EXPERIMENT NO. 1

Object: Introduction to safety and working in chemical laboratory.

Theory: The real understanding of the principles which includes all laboratory techniques and procedure is possible only if a student plans his/her work carefully in advance and work purposefully during each laboratory period. For efficient working in the laboratory following points must be bore in mind.

1. Careful planning in advance will enable you to work fast and efficiently.

2. While performing the experiment record all the observations on left hand side page of practical notebook and get it signed by the instructor/faculty members.

3. Be aware of what you are doing and why you are doing it. As you work, think over the probable questions, if after your determined efforts you cannot answer them, do not hesitate to ask your teacher.

4. Always follow the experimental instructions exactly

5. All glassware's must be scrupulously clean, if not, then clean it with chromic acid (potassium dichromate + sulphuric acid), washed with tap water and-then rinsed with distilled water.

6. It should be regarded a normal practice that all determinations are performed in duplicate While working in the laboratory suitable precautions should be observed to prevent accidents:

1. Never work alone in the laboratory unless a demonstrator or teaching assistant is present.

2. To protect clothing from spoilage and damage by chemicals and accidents, the laboratory coat (white) should be worn while working in the laboratory.

3. Read the label carefully before using the chemical from the container.

4. Under no circumstances should the working surface of the bench become cluttered with apparatus, if they will be needed at a later stage, it may be placed at the back of the bench.

5. Never taste any chemical unless instructed to do so.

6. Do not add any porous pieces or any solid to a boiling liquid; add only after allowing the liquid to cool a little.

Even after all precautions, if accident occurs, do not panic and inform the instructor at once and act as suggested below:

1. Small Burns: Immediately plunge the burned area for 4 -5 min. Into the cold the cold water, preferably with ice in it, then gently dry and apply an ointment.
2. Severe Burns: Do not apply any ointment but seek medical treatment at once.

3. Acid Burns: Wash with plenty of water, then with very dilute sodium bicarbonate solution and finally with distilled water
4. Base Burns: Wash with plenty or water, then with very dilute acetic acid solution and finally with distilled water
5. Reagents sucked in Mouth: If the reagent is sucked, spit at once and wash the mouth thoroughly with water.

TERM USED IN CHEMICAL ANALYSIS:

Chemical analysis is carried out in two ways:

1. Qualitative analysis   **2. Quantitative analysis**

1. Qualitative analysis is the detection of ions or radicals in an inorganic salt whereas quantitative analysis involves the determination of quantity of a particular component present in a substance. Quantitative analysis can be carried out in two ways:
   (i)   Gravimetric analysis   **(ii) Volumetric analysis**

When the analysis is based on the measurement of weight then it is called gravimetric analysis. On the other hand when it is based on measuring the volume of the solution of a substance then it is called volumetric analysis,

TERMS USED IN VOLUMETRIC ANALYSIS

1. **Titration:** The process of finding out the volume of one of the solution required to react completely with the definite volume of the other solution is known as titration. Titration can be classified into four categories:

   (i)   Acid – Base titration/ Neutralization titration
   (ii)   Redox Titration/ oxidation- reduction titration
   (iii) Precipitation Titration
   (iv)   Complexometric titration

2. **Titrant:** The solution of known strength is called the titrant.
3. **Titrand:** The solution which contains a substance to be estimated or whose strength is to be estimated.
4. **End point and Equivalence point:** The point at which the completion of reaction occurs is called equivalence point whereas an end point is an observable physical change that occurs near the equivalence point.
5. **Indicator:** The substance which indicates the end point of titration is called indicator. The indicator indicates the completion of reaction by change in colour at the end point. There are three types of indicators

   (i)   Self Indicator: If one the reacting solution is strongly coloured and is decolorized or changes into a deterrent colour by the substance that is being determined then it is called self indicator Or it can defined as either titrant or titrand changes its colour at the end point eg. Potassium permanganate.

(ii) **Internal Indicator:** Internal indicator are the substances which are added into the conical flask in which titration is carried out. Eg. Phenolphthalein, methyl orange, Diphenylamine

(iii) **External Indicator:** External indicator is the substance, which is not addedinto the conical flask taken outside on the white tile or spot plate. Eg. Potassium ferricyanide

6. **Normality Equation:** According to the law of equivalence, the substances react with each other in a definite ratio by mass. For example, if an acid titrated against a base then at the end point according to normality equation.

