

Unit - IIA. Volumetric AnalysisIntroduction

Analytical chemistry is a branch of Chemistry which deals with the analysis of substance.

It is divided into two classes

- (i) Qualitative analysis
- (ii) Quantitative analysis

Qualitative analysis determine types of chemical substance present in the given sample while

Quantitative analysis determine the amount of chemical substance present in the given sample.

There are various methods of quantitative analysis such as volumetric analysis, gravimetric analysis, spectrophotometry, polarimetry, fluorimetry, chromatography and biological methods.

Volumetric Analysis

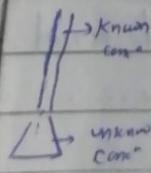
It is quantitative analysis in which volume of known concentration solution (std. soln) required to reacts with solution of unknown concentration.

- It is easy, accurate and faster method in comparison with other quantitative methods.

$\xrightarrow{\text{vol}^m}$  Important terms

volume

① Titration:

 The process in which  $\text{vol}^m$  of known concentration solution required to reacts with solution of unknown concentration is called as titration.

② Titrant and titrate:

The solution taken in burette during titration is called as titrant. While solution taken in a conical flask is called titrate.

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③ Equivalence point or Theoretical end point:

The volume at which the reaction is completed by addition of stoichiometric amount of titrant is known as equivalence point or theoretical end point.

④ Indicator:

The substance which is used for the detection of end point (or completion of <sup>particular</sup> reaction) visually is called as indicator.

⑤ End Point:

The volume at which the completion of reaction is observed by using an indicator is called as end point.

⑥ Titration error:

The difference between equivalence point (Theoretical end point) and end point is called as titration error.

### Requirements of volumetric analysis:

- ① The chemical reaction must be simple.
- ② The reaction must form product.
- ③ The reaction must show marked change at equivalence pt.
- ④ The reaction must be stoichiometric.
- ⑤ The reaction should not form any side reaction.
- ⑥ The reaction should be specific for the substance to be analysed.
- ⑦ The end point of reaction should be well defined and shows visible change by using indicator.
- ⑧ The reaction should be relatively fast.

### Advantages of Volumetric analysis:

- ① It required simple apparatus like burette, pipette, conical flask.
- ② It is simple process of analysis. (and does not involved laborious operations)

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- (3) It gives quick and correct result
- (4) It is more precise and accurate method.

### Definitions

#### ① standard solution:

The solution of known concentration (strength) is called as standard solution.

It is prepared by dissolving accurate quantity of highly pure substance.

#### ② primary standard substance:

The highly pure substance which is used to prepare standard solution by direct weighing is called as primary standard substance.

X - The ~~constant~~ substance whose solution can not be prepared by direct weighing and not used as primary standard substance is called secondary standard solution.

### Requirements of primary standard solution:

- ① It should be highly pure.
- ② Its composition should not change in air or during storage.
- ③ The impurities present in it should not be exceed 0.01 - 0.02%.
- ④ The substance should be readily soluble in a given solvent under experimental conditions.
- ⑤ It must possess high molar mass to minimize weighing error.
- ⑥ Its solution should be stable on keeping for longer time.

e.g. The primary std. solutions used in titration are

- ① Acid base titration → sodium carbonate, potassium hydrogen phthalate, succinic acid, Benzoic acid

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- (b) Redox titration  $\rightarrow$  potassium dichromate, potassium iodate, oxalic acid, sodium oxalate, Arsenious oxide
- (c) precipitation titration  $\rightarrow$  silver, silver nitrate, sodium chloride, potassium chloride.
- (d) complex formation titration  $\rightarrow$  Zn, Mg, disodium salt of EDTA.

Note: Generally hydrated salts are not used as primary standards because these substances loss water molecule on drying. The primary standard solution substances are used after drying between 105-110°C.

### Terms to express concentration

The concentration of solution is expressed on the basis of mass of solute dissolved in solvent or solution.

#### ① Molarity [M]:

The number of gram moles of solute (substance) dissolved in sufficient solvent to form  $1\text{dm}^3$  of solution is called as molarity.

- It is the ratio of wt. of solute per  $\text{dm}^3$  to molecular wt. of solute.
- It is determined by formula.

$$\text{Molarity (M)} = \frac{\text{wt. of solute per dm}^3}{\text{molecular wt. of solute}}$$

#### ② Normality (N):

The number of gram equivalent of solute (substance) dissolved in sufficient solvent to produce  $1\text{dm}^3$  of solution is called Normality.

It is determined by formula.

$$\text{Normality (N)} = \frac{\text{wt. of solute per dm}^3}{\text{Equivalent wt. of solute.}}$$

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Equivalent wt. depends upon type of reaction involved in the titration

(a) For acid-base titration

Eq. wt. is equal to molecular wt. of acid or base divided by no. of replaceable  $H^+$  or  $OH^-$  ions in acid or base respectively.

$$\text{Eq. wt. of an acid} = \frac{\text{molecular weight}}{\text{No. of replaceable } H^+ \text{ ions}}$$

$$\text{Eq. wt. of a base} = \frac{\text{molecular weight}}{\text{No. of replaceable } OH^- \text{ ions}}$$

(b) For oxidation-reduction titration

The equivalent wt. of an oxidizing or reducing agent is equal to molecular wt. of oxidizing or reducing agent divided by no. of electrons gained or lost per molecule (or ion) of the substance.

