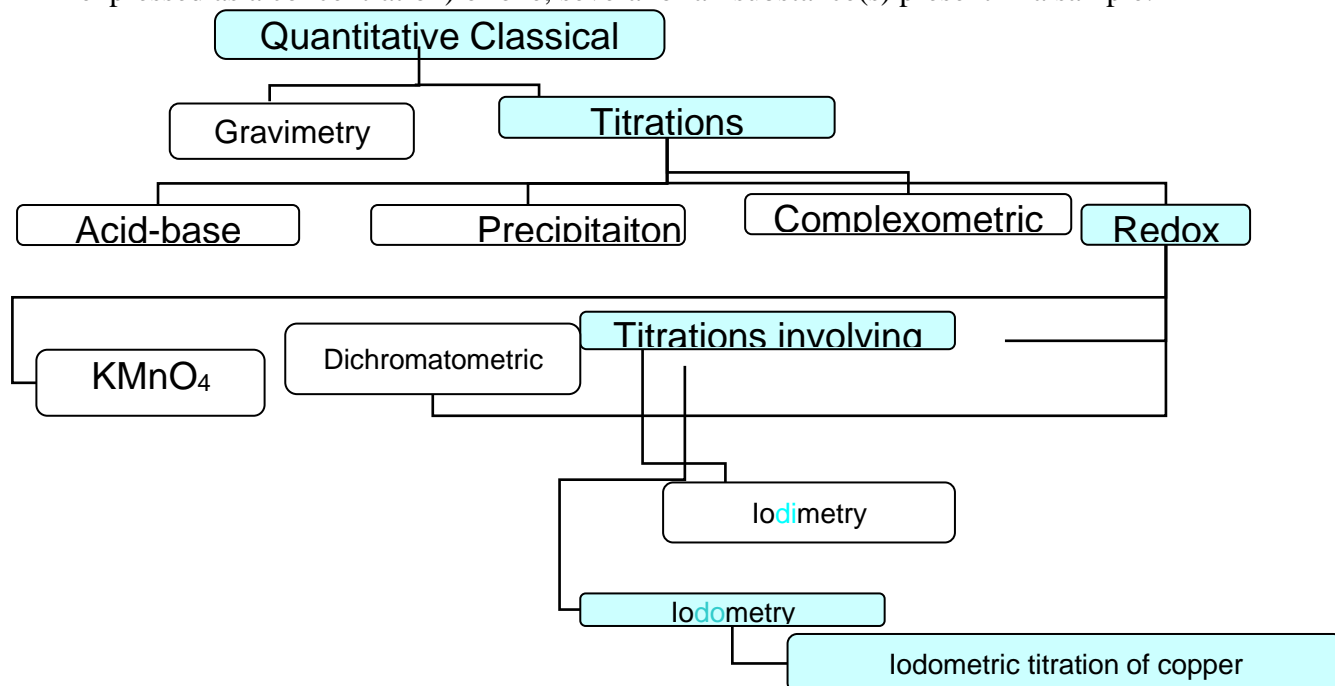


Introduction:

Quantitative analysis: is the determination of the absolute or relative amount (often expressed as a concentration) of one, several or all substance(s) present in a sample.



Titration: is the process, operation, or method of determining the concentration of a substance (analyte) in solution by adding to it a standard reagent (titrant) of known concentration in carefully measured amounts until a reaction of definite and known proportion is completed, as shown by a color change or by electrical measurement, and then calculating the unknown concentration.

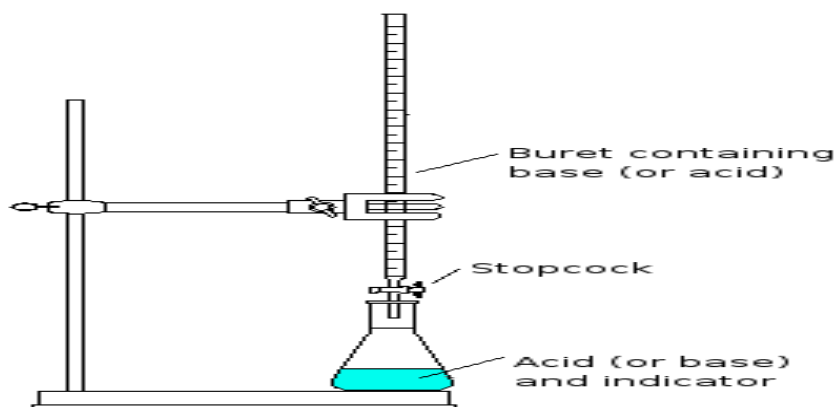
Equivalence point:

The point in a titration where the amounts of titrant and material being titrated are equivalent chemically.