Number of gram equivalents of acid = Number of gram equivalents of the base

$$N_1 V_1 = N_2 V_2$$

When N_1 and N_2 are normality's of acid and base and V_1 and V_2 are the volumes of acid and base respectively. This is known as the normality equation and is not fundamental principle of chemistry.

7. **Strength:** The amount of substance dissolved in I litre of solution, when expressed in grams is termed as strength of a solution. Strength of solution can also be expressed in any of the following ways:

(i) **Normality:** It is the number of gram equivalents of the substance dissolved per litre of the solution. It is denoted by N. If one gram equivalent of a substance is dissolved per litre of the solution, it is called normal solution.

(ii) **Molarity:** It is the number of moles of the solute present per litre of the solution it is denoted by M. Is denoted by m.

(iii) **Molality:** It is the number of moles of the substance dissolved in 1000gm or 1kg of the solvent. It is denoted by m.

(iv) **Formality:** It is the number of gram formula weight of the substance dissolved in one litre of the solution. It is denoted by F.

8. **Equivalent Weight:** The equivalent weight of a substance is define as the number of parts by weight of it that combine with or displace one part by weight of hydrogen or eight part of oxygen or 35.5 parts by weight or chlorine. Equivalent weight expressed in grams is called gram equivalent weight.

(i) **Equivalent weight of an acid**

$$\frac{\text{Molecular weight of acid}}{\text{Number of replaceable hydrogen atoms in one molecule of acid (Basicity of acid)}}$$

(Basicity - number of replaceable hydrogen atoms in an acid. Example HCL, H_2SO_4, H_3PO_4 are monobasic, dibasic and tribasic as they contain 1, 2 and 3 replaceable hydrogen atoms respectively)

(ii)   Equivalent weight of a base

$$\frac{\text{Molecular weight of base}}{\text{Number of replaceable OH – groups present in one molecule of acid (Acidity of base)}}$$

(Acidity = number of replaceable hydrogen OH groups in one molecule of a base. Example N_aOH, Ba $(OH)_2$ and Al $(OH)_3$ are mono, di and tri acid bases they contain 1 2 and 3 replaceable OH groups respectively)

(iii)   Equivalent weight of an oxidizing or reducing agent

$$= \frac{\text{Molecular mass of the substance}}{\text{Number of electrons gained / lost by one molecule in the redox reaction}}$$

9. **Standard Solutions:** A solution of known concentration is known as standard solution. There are many types of substances which are generally employed for preparing solution as explained below.

   (i)   Primary standard substance: Any substance whose standard solution can be prepared directly by dissolving and accurately weighting its amount and making up the solution to a known volume by dilution with water. A primary standard substance possesses the following characteristics:
   - It should be easily available in highly pure state. The impurities. If present must be inert with respect to the substance with which it is brought to react.
   - It should have a high equivalent weight or molar mass so that error due to weighing is minimized.
   - It should be readily soluble in water or the desired solvent.
   - It should neither be hygroscopic not efflorescent.
   - It should be stable at oven temperature used for drying. The hydrated substances are seldom used as primary standards.
   - It should be stable and unaffected by air.
   - Its composition should not change on standing during storage.
   - Crystalline oxalic acid, anhydrous sodium carbonate, dried KCL $AgNO_3$ $FeSO_4(NH_4)_2SO_4.6H_2O$ are used as primary standards.

   (ii)   **Secondary Standard Substance**: The substances which do not fulfil the above requirements and their standard solutions are not prepared directly by weighing are called secondary standard standard substances.

To prepare the standard solution of secondary standard and approximate weight of the substance is dissolved in a known volume of the solvent (water) Then the exact strength of the solution is found by titrating it against some primary standard. The process is called standardization.

The common Secondary standards are:

- Alkali hydroxides like NaOH, KOH etc. As they are hygroscopic and their weight keep on changing during weighing.
- $KMnO_4$ as it is not available in pure form and is associated with manganese dioxide which catalyzes the auto decomposition of permanganate solution on standing.
- Inorganic acids HCl, H_2SO_4 etc. Because their concentrations are known only approximately.