(3) Molality (m):

The number of gram moles of solute (substance) dissolved in sufficient solvent to form 1 kilogram of solvent is called as molality.

$$\text{molality (m)} = \frac{\text{wt. of solute per kg of solvent}}{\text{molecular wt. of solute}}$$

(4) Mole Fraction (x)

The ratio of number of moles of the solute to the total number of moles present in the solution is called mole fraction.

Suppose a solution containing two components A and B, suppose

$x_A$  - mole fraction of component A

$x_B$  - mole fraction of component B

$n_A$  - Number of moles of component A

$n_B$  - Number of moles of component B

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Then

$$x_A = \frac{n_A}{n_A + n_B} \quad \text{and} \quad x_B = \frac{n_B}{n_A + n_B}$$

The sum of mole fraction of all component in the solution = 1

for binary solution (sol<sup>n</sup> of two components)  $x_A + x_B = 1$

for ternary solution (sol<sup>n</sup> of three components)  $x_A + x_B + x_C = 1$

### (v) percent composition

#### a) By weight (w/w)

The percent composition by weight is the number of grams of solute present in 100 g of solution

#### b) By volume (v/v)

The percent composition by volume is the volume of solute present in 100 cc of solution

e.g. 20% of ethanol solution is prepared by addition of 20ml of ethanol in 80ml of water.

#### c) By weight per volume (w/v)

The number of grams of solute present in 100 cc of solvent.

Numerically

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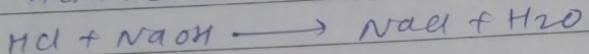
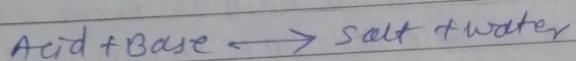
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Classification of titrimetric or volumetric methods

Depending upon nature of chemical reaction, titrimetric methods are classified into following types

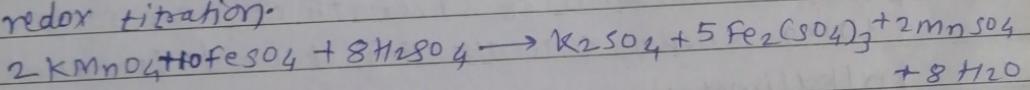
① Acid-Base or neutralization titration

When acid reacts with base to salt and water is called acid-base titration or neutralisation reaction/titration.



② Redox-titration:

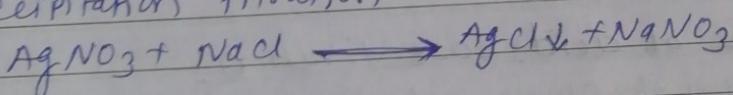
The titration in which one substance ~~reacts~~ is oxidised while other substance is reduced is called as redox titration.



In this redox reaction,  $\text{KMnO}_4$  is oxidizing agent while  $\text{FeSO}_4$  is reducing agent.

③ Precipitation titration:

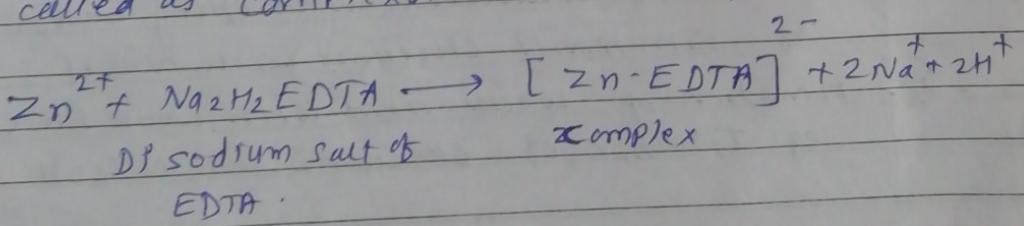
The titration which involves formation of precipitate when reactants reacts each other is called as precipitation titration.



insoluble

④ Complexometric titration:

The titration which involves formation of complex when metal ion reacts with complexing agents is called as complexometric titration.

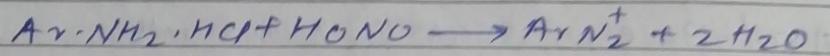
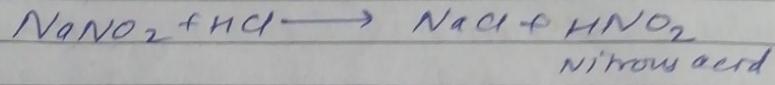


⑤ Diazotization titration:

The titration in which simple aromatic amino ~~acid~~ compound reacts with sodium nitrate solution to form

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diazonium salt is called as diazotization reaction.

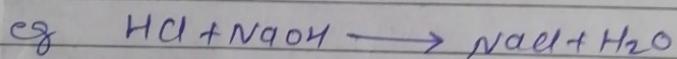


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#### \* Acid-Base OR Neutralisation Titration

When acid reacts with base to form salt and water is called acid-base reaction or neutralisation reaction or titration.



