Acid & base

Merits

–It is wider concept as compared to arrherenious concept it covers large variety of substances as base eg OH^-, $NH_{2,}$Pyrydine.

- This concept can used to explain Acid base reaction in non aqueous solvent

- Relative strength of acid & bases can be determine with the help of this concept

Demerits

- Not satisfactory to explain non protonic acid base reaction
- It gives more importance to protonic exchange but there are several acid base reaction in which protons are not involved .
- Lewis concept(electronic concept)

-Define Acid & base in terms of electrons

- A base is defined as a substance which can give an electron pair to form a co-valent co-ordinate bond while an acid is a substance which has tendency to accept an electron pair from a base to form a covalent co-ordinate bond

- Hence lewis base possess a lone pair of electron and act as a electron pair donar

Eg OH^- , Cl^- , CN^-, NH^{3-}

- lewis aid possess either an incomplete octate & thereby act as as electron pair acceptor

Eg SO_3^+ ,$AlCl_{3,}ZnCl_{3,}BF_3$

Eg of lewis base –acid reaction-

In this reaction the central boron atom in the acid causes an incomplter octate & can take a lone pair of electron where as the nitrogen atom of the base NH_3 possess a lone pair of electron therefore they combine together to form a complex.

It also include those reaction in which no of ions are form and no transparence of H^+ ion or other ions takes place

Eg $2\ NH_3 + Ag$----------------------[$Ag(NH_3)_2$

Merits

Acid base reaction not involving proton are covered by this concept

-According to this concept Acid base behavior do not involve any particular species

- Acid base behavior does not depend on presence or absence of any solvent.

- Basic properties of metal oxide & Acidic properties of non metal oxides can be explained.

Demerit

- There is no uniform scale of acid base strength & strength depends upon reaction

- It is also broad concept of acid & base & creates unnecessary complications.

Conjugate pairs of acid & base

According to this concept acid base reaction can be expressed as

Acid $\longleftrightarrow$ Base $+H^+$

Therefore acid or base are related to each other

- Every acid changes into base after releasing one proton & every base on accepting a proton changes into acid. Acid & base thus exist in pairs & these pairs are called conjugate pairs.

- Thus the conjugate acid differ from its conjugate base by one proton

Eg $HCl+H_2O \longrightarrow H_3O + Cl^-$

Acid Base conjugate acid conjugate base

- In this reaction HCl donates a proton & changes into Cl^- ion thus HCl is an acid & Cl^- is its conjugate base

H_2O molecule accept the proton given by HCl & changes to H_3O^+ ion therefore H_2O act as base & H_3O as its conjugate acid.

- Since H_3O^+ has the tendency to give a proton & Cl^- has a tendency to accept it the exchange of electron is reversible process.

Law of mass action

The rate of chemical reaction is α to the active masses of the reactant raise dto the power equal to the stochiometry coefficient of that species in the chemical reaction

Then according to law of mass action

Rate of reaction α Active mass of $[A]^{a}$ & $[B]^{b}$ or Rate of reaction = $K[A]^{a} [B]^{b}$

Where K is the constant of proportionality and is known as rate constant

[A] & [B] represent active masses of reactant A and B respectively

$aA+bB \longleftrightarrow cC+dD$

rate forward Rate of backward

Rate of forward $R_e^n = [A]^{a} [B]^{b} / c$

Law of chemical equilibrium

Let us consider a general R_e^n

$aA+bB \longleftrightarrow cC+dD$

-In which an chemical equilibrium exist between['A' & 'B'] and product ['C'& 'D'] let [A] ,[B] &[C] [D] represent active masses.

Thn according to law of mass action

Rate of forward R_e^n α $[A]^{a} [B]^{b}$

Or Rate of forward $R_e^n = K_1[A]^{a} [B]^{b}$

Rate of backward R_e^n α $[C]^{c} [D]^{d}$

Rate of backward $R_e^n = K_2 [A]^{a} [B]^{b}$

At equilibrium the rate of two opposite reaction becomes equal

Therefore

Rate of forward R_e^n = Rate of backward R_e^n

$K_1[A]^{a}$ & $[B]^{b} = K_2 [A]^{a} [B]^{b}$

$$\frac{K_1}{K_2} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

A particular temperature K_1 &K_2 are constant therefore the ratio of K_1/K_2 will be constant this is represent by 'K' and is called equilibrium constant and the above equilibrium can be written as

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Therefore K= equilibrium constant

Note – larger the value of ‘k’ greater is the extent to which reactant are converted to product

Relative strength of acid and base

The strength of an acid is determined by its tendency to loose proton. Higher the tendency of an acid to loose proton greater its strength like HCl ,$HNO_{3,}H_2SO_{4-}$ (possess very high tendency to loose proton therefore they are strong acid

- On the other hand acid are like CH_3COOH,CN,OH^-,NH_3 possesses little tendency to loose proton & are weak acids

- Similarly the strength of the base is determined by its tendency to gain proton.

- The bases like CH_3COO^-, CN^-,OH^-, NH_3^- etc are strong bases because they possesses very high tendency to gain proton

- But bases like Cl^-, NO_3^-,SO_4^{2-} are weak bases because they have little tendency to accept proton.

Note The conjugate strong acid is always a weak base & the conjugate of weak acod is always a strong base.

Eg

Relative strength of acid

Quantitatively the strength of an acid may be defined as the concentration of H_3O^+ i.e. H^+ ions in its aqueous solution at a particular temperature .

