2} \text{PK}_b - \frac{1}{2} \text{Log } C \quad \text{Now PK}_w \text{ is 14}$$

$$\text{pH} = 7 - \frac{1}{2} \text{PK}_b - \frac{1}{2} \text{Log } C$$

It is clear from the equation that pH of solution of weak base and strong acid will always be acidic

**(c) Salts of weak acid and weak base**

In this type of salt both the anion of weak acid ( $A^-$ ) and the cation of weak base ( $B^+$ ) undergo hydrolysis simultaneously.

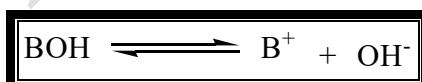
**Hydrolysis constant**

$$K_w = \frac{[HA][BOH]}{[B^+][A^-]}$$

**Relation between  $K_h$ ,  $K_w$ ,  $K_a$  and  $K_b$** 

Dissociation constant for weak acid is

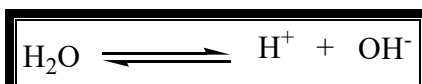
$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \dots \dots \dots (1)$$



Dissociation constant for weak base is

$$K_b = \frac{[BH^+][OH^-]}{[BOH]} \dots \dots \dots (2)$$

Dissociation constant for water



$$K_w = [H^+][OH^-] \dots \dots \dots (3)$$

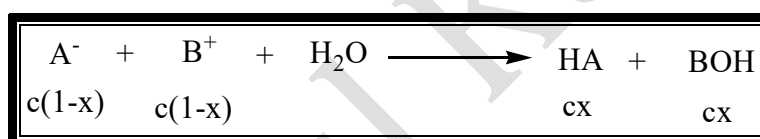
Dividing equation 3 by 1 and 2

$$\frac{K_w}{K_a \times K_b} = \frac{[HA][BOH]}{[B^+][A^-]} \dots \dots \dots (4)$$

$$K_h = \frac{K_w}{K_a \times K_b} \dots \dots \dots (5)$$

### Relation between hydrolysis constant and degree of hydrolysis

If the initial concentration of the salt is C moles per litre and x is the degree of hydrolysis then equilibrium concentration will be like following



Put the values of concentration in equation 4

$$K_h = \frac{C^2 X^2}{C^2 (1-X)^2} = \frac{X^2}{(1-X)^2}$$

If we neglect x as compare to 1

$$K_h = X^2$$

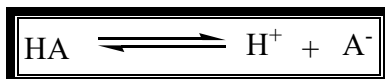
$$X = \sqrt{K_h}$$

$$X = \sqrt{\frac{K_w}{K_a \times K_b}}$$

From this equation we can say that degree of hydrolysis will be higher if the acid or base is weaker. Degree of hydrolysis is not depended on the concentration of solution.

### Derivation of pH

Hydrogen concentration of the solution of a salt of weak acid and weak base can be derived from the ionic equation of the weak acid.



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

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

From the hydrolysis reaction of the salt we can say that

$$[\text{HA}] = Cx \text{ and } [\text{A}^-] = C(1-x)$$

$$[\text{H}^+] = K_a X$$

Now substituting value of X

$$[\text{H}^+] = K_a \sqrt{\frac{K_w}{K_a \times K_b}}$$

$$[\text{H}^+] = \sqrt{\frac{K_w K_a}{K_b}}$$

Now take negative logarithm at both the side

$$-\text{Log}[\text{H}^+] = -\frac{1}{2}\text{Log}K_w - \frac{1}{2}\text{Log}K_a + \frac{1}{2}\text{Log}K_b$$

$$pH = \frac{1}{2}PK_w + \frac{1}{2}PK_a - \frac{1}{2}PK_b$$

$$pH = 7 + \frac{1}{2}PK_a - \frac{1}{2}PK_b$$

If  $PK_a = PK_b$  then the dissociation constant of the acid is equal to that of base then  $pH = 7$ . Thus the solution will be neutral although hydrolysis has been taken place. The solution of ammonium acetate will be neutral as dissociation constant for acetic acid and ammonium hydroxide is same.