Multiple Choice Questions:

1. Phenolphthalein changes colour in

   i)Acids   ii)alkalis   iii)water   iv) salt solutions

   a)

2. Which of the following combinations **cannot** produce a buffer solution?

   i) HNO_2 and $NaNO_2$

   ii) HCN and NaCN

   iii) $HClO_4$ and $NaClO_4$

   iv) NH_3 and $(NH_4)_2SO_4$

3. A pipette is used to transfer a base into a flask kept below a burette filled with acid. The pipette, the flask and the burette should, respectively, be rinsed with....

   i)Distilled water, base and acid.

   ii)Base, Distilled water and acid.

   iii)Acid, Base, Distilled water.

   iv)Distil water in all cases.

4. Properties of a primary standard for use in acid-base titrations include……

   i) Stability and high purity

   ii) High purity and low solubility

   iii) Reactive with air and low molar mass

   iv) None of the above

EXPERIMENT NO: 2

Object: Determination of chloride content in the given sample by Mohr's Method. (Argentometric titration).
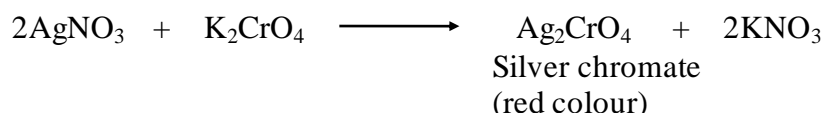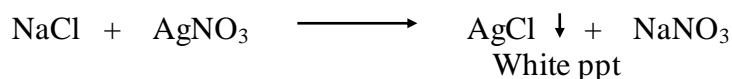
Apparatus: Pipette, burette, conical flask.

Theory: Chloride are present in water usually as $NaCl$, $MgCl_2$, $CaCl_2$ and may be due to leaching of marine sedimentary deposits, pollution from sea water, industrial or domestic wastes etc. Although chlorides are not harmful as such, their concentration over 250 ppm imparts a salty taste to the water, thus rendering the water unacceptable for drinking purposes from aesthetic point of view. Presence of chloride is also undesirable in boiler feed water because they leads to problems like priming and foaming salts like $MgCl_2$ may undergo hydrolysis under high pressure and temperature prevailing in the boiler, generating hydrochloric acid, which causes corrosion in boiler parts. Chloride in form of $MgCl_2$ and $CaCl_2$ cause permanent hardness.

When silver nitrate solution is added to a solution of NaCl containing a few drops of potassium chromate, white silver chloride is precipitated initially. As soon as all the chloride ions have been precipitated out, even a drop of silver nitrate added in excess gives a red precipitate of silver chromate, indicating the end point. This method is based on the fact that silver chloride is more insoluble than silver chromate because the solubility product of silver chloride (1.2×10^{-10}) is ower than that of silver chromate (1.7×10^{-10}). Hence so long the chloride ions are available the less soluble silver chloride is precipitated and no silver chromate is formed. In fact silver chromate, even if formed, will immediately change to silver chloride by interaction with chloride ions.

$$Ag_2CrO_4 + 2\,Cl^- \longrightarrow 2\,AgCl \downarrow + CrO_4^{2-}$$
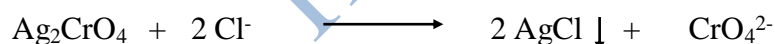
As soon as all chloride ions used, even a slight excess of Ag^+ produces insoluble silver chromate, which is red in colour.

$$NaCl + AgNO_3 \longrightarrow AgCl \downarrow + NaNO_3$$
White ppt

$$2AgNO_3 + K_2CrO_4 \longrightarrow Ag_2CrO_4 + 2KNO_3$$
Silver chromate
(red colour)

However, it should be noted that the water sample used for chloride determination should be practically neutral or only faintly alkaline (pH 7-8) since silver chromate is readily soluble in dilute acids, whereas in strongly alkaline solutions. Ag_2O may get precipitated as AgOH and in ammonia solutions, AgCl itself is soluble.

