IONIC EQUILIBRIA

ACID – BASE THEORY

An acid is:

- A substance that donates a proton ***OR***
- A substance that can accept a pair of electrons

A base is:

- A substance that accepts a proton ***OR***
- A substance that donates a pair of electrons

- When an acid also called the *conjugate acid of the base* donates a proton, a base called the *conjugate base of an acid* is formed. For example:

Conjugate acid	Conjugate base
HCl	Cl^-
HNO_3	NO_3^-
H_2O	OH^-
NH_4^+	NH_3
$[Al(H_2O)_6]^{3+}$	$[Al(H_2O)_5OH]^{2+}$

- When bases accept protons, they form the *conjugate acids of the bases.* For example, ammonia accepts a proton to form the ammonium ion which by definition is a conjugate acid of ammonia.

$$NH_3(aq) + \; H^+(aq) \longrightarrow NH_4^+(aq)$$

Strength of acids and bases

- The strength of an acid is measured by the ease with which it releases a proton.
- *Strong acids:* easily release protons and are completely ionized in the solvents.
- *Weak acids:* do not easily release protons, and are partially ionized in the solvents.

Factors affecting acid strength

Nature of the solvent

- The more basic the solvent, the stronger will be the acid in such a solvent because the acid will easily donate its proton. If the solvent is of weaker base strength, the acid cannot easily donate its proton to it, hence behaving as a weak acid instead.
- Hence, ethanoic acid will show much more acid properties when dissolved in ammonia than when dissolved in water, because ammonia is stronger base than water.

Proton – conjugate base bond strength

- The stronger the proton – conjugate base bond, the weaker the acid will be. This is because it is difficult to break the bond and release the proton.

- The weaker the proton – base bond, the stronger the acid will be. This is because the bond can be easily broken and the proton easily released
- Hence HI is a stronger acid in aqueous solution than HF because the $H-I$ bond is weaker than the $H-F$ bond and can easily be broken to release protons more readily than that in $H-F$

Comparing acid strength

By using their degree of dissociation.

- Degree of dissociation is the fraction of each mole of an electrolyte that exists as ions. It can also be expressed as a percentage.
- A stronger acid has a higher degree of dissociation compared to a weak one.

By using their dissociation constants, $\boldsymbol{K_a}$, (weak acids)

- Since a weak acid partially ionizes, a solution of a weak acid has the ions and the molecules of an acid present in equilibrium with each other.
- Hence the law of mass action can be applied to give the dissociation constant. i.e. for a weak acid HX,

$$HX(aq) \leftrightharpoons H^+(aq) + X^-(aq)$$

$$K_a = \frac{[H^+][X^-]}{[HX]}$$

- An acid with a higher K_a value would have ionized more than the one with the lower value. Hence an acid with a higher K_a value is a stronger acid than the one with a lower value.

Dissociation of water

- Water is a weak electrolyte because it is slightly ionized

$$H_2O(l) \leftrightharpoons H^+(aq) + OH^-(aq)$$

- By applying the law of mass action the equation obtained is

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

- But since the dissociation of water is very small,

$$[H_2O] \approx 1$$

- Hence, equation (1) becomes

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

- Which is called the *the ionic product of water*
- The numerical value of the ionic product of water is given by

$$\boldsymbol{K_w = 1 \times 10^{-14} mol^2 dm^{-6}}$$

pH

- This is defined as *the negative logarithm to base ten of the hydrogen ion concentration of a given solution*

i.e. $\boldsymbol{pH = -\log_{10}[H^+]}$

pH of water

- From $K_w = [H^+][OH^-] = 1 \times 10^{-14}$
- But $[H^+] = [OH^-]$

$$\therefore [H^+]^2 = 1 \times 10^{-14}$$

$$[H^+] = \sqrt{(1 \times 10^{-14})}$$

$$pH = -\log_{10}\left(\sqrt{(1 \times 10^{-14})}\right)$$

$$\underline{\underline{pH = 7}}$$

pH of acids

- ***Strong acids***
- These are completely ionized in aqueous solution.
- Thus their $pH = -\log[H^+]$