If  $PK_a > PK_b$  then solution will be basic and if  $PK_a < PK_b$  then the solution will be acidic.

### Buffer solutions

For many purposes in chemistry, industrial chemistry, and biology, some kind of solutions are required whose pH do not change on addition of small amounts of strong acid or bases. Such solutions are referred as buffer solutions.

The solutions which resist change in pH on dilution or with the addition of small amounts of acid or base are called buffer solutions.

There are two types of buffer solutions (1) Acidic buffer solutions (2) Basic buffer solutions.

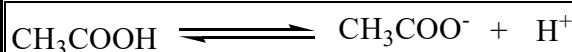
(1) Acidic buffer solutions: It is mixture of weak acid and salt of weak acid and strong base. For example,  $CH_3COOH + CH_3COONa$

(2) Basic buffer solutions: It is mixture of weak base and salt of weak base and strong acid. For example,  $NH_4OH + NH_4Cl$

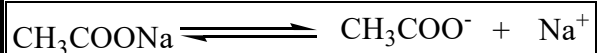
### Mechanism of buffer solutions

#### (1) Mechanism of acidic buffer solution

The pH of the acidic buffer is controlled by the equilibrium.

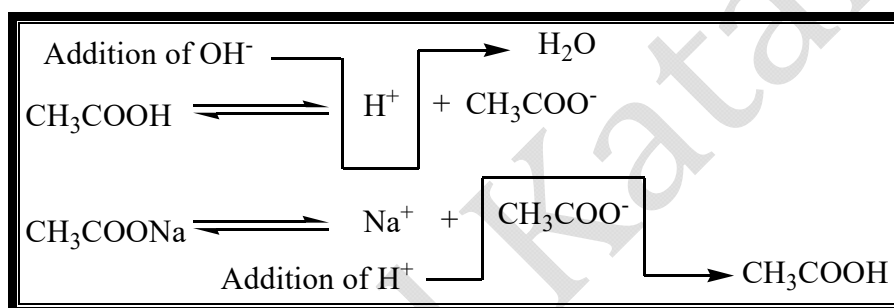


The buffer solutions has a large amount of  $\text{CH}_3\text{COO}^-$  ions due to the complete dissociation of salt  $\text{CH}_3\text{COONa}$



On the dissociation of acid, the increase of  $\text{H}^+$  ions is taken up immediately by  $\text{CH}_3\text{COO}^-$  ions to form undissociated  $\text{CH}_3\text{COOH}$ .

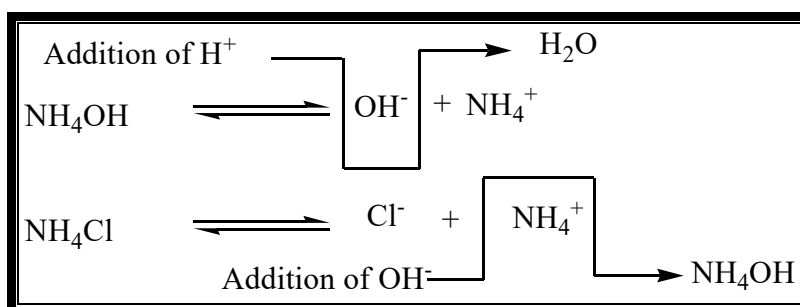
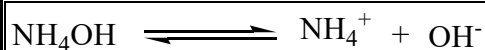
Thus the added  $\text{H}^+$  ions are neutralized and the pH of the solution remains almost constant.



When the base is added to the buffer solution, the additional  $\text{OH}^-$  ions are joined to  $\text{H}^+$  to form Water molecule. Thus the added hydroxyl ions are neutralized and the pH does not change.

## (2) Mechanism of basic buffer

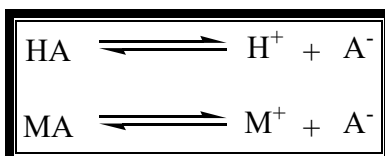
The pH of basic buffer is controlled by the equilibrium.