- The determination of strength of acid solution by using known concentration ~~of~~ of base is called as acidimetry, whereas
- The determination of strength of base solution by using known concentration of acid is called as alkalimetry.
- The indicator shows end point of titration. The indicator have one colour in acid solution while different colour in alkaline solution.
- At the equivalence point, the pH of the solution may be equal to, greater than or less than 7, depending upon relative strength of acid and alkali.

#### Types of acid-base titration:

- I Titration of strong acid with strong base  
eg Titration of HCl with NaOH
- II Titration of strong acid with weak base.  
eg Titration of HCl with NH<sub>4</sub>OH
- III Titration of weak acid with strong base.  
eg Titration of CH<sub>3</sub>COOH with NaOH
- IV Titration of weak acid with weak base.  
eg Titration of CH<sub>3</sub>COOH with NH<sub>4</sub>OH

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### pH Variation during acid-base titration

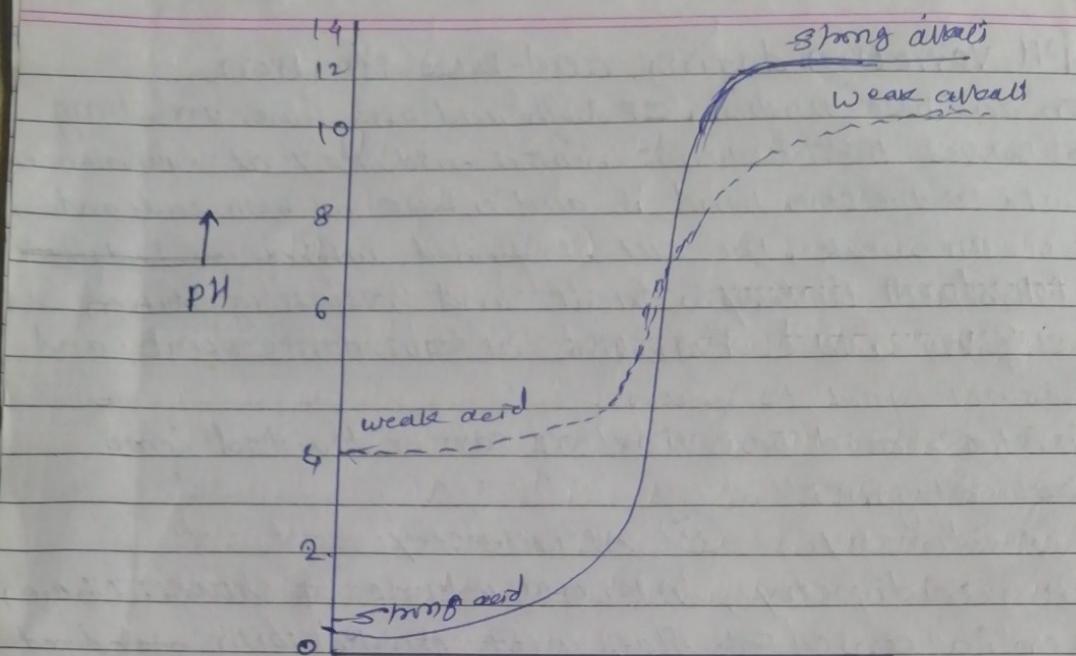
In acid base-titration, IF both acid and base are strong electrolytes then solution is neutral and pH=7 at equivalence point. on the other hand if acid or base or both acids and bases are weak, the salt is formed which ~~are hydrolyzed~~ is hydrolysed to certain extent and resulting solution is slightly acidic or alkaline at equivalence point and pH is not equal to seven.

Therefore acid base titration can be divided into two categories

#### (i) Acidimetry      (ii) Alkalimetry

- In acidimetry, A known volume of alkali base taken in conical ~~flask~~ flask and titrated with standard solution acid taken in burette. The pH of the solution equal to, less than or greater than 7 depend on strong and weak nature of acid or base.
- In alkalimetry, A known volume of acid taken in conical flask and titrated with standard solution of base taken burette. The pH of the solution equal to, less than or greater than 7 depend on strong and weak nature of acid or base.
- When base is taken in a burette and acid is taken in a conical flask, then, all  $H^+$  ions in acid is consumed by base at the equivalence point. After that concentration of  $OH^-$  ion increases due excess addition of base and pH increases suddenly.
- The pH range near the equivalence point is different for different type of acid-base titration.

Type of titration	pH range
Strong acid with strong base	3.3 to 10.5
Strong acid with weak base	3.5 to 7.5
Weak acid with strong base	6.5 to 7.5
Weak acid with weak base	6.5 to 7.5



ml. of alkali added →  
Variation of pH during Acid-base titration

### Acid-base indicator or Neutralisation indicators

- In acid base titration, the indicator is used to show end point of titration.
- Indicator shows one colour in acidic solution while different colour in alkaline solution.
- At the end point, indicator shows sharp ~~end point~~ colour change.
- The colour change of acid base ~~titration~~ indicator is not sudden but takes place within small range of pH
- The pH range of solution in which indicator shows change in colour, this range is called as pH range of Indicator.

The pH range of various acid base indicators are given below.