- ***Weak acids***
- Weak acids do not completely dissociate even in very dilute solution. The $[H^+] \neq [Acid]$. The hydrogen ion concentration depends on the degree of dissociation of the acid.
- Consider a weak acid HX which ionizes in aqueous solution as follows

	$HX(aq)$	$\leftrightharpoons$	$H^+(aq)$	$+$	$X^-(aq)$
Initial moles:	1		0		0
Equilibrium moles:	$1-\propto$		$\propto$		$\propto$
Equilirium concetration	$\frac{1-\propto}{V}$		$\frac{\propto}{V}$		$\frac{\propto}{V}$

Applying the law of mass action:

$$K_a = \frac{[H^+][X^-]}{HX}$$

$$K_a = \frac{\left(\frac{\propto}{V}\right)\left(\frac{\propto}{V}\right)}{\left(\frac{1-\propto}{V}\right)}$$

$$K_a = \frac{\propto^2}{V(1-\propto)}$$

But

$$\frac{1}{V} = C$$

- For weak acids, the degree of dissociation is very small such that

$$(1-\propto) \approx 1$$

- Hence

$$\boldsymbol{K_a = C \propto^2}$$

- From the above equation it can be seen that

$$\boldsymbol{[H^+] = C \propto}$$

- Also

$$\boldsymbol{[H^+] = \sqrt{CK_a}}$$

pH of bases

- *Strong bases*

These are assumed to be completely ionized. In solution, these produce hydroxide ions in the solution and not hydrogen ions. For this reason, the pH of the solution is determined indirectly from the ionic product expression.

i.e

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

$$[H^+] = \frac{K_w}{[OH^-]}$$

Introducing $-\log_{10}$ $both\ sides$

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

Hence $pH = pK_w - pOH$

But

$$pK_w = 14$$

Therefore

$$pH = 14 - pOH$$

Weak bases

These are partially dissociated in solution. The hydroxide ion concentration in the solution as it was with the weak acids is dependent on the base dissociation constant, K_b, or the degree of dissociation ($\propto$)

Hence

$$\boldsymbol{K_b = C \propto^2}$$

$$\boldsymbol{[OH^-] = C \propto}$$

$$\boldsymbol{[OH^-] = \sqrt{CK_b}}$$

SALT HYDROLYSIS

- *Is the reaction of a salt with water to form a solution whose pH is greater or less than seven*
- Typically, salts are thought to give neutral solutions when dissolved in water. However, this is only true for salts derived from strong acids and strong bases. Other combination of salts when dissolved in water, give solutions whose pH is not exactly seven.
- Hydrolysis can occur in three different ways, all of which produce changes in pH

Salts of strong bases and weak acids

- When such salts are dissolved in water, they give alkaline solutions. (pH is greater than seven)
- Examples include: sodium ethanoate, potassium fluoride, sodium carbonate, potassium cyanide, sodium sulphite.

- The anion being a conjugate base of a weak acid, easily accepts protons from the water molecules to form an unionized weak acid and the hydroxide ion in solution. This makes the solution alkaline. Consider a salt such as sodium methanoate.
- Sodium methanoate in water dissociates into sodium and methanoate ions.

$$HCOONa\,(aq) \longrightarrow HCOO^-(aq) + Na^+(aq)$$

- The methanoate ions then react with water molecules

$$HCOO^-(aq) + H_2O(l) \leftrightharpoons HCOOH(aq) + OH^-(aq)$$

- The free hydroxide ions in the solution make it alkaline.

- From the above equation, the law of mass action can be applied, to give

$$K = \frac{[HCOOH][OH^-]}{[\,HCOO^-][H_2O]}$$

- But since water is in large excess, its concentration does change much so that at equilibrium $[H_2O] \approx 1$.