The dissociation of an acid HA can be written as

$HA + H_2O \longleftrightarrow H_3\,O + A$

According to the law of mass action log of equilibrium

Where Ka = dissociation constant & ionization constant

From the above equation it is clear that H_3O^+ concentration depend upon the value of dissociation constant or ionization constant [Ka] of the Acid.

Hence the value of Ka for particular Acid can be regarded as a quantitative measure of its strength .

Relative strength of base

- The strength of base is depended upon its tendency to gain proton.

- Therefore strength of base can be quantitatively determined by measuring the dissociation constant of base [Kb]

- Let us consider the example in which we gain proton from water

According to law of mass action & chemical equlilibrium

$$B + H_2O \longrightarrow BH + OH$$

$$Kb = \frac{[BH] [OH]}{[B]}$$

Where Kb = dissociation constant or ionization constant of base

When the value of Kb is large the formation of OH ion is favoured this implies that B has a greater tendency to gain H^+ & therefore is strong base

- On the other hand of the value of Kb is smaller indicates that B has lesser tendency to gain proton (H^+) i.e it is weak base.

Thus the higher value of Kb greater is the strength of base .

Common Ion effect

The suppression of dissociation of weak electrolyte on addition of strong electrolyte containing a common ion is called common ion effect.

General reaction

AB A+ B

AC A+C

Suppose AB is weak electrolyte in a solution which partially dissociate into A^+ and B^- ion and following equilibrium is obtained

AB A+B

$$K = \frac{[A][B]}{AB}$$

Now if strong electrolyte AC is added which is capable of giving A ion is added to this solution the concentration of A^+ ion increases which disturbs the equilibrium & system counter reacts this increase.Therefore A+ ion combines with B^- ions undissociated AB molecule Thus the dissociation of AB gets suppressed. Shift the equilibrium in the reverse direction and the concentration of B^- ion decreases.

Buffer solutions and common ion effect

A **buffer solution** resists (or buffers) a change in its **pH**. That is, we can add a small amount of an acid or base to a buffer solution and the pH will change very little.

How to calculate pH of buffer solution containing both acid and conjugate base? Dissociation constant definition 1.1 can be rearranged into

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

or

$$pH=pK_a+\log(\frac{[A^-]}{[HA]})$$

(note that due to sign change $[A^-]$ was moved to nominator).

This is so called **Henderson-Hasselbalch equation** (or **buffer equation**). It can be used for pH calculation of solution containing pair of acid and conjugate base - like HA/A^-, HA^-/A^{2-} or B^+/BOH. For solutions of weak bases sometimes it s more convenient to use equation in the form

$$pOH=pK_b+\log(\frac{[B^+]}{[BOH]}) \quad 15.3$$

Two common types of **buffer solutions** are :

(1) a weak acid together with a salt of the same acid with a strong base. These are called **Acid buffers** e.g. CH3COOH + CH3COONa.

(2) a weak base and its salt with a strong acid. These are called **Basic buffers**. e.g.NH4OH + NH4Cl.

Let us illustrate buffer action by taking example of a common **buffer system consisting of solution of acetic acid and sodium acetate** (CH3COOH/CH3COONa).
CH3COOH --- H+ + CH3COO–
CH3COONa ---- Na+ + CH3COO-

since the salt is completely ionised, it provides the common ions CH3COO– in excess. The common ion effect suppresses the ionisation of acetic acid. This reduces the concentration of H+ ions which means that pH of the solution is raised. Thus, a 0.1 M acetic acid solution has a pH of 2.87 but a solution of 0.1 M acetic acid and 0.1 M sodium acetate has a pH of 4.74. Thus 4.74 is the pH of the buffer. On addition of 0.01 mole NaOH the pH changes from 4.74 to 4.83, while on the addition of 0.01 mole HCl the pH changes from 4.74 to 4.66. Obviously the buffer solution maintains fairly constant pH and the changes in pH could be described as marginal.

Buffer Action:

A buffer solution containing equimolar amounts (0.10 M) of acetic acid and sodium acetate has pH 4.74. Now we proceed to discuss how the addition of a small amount of HCl or NaOH to the buffer solution affects its pH. The pH of the buffer is governed by the equilibrium

CH3COOH --- CH3COO– + H+

The buffer solution has a large excess of CH3COO– ions produced by complete ionisation of sodium acetate,

CH3COONa ---CH3COO- + Na+

(1) **Addition of HCl**.

Upon the addition of HCl, the increase of H+ ions is counteracted by association with the excess of acetate ions to form unionised CH3COOH. Thus the added H+ ions are neutralized and the pH of the buffer solution remains virtually unchanged. However owing to the increased concentration of CH3COOH, the equilibrium shifts slightly to the right to increase H+ ions. This explains the marginal increase of pH of the buffer solution on addition of HCl.

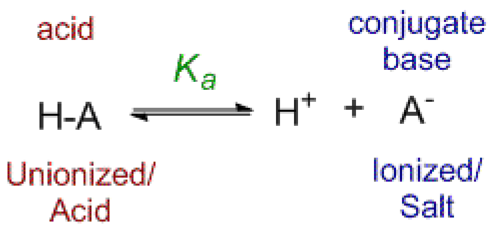
(2) **Addition of NaOH**.