The end point :

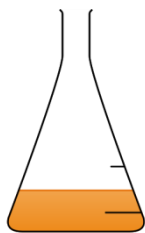
The physical change which results when the equivalence point has been reached. In colorimetric titrations, this is a color change of the indicator

Titration set up:

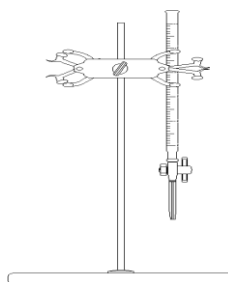


The apparatus

Conical flask



Burette



Funnel



Pipette

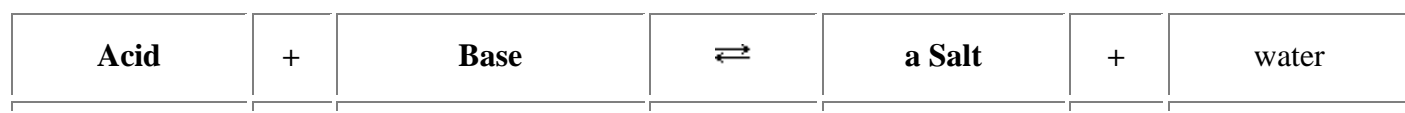


Types of titration that will be encountered in 250 chem lab. :

- 1- Neutralization titration (Acid –base reaction)
- 2- Precipitation titration.
- 3- Complexometric titration.
- 4- Redox titration.

Acid –base reactions

These titrations are based on the neutralization reaction that occurs between an acid and a base, when mixed in solution.

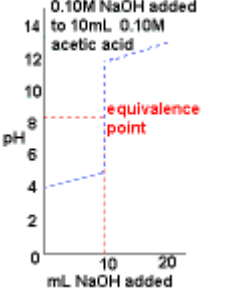
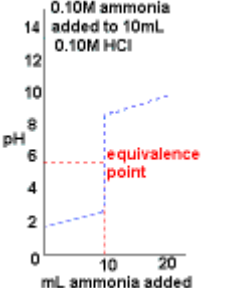
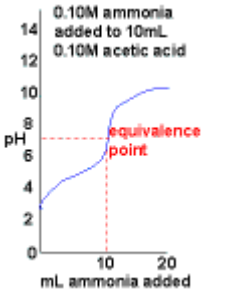


Key Concepts:

- Acid-base reactions involve a proton transfer
- The acid donates a proton to the base
- Acid-base reactions are also known as neutralization reactions
- Equivalence point is the point at which the moles of H^+ is equal to the moles of OH^-
- An indicator is used to show the equivalence point during a titration

Acid-base Titration curves:

General Type	Example	Typical Titration Curve	Features of Curve
Strong Acid and Strong Base	HCl added to NaOH	<p style="font-size: small;">0.10M HCl added to 10mL 0.10M NaOH</p>	<p>Curve begins at high pH typical of strong base and ends at low pH typical of strong acid.</p> <p>There is a large rapid change in pH near the equivalence point (pH =7).</p>
Strong Base and strong Acid	NaOH added to HCl	<p style="font-size: small;">0.10M NaOH added to 10mL 0.10M HCl</p>	<p>Curve begins at low pH typical of strong acid, and ends at high pH typical of strong base.</p> <p>There is a large rapid change in pH near the equivalence point (pH=7).</p>

Weak Acid and Strong Base	NaOH added to acetic acid (CH ₃ COOH)		<p>Curve begins at a higher acidic pH and ends at high basic pH.</p> <p>The pH change at the equivalence point (pH > 7) is not so great.</p>
Strong Acid and Weak Base	Ammonia (NH ₃) added to HCl		<p>Curve begins at low pH and ends at a less high basic pH.</p> <p>The pH change at the equivalence point (pH < 7) is similar to that for Strong Base and Weak Acid.</p>
Weak Acid and Weak Base	Ammonia (NH ₃) added to Acetic acid (CH ₃ COOH)		<p>Curve begins at higher acidic pH and ends at low basic pH.</p> <p>There is not a great pH change at the equivalence point (pH ~ 7) making this a very difficult titration to perform.</p>

Volumetric analysis to prepare and standardize Hydrochloric Acid

*prepare 0.1 M HCl.