Hence

$$\boxed{K_h = \frac{[HCOOH][OH^-]}{[\,HCOO^-]}}$$

The above expression is called the *expression for the hydrolysis constant, K_h, of the salt, sodium methanoate.*

K_h is called the hydrolysis constant

pH of the solution

From the expression,

$$K_h = \frac{[HCOOH][OH^-]}{[\,HCOO^-]}$$

But

$$[HCOOH] = [OH^-]$$

$$[\,HCOO^-] \approx [salt]$$

Hence

$$K_h = \frac{[OH^-]^2}{[salt]}$$

$$\boxed{\boldsymbol{[OH^-] = \sqrt{(K_h[salt])}}}$$

And

$$pH = 14 - pOH$$

Note

$$K_h = \frac{[HCOOH][OH^-]}{[\,HCOO^-]}$$

- Multiplying through the numerator and denominator by $[H^+]$

$$K_h = \frac{[HCOOH][OH^-]}{[\,HCOO^-]} \times \frac{[H^+]}{[H^+]}$$

- Re-arranging

$$K_h = \frac{[HCOOH]}{[\,HCOO^-][H^+]} \times [H^+][OH^-]$$

- But

$$\frac{[HCOOH]}{[\,HCOO^-][H^+]} = \frac{1}{K_a}$$

And

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

Therefore

$$\boxed{K_h = \frac{K_w}{K_a}}$$

Salts of weak bases and strong acids

- When such salts are dissolved in water, they give acidic solutions. (pH is less than seven)
- Examples include: ammonium chloride, ammonium nitrate, methylammonium chloride, dimethylammonium nitrate.
- The cation of the salt being a conjugate acid of a weak base, easily releases protons to form an unionized weak base and a proton in solution. This makes the solution acidic
- For example, a solution of ammonium chloride is acidic will react with strongly electropositive metals such as zinc to liberate hydrogen. This is because
- Ammonium chloride dissociates fully in water

$$NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

- The ammonium ions then react with water to form an acidic solution.

$$NH_4^+(aq) + H_2O(l) \leftrightharpoons NH_3(aq) + H_3O^+(aq)$$

- The oxonium ions produced then react with the metal to liberate hydrogen gas

$$Zn(s) + 2H_3O^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g) + 2H_2O(l)$$

- From the above equation, the law of mass action can be applied, to give

$$K = \frac{[NH_3][\,H_3O^+]}{[NH_4^+][H_2O]}$$

- But since water is in large excess, its concentration does change much so that at equilibrium $[H_2O] \approx 1$. Hence

$$K_h = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

- The above expression is called the *expression for the hydrolysis constant, K_h, of the salt, ammonium chloride*

- ***pH of the solution***
- From the expression,

$$K_h = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

- But
  $[NH_3] = [H_3O^+]$ and $[NH_4^+] \approx [salt]$

Hence

$$K_h = \frac{[H_3O^+]^2}{[salt]}$$

$$\boxed{[\boldsymbol{H_3O^+}] = \sqrt{(\boldsymbol{K_h[salt]})}}$$

And

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

- ***Note***

It is also true that

$$K_h = \frac{K_w}{K_b}$$

Salts containing heavily hydrated cations

- A number of normal salts when dissolved in water give an acidic solution for example iron(III) chloride. This is because; the hydrated metal ion behaves as an acid. The high charge density of the cation causes greater attraction of the lone pairs in the water molecules. This attraction extends to $O-H$ bonds which becomes weaker, so that a proton is lost to the solution

$$[Fe(H_2O)_6]^{3+}(aq) \quad \leftrightharpoons \quad [Fe(H_2O)_5OH]^{2+}(aq) \quad + \quad H^+(aq)$$

BUFFER SOLUTION

- *This is a solution which resists a change in pH when a small amount of acid or alkali is added.*
- A buffer solution consists of either a *weak acid and its salt with a strong base (a conjugate base)* or a *weak base (alkali) and its salt with a strong acid*

Types of Buffers

Acidic buffers

- These contain a weak acid and its salt with a strong base. For example, methanoic acid and sodium methanoate, ethanoic acid and potassium ethanoate, carbonic acid and sodium carbonate.