Indicator	pH-range	colour in acid	colour in alkali
phenolphthalein	8.2 - 10	colourless	Pink
methyl Red	4.8 - 6	Yellow	Red
Methyl orange	3.2 - 4.4	Red	Yellow
Litmus	4.5 - 8.3	Red	Blue
Thymol blue	1.2 - 2.8	Red	Yellow

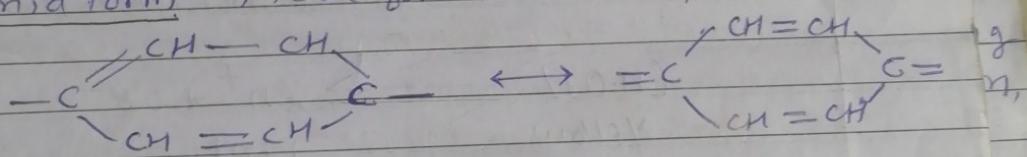
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+ 1720  
1750  
16855

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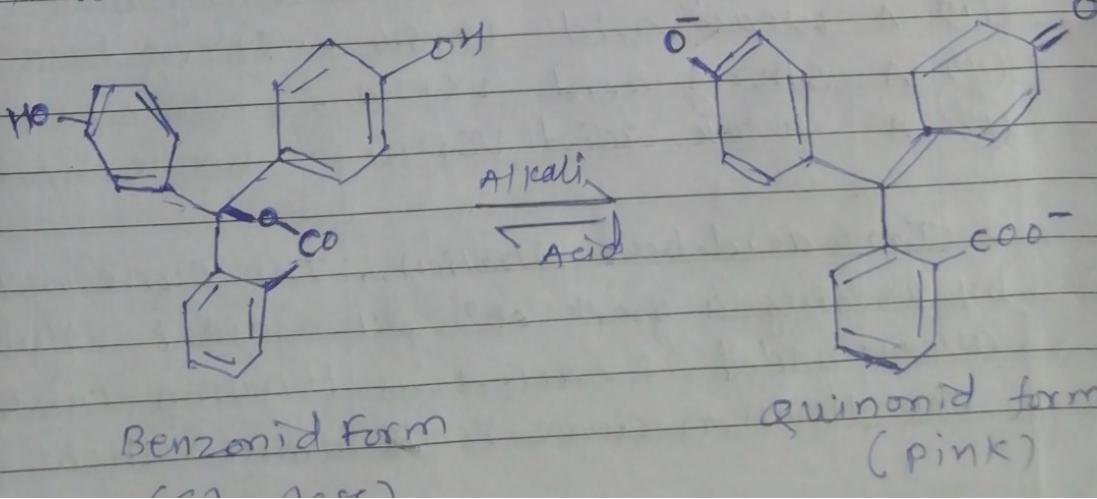
Bromocresol Green	3.8 - 5.4	Yellow	Blue
Bromothymol blue	6.0 - 7.6	Yellow	Blue
Alizarin yellow	10. - 12.	Yellow	orange Red

Modern theory of acid-base Indicator. OR  
Quinonoid Theory of acid-base Indicator

- The substance which indicate end point of titration is called as indicators
- Indicator changes its colour at different pH
- This theory is used to explain colour change of acid-base indicator with change in pH.
- According to modern theory,
- (a) The acid base indicator exist in two tautomeric forms, one is benzonid form and other is quinonoid form. These forms are in equilibrium.

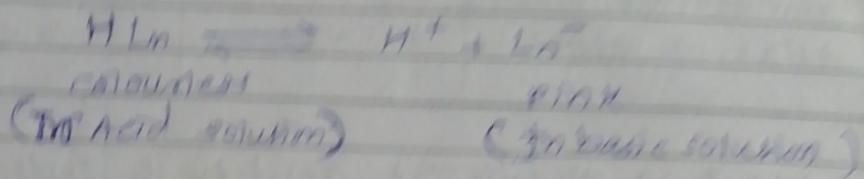


- (b) This indicator shows colour change due to the interconversion of one tautomeric form into other.
- (c) Out of these two tautomeric, one form exist in acidic medium while other form exist in alkaline medium.
- (d) During acid base titration, the medium changes from acidic to alkaline and vice versa.
- (e) The benzonid form of phenolphthalein is colourless in acidic medium and pink in alkaline medium.



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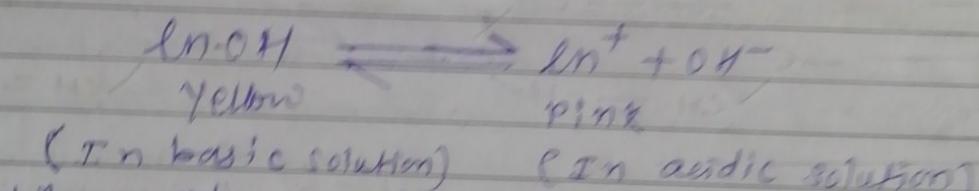
Phenolphthalein is weak acid it dissociates as



When acid is taken in conical flask, phenolphthalein is in undissociated form due to the presence of more concentration of  $\text{H}^+$  ion, therefore solution is colourless. At end point, the colour changes from colourless to pink, because in basic solution, phenol-phthalein undergoes dissociation and solution becomes pink in colour.

When alkali is taken in conical flask colour changes from pink to colourless.

Similarly, methyl orange ( $\text{C}_{20}\text{H}_{14}\text{O}_4$ ) shows different colour in dissociated and nondissociated form.