*The reaction between sodium carbonate and hydrochloric acid takes place in two stages:

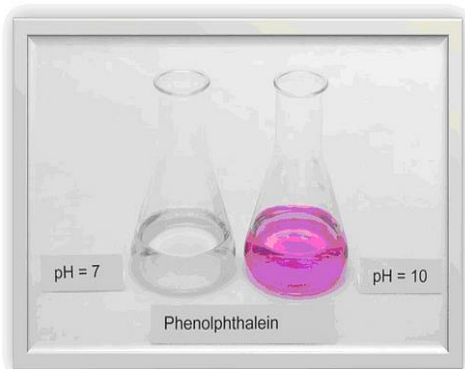


Two indicators are needed to cover both stages:

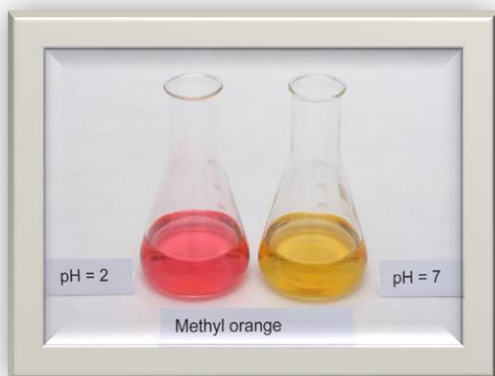
- In stage 1, phenolphthalein is most suitable, and will respond to the pH change associated with the formation of sodium hydrogen carbonate, NaHCO₃.
- In stage 2, methyl orange is most suitable, and will respond to the pH change associated with the final formation of sodium chloride, NaCl.

Procrdure:

1. Transfer a 10 ml aliquot (portion) of sodium carbonate solution to a 250 cm³ capacity conical flask. Add a few drops of phenolphthalein indicator solution.
2. Titrate with the hydrochloric acid. The end-point of the titration is when the solution just changes from pink to colorless. Equation (1)



- 3-repeat the process by methyl orange indicator solution, the end-point of the titration is when the solution just changes from yellow to orange equation (2)



- 4- Repeat steps 1 - 3 until concordance (i.e. until the readings are the same or within 0.2cm³).

- 5-Tabulate your titration results.

Results:

Burette reagent	
Conical flask reagent	
Indicator	

Volume 1	Volume 2	Volume 3	Mean volumes

- 6- Do the calculations using the following equation:

$$V_1 M_1 = V_2 M_2$$

Where:

V_1 = volume of titrant used for the known solution

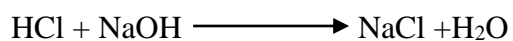
V_2 = volume of titrant used for the unknown solution

M_1 = Molarity of the known solution

M_2 = Molarity of the unknown solution

Titration of Sodium Hydroxide with Hydrochloric Acid.

The reaction:

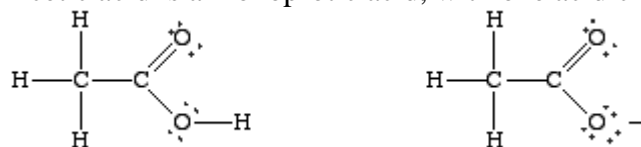


procedure :

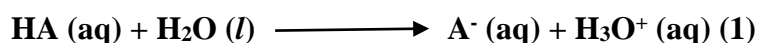
- 1- Pipette 10 ml of Sodium hydroxide solution into 250 ml conical flask.
- 2- Add 1-2 drops of Phenolphthalein solution.
- 3- Titrate with hydrochloric acid solution till the first color change.
- 4- Calculate the concentration of Sodium Hydroxide .

Titration of Acetic acid By Sodium hydroxide

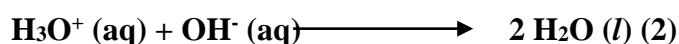
Acetic acid is a monoprotic acid, with one acidic hydrogen atom.