Action of an acidic buffer

- Consider a buffer solution made of methanoic acid and sodium methanoate.
- Sodium methanoate fully ionizes in aqueous solution

$$HCOONa(aq) \longrightarrow HCOO^-(aq) + Na^+(aq)$$

- Methanoic acid partially ionizes.

$$HCOOH(aq) \leftrightharpoons HCOO^-(aq) \quad + \quad H^+(aq)$$

- The presence of methanoate ions from the salt suppresses the ionization of methanoic acid further so that the solution contains large amount on methanoate ions and methanoic acid molecules.
- If a small amount of the acid is added to the solution, the hydrogen ions added react with methanoate ions to methanoic acid molecules.

$$HCOO^-(aq) \quad + \quad H^+(aq) \quad \longrightarrow \quad HCOOH(aq)$$

- If a small amount of the alkali is added, the excess methanoic acid molecules react with the hydroxyl ions added to form the salt and water.

$$HCOOH(aq) \; + \; OH^-(aq) \; \longrightarrow \; HCOO^-(aq) \; + \; H_2O(aq)$$

- Hence the pH of the solution remains unchanged

pH of an acidic buffer

- Methanoic acid in the solution is partially ionized.

$$HCOOH(aq) \; \leftrightharpoons \; HCOO^-(aq) + H^+(aq)$$

- By law of mass action,

$$K_a = \frac{[HCOO^-][H^+]}{[HCOOH]}$$

- But since the acid is only slightly ionized,

$$[HCOO^-] \approx [salt]$$

$$[HCOOH] \approx [acid]$$

Therefore

$$K_a = \frac{[salt][H^+]}{[acid]}$$

$$[\boldsymbol{H^+}] = \frac{\boldsymbol{K_a[acid]}}{\boldsymbol{[salt]}}$$

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

Basic buffers

- These contain a weak base, and its salt with a strong acid. For example, ammonia solution and ammonium chloride, methylammonium nitrate and methylamine solution.

Action of a basic buffer

- Consider a solution containing ammonia solution and ammonium chloride.
- Ammonium chloride is fully dissociated

$$NH_4Cl(aq) \; \longrightarrow \; NH_4^+(aq) \; + \; Cl^-(aq)$$

- While ammonia is partially ionized

$$NH_3(aq) \; + \; H_2O(l) \; \leftrightharpoons \; NH_4^+(aq) \; + \; OH^-(aq)$$

- The presence of ammonium ions from the salt suppresses the ionization of ammonia molecules so that the solution contains a large amount of ammonium ions from the salt and unionized ammonia molecules.

- If a small amount of the acid is added to the solution, the hydrogen ions from the acid react with ammonia molecules to form ammonium ions.

$$NH_3(aq) \quad + \quad H^+(aq) \quad \longrightarrow \quad NH_4^+(aq)$$

- If a small amount of the alkali is added, the excess ammonium ions react with the hydroxyl ions added to form ammonia molecules and water

$$NH_4^+(aq) \; + \; OH^-(aq) \; \longrightarrow \; NH_3(aq) \; + \; H_2O(l)$$

Hence the pH of the solution remains unchanged

pH of an acidic buffer

- Ammonia in the solution is partially ionized.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

By law of mass action,

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3(aq)]}$$

But since the acid is only slightly ionized,

$$[NH_4^+] \approx [salt]$$

$$[NH_3] \approx [base]$$

Therefore

$$K_b = \frac{[salt][OH^-]}{[base]}$$

$$[\boldsymbol{OH^-}] = \frac{\boldsymbol{K_b[base]}}{\boldsymbol{[salt]}}$$

But $pH = 14 - pOH$

Applications of buffer solutions

- ➢ Maintain constant pH of blood and tissue fluids
- ➢ In fermentation buffers prevent pH changes that would reduce the activity of enzymes
- ➢ In medicine, Solutions for intravenous injections are buffered so that pH does not change.
- ➢ in biochemical assays depend on enzymes and buffers are used to maintain the pH constant
- ➢ in industrial products such as shampoos and lotions
- ➢ in manufacture of drug