When acid taken in a conical flask, the colour changes from pink to yellow while in case of alkali colour changes from yellow to pink.

### Choice of suitable indicator for different acid-base titration

There are four types of acid base titration

- (I) A strong acid versus a strong base
- (II) A weak acid versus a strong base
- (III) A strong acid versus a weak base
- (IV) A weak acid versus a weak base

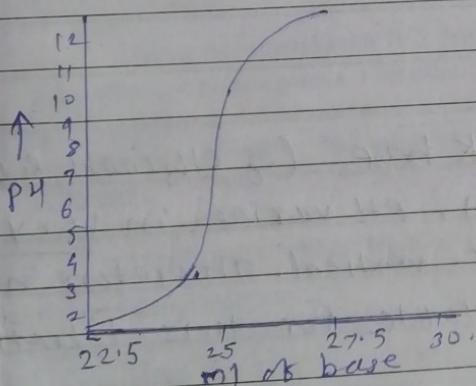
- In acid-base titration, the curve obtained by plotting a graph of pH against volume of alkali added is called as titration curve

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- distance and then bends away.
- The ~~p~~ region indicate change in colour pH at equivalence point.
  - The colour change of acid-base indicator takes place within small range of pH value. This range is called as pH-range of indicator.
  - The selection of indicator depends upon pH range of indicator matches with pH-range near equivalence point of concern acid-base titration.

### ① Strong acid versus strong base (e.g. HCl + NaOH)

The pH curve (titration curve) of strong acid (HCl) and strong base (NaOH) is almost vertical over the pH range 3.3 - 10.5. The titration curve indicate that, upto end point, pH increases upto 3.3. After addition of excess of NaOH, concentration of OH<sup>-</sup> increases and pH suddenly increases to 10.5. The indicator pH range matches with selected strong acid and strong base titration pH range 3.3 - 10.5. So phenolphthalein, methyl orange, methyl red are suitable indicator for such titration.

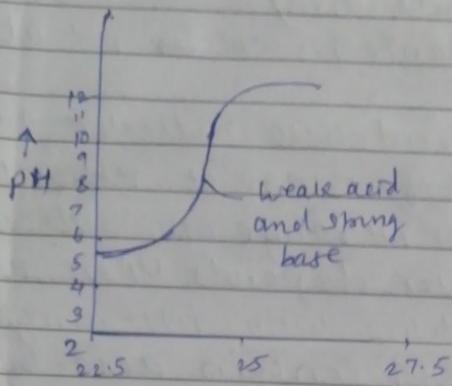


Suitable Indicator	pH range
methyl orange	3.2 - 4.5
Methyl Red	4.4 - 6.5
Litmus	5.5 - 7.5
phenolphthalein	8.4 - 10.5

### ② Weak acid versus strong base (e.g. CH<sub>3</sub>COOH and NaOH)

The titration curve of weak acid (CH<sub>3</sub>COOH) and strong base (NaOH) is almost vertical over the pH range 6.5 to 10.5. Due to weak acid, the solution is alkaline at end point. The phenolphthalein is suitable indicator for weak acid and strong base titration.

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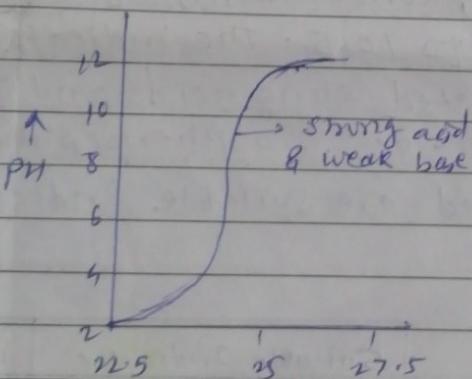


Suitable Indicator	pH-range
Phenolphthalein	8.4 - 10.5
Bromoethy moly Blue	6 - 7.6

ml of base →

### (3) Strong acid versus weak base (e.g HCl & NH<sub>4</sub>OH)

The titration curve of strong acid (HCl) with weak base (NH<sub>4</sub>OH) is <sup>almost</sup> vertical over the pH range 3.5 to 7.0. After the neutralisation, pH varies from 3.5 to 7.0 so methyl red and methyl orange are suitable for such titration

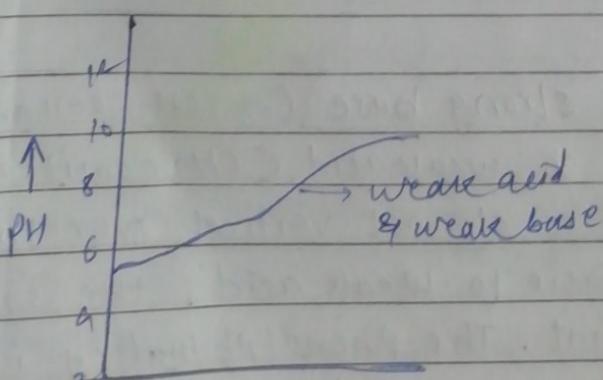


Suitable indicator	pH range
methyl orange	3.2 - 4.5
methyl Red	4.4 - 6.5

ml of base →

### (4) Weak acid versus weak base. (e.g CH<sub>3</sub>COOH & NH<sub>4</sub>OH)

In this type of titration, pH varies in very narrow range and curve is not vertical. Therefore no suitable indicator is available for this titration.