Procedure:

1. Standard N/20 NaCl solution:- Weight 0.2922g of pure and dry A.R. (Analytical Reagent) NaCl (Mol. Wt. =58.44) in a clean and dry watch glass. Dissolve it in distilled water and make up the volume up to the mark in a 100ml standard flask.

2. Standardization of AgNO₃ solution: Fill the burette with unknown AgNO₃ solution and note the initial reading. Pipette out 10ml of standard 0.05N sodium chloride solution into a conical flask and add 1ml of indicator [K₂CrO₄] solution. Add silver nitrate solution slowly from a burette, swirling the liquid constantly; a white precipitate of AgCl is obtained. After the addition of few ml of AgNO₃, a red colour appear in the flask but disappears quickly upon shaking. As the end point is approached, the red colour disappears slowly. Continue the addition of AgNO₃ solution drop by drop, till a permanent reddish brown colour is obtained. The colour persists even after shaking. This will be the end point. Note the reading and repeat the titration until concordant reading obtained.

3. Titration against unknown sample (NaCl): Repeat the above procedure with the unknown sample provided

4. Blank Correction with distilled water: Take 10ml of distilled water sample in a conical flask and add 1ml of indicator [K₂CrO₄] to it. Titrate it against AgNO₃ solution till red colour is obtained having the same intensity as in (1)

Observations:

1. Blank Correction with distilled water

S.N.	Volume of distilled water sample taken	Burette reading		Volume of AgNO₃ Used	Blank Correction (BC) Reading
		Initial	Final		
1	10				
2	10				
3	10				

2. Titration of silver nitrate with sodium chloride (0.05N)

S.N.	Volume of known NaCl solution taken (V_1)	Burette reading		Volume of AgNO₃ Used (V_2^*)	Concordant reading	Final Reading = $V_2^* - BC = V_2$
		Initial	Final			
1	10	0				
2	10	0				
3	10	0				

3. Titration of silver nitrate with unknown sample

S.N.	Volume of unknown NaCl solution taken (V_4)	Burette reading		Volume of AgNO₃ Used (V_3^*)	Concordant reading	Final Reading = $V_3^* - BC = V_3$
		Initial	Final			
1	10	0				
2	10	0				
3	10	0				

Calculations:

V_1 = Volume of NaCl taken = 10 ml

N_1 = Normality of NaCl taken = 0.05N

V_2 = Volume of AgNO$_3$ consumed = -----ml

N_2 = Normality of AgNO$_3$ solution = ------N

Since N_1V_1 = N_2V_2

Normality of NaCl provided x volume = Normality of AgNO$_3$ x volume

N_2 = N_1V_1/ V_2

Similarly $N_3 V_3$ = $N_4 V_4$

N_3 = Normality of AgNO$_3$ which is equal to N_2 = ----- N

V_3 = Volume of AgNO$_3$ used = --------ml

N_4 = Normality of unknown solution = ---------N

V_4 = Volume of unknown sample taken = --------ml

$$N_4 = \frac{N_3 V_3}{V_4} \qquad (N_3 = N_2)$$

Strength = N_4 x Eq. wt. of Cl$^-$ g/l

(Equivalent weight of Cl$^-$ = 35.5)

Strength = N_4 x 35.5 g/l

Result:

Chloride present in the unknown sample = -----------g/l

= -----------mg/l

= -----------ppm

Precautions:

1. The end point should be noted when a tinge of brownish red colour persists.

2. Store AgNO$_3$ in a coloured bottle.

3. The reaction mixture should be briskly shaken during the titration.

Multiple Choice Questions:

1. The titration in which insoluble colored precipitates are formed at end point is known as
   i) Neutralization titration   ii) Complexometric titration
   iii) Precipitation titration   iv) Redox titration

2. The pH of the sample in Mohr's Method lies between
   i) 4-5   ii) 8-9   iii) 7-8   iv) 9-10

3. Presence of chloride is undesirable in boiler feed water because
   i) They cause priming and foaming   ii) They undergo hydrolysis and cause corrosion
   iii) They cause permanent hardness   iv) All of the above

4. Sample required for blank correction reading in Argentometric titration is
   i) Sodium Chloride solution   ii) Distilled water
   iii) Brine solution   iv) Silver salt solution

EXPERIMENT NO. 3

Object: Determination of iron content in the given sample by using external indicator.