SOLUBILITY PRODUCT

- This applies to a sparingly soluble salt.
- When a sparingly salt such as lead(II) sulphate is added to water, little of it dissolves and produces ions in the solution while most of it remains undissolved. This there is equilibrium between the solid and its ions. Consider a sparingly soluble salt, MX which dissolves in water according to the equation.

$$MX(s) \rightleftharpoons M^+(aq) \; + \; X^-(aq)$$

- Since the ions are in contact with the solid, the solution is said to be saturated.
- By law of mass action,

$$K = \frac{[M^+][X^-]}{[MX]}$$

- But since the solubility of the salt is very small, the $[MX] \approx 1$.
- Hence the equation becomes

$$K_{sp} = [M^+][X^-]$$

- Which is the *solubility product expression* for a sparingly soluble salt, MX.
- K_{sp} is called the *solubility product constant.*

- *The **solubility product** of a sparingly soluble salt is the product of the molar concentration of the ions produced by the salt raised to their stoichiometric powers in a saturated solution at a given temperature.*

- ***Solubility of a salt***:
  Is the mass of a salt required to saturate 100g of water at a given temperature **OR** *The mass of the salt that can be dissolved in 100g of water to form a saturated solution at a given temperature*

- ***Saturated solution:***
  Is a solution that cannot dissolve any more solute at a given temperature in the presence of un-dissolved solute.

- The solubility of a sparingly soluble salt can be determined by conductivity measurements e.g. for barium sulphate or titration and the solubility product calculated e.g. magnesium hydroxide, calcium iodate.

Note:

When

- $K_{sp} = [M^+][X^-]$; The solution is said to be saturated
- $K_{sp} > [M^+][X^-]$; The solution is unsaturated
- $K_{sp} < [M^+][X^-]$; Precipitation occurs

Determination of the solubility product of sparingly soluble salt such as silver oxalate

This can be done by titration method.

Procedure

- Excess silver oxalate is added to a given volume of water in a container.
- The container is stoppered and shaken occasionally for about two hours.
- The solution is filtered to removes the excess solid
- An aliquot of the filtrate is pipetted into a conical flask and **warmed**.
- The **warm** solution is titrated with a standard solution of potassium manganate(VII).
- The concentration of the oxalate ions in the solution is calculated.

Treatment of results

$$Ag_2C_2O_4(s) \leftrightharpoons 2Ag^+(aq) + C_2O_4^{2-}(aq)$$

- Let $[C_2O_4^{2-}] = x$
- $[Ag^+] = 2x$

- From
- $K_{sp} = [Ag^+]^2[C_2O_4^{2-}]$

- $K_{sp} = (2x)^2x$
- $K_{sp} = 4x^3$

Factors which affect the solubility of a sparingly soluble salt

Formation of complex ion

- Consider a sparingly salt such as silver oxalate.

$$Ag_2C_2O_4(s) \leftrightharpoons 2Ag^+(aq) + C_2O_4^{2-}(aq)$$

- The solubility of this salt can be increased by adding ammonia solution. This is because ammonia reacts with silver ions to form the diamminesilver(I) complex ions.

$$Ag^+(aq) + 2NH_3(aq) \longrightarrow [Ag(NH_3)_2]^+(aq)$$

- This reduces the concentration of silver ions in equilibrium. And in order to restore the K_{sp}, more silver oxalate dissolves.
- Hence, *formation of a complex ion increases the solubility of a sparingly soluble salt.*
- The solubility of lead(II) chloride is higher in concentrated hydrochloric acid than water or dilute hydrochloric acid du formation of a complex ion, tetrachloroplumbate(II).

$$PbCl_2(aq) + 2Cl^-(aq) \longrightarrow [PbCl_4]^{2-}(aq)$$

- Copper(I) salts are also more soluble in aqueous ammonia than water because of formation of the complex ion, diamminecopper(I) ion.

$$Cu^+(aq) + 2NH_3(aq) \longrightarrow [Cu(NH_3)_2]^+(aq)$$

Common ion effect

- *This is the precipitation of a sparingly soluble ionic solute from a saturated solution by adding to the solution another electrolyte containing an ion common to that of the sparingly soluble compound.*

- The *common ion effect reduces the solubility of a sparingly soluble salt*.
- Consider a sparingly soluble salt such as silver chloride.

$$AgCl(s) \leftrightharpoons Ag^+(aq) + Cl^-(aq)$$

- When silver nitrate is added to such a solution, the concentration of silver ions in the solution increases, the ionic product exceeds the K_{sp}, the excess silver ions react with chloride ions to form silver chloride solid and the K_{sp} is restored.