Indicator → NO  
suitable Indicator

## Redox Titration

The titration in which one reactant is oxidized and the other is reduced is known as redox titration. The titration reaction involves a transfer of electron from one substance to another.

The process of releasing electron is oxidation and the process of gaining electron is known as reduction. In redox titration, both oxidation and reduction process takes place simultaneously.

The reagent which oxidizes to other substance and itself reduces; this substance is called as oxidizing agent (oxidant) i.e. oxidizing agent gain electrons and reduced itself to lower valency state. The reagent which reduces to other substance and itself oxidizes this

substance is called as reducing agent (reductant) i.e. reducing agent losses electron and itself oxidized to higher valency state.

The oxidizing agents are potassium permanganate, potassium dichromate, potassium iodate, ceric salts and  $I_2$  solution etc. The reducing agents are sodium oxalate, oxalic acid, Ferrous sulphate, ferrous ammonium sulphate (Mohr's Salt) etc.

Electrode potential measures the electron releasing tendency of a redox system. The electrode potential of redox system can be determined by the combination of two half cells. One half cell which release electron (oxidation) and other half cell which gain electron (reduction)

### **2.15 Important oxidation-reduction titration reagent**

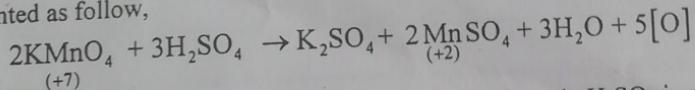
#### a) Potassium permagnate ( $KMnO_4$ )

Potassium permagnate ( $KMnO_4$ ) is most useful oxidizing agent. The colour of  $KMnO_4$  solution is pink. In order to prepare 1M solution  $KMnO_4$ , 158 g  $KMnO_4$  dissolve while 31.6 g  $KMnO_4$  dissolve to prepare 1N solution.

$$\text{Equivalent weight of } KMnO_4 = \frac{\text{Molecular weight of } KMnO_4}{\text{Number of } e^- \text{ accepted by one molecule of oxidising agent}}$$

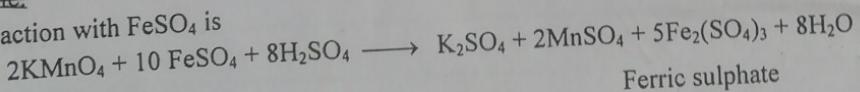
$$= \frac{158}{5}$$

Potassium permagnate widely used in acidic medium. In acidic medium, manganese in  $KMnO_4$  reduces from  $Mn^{+7}$  to  $Mn^{+2}$ . The chemical reaction of  $KMnO_4$  in acidic medium represented as follow,



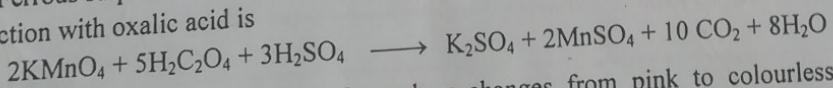
Among the mineral acids  $HCl$ ,  $HNO_3$  and  $H_2SO_4$ , only  $H_2SO_4$  is most suitable for use with potassium permanganate. Potassium permanganate cannot be used with  $HCl$  because of its reducing action and cannot be used with  $HNO_3$  because  $HNO_3$  is itself oxidizing agent. The redox titration with  $KMnO_4$  can be performed using reducing agent like  $FeSO_4$ , oxalic acid, etc.

The reaction with  $FeSO_4$  is



Ferrous sulphate

The reaction with oxalic acid is

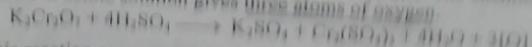


In redox titration with  $KMnO_4$ , colour changes from pink to colourless due to formation of colourless  $K_2SO_4$  and  $2MnSO_4$ . The advantage of potassium permanganate is that it itself act as an indicator. The following are drawbacks of its,

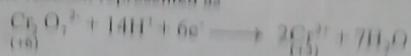
- i) Its solution protected from sunlight.
- ii) It is less stable in alkaline and acidic medium.
- iii) It cannot be used as a primary standard.

### b) Potassium dichromate ( $K_2Cr_2O_7$ )

Potassium Dichromate is strong oxidizing agent and more useful than  $K_2CrO_7$ . Potassium dichromate is a salt of chromic acid. The chemical reaction of potassium dichromate in acidic solution gives three atoms of oxygen.



The ionic reaction represented as

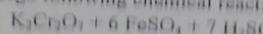


During reaction of potassium dichromate in acidic solution, a molecule of potassium dichromate gain 6 electron and oxidation state of chromium reduces from 6 to 3.

$$\text{Equivalent wt. of } K_2Cr_2O_7 = \frac{\text{Molecular wt. of } K_2Cr_2O_7}{6}$$

$$= \frac{294}{6} = 49$$

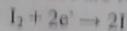
The acidic solution of  $K_2Cr_2O_7$  with Ferrous ammonium sulphate (Molar's salt) undergo following chemical reaction,



Potassium dichromate solution is stable towards light and used as a primary standard.