Apparatus: Burette, pipette, Standard flask, Spot plate, Glass rod, Conical flask.

Theory: Iron content can be determined by taking ferrous ammonium sulphate as sample. This titration can be categorized under redox titration. Ferrous ions present in Mohr's Salt are oxidized to ferric ions by potasssium dichromate (strong oxidizing agent) in the presence of an acid (dil HCl or dil H_2SO_4) Each molecule of $K_2Cr_2O_7$ gives up three atoms of oxygen, which are used for oxidation of ferrous ion to ferric ion, leaving ammonium sulphate unchanged. Also in the presence of acid (H^+ ions), each chromium atom reduces from Cr^{6+} to trivalent Cr^{3+} ion (by gaining three electron form reducing agent). The reaction takes place in the following manner.

$$K_2Cr_2O_7 \quad + \quad 4H_2SO_4 \longrightarrow K_2SO_4 \ + \ Cr_2(SO_4)_3 \ + 4\,H_2O \ + \ 3[O]$$

$$Or \quad [Cr_2O_7]^{2-} \quad + \quad 8H^+ \longrightarrow 2Cr^{3+} \ + \ 4H_2O \ + 3[O]$$
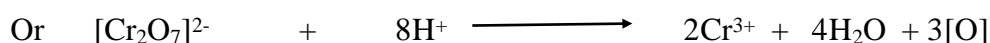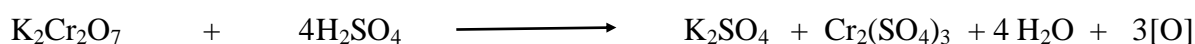
Hence complete reaction is:

$$K_2Cr_2O_7 \ + \ 6FeSO_4 \ + \ 7H_2SO_4 \longrightarrow K_2SO_4 \ + \ Cr_2(SO_4)_3 \ + \ 7H_2O \ + \ 3Fe(SO_4)_3$$

$$Or \ [Cr_2O_7]^{2-} \ + \ 14H^+ \ + \ 6Fe^{2+} \longrightarrow 6Fe^{3+} \ + \ 2Cr^{3+} \ + \ 7H_2O$$
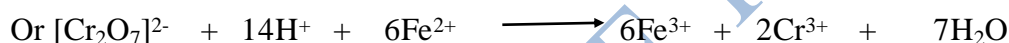
An external indicator (0.1 % potassium ferricyanide) is taken on white tile. From time to time during titration, a drop of titrated solution is mixed with an indicator on tile. If much ferrous ions (Fe^{2+}) are present a strong blue color appears due to the formation of ferroferricyanide complex.

$$2K_3[Fe(CN)_6] \ + \ 3FeSO_4 \longrightarrow Fe_3[Fe(CN)_6]_2 \quad + \quad 2K_2SO_4$$
$$\text{Ferrous ferricyanide (Dark blue complex)}$$

As the titration proceeds, blue colour becomes fainter because ferrous ion present in Mohr's salt keepon oxidizing to ferric ion. At the end point yellowish brown colored complex of ferriferricyanide is formed indicating that all the ferrous ion are oxidized to ferric ions by potassium dichromate.

$$3Fe_2(SO_4)_3 \quad + \quad 2[K_3Fe(CN)_6] \longrightarrow 3\ K_2SO_4 \ + \ 2Fe[Fe(CN_6)]$$
$$\text{Ferri ferricyanide(Yellowish Brown)}$$
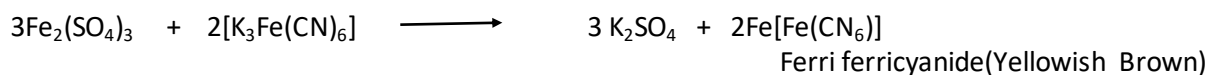
If potassium ferricyanide (indicator) is used internally then some of the ferrous ions of FAS form ferroferricyanide complex (which is blue in color) and some of the ferrous ions of FAS will undergo oxidation in presence of $K_2Cr_2O_7$ forming ferriferricyanide (whch is yellow in color). At the same time the reduction of chromium form +6 state in $K_2Cr_2O_7$ to +3 state in $Cr_2(SO_4)_3$ occurs, which is of light green color. Thus,due to the formation of different colors i.e.yellow color is masked by green and blue color and therefore we are unable to detect the end point.