When NaOH is added to the buffer solution, the additional OH– ions combine with H+ ions of the buffer to form water molecules. As a result the equilibrium (1) shifts to the right to produce more and more H+ ions till practically all the excess OH– ions are neutralised and the original buffer pH restored. However, a new equilibrium system is set up in which [CH3COOH] is lower than it was in the original buffer. Consequently [H+] is also slightly less and pH slightly higher than the buffer pH values Operation of a Basic buffer as NH4OH/NH4Cl can also be explained on the same lines as of an acid buffer upon addition of HCl the H+ ions combine with OH– ions of the buffer to form water molecules. The equilibrium,

NH4OH--- NH4+ + OH- is shifted to the right till all the additional H+ ions are neutralised and the original buffer pH restored. When NaOH is added to the buffer solution, OH– ions associate with excess of NH4+ ions to form unassociated NH4OH. Thus the pH of the buffer is maintained approximately constant.

Derivation of Henderson-Hasselbalch Equation

For Acids



Acid Dissociation

According to the law of dissociation, the acid dissociation constant K_a can be defined by the equation:

$K_a = [H^+][A^-]/[HA]$

where $[H^+]$ and $[A^-]$ are the concentrations of the ionized form of the acid, while [HA] is the concentration of the unionized form.

Taking log on both sides you get:

$\log K_a = \log([H^+][A^-]/[HA])$

Splitting the log terms into separate components gives you:

$\log K_a = \log[H^+] + \log([A^-]/[HA])$

Since $pK_a = -\log_{10} K_a$ and $pH = -\log_{10}[H^+]$, therefore:

$-pK_a = -pH + \log([A^-]/[HA])$

Rearranging the terms we get the Henderson-Hasselbalch equation for acids as:

$pH = pK_a + \log([A^-]/[HA])$

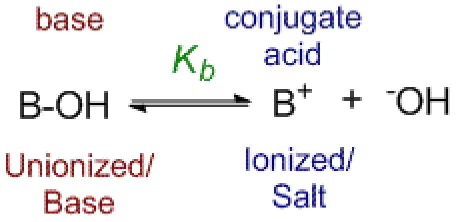
This equation can also be written as:

$pH = pK_a + \log[(\text{salt})/(\text{acid})]$

or

$pH = pK_a + \log([\text{ionized}]/[\text{unionized}])$

Similarly for bases:



Base Dissociation

According to the law of dissociation, the base dissociation constant K_b can be defined by the equation:

$K_b = [OH^-][B^+] / [BOH]$

where $[B^+]$ and $[OH^-]$ are the concentrations of the ionized form of the base, while [BOH] is the concentration of the unionized form.

Taking log on both sides you get:

$\log K_b = \log([OH^-][B^+] / [BOH])$

Splitting the log terms into separate components gives you:

$\log K_b = \log[OH^-] + \log([B^+] / [BOH])$

Since $pK_b = -\log_{10} K_b$ and $pOH = -\log_{10}[OH^-]$, therefore:

$-pK_b = -pOH + \log([B^+]/[BOH])$

Rearranging the terms we get the Henderson-Hasselbalch equation for bases:

$pOH = pK_b + \log ([B^+]/[BOH])$
This equation can also be written as:

$pOH = pK_b + \log [(salt)/(base)]$
or
$pOH = pK_b + \log ([ionized]/[unionized])$

pK_a And pH Can Be Used Universally For Both Acids and Bases

Generally the term pK_a can be used to measure the strength of an acid and pK_b for bases. However, in order to compare acidity with basicity the pK_a of a base may also be calculated in order to keep a single scale of comparison. To derive the relationship for bases in terms of pH and pK_a we must look at the relationship between pK_a and pK_b as well as the relationship between pH and pOH.

The product of K_a and K_b is the dissociation constant of water:

$K_a . K_b = K_w = [H^+][OH^–]$
Since $[H^+][OH^–] = K_w = 10^{–14}$, therefore:

$K_a . K_b = 10^{–14}$
Therefore taking logs:

$\log K_a + \log K_b = \log 10^{–14}$
thus, since $pK_a = -\log K_a$ and $pK_b = -\log K_b$:

$pK_a + pK_b = 14$
and it is known that

$[H^+] [OH^–] = K_w = 10^{-14}$
taking logs:

$\log [H^+] + \log [OH^–] = \log 10^{-14}$
Since $pH = -\log [H^+]$ and $pOH = -\log [OH^–]$

$pH + pOH = 14$
Thus for bases, the Henderson-Hasselbalch equation:
$pOH = pK_b + \log ([B^+]/[BOH])$ may be rewritten as:

$14 – pH = 14 – pK_a + \log ([B^+]/[BOH])$
subtracting 14 on both sides and multiplying both sides by -1 we get the Henderson-Hasselbalch equation for bases in terms of pKa and pH:
$pH = pK_a – \log ([B^+]/[BOH])$
or

$pH = pK_a – \log ([salt]/[base])$
or
$pH = pK_a – \log ([ionized]/[unionized])$

Buffer capacity is a measure of the efficiency of a buffer in resisting changes in pH. Conventionally, the buffer capacity (β) is expressed as the amount of strong acid or base, in gram-equivalents, that must be added to 1 liter of the solution to change its pH by one unit.