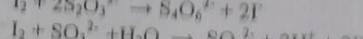
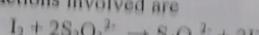
### c) Iodine ( $I_2$ ) solution

Iodine is mild oxidizing agent and oxidizes ions such as thiosulphate ( $S_2O_3^{2-}$ ), sulphite ( $SO_3^{2-}$ ), arsenite ( $AsO_3^{3-}$ ) and Ferrous ions quantitatively in neutral or moderately acidic solution. There are two types of titration involving iodine namely iodometry and iodometry.



i) **Iodometry:** The titration in which standard iodine solution is used as oxidant and directly treated with a reducing agent is known as Iodometry. It includes the determination of thiosulphate, sulphilite, arsenites, etc.

The reactions involved are



ii) **Iodometry:** The titration in which Iodine is liberated by oxidation of an iodine ion (usually potassium iodide) by a strong oxidizing agent in neutral or slightly acidic solution.



Iodine is involved in an equivalent amount and is titrated with a standardized solution of a reducing agent, generally sodium thiosulphate.

### 2.16 Redox indicators

The indicators used in oxidation-reduction titrations are of following types

#### Internal redox indicator

The indicators added during redox titration are known as internal redox indicator. The internal indicator exists in two different colours, one colour in oxidized and other colour in reduced form.



Diphenyl amine is colorless molecule in the reduced form and deep violet in oxidized form.



Diphenylamine

Diphenyl benzidine (colourless)



Diphenyl benzidine (violet)

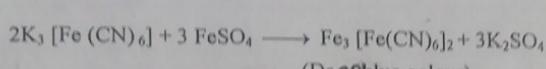
Diphenyl amine is sparingly soluble in water. In diphenyl amine, the reduced form of indicator is predominant at potential between 0.7 and 1.0 V and solution remains colourless above 1.25 V potential, oxidized form is predominant and the solution becomes violet in colour. The suitability of internal indicator in redox titration depends on the change of reduction potential range.

### **External Indicator**

External indicator used in redox titration when no internal indicator is available for such titration. The external indicators are not directly added to the reaction due to following reasons.

- ✓ i) A sharp change in colour is not visible at the end point in the case of dark coloured liquids.
- ✓ ii) After addition of the indicator to the reaction.

Indicator forms an insoluble precipitate with the reaction mixture. External indicator used for a spot test. A freshly prepared solution of external indicator is placed in grooves of a white tile. A drop of reaction mixture added externally on this spot test plate. The indicator shows change in colour when the titration is complete. Potassium ferricyanide  $K_3[Fe(CN)_6]$  used as an external indicator in the titration of  $K_2Cr_2O_7$  and  $FeSO_4$  ( $NH_4)_2SO_4 \cdot 6H_2O$ . The reaction is



Potassium ferricyanide solution placed in a groove of a white tile. Addition of a drop of reaction mixture gives a blue colour till ferrous ions are present in solution. When titration is completed, addition of reaction mixture not produced blue colour.

### **Starch as an indicator**

Starch is used as an indicator with iodine because iodine forms deep blue colour complex. So the solution remains colourless till iodine is consumed. Excess addition of iodine changes the colour of solution to deep blue. When starch is added to iodine in the reaction mixture, colour change from blue to colourless indicated at the end point.

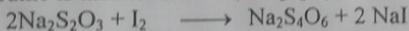
### **Iodometric estimation of Cu (II)**

In the iodometric estimation of Cu (II), the equivalent amount of iodine liberated by the reaction between copper sulphate and KI and estimated volumetrically by titrating with sodium thiosulphate solution. In these reactions, Cu (II) is reduced to Cu (I) and I<sup>-</sup> is oxidized to iodine.



The ionic reaction is  $2Cu^{2+} + 4 I^- \longrightarrow Cu_2I_2 + I_2$

This liberated iodine is then titrated with  $Na_2S_2O_3$ .



Starch is indicator use in this titration shows colour change from blue to colourless. The strength of copper sulphate determine from end point of titration.

**Procedure:** The iodometric estimation of Cu (II) undergo by following steps.

#### **a) Preparation of standard copper sulphate solution**

The N/20 (0.05N) standard solution of copper sulphate pentahydrate ( $CuSO_4 \cdot 5H_2O$ ) can be prepared by weighing accurately 1.25 g of copper sulphate pentahydrate and transfer it to 100 ml volumetric flask containing nearly 20 ml distilled water. Add 1-2 ml of dil sulphuric acid and make up volume up to 100 ml with distilled water.

#### **b) Standardization of sodium thiosulphate (hypo) solution**

Pipette out 20 ml Copper sulphate solution in a conical flask and add drop wise dilute ammonia with shaking till light turbidity is obtained. Add dilute acetic acid drop wise with shaking to remove the turbidity. Then add 10 ml of 10% KI solution. Fitted this flask with cork, keep in dark. That solution becomes a dark brown colour due to the liberated iodine. This solution titrated with sodium thiosulphate up to yellow colouration. At this stage, add 4-5 drops of starch indicator and pinch of solid KCNS or  $NH_4CNS$ . The solution become blue colour due to formation of starch-iodine complex and continues the titration till the blue colour disappears. Repeat the titration to obtain three concordant readings.

#### **c) Determination of strength of unknown copper (II) solution**

The volume of given unknown copper sulphate solution is made up to 100ml. This 20 ml unknown copper (II) solution titrated with same thiosulphate (hypo) solution and repeats the procedure similar to standardization of sodium thiosulphate solution to get three concordant readings.