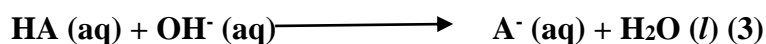
A weak acid is a compound that partially ionizes in aqueous solution producing hydronium (H_3O^+) ions. The general equation for the dissociation of any weak acid can be written as:



The addition of a strong base results in a neutralization reaction in which hydroxide ions (OH^-) react with hydronium to produce water:



As hydronium is consumed in the neutralization reaction, the equilibrium in equation 1 is shifted to the right according to Le Chatelier's Principle. Neutralization process can be written as the sum of equations (1) and (2):



The concentration of the unknown solution can be determined by measuring the volume of titrant added to reach the equivalence point. The equivalence point occurs when all of the acid has been neutralized by the base. And it will be determined by using an indicator that changes color at the equivalence point

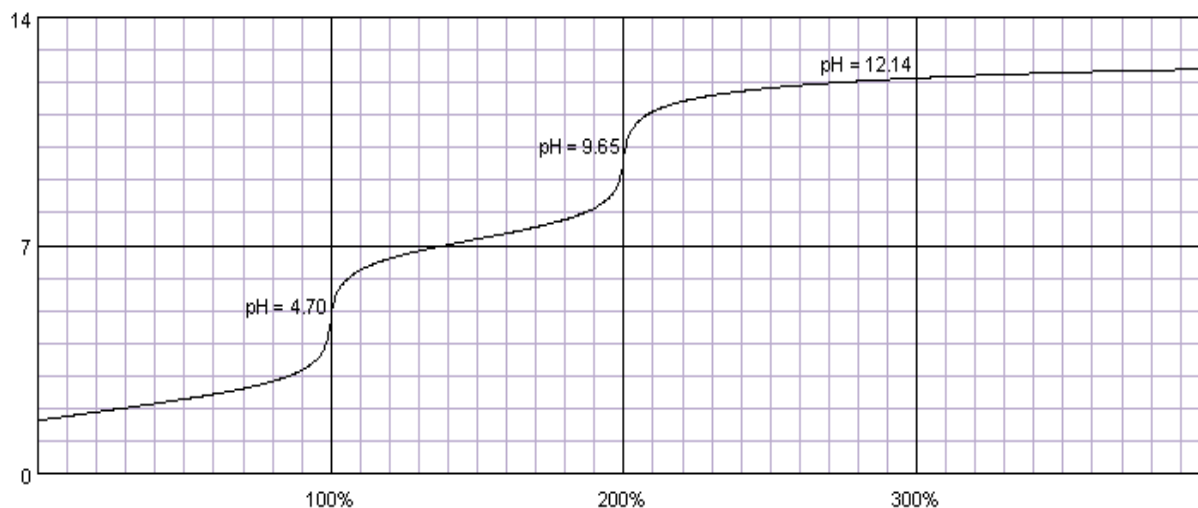
procedure:

- 1-Pipette aliquot(10 ml) of acetic acid solution into 250mL conical flask..
- 2-Add 2-3 drops of phenolphthalein solution.
- 3-Titrate with NaOH solution till the first color change.
- 4-Calculate the concentration of Acetic Acid solution.

Titration of phosphoric acid with sodium hydroxide

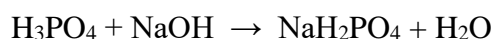
Phosphoric acid is relatively weak, with $pK_{a1}=2.15$, $pK_{a2}=7.20$ and $pK_{a3}=12.35$.

That means titration curve contains only two inflection points and phosphoric acid can be titrated either as a monoprotic acid or as a diprotic acid. In the first case acid has to be titrated against indicator changing color around pH 4.7 (for example methyl orange) in the second case - against indicator changing color around pH 9.6 (for example phenolphthalein).

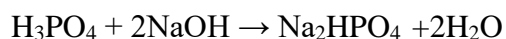


reaction

Depending on the indicator used reaction taking place is either:



Or



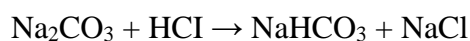
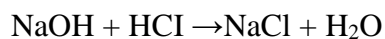
The procedure:

- Pipette aliquot of phosphoric acid solution(10ml) into 250 mL conical flask.
-
- Add 2 drops of methyl orange or 2 drops of phenolphthalein solution
- Titrate with NaOH solution till the first color change.
- Calculate the concentration of phosphoric acid solution.

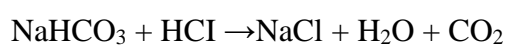
Titration the Mixture of Sodium Hydroxide and Sodium Carbonate

The composition of the solution can be deduced from the relative volumes of acid needed to titrate equal volumes of the sample.