Calculate the buffer capacity as:

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

ΔB = gram equivalent of strong acid/base to change pH of 1 liter of buffer solution
ΔpH = the pH change caused by the addition of strong acid/base

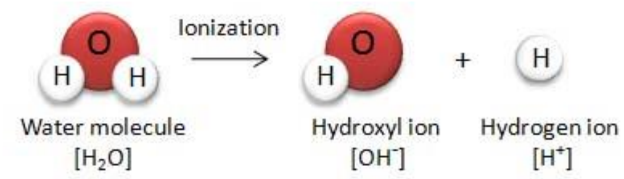
In practice, smaller pH changes are measured and the buffer capacity is quantitatively expressed as the ratio of acid or base added to the change in pH produced (e.g., mEq./pH for x volume). The buffer capacity depends essentially on 2 factors:

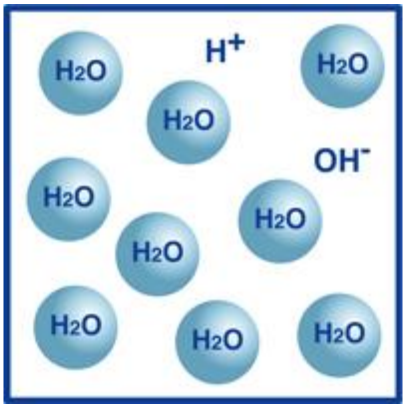
1. Ratio of the salt to the acid or base. The buffer capacity is optimal when the ratio is 1:1; that is, when pH = pKa

Ionic Product of Water

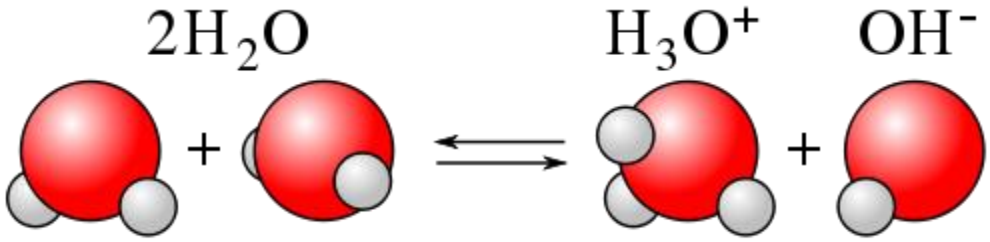
Pure water is a weak electrolyte and it undergo self ionization or auto-protolysis. In this process water molecules splits into hydrogen ion (H+) and hydroxide ion (OH-).

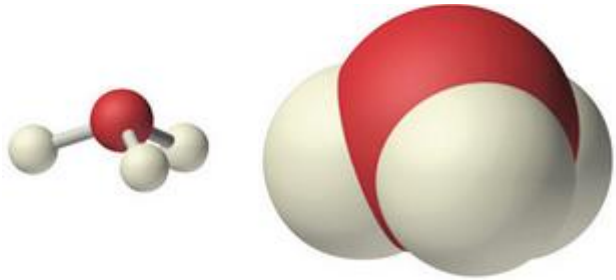
The equation is shown as:





As we know hydrogen ion is very reactive and it reacts further with water molecules to form hydronium ion(H_3O^+)





Hydronium ion,
H_3O^+

Applying law of mass action at equilibrium, the value of dissociation constant, K comes to

$$K = [H^+]\,[OH^-]/[H_2O]$$

$$\text{or}\quad [H^+][OH^-] = K[H_2O]$$

Since dissociation takes place to a very small extent, the concentration of undissociated water molecules, $[H_20]$, may be regarded as constant. Thus, the product #$[H_20]$ gives another constant which is designated as K_w. So,

$$[H^+][OH^-] = K_w$$

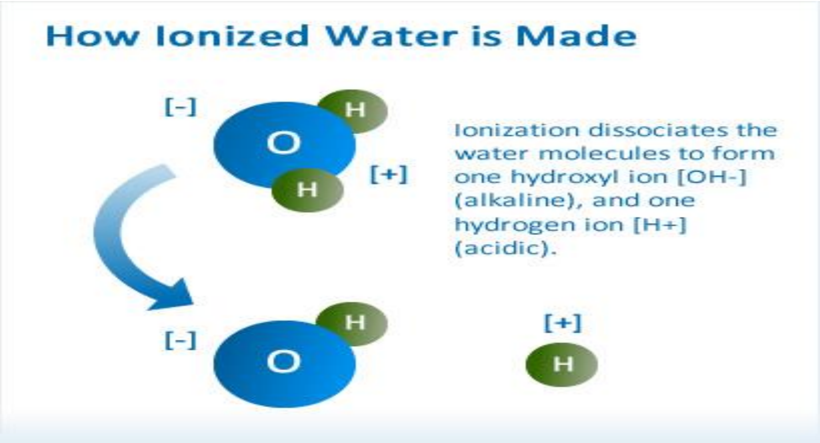
The constant, K_w, is termed as **ionic product of water**.

It is only because of the self ionization of water that it can act as both acid as well as base.

Any substance which increases the concentration of H^+ ion would make water acidic.

Similarly, any substance which increases the concentration of OH- ion, would make water basic.

But in pure water, the hydrogen ion (hydroxonium ion) concentration is always equal to the hydroxide ion concentration. For every hydrogen ion formed, there is a hydroxide ion formed as well.



How Ionized Water is Made

Ionization dissociates the water molecules to form one hydroxyl ion [OH-] (alkaline), and one hydrogen ion [H+] (acidic).

The product of concentrations of H^+ and OH^- ions in water at a particular temperature is known as ionic product of water. The value of K_w increases with the increase of temperature, i.e., the concentration of H^+ and OH^- ions increases with increase in temperature.

The value of K_w at 25°C is 1×10^{-14}. Since pure water is neutral in nature, H^+ ion concentration must be equal to OH^- ion concentration.

$$[H^+] = [OH^{\sim}] = x$$

or $\mathbf{[H^+][OH^-]=x^2= 1 \times 10^{-14}}$

or $\mathbf{x = 1 \times 10^{-7}\ M}$

or $\mathbf{[H^+] = [OH^-] = 1 \times 10^{-7}\ mol\ litre^{-1}}$

This shows that at 25°C, in 1 litre only 10^{-7} mole of water is in ionic form out of a total of approximately 55.5 moles.