On the addition of acid,  $H^+$  ions join with  $OH^-$  ions to form  $H_2O$  molecules. On the addition of base the  $OH^-$  ions join with  $NH_4^+$  ions to form undissociated  $NH_4OH$ . In both the cases pH does not change.

### Equation for the pH of acidic buffer solution

The dissociation of the weak acid HA and salt MA may be represented as follows.



$$K_a = \frac{[H^+][A^-]}{[HA]} \dots\dots\dots(1)$$

$$[H^+] = K_a \frac{[HA]}{[A^-]} \dots\dots\dots(2)$$

The weak acid HA dissociates to a small extent and the dissociation further depressed by the addition of  $A^-$  ions due to common ion effect. As a result the equilibrium concentration of unionized acid is almost equal to initial concentration of the acid.

$$[HA] = [\text{Acid}]$$

Where  $[\text{Acid}]$  is the initial concentration of the acid and  $[\text{Salt}]$  is that of the salt. At the equilibrium  $[A^-]$  is presumed to be equal to the initial concentration of the salt since it is completely dissociated.

$$[A^-] = [\text{Salt}]$$

So equation 2 will be

$$[H^+] = K_a \frac{[\text{Acid}]}{[\text{Salt}]} \dots\dots\dots(3)$$

Taking negative logarithm at both sides



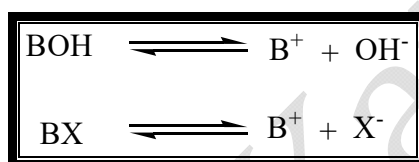
$$-\text{Log}[\text{H}^+] = -\text{Log } K_a - \text{Log} \frac{[\text{Acid}]}{[\text{Salt}]}$$

$$\text{pH} = \text{p}K_a - \text{Log} \frac{[\text{Salt}]}{[\text{Acid}]}$$

The equation is known as Henderson-Haselbalch equation.

### Equation for pH basic buffer solution

The dissociation of the weak base BOH and salt BX may be represented as follows.



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

$$[\text{OH}^-] = K_b \times \frac{[\text{BOH}]}{[\text{B}^+]} \dots \dots \dots (1)$$

At equilibrium  $[\text{BOH}] = [\text{Base}]$  due to slight dissociation of weak base and common ion effect.  $[\text{B}^+] = [\text{Salt}]$  since the salt is completely dissociated where  $[\text{base}]$  is the initial concentration of base. And  $[\text{Salt}]$  is that of the salt. Thus we can write (1) as

$$[\text{OH}^-] = K_b \times \frac{[\text{Base}]}{[\text{Salt}]} \dots \dots \dots (2)$$

Taking negative logarithm at both side

$$-\text{Log}[\text{OH}^-] = -\text{Log}K_b - \text{Log} \frac{[\text{Base}]}{[\text{Salt}]} \dots \dots \dots (2)$$

$$pOH = pK_b + \text{Log} \frac{[Salt]}{[Base]} \dots \dots \dots (3)$$

This equation is also known by Handerson-Hasselbalch equation for basic buffer.

Now  $pH = 14 - pOH$ , on the basis of same we can find the pH of the buffer solution.

$$pOH = pK_b + \text{Log} \frac{[Salt]}{[Base]} \dots \dots \dots (4)$$

$$pH = 14 - pK_b - \text{Log} \frac{[Salt]}{[Base]} \dots \dots \dots (5)$$

Buffer solutions are most effective when the concentration of acid or base and salt are about equal.

Buffer Capacity (Buffer Index)

The change in the concentration of acid or base of the buffer solution required for changing its pH by one is called buffer capacity, and is denoted by  $\beta$ .

$$\text{Buffer Capacity} = \frac{\text{moles of acid or base added}}{\text{change in pH}}$$

$$\beta = \frac{\partial[HA]}{\partial[pH]} \quad \text{Or} \quad \beta = \frac{\partial[BOH]}{\partial[pH]}$$

The buffer capacity is also defined as the number of moles of an acid or a base which when added to a litre of a buffer solution changes its pH by unity.

*I have work hard preparing this material.....  
You also work hard preparing from this material!!!!  
Best Luck....*

Dr Vipul Kataria