Procedure :

Standard (N/20) solution of Ferrous Ammonium Sulphate:

Weight 1.9600 g of pure A.R. grade Ferrous ammonium sulphate (Eq. wt. = 392.12) and transfer into a 100ml volumetric flask. Add 5ml of conc.H_2SO_4 dissolve the salt completely and then make up to the mark with distilled water.

Titration of $K_2Cr_2O_7$ solution with known ferrous ammonium sulphate solution:

Rinse the burette with potassium dichromate solution and fill it. Pipette out 10ml of ferrous ammonium sulphate solution of known concentration in a clean conical flask and add to it about equal volume of 2N H_2SO_4 with the help of measuring cylinder. Put a series of drops of external indicator (0.1% potassium ferricyanide solution) with the help of a glass rod, on a tile. Run $K_2Cr_2O_7$ solution from the burette into the conical flask having acidified Mohr's salt solution. After adding one ml of $K_2Cr_2O_7$ solution, with drawn a drop of the solution form conical flask with a thin glass rod and mix it with one drop of Potassium ferricyanide on the tile. The appearance of blue colour shows the presence of ferrous ions in the solution that is being titrated and indicates that the end point has not yet reached. Now add another ml of $K_2Cr_2O_7$ again and do the test with another drop of potassium ferricyanide. Continue the addition of the dichromate in one ml lots till no blue colour is obtained.

Supposed in experiment there is a blue colour on the addition of 18ml of potassium dichromate solution, but no blue colour on the addition of 19ml of potassium dichromate solutions. It means that the end point lies between 18ml and 19ml. Now repeat the titration by adding 18ml of potassium dichromate without withdrawing any drop of the reaction mixture. After this add 0.1 ml of potassium dichromate solution every time and test a drop of the reaction mixture with potassium ferricyanide. Continue adding dichromate in 0.1ml lots till a drop of the reaction mixture does not give a blue colour with potassium ferricyanide. Repeat this titration to yield concordant reading.

Titration of $k_2Cr_2O_7$ solution with unknown ferrous ammonium sulphate solution:

The titration will be carried out exactly in the same way as mentioned above except in place of known ferrous ammonium sulphate solution, unknown ferrous ammonium sulphate solution will be taken.

Observations:

a) Titration of $K_2Cr_2O_7$ solution with known ferrous ammonium sulphate solution:

S.N.	Volume of Known FAS solution taken	Burette reading		Volume of $K_2Cr_2O_7$ Used	Concordant Reading
		Initial	Final		
1	10 ml				
2	10ml				
3	10ml				

b) Titration of $K_2Cr_2O_7$ solution with unknown ferrous ammonium sulphate solution:

S.N.	Volume of unknown FAS solution taken	Burette reading		Volume of $K_2Cr_2O_7$ Used	Concordant Reading
		Initial	Final		
1	10 ml				
2	10ml				
3	10ml				

Calculation:

N_1 = Normality of known ferrous ammonium sulphate

V_1 = Volume of known ferrous ammonium sulphate solution taken.

V_2 = Volume of $K_2Cr_2O_7$ used.

N_2 = ? (Normality of $K_2Cr_2O_7$)

Volume x Normality of known solution = Volume x Normality of $K_2Cr_2O_7$

$N_1V_1 = N_2V_2$

$0.05 \times 10 = N_2 \times V_2$

$N_2 = \dfrac{0.05 \times 10}{V_2}$

Normality of known $K_2Cr_2O_7$ ....N

In the titration against unknown

$N_3 V_3 = N_4 V_4$ ($N_2 = N_3$)

Where , N_4 = Normality of unknown ferrous ammonium sulphate

V_4 = Volume of unknown ferrous ammonium sulphate solution taken.

V_3 = Volume of $K_2Cr_2O_7$ used.