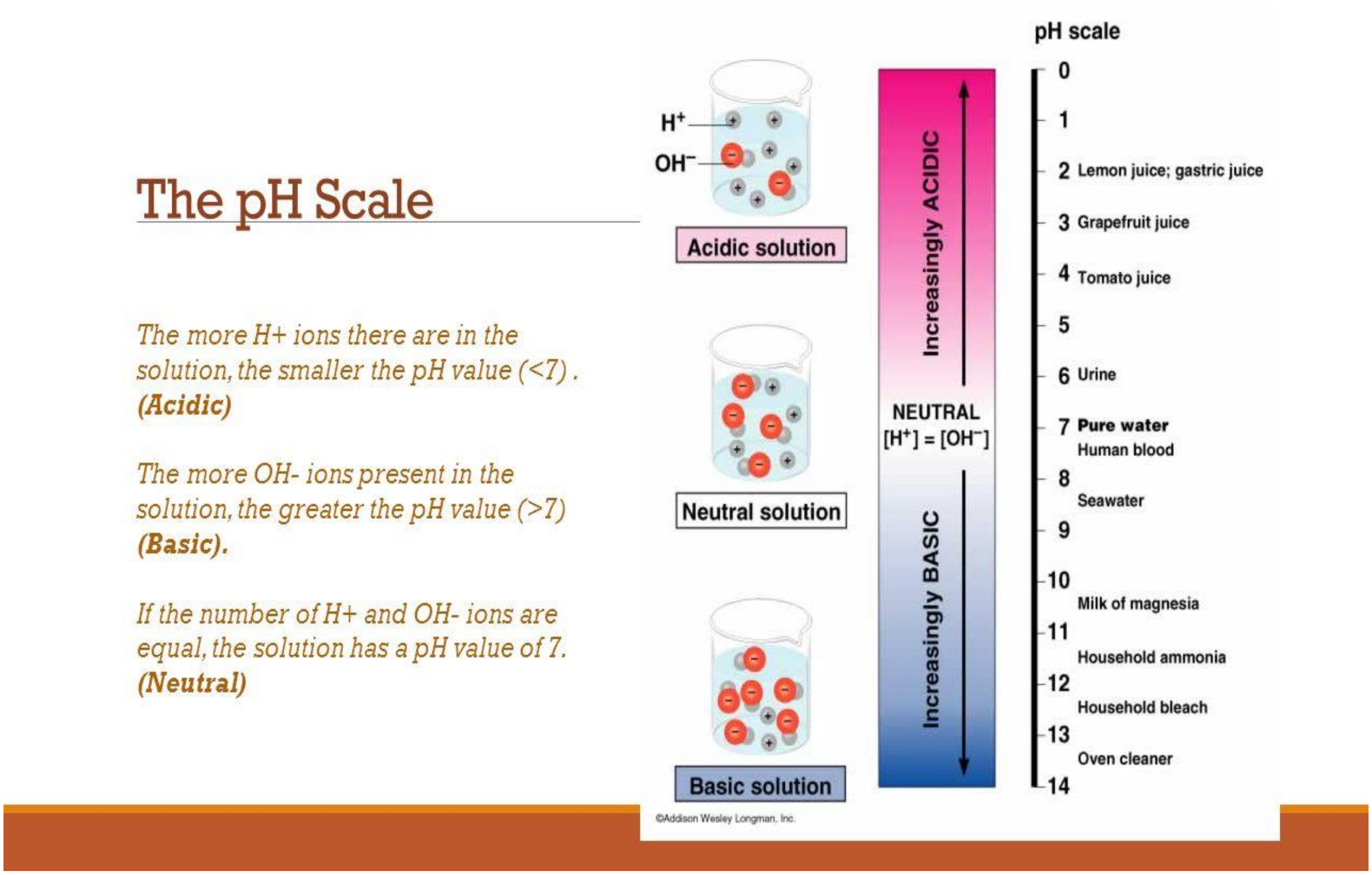
When an acid or a base is added to water, the ionic concentration product, $[H^+][OH^-]$, remains constant, i.e., equal to K_w but concentrations of H^+ and OH^- ions do not remain equal. The addition of acid increases the hydrogen ion concentration while that of hydroxyl ion concentration decreases,

pH of the solution

In chemistry, **pH** (/piːˈeɪtʃ/) is a numeric scale used to specify the acidity or basicity of an aqueous **solution**. It is approximately the negative of the base 10 logarithm of the molar concentration, measured in units of moles per liter, of hydrogen ions.

The pH of an aqueous solution is the measure of how acidic or basic it is. The pH of an aqueous solution can be determined and calculated by using the concentration of hydronium ion concentration in the solution

The pH of an aqueous solution is based on the pH scale which typically ranges from 0 to 14 in water (although as discussed below this is not an a formal rule). A pH of 7 is considered to be neutral. A pH of less than 7 is considered acidic. A pH of greater than 7 is then considered basic. Acidic solutions have high hydronium concentrations and lower hydroxide concentrations. Basic solutions have high hydroxide concentrations and lower hydronium concentrations.