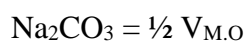
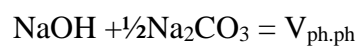
Titration with hydrochloric acid to a phenolphthalein end point ($V_{\text{ph,ph}}$):



Titration with hydrochloric acid to a methyl orange end point ($V_{\text{M.O}}$):



Components in sample Relationship between ($V_{\text{ph,ph}}$) and ($V_{\text{M.O}}$) in the titration of an equal volume of sample



Procedure:

1. Load a burette with 0.1 N hydrochloric acid solution.
2. To conical flask pour in 10 ml aliquot of sample (V_{sample}).
3. Introduce 2-3 drops of phenolphthalein solution, and titrate with 0.1 N hydrochloric acid solution until the solution lost the color. Read the burette mark ($V_{\text{ph,ph}}$).
4. To the same conical flask, introduce 2-3 drops of methyl orange solution, and titrate with 0,1 N hydrochloric acid solution until the solution just begin to change colour. Read the burette mark ($V_{\text{M.O}}$).
6. Repeat titration also two times. Calculate the median volumes of used hydrochloric acid solution.
7. Calculate the concentration of NaOH and Na_2CO_3

Precipitation titration:

Introduction

Titration is a process by which the concentration of an unknown substance in solution is determined by adding measured amounts of a standard solution that reacts with the unknown. Then the concentration of the unknown can be calculated using the stoichiometry of the reaction and the number of moles of standard solution needed to reach the so called end point.

Precipitation titrations: are based upon reactions that yield ionic compounds of limited solubility.

General Principles:

The major precipitation reaction used is that of silver with a range of anions. These anions include:

- Chloride
- Bromide
- Iodide
- Thiocyanate

Titration involving silver are termed argentometric, from the old name for silver, argentum.

The reaction ratio is 1:1 and silver salts formed are generally quite insoluble.

Silver nitrate solutions slowly decompose when exposed to light, so they should be kept in dark bottles.

Chemical Indicators:

There are three common chemical indicators that are associated with argentometric titrations:

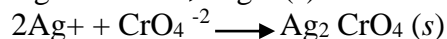
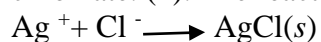
1. The chromate ion, CrO_4^{2-} (the Mohr method);
2. The ferric ion, Fe^{3+} (the Volhard method);
3. Adsorption indicators such as fluorescein (the Fajans method)

Comparison of silver titration methods:

Method	Advantages	Disadvantages
Mohr □	Simple	Alkaline solutions only Not suitable for iodide
Volhard halide analyses	Capable of direct silver and	Must be 1M nitric acid solution indirect

Mohr method:

The Mohr method uses chromate ions as an indicator in the titration of chloride ions with a silver nitrate standard solution. After all the chloride has been precipitated as white silver chloride, the first excess of titrant results in the formation of a silver chromate precipitate, End point is signalled by the appearance of the red silver chromate. (1). The reactions are:



By knowing the stoichiometry and moles consumed at the end point, the amount of chloride in an unknown sample can be determined.

Solution during titration should be close to neutral.6-9.

Above this pH, silver starts to react with hydroxide anions, precipitating in form of AgOH and Ag₂O.

Below this pH chromate converts to dichromate, a bright orange colour thereby obscuring the endpoint

Mohr's method is suitable only for titration of chloride, bromide and cyanide
Determination of unknown of Chloride sample.

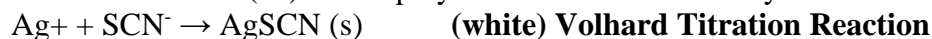
Procedure:

- 1-Pipette aliquot of chlorides solution into 250 mL Erlenmeyer flask.
- 2-Add 1 mL of 5% potassium chromate solution.
- 3-Titrate with silver nitrate solution till the first color change.
- 4- calculate the Concentration of NaCl

Volhard method

The Theory:

The Volhard method is based on the precipitation of silver thiocyanate in nitric acid solution with iron (III) ion employed to detect excess thiocyanate ion:

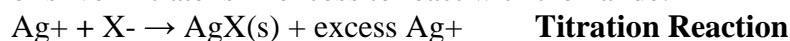


The solution turns red with first slight excess of thiocyanate ion:



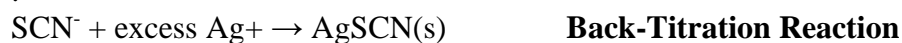
The titration with thiocyanate is carried out in acidic solution. When the silver (I) has been precipitated as white silver thiocyanate, the excessive titrant will react with the iron (III) indicator and form a soluble red complex. The color change at the end point is not extremely sharp, but it can be detected with a little practice

In the Volhard method for determination of chloride and other anions, a known amount of standard silver nitrate solution is added to the sample solution; the amount of silver nitrate is in excess to react with the halide:



The excess silver (I) is then back-titrated with standard thiocyanate

:



procedures:

Part I: *Determination of unknown silver sample by Volhard method*

1-Pipette 10 ml silver nitrate solutions to a 250 ml conical flask

2-Add 5 ml of 1:1 nitric acid and 1 ml of ferric indicator

3-. Titrate with thiocyanate solution, shaking the solution thoroughly between additions of drops. The end point is marked by the permanent appearance of the reddish orange color of the ferricthiocyanate complex.