**Q) Observation and calculations**

- Weight of copper sulphate dissolved in 100 ml of standard solution = W g
- End point of titration of copper sulphate (A) solution with sodium thiosulphate = V<sub>1</sub> ml
- End point of titration of copper sulphate (B) solution with sodium thiosulphate = V<sub>2</sub> ml
- Equivalent weight of copper sulphate pentahydrate = 249.5
- Volume of CuSO<sub>4</sub> used in the titration = 10ml
- Normality of CuSO<sub>4</sub> A solution =  $\frac{W_1 \times 10}{249.5} = N_1$
- Normality of sodium thiosulphate solution =  $\frac{N_1 \times 10}{V_1} = N_2$
- Normality of CuSO<sub>4</sub> B solution =  $\frac{N_2 \times V_2}{10} = N_3$
- Weight per litre of CuSO<sub>4</sub>.5H<sub>2</sub>O in copper sulphate B solution = N<sub>3</sub> × 249.5 g
- Weight of CuSO<sub>4</sub>.5H<sub>2</sub>O in 100 ml copper sulphate B solution =  $\frac{N_3 \times 249.5}{10}$  g

**B. GRAVIMETRIC ANALYSIS****2.17 Introduction**

**G**ravimetric analysis is a method of quantitative determination of a substance by weight. Gravimetric analysis involves precipitation and estimation of insoluble salt of an element or compound from a solution. The estimation of insoluble salt or compound goes through the process of filtration, washed to free from impurities, drying or converting it into a pure form and finally weighing.

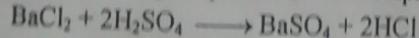
The gravimetric analysis is slow, tedious and time consuming method as compare to volumetric analysis. The accurate results from gravimetric analysis depend on the choice of precipitant, its amount and the condition of precipitation. The gravimetric analysis is applicable only to those compounds which form metallic compound on ignition and do not contain any relative matter.

**2.18 Steps involved in gravimetric analysis with reference to estimation of barium as barium sulphate**

The gravimetric estimation of barium as a barium sulphate is carried out by performing the following steps.

- Precipitation
- Digestion
- Filtration
- Washing
- Drying
- Incineration
- Weighing
- Calculation

**i) Precipitation:** Gravimetric analysis is a quantitative method for accurately determining the amount of a substance by selective precipitation of the substance from an aqueous solution. The precipitate is separated from the aqueous solution by filtration and then weighed. The barium chloride solution is titrated with dilute sulphuric acid and barium precipitate as barium sulphate. The precipitated barium sulphate is separated and weighed.



The precipitate in gravimetric estimation should have following characteristics;

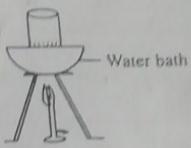
- It must be highly insoluble so that the constituent being estimated is quantitatively precipitated.
- The precipitate should be filterable.
- It must have a known stable composition.
- It should be of high purity and free from co-precipitation.

(19)

**ii) Digestion:** In the estimation, the precipitate is allowed to stand for a few hours to overnight with mother liquor or by warm on steam bath. This process is known as digestion. The digestion of obtained precipitate is important due to following reasons

- The very fine particles formed during precipitation may pass through filter paper. To avoid these, large particles with regular shape gets precipitated while cooling during digestion, which makes filtration fast and easy.
- Digestion decreases the undesirable impurity that gets precipitate along with the desired precipitate tends to dissolve in mother liquor i.e. decreases the effect of co-precipitation.

In gravimetric estimation of barium as barium sulphate, keep the beaker on a boiling water bath for half an hour to digest the precipitate for complete precipitation.



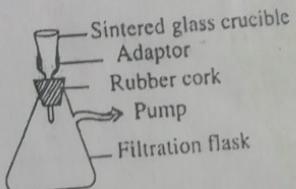
**iii) Filtration:** The precipitate from the solution separated by filtration carried out either by filter paper or sintered glass crucible.

**1) By using a filter paper:** The different type of filter paper is used for different kind of filtration. The filter paper for filtration must be selected in such a way that the pores of filter paper must be smaller than the size of the particles of the precipitate. The precipitate is separated by filtration either through crucibles or Whatmann's No 40, 41 or 42 filter papers because they are having very negligible ash values. The diameter of filter paper may vary according to the bulkiness of the precipitate. For filtration, Whatmann's filter paper No. 40 used for bigger size particles, 41 for gelatinous and flocculent precipitate and 42 for fine particles.

Whatmann's folded filter paper is fitted into the funnel. A round filter paper folded exactly in half and then in quarter. Folded filter paper three part open on one side and one on other side. Then it is placed in a funnel moistened with water and press to remove the air. The liquid is transferred into the funnel with the help of glass rod taking care that the liquid does not fill the funnel more than half at a time.



**2) By using a sintered glass crucible:** The sintered glass crucible numbered 1, 2, 3, and 4 having different types of porosity. A sintered glass crucible fitted with the help of adapter into filtration flask and attach to a vacuum pump for filtration. The liquid is transferred into the funnel with the help of glass rod, retaining more precipitate possible in a beaker.



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END