The pH Scale

The more H+ ions there are in the solution, the smaller the pH value (<7) . ***(Acidic)***

The more OH- ions present in the solution, the greater the pH value (>7) ***(Basic).***

If the number of H+ and OH- ions are equal, the solution has a pH value of 7. ***(Neutral)***

$[H^+] > [OH^-]$; (Acidic solution)

Similarly, when a base is added, the OH^- ion concentration increases while H^+ ion concentration decreases,i.e.,

$[OH^-] > [H^+]$; (Alkaline or basic solution)

In neutral solution,

$[H^+] = [OH^-] = 1 \times 10^{-7}$ M

In acidic solution,

$[H^+] > [OH^-]$

or $[H^+] > 1 \times 10^{-7}\ M$

and $[OH^-] < 1 \times 10^{-7}\ M$

In alkaline solution,

$[OH^-] > [H^+]$

or $[OH^-] > 1 \times 10^{-7}\ M$

and $[H^+] < 1 \times 10^{-7}\ M$

Thus, if the hydrogen ion concentration is more than 1×10^{-7} M, the solution will be acidic in nature and if less than 1×10^{-7} M, the solution will be alkaline.

It is, thus, concluded that every aqueous solution, whether acidic, neutral or alkaline contains both H^+ and OH^- ions. The product of their concentrations is always constant, equal to 1×10^{-14} at 25°C. If one increases, the other decrease accordingly so that the product remains 1×10-14 at 25^o C.

<u>Relation between pH & pOH</u>

pH concept can also be used to express small quantities as OH & Kw

pOH = -log [OH^-]

pKw = - log Kw

let us consider log form of the expression

Kw = [H^+] [OH^-]

That is Log Kw = log H +log OH

Or – log Kw = - log H – log OH

Thus pKw = pH + pOH

Since Kw = 1.0 X 10^{-14} mol /litre

Therefore p Kw =- log 1.0 X 10^{-14} mol /litre=14

Hence for any aqueous solution a time 25 ^{0} C

pH + pOH add upto 14

i.e pH + pOH = 14

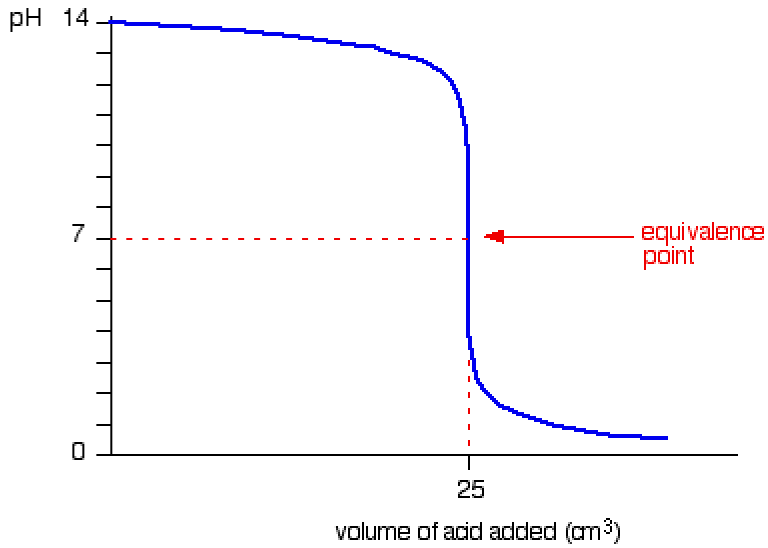
Neutralization Curve of Acid & Base

Titration curves for strong acid v strong base

We'll take hydrochloric acid and sodium hydroxide as typical of a strong acid and a strong base.

$$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$$

Running acid into the alkali



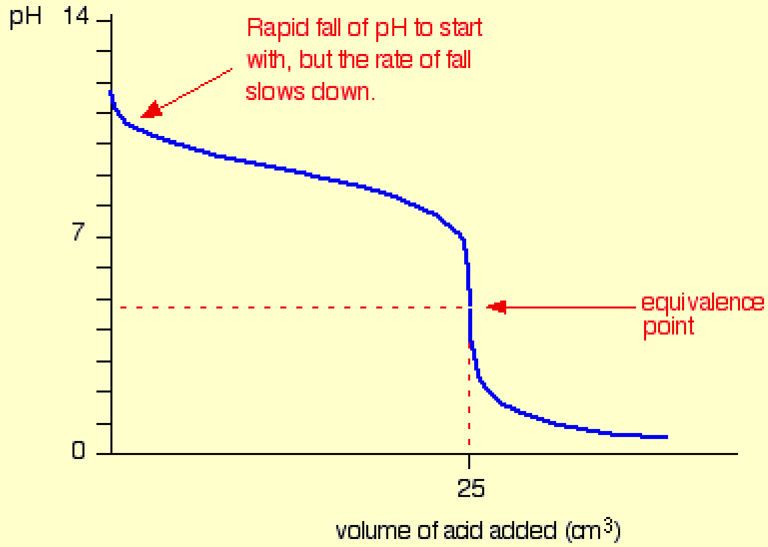
You can see that the pH only falls a very small amount until quite near the equivalence point. Then there is a really steep plunge.

Titration curves for strong acid v weak base

This time we are going to use hydrochloric acid as the strong acid and ammonia solution as the weak base.

$$NH_{3(aq)} + HCl_{(aq)} \longrightarrow NH_4Cl_{(aq)}$$

Running acid into the alkali



Because you have got a weak base, the beginning of the curve is obviously going to be different. However, once you have got an excess of acid, the curve is essentially the same as before.

At the very beginning of the curve, the pH starts by falling quite quickly as the acid is added, but the curve very soon gets less steep. This is because a buffer solution is being set up - composed of the excess ammonia and the ammonium chloride being formed.