- The same thing would occur if sodium chloride was added to a saturated solution of silver chloride

Applications of common ion effect

Purification of common salt.

- Common salt contains calcium and magnesium chloride as impurities. Bubbling hydrogen chloride through a saturated solution of impure sodium chloride will precipitate sodium chloride while leaving calcium and magnesium chlorides in the solution

Salting out of soap

- In the preparation of soap, a concentrated solution of sodium chloride is added to the reaction mixture to precipitate soap.

Selective precipitation of compounds in qualitative analysis

- This also uses the knowledge of solubility product and common ion effect, for example the precipitation of sulphides.
- Certain metal sulphides are precipitated by passing hydrogen sulphide into a solution of the metal ion in presence of an acid while others in the presence of alkali.
- The choice of the conditions depends on the solubility product of the sulphide.
- Precipitation of sulphides such as ZnS, MnS, and NiS occurs in alkaline medium (presence of dilute ammonia).
- Hydrogen sulphide ionizes in water as follows

$$H_2S(aq) \leftrightharpoons 2H^+(aq) + S^{2-}(aq)$$

- In the presence of an alkali, hydrogen sulphide reacts with the alkali the hydrogen ions react with the hydroxide reducing their concentration in equilibrium. This causes further ionization of hydrogen sulphide and the concentration of the sulphide ions increases. The high K_{sp} of the sulphides is reached which enables them to precipitate.
- While, sulphides such as CuS, SnS and CdS with low K_{sp} values are precipitated in acidic medium (presence of dilute hydrochloric acid). The hydrogen ions from the acid suppress the ionization of hydrogen sulphide. Very low concentration of sulphide ions occur in solution but enough to reach the K_{sp} of the metal sulphides hence precipitated.

Use of potassium chromate(IV) in silver titration

- When silver nitrate solution is titrated with sodium chloride solution containing a little potassium chromate(IV), only silver chloride is precipitate as long as there are any chloride ions in the solution. The red precipitate of silver chromate(VI) appears when all the chloride ions are reacted.
- This is explained by the solubility products of the two silver salts.

$K_{sp}(AgCl) = 1 \times 10^{-10} mol^2 dm^{-6}$ and $K_{sp}(Ag_2CrO_4) = 2.5 \times 10^{-12} mol^3 dm^{-9}$.

- Suppose the concentration of Cl^{-} and $CrO_4^{2-}$are both $0.1\,moldm^{-3}$ then the concentration of silver ions needed to precipitate silver chloride

$$=\frac{1\times10^{-10}}{0.1}=1\times10^{-9}\,moldm^{-3}$$

- Concentration of silver ions needed to precipitate silver chromate

$$=\sqrt{\left(\frac{2.5\times10^{-12}}{0.1}\right)}=5\times10^{-6}\,moldm^{-3}$$

- Thus even if the concentration of chloride and chromate ions in the solution is the same, it is easier by adding silver ions to reach the solubility product of silver chloride than that of silver chromate in spite of the lower solubility product of the latter.

ACID – BASE INDICATORS

- Acid – base indicators are substances which can change colour according to the hydrogen ion concentration of the liquid in which they are placed.
- They are weak acids, hence they are slightly dissociated when dissolved in water. The colour of the indicator depends on the colour of the undissociated molecules and the colour of the ions produced.

Action of an indicator

- Consider an indicator, HIn, when put in water, it ionizes as follows

$$HIn(aq) \leftrightharpoons H^{+}(aq) + In^{-}(aq)$$

- And at this point, there are indicator molecules (HIn) and ions in the solution and the colour of the solution will be an intermediate of the two. e.g. in water methyl orange is orange, while phenolphthalein is colourless.