Part II: *Determination of unknown KBr sample by Volhard method*

1-Pipette 10 ml of KBr solution to 250 ml conical flask.

2-add 20 ml of AgNO₃ ,5 ml of 6N HNO₃ and 1ml of ferric indicator

3- titrate the excess of AgNO₃ by solution of KSCN from the burette ,shaking will till reach the end point .

4- make the blank,and calculate the concentration of KBr

Complexometric titration:

Introduction:

These titrations are based on the formation of a complex between the analyte and the titrant. The chelating agent EDTA is very commonly used to titrate metal ions in solution. These titrations generally require specialized indicators that form weaker complexes with the analyte.

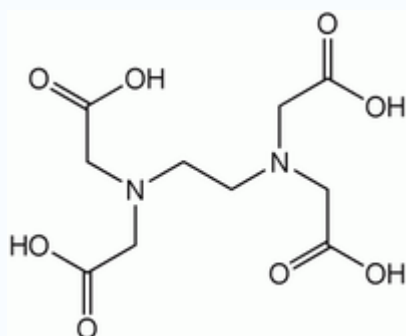
A common example is Eriochrome Black T for the titration of calcium and magnesium ions or Murexide for the titration of Calcium.

Chelating agent

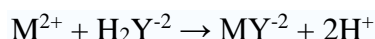
Ligands having more than one electron donating groups are called **chelating agents**

Complexometric titration with EDTA

ethylenediaminetetraacetic acid, has four carboxyl groups and two amine groups that can act as electron pair donors, or Lewis bases. The ability of EDTA to potentially donate its six lone pairs of electrons for the formation of coordinate covalent bonds to metal cations makes EDTA a **hexadentate** ligand.



EDTA forms an octahedral complex with most 2^+ metal cations, M^{2+} , in aqueous solution.



EDTA has the widest general application in analyses because of the following important properties:

- It has low price.
- The special structure of its anion which has 6 ligand atoms
- The formation constant for most metal cation-EDTA complexes is very high

Factors influencing EDTA reactions:

- The nature and activity of metal ion.
- The pH at which the titration is carried out.
- The presence of interfering ions such as CN
- Organic solvents also increase the stability of complex

EDTA Determination of Total Water Hardness

Purpose:

Determine the hardness in tap water samples.

Water hardness is an expression for the sum of the calcium and magnesium cation concentration in a water sample. These cations form insoluble salts with soap, decreasing soaps cleaning effectiveness. They also form hard water deposits in hot water heaters. The standard way to express water hardness is in ppm CaCO_3 which has the formula weight of 100.1 g/mole.

Procedure:

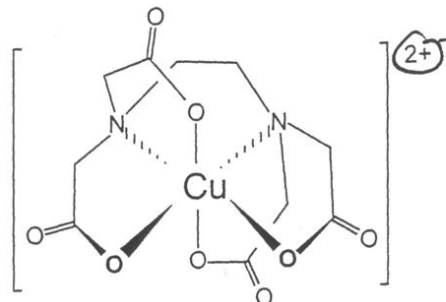
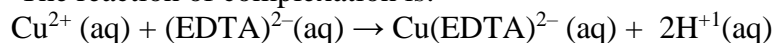
- 1-Transfer a100 ml of tap water by graduated cylinder to the conical flask.
- 2-Add 1ml of buffer solution (PH10) and little particles of EBT indicator.
- 3-Titrate by standard solution of EDTA (0.01M), till the first color change (wine red to Blue).
- 4-Calculate the total water hardness as concentration of CaCO_3 in ppm.

Copper Analysis by Complexometric Titration

The complexing agent will be ethylenediaminetetraacetic acid (EDTA) in the form of its disodium salt, EDTA forms complexes with many metal

This particular method can only be used in the absence of such ions as Ca^{2+} , Ni^{2+} , etc.

The reaction of complexation is:



The stoichiometry is one metal cation to one EDTA anion.