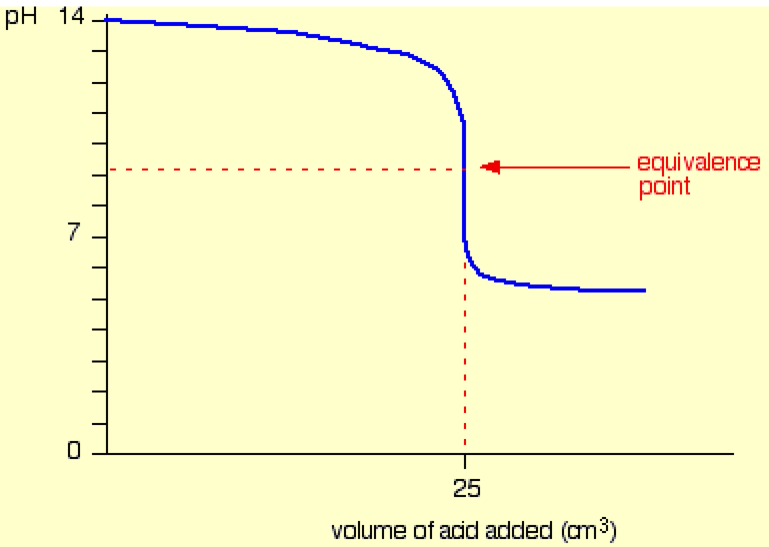
. itration curves for weak acid v strong base

We'll take ethanoic acid and sodium hydroxide as typical of a weak acid and a strong base.

$$CH_3COOH_{(aq)} + NaOH_{(aq)} \longrightarrow CH_3COONa_{(aq)} + H_2O_{(l)}$$

Running acid into the alkali

For the first part of the graph, you have an excess of sodium hydroxide. The curve will be exactly the same as when you add hydrochloric acid to sodium hydroxide. Once the acid is in excess, there will be a difference.



Past the equivalence point you have a buffer solution containing sodium ethanoate and ethanoic acid. This resists any large fall in pH.

Titration curves for weak acid v weak base

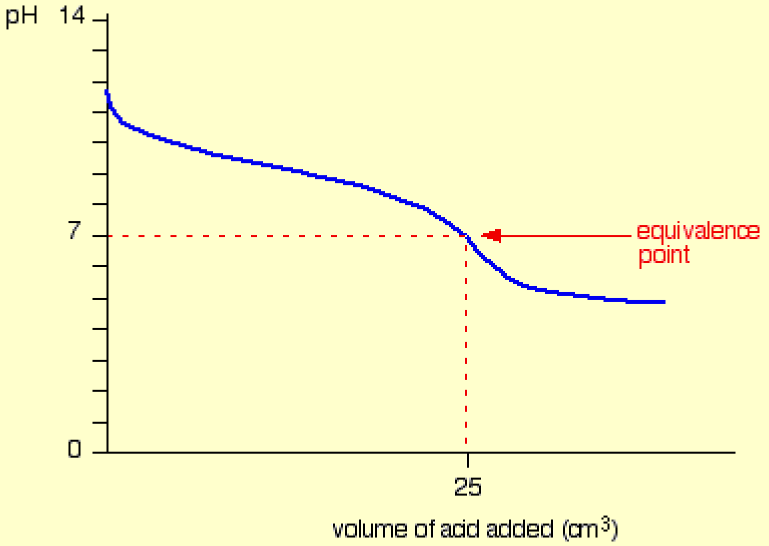
The common example of this would be ethanoic acid and ammonia.

$$CH_3COOH_{(aq)} + NH_{3(aq)} \longrightarrow CH_3COONH_{4(aq)}$$

It so happens that these two are both about equally weak - in that case, the equivalence point is approximately pH 7.

Running acid into the alkali

This is really just a combination of graphs you have already seen. Up to the equivalence point it is similar to the ammonia - HCl case. After the equivalence point it is like the end of the ethanoic acid - NaOH curve.



Notice that there isn't any steep bit on this graph. Instead, there is just what is known as a "point of inflexion". That lack of a steep bit means that it is difficult to do a titration of a weak acid against a weak base.

Theory of Indicators

An **indicator** is a substance which show characteristic change in its colour when comes in contact with acid or base and thus it is used to determine **dicators** the degree of acidity or basicity of any solution. For example litmus solution or litmus paper.

Role of indicators in chemistry is very important. They are used are also used to find out the end point in a titration.

In acid-base **titrations**, organic substances (weak acids or weak bases) are generally used as **indicators**.

Indicators change their colour within a certain pH range.The colour change and the pH range of some common **indicators used** are tabulated below:

ndicator	**pH Range**	**Colour of Acidic Solution**	**Colour of Basic Solution**
Methyl Orange	**3.2-4.5**	**Orange**	**Yellow**
Methyl Red	**4.4 – 6.5**	**Red**	**Yellow**
Bromothymol blue	**6.0 -7.8**	**Yellow**	**Blue**
Phenolphthalein	**8.3- 10.0**	**Colourless**	**Pink**
Alizarin Yellow	**10.1 – 12.1**	**Yellow**	**Red**
Litmus	**5.5-7.5**	**Red**	**Blue**
Phenol red	**6.8-8.4**	**Yellow**	**Red**

There are two theories which explain the change of colour **indicators** with change in pH.