- *Addition of an acid*, increases the hydrogen ion concentration in the solution. These combine with the In^{-} in the solution to form the unionized HIn indicator molecules. The HIn molecules of litmus and methyl orange are red, while those of phenolphthalein are colourless.

- *Addition of an alkali,* provides hydroxide ions which react with the hydrogen ions from the indicator. This reduces the concentration of the hydrogen ions in equilibrium. More of the indicator molecules ions, increasing the concentration of the In^{-} ions in the solution, hence the colour of the solution also changes to that of the In^{-} ions. e.g. the In^{-} ions of litmus are blue, methyl orange are orange, and phenolphthalein pink

Choice of an indicator

- The true point of neutralization in any titration occurs when the amounts acid and base added together are chemically equivalent to each other. i.e. complete neutralization has taken place and a salt and water have been produced.

- However sometimes, the pH is not equal to 7 even at this point. This is because the salt formed at endpoint may undergo hydrolysis. The choice of the indicator will therefore depend on the pH of the solution at end point.
- Every indicator has a definite range of pH over which it changes colour, and if the pH at the end point of the titration falls within this range, then the indicator will be the ideal choice.

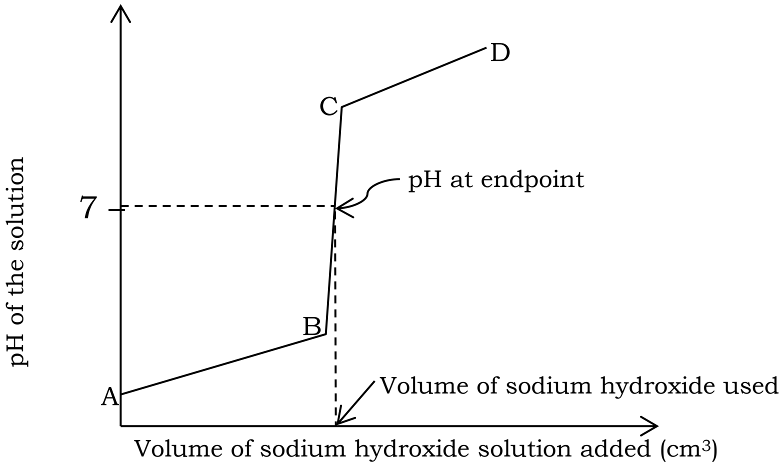
Table showing the ranges of some common indicators

Indicator	**pH range**
Methyl orange	2.9 – 4.6
Phenolphthalein	8.3 – 10.0
Litmus	5.0 – 8.0
Methyl red	4.2 – 6.3

- A titration between a strong acid (hydrochloric acid) and a weak base (aqueous ammonia), produces a salt, ammonium chloride which undergoes hydrolysis to form an acidic solution. Hence end point, the solution has a pH lower than seven. Methyl orange, litmus and methyl red would be ideal choices. (methyl range is commonly used)
- A titration between a weak acid (ethanoic acid) and a strong base, (sodium hydroxide) produces sodium ethanoate which hydrolyses in water to form an alkaline solution, with pH greater than seven. Phenolphthalein is the indicator of choice.
- A titration between a strong acid and a strong base forms a salt that does not undergo hydrolysis. pH of the solution at endpoint is seven and any indicator can be used for the titration.