The indicator used for the titration is called murexide. This indicator is highly colored and will complex with the copper ion to give different colored species. During the titration, the EDTA^{2-} forms a more stable complex and frees the indicator, which then displays its original color. The appearance of the free indicator means that all metal ions have been complexed by EDTA, which signals the end point.

Procedure:

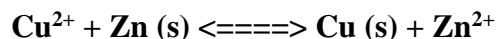
- 1- Pipette 10 ml of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ to the conical flask.
- 2- add 1 ml of NH_3 , 10 ml of distilled water and the Murexide indicator.
- 3- Titrate by 0.01M of EDTA till the first color change.
- 4- calculate the concentration of Cu.

Oxidation/Reduction Reactions

Introduction:

Oxidation/Reduction Reactions :is the Reactions in which electrons are transferred from one reactant to another

Example



Oxidizing reagent : A reagent which tends to remove electrons from another reactant. its oxidation number becomes less positive after it reacts.

In the above reactant Cu^{2+} is the oxidizing agent. It has been reduced.
 $\text{Cu}^{2+} + 2\text{e} \rightleftharpoons \text{Cu (s)}$

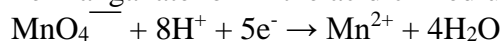
Reducing agent: A reagent which tends to give up electrons to another reactant. Its oxidation number becomes more positive after it reacts.

In the above reaction Zn is the reducing agent. It has been oxidized.
 $\text{Zn (s)} \rightleftharpoons \text{Zn}^{2+} + 2\text{e}$

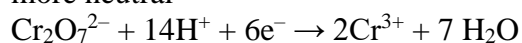
Examples of Oxidizing agents:

1-. KMnO_4 ,

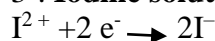
Permanganate ion in the acidic medium is a very strong oxidizing agent



2-. $\text{K}_2\text{Cr}_2\text{O}_7$ in dil. H_2SO_4 is moderately strong oxidizing agent; oxidizing ability depends strongly on pH, decreasing rapidly as solution becomes more neutral



3-. Iodine solution



Type of Redox Indicators:

Self Indicators: the titrant itself may be so strongly coloured that after the equivalence point, a single drop of the titrant produces an intense colour in the reaction. e.g. potassium permanganate
Such Indicators are called self indicators.

starch indicator: this indicator is used for titration involving iodine.

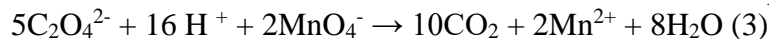
Redox indicators: such as Diphenylamine

Titration of Oxalic acid (H₂C₂O₄) by Potassium permanaganate

Oxalic acid and Potassium permanaganate react in an acid medium according to the following half-cell reactions:



The two half-cell reactions are combined to obtain the complete redox reaction:

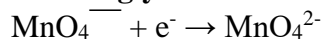


From this balanced equation, you can see that there is a 5:2 stoichiometric ratio between the moles of oxalate and the moles of permanganate.

pH dependence of oxidizing behavior

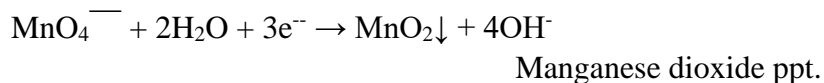
It is important to note that for many oxidants the pH of the medium is of great importance and hence their oxidizing strength may vary depending on the medium in which its reaction is studied. For example potassium permanganate is oxidizing agent in all three mediums, acid, alkaline and neutral. However it is strongest in acidic medium.

a. Strongly alkaline medium

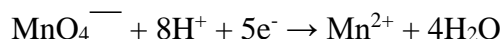


Permanganate ion Manganate ion

b. Neutral medium



c. Acidic medium



Procedure

- 1-pipette a 10 ml of H₂C₂O₄ to the conical flask.
- 2- Add 10 ml of H₂SO₄ acid
- 3- Heat the solution to 60-90°C to speed the reaction.
- 4- Titrate the hot solution till reach the end point (pink color of the KMnO₄)
- 5- Calculate the concentration of the Oxalic acid.

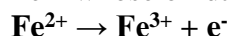
Titration of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ sample by Potassium dichromate solution.

Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) is a very strong oxidizing agent. However it is not as strong oxidizing agent as permanganate is. Potassium dichromate acts as oxidizing agent in acidic medium only.

it can't be used as a self indicator like KMnO_4 . this is because its reduction product (Cr^{3+}) is green which hinders in the visual detection of end point by observing dichromate colour. Thus an indicator is must in this titration.