Ostwald's Theory:

According to Ostwald’s theory

- The colour change of any indicator is due to its ionisation. The unionised form of indicator has different colour than its ionised form.
- An inidicator is either a weak acid or base, so its ionisation is highly affected in acids and bases. If an **indicator** is a weak acid, its ionisation would be very much low in acids due to common H^+ ions while it is fairly ionised in alkalies. In the same way, if the **indicator** is a weak base, its ionisation is large in acids and low in alkalies due to common OH^- ions.

Let’s take examples of two important indicators **phenolphthalein**which is a weak acid and **methyl orange** which is a weak base.

1. Phenolphthalein:

It is represented as HPh. This indicator being a weak acid ionises in solution to a small extent as follows:

$$HPh \rightleftharpoons H^+ + Ph^-$$

Colourless Pink

Applying law of mass action, we get

$K = [H^+][Ph^-]/[HPh]$

The undissociated molecules of **phenolphthalein** are colourless while the Ph^- ions are pink in colour. In presence of an acid , ionisation of HPh is practically negligible as the equilibrium shifts to left hand side due to high concentration of H^+ ions. Thus, the solution would remain colourless. On addition of alkali, hydrogen ions are removed by OH^- ions in the form of water molecules and the equilibrium shifts to right hand side. Thus, the concentration of Ph^- ions increases in solution and they impart pink colour to the solution.

2. Methyl orange:

It is a very weak base and can be represented as MeOH. It is ionized in solution to give Me^+ and OH^- ions.

$\mathbf{MeOH \rightleftharpoons Me^+ + OH^-}$

Yellow Red

Applying law of mass action,

$\mathbf{K = [Me^+][OH^-]/[MeOH]}$

In presence of an acid, OH^- ions are removed in the form of water molecules and the above equilibrium shifts to right hand side. Thus, sufficient Me^+ ions are produced which impart red colour to the solution. On addition of alkali, the concentration of OH^- ions increases in the solution and the equilibrium shifts to left hand side, i.e., the ionisation of MeOH is practically negligible. Thus, the solution acquires the colour of unionised **methyl orange** molecules, i.e., yellow.

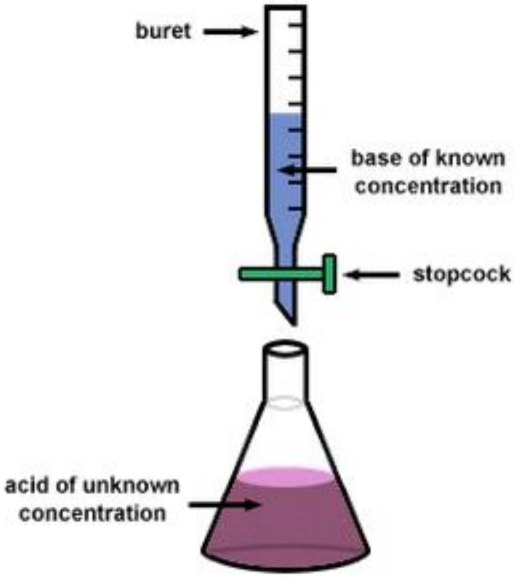
This theory also explains the reason why **phenolphthalein** is not a suitable **indicator** for **titrating** a weak base against strong acid. The OH^- ions furnished by a weak base are not sufficient to shift the equilibrium towards right hand side considerably, i.e., pH is not reached to 8.3. Thus, the solution does not attain pink colour. Similarly, it can be explained why **methyl orange** is not a suitable **indicator** for the **titration** of weak acid with strong base.

- **Quinonoid theory**

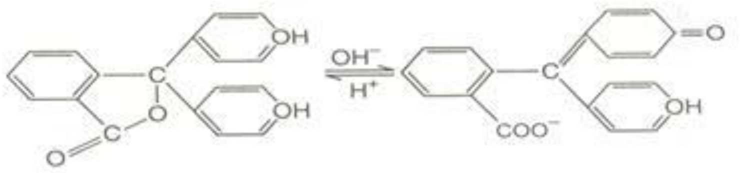
According to quinonoid theory, an **acid-base indicators** exist in two tautomeric forms having different structures which are in equilibrium. One form is termed benzenoid form and the other quinonoid form.

The two forms have different colors. The color change is due to the interconversation of one tautomeric form into other. One form mainly exists in acidic medium and the other in alkaline medium.

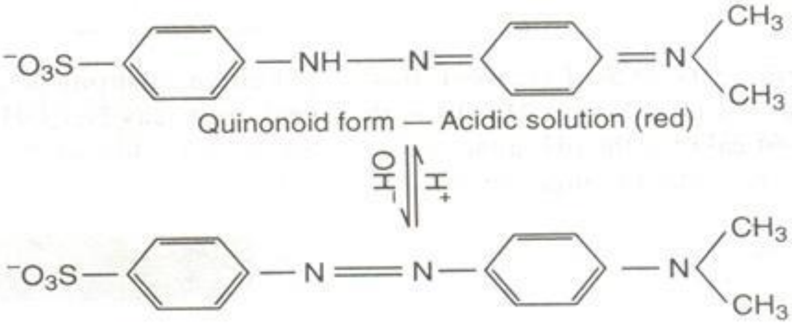
Thus, during **titration** the medium changes from acidic to alkaline or vice-versa. The change in pH converts one tautomeric form into other and thus, the colour change occurs.



Phenolphthalein has benziod form in acidic medium and thus, it is colourless while it has quinonoid form in alkaline medium which has pink colour.



Methyl orange has quinonoid form in acidic solution and benzenoid form in alkaline solution. The color of benzenoid form is yellow while that of quinoniod form is red.



Quinonoid form — Acidic solution (red)