pH CURVES

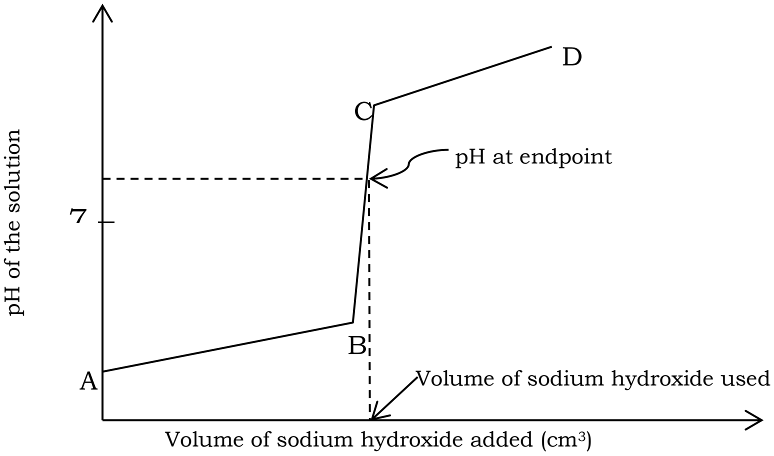
Titration of a strong acid against a strong alkali (hydrochloric *acid and* sodium hydroxide)



Explanation

- Initially, pH is low. Because hydrochloric acid is a strong acid the fully ionizes to give a high concentration of hydrogen ions.
- There is a gradual increase in pH between AB. This is because the acid is still in excess. The hydrogen ions gradually neutralized by the hydroxide ions from the alkali
- There is a rapid increase in pH between BC because the end point has been reached. A small amount of sodium hydroxide causes a big increase in pH.
- The pH continues to increase further between CD, due to addition of excess sodium hydroxide.
- The pH at endpoint is 7 because the salt formed (sodium chloride) does not undergo hydrolysis

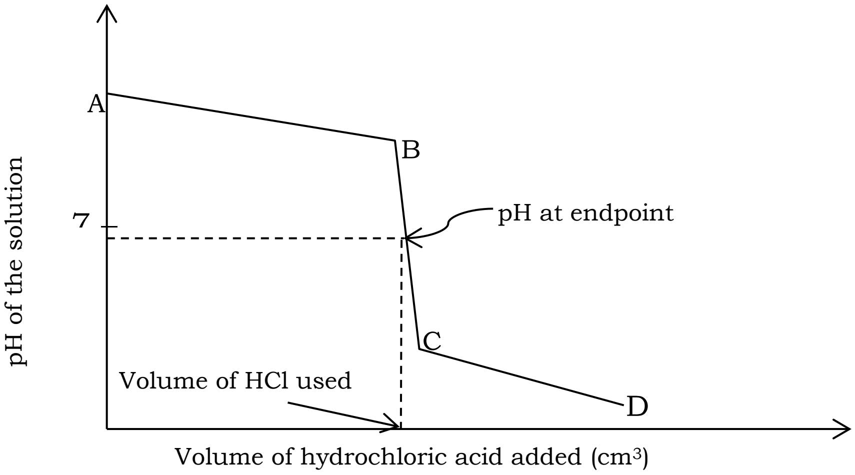
Titration of a weak acid against a strong alkali (ethanoic acid sodium hydroxide)



Explanation

- Initially the pH is not very low. Because ethanoic acid is a weak acid that partially ionizes to give a lower concentration of hydrogen ions
- The pH increase gradually along AB as the alkali is added because of the gradual neutralization of the excess hydrogen ions by hydroxide ions. A buffer solution is formed that does not allow pH to change rapidly.
- pH increases rapidly along BC because the end point has been reached. Small amount of sodium hydroxide causes a big change in pH.
- The pH increase along CD because of excess sodium hydroxide added.
- The pH at end point is greater than 7 because of salt hydrolysis to form an alkaline solution

Titration of a weak alkali against a strong acid (aqueous ammonia and hydrochloric)



Explanation

- Initially at A, the pH is not very high. Because aqueous ammonia is a weak base that partially ionizes to give fewer hydroxide concentration in the solution.
- The pH then decreases gradually along AB. This is because of addition of the hydrogen ions that neutralizes the hydroxide ions. The alkali is still in excess and together with the salt formed form a buffer solution that resists a rapid change in pH.
- The pH then decreases rapidly along BC when a small amount of the acid is added because the endpoint is reached.
- Along CD pH decreases gradually because of addition of excess acid
- The pH at endpoint is less than seven because the salt formed undergoes hydrolysis to produce hydrogen ions that make the solution acidic.