Mohr's Salt

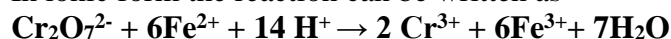
The reducing agent used in this titration is **Mohr's salt** which is a double salt. Its composition is $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. the redox active species in this compound is Fe^{2+} whose oxidation can be represented as:



The reaction:



In ionic form the reaction can be written as



Orange

green

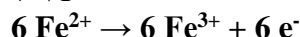
This redox reaction can be split apart in two parts- one showing the oxidation and the other reduction



+ VI

+III

reduction
(Oxidation number has decreased)



+II

+III

oxidation
(Oxidation number has increased)

The end point of the titration as indicated earlier has to be defined with the help of an indicator.

Diphenylamine is use as redox indicator

The end point is marked with an intense blue violet color.

Procedure:

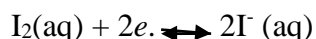
- 1-Pipette 10 ml of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ to the conical flask.
- 2-Add 10 ml of H_2SO_4 (2M) ,5 ml of Phosphoric acid and 1ml of Diphenyl Amine indicator.
- 3- Titrate the solution by standard solution of $\text{K}_2\text{Cr}_2\text{O}_7$ till reach the end point (dark blue).
- 4- Calculate the concentration of the $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ sample.

REDOX TITRATIONS WITH IODINE

Introduction:

Titrimetric titrations that create or consume I_2 are widely used in **quantitative analysis**.

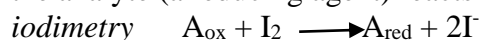
Iodine is a moderately weak oxidizing agent; it is reduced to form the iodide anion, as follows:



The above redox reaction is completely reversible, and so the iodide anion is a moderately weak reducing agent that will react with oxidizing analytes to produce iodine.

In iodimetric titrations, (direct titration)

the analyte (a reducing agent) reacts with iodine to produce iodide:



where A_{ox} and A_{red} are the oxidized and reduced forms, respectively, of the analyte.

conditions:

neutral or mildly alkaline (pH = 8) to weakly acid solutions

If the pH is too alkaline, I_2 convert to Hypo iodate and Iodide

If the solution is too acid the starch used for the end point detection tend to hydrolyze or decompose in this medium

iodometric (indirect titration)

When an analyte that is an oxidizing agent is added to excess iodide to produce iodine, and the iodine produced is determined by titration with sodium thiosulfate, the method is called "iodometry".

Example:



Then the iodine (I_2) is usually titrated with standard **thiosulfate**

as follows:



The iodine produced in this reaction is stoichiometrically related to the amount of analyte originally present in the sample.

The end point is detect with starch.

The disappearance of the blue starch- I_2 complex color indicates the end of the titration.

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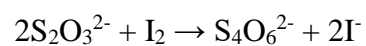
The reason for such timing:

Starch is added just before the end point(the color become pale yellow)

because:

1. iodine-starch complex is slowly dissociated.
2. starch has a tendency to hydrolyze in acid solution.

Titration of Sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) by Iodine (I_2)



Procedure :

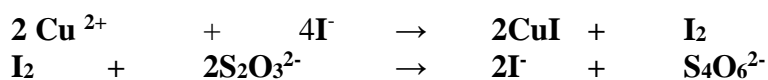
- 1-Pipette 10 ml of $\text{Na}_2\text{S}_2\text{O}_3$ to the conical flask.
- 2-Add 1ml of Starch indicator.
- 3-Titrate the solution By I_2 solution and shaking till reach the blue color of the I_2 – starch complex.
- 4-Calculate the concentration of the I_2 solution

Iodometric titration of copper.

Iodometric determination of copper is based on the oxidation of iodides to iodine by copper (II) ions, which get reduced to Cu^+

For the best results reaction should take place in the slightly acidic solution (pH around 4-5),

To detect titration end point we will use a standard indicator for iodine titrations - starch. We start with a solution containing relatively high concentration of iodine, so indicator has to be added close to the end point.



Procedure:

1-Pipette aliquot containing copper (II)(10ml) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ into 250 ml conical flask with a glass stopper.

2-Add 20 ml of potassium Iodide 10%.

3-Add 20ml of (2M) H_2SO_4 and dilute the solution by 20 ml distilled water.

4- Titrate the solution till reach the pale yellow color

5 -add 1ml of starch indicator.

6-Continue the titration until blue color disappears.

7 Calculate the Concentration of the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$