N_3 = Volume of $K_2Cr_2O_7$ used. Which is equal to N_2

$N_4 = \dfrac{N_3 \ V_3}{V_4}$

By substituting the values in the above equation we calculate the normality of unknown ferrous ammonium sulphate.

Strength of unknown solution = 392.12 x N_4 g/l

(Equivalent weight of Mohr's = 392.12)

392.12 g of FAS contain = 56g of Fe

Result:

Strength of ferrous contents in unknown solution = 56 x N_4 g/l

Precautions:

1. The glass rod must be washd each time before use for withdrawing a drop from the titration flask.

2. Always uses dilute H_2SO_4 as a reducing agent because $K_2Cr_2O_7$ acts as an oxidant in acidic medium.

Multiple Choice Questions:

1. The formula of Mohr's salt is…………….……

2. What is the oxidation state of chromium in $K_2Cr_2O_7$?
   i)   + 6   ii) +3   iii) +2   iv) + 4

3. What is the oxidation state of chromium in $Cr_2(SO_4)_3$?
   i)   + 6   ii) +3   iii) +2   iv) + 4

4. The .... of chromium form +6 state in $K_2Cr_2O_7$ to +3 state in $Cr_2(SO_4)_3$ occurs.

EXPERIMENT NO. 4

Object: Determination of total, permanent and temporary hardness in water sample using EDTA as standard solution.

Apparatus: Burette, conical flask, funnel, volumetric flask(250 ml).

Theory: Hardness is defined as the soap precipitating power of the water. Any salt which precipitates soap is responsible for hardness. As soaps are sodium or potassium salts of higher fatty acids and the sodium and potassium salts do not precipitate soap therefore they do not cause any hardness. The divalent salts e.g. $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, $CaSO_4$, $MgSO_4$, $CaCl_2$ and $MgCl_2$ etc, are generally found in appreciable amount and are thus considered reasonable for hardness in ground water, the presence of $FeSO_4$, $Al_2(SO_4)_3$ also cause hardness although their presence are not very common.

$C_{17}H_{35}COONa$ + NaCl $\longrightarrow$ $C_{17}H_{35}COONa$ + NaCl
Soap   or any   no ppt
                    Soluble salts
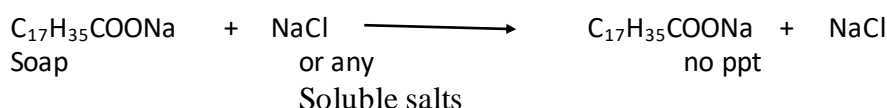
Exchange of sodium ion, thus sodium ion is not responsible for hardness.

Hardness may be of two types- Temporary hardness (cause due to bicarbonate of Ca^{2+} & Mg^{2+}) and permanent hardness (caused due to chloride and sulphate of Ca^{2+} & Mg^{2+})

Both temporary and permanent hardness of water are expressed in their equivalents of $CaCO_3$ in parts per million (1,00,000 parts of water). This is referred to as degree of hardness of water.

EDTA (versanate) forms a stable and soluble complex with a large number of metal ions responsible for hardness. This method is the best method available for the estimation of hardness as it is simple, inexpensive and gives accurate results. The determination is based upon the fact that when EBT is added to water sample at pH10 (ammonia buffer) gives wine red coloured unstable complex with calcium and magnesium ions present in water due to the formation of less stable metal- indicator complexes. The addition of versenate solution results in the formation of more stable metal- EDTA complexes as compared to metal indicator complexes. The versenate first reacts with hardness producing metal ions present in water and when they are consumed it reacts with metal ions released from the less stable metal-indicator which gives rise to its original blue colour at the end point.
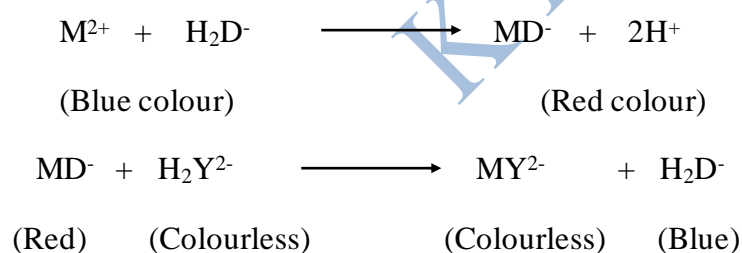
The formula of the versenate is:

HOOCCH₂   CH₂COONa   HOOCCH₂   CH₂COO-
       \   /   \   /
        NCH₂CH₂N $\longrightarrow$ NCH₂CH₂N   +2 Na⁺
       /   \   /   \
NaOOCCH₂   CH₂COOH   -OOCCH₂   CH₂COOH
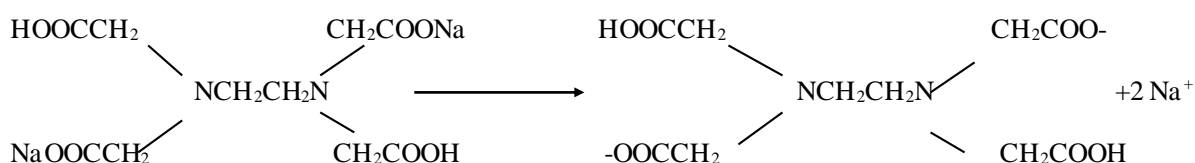
The above equation can be written as:

$$Na_2H_2Y \longrightarrow H_2Y^{2-} + 2Na^+$$

(Solid)   (in solution)

$$M^{2+} + H_2Y^{2+} \longrightarrow MY^{2-} + 2H^+ \quad (M^{2+} = Ca^{2+} \text{ or } Mg^{2+})$$
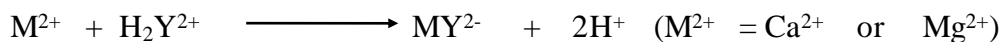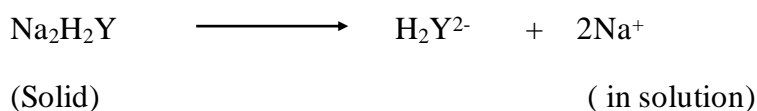
The metal ions get attached in place of hydrogen atoms of the carboxylic acid groups present in the versenate forming stable complexes and not through the carboxylate ions created by the ionization of Na^+ in solution.
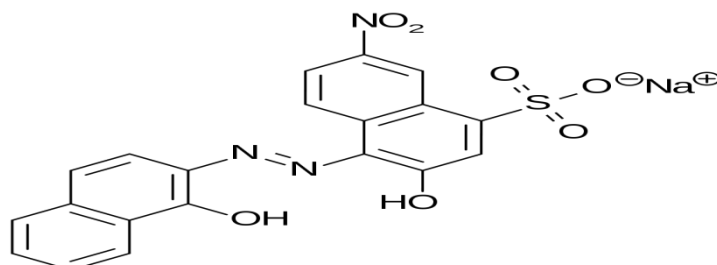
EBT polymerize in strongly acidic solutions to a red brown product and hence the indicator is generally used in EDTA titration with solutions having pH greater than 6.5. The sulphuric acid group loses its proton much before the pH range of 7 – 12. The sulphuric acid group losses its proton much before the pH ranges of 7 – 12. The dissociation of the hydrogen atoms of the phenolic groups only should therefore be considered and hence in solution it can be represented by the formula H_2D. Initially, when it is added to hard water along with buffer solution of pH = 10, the reaction is;

$$M^{2+} + H_2D^- \longrightarrow MD^- + 2H^+$$

(Blue colour)   (Red colour)

$$MD^- + H_2Y^{2-} \longrightarrow MY^{2-} + H_2D^-$$

(Red)   (Colourless)   (Colourless)   (Blue)

On addition of EDTA, the red colour diminishes and ultimately at the end point changes from wine red to sky blue.

Method:

1. Preparation of Standard CaCl$_2$ solution:

Weight out accurately about 0.05g of pure $CaCO_3$ on a watch glass and transfer it into a well clean conical flask rinsed with distilled water. Add 3ml of dilute hydrochloric acid to dissolve all the $CaCO_3$, add distilled water, heat for 5 minutes to remove CO_2, cool and neutralize the excess of acid with pure dilute ammonia using litmus paper as indicator which changes from red to blue. Transfer it to a clean 250mL Volumetric flask rinsed with distilled water 2 or 3 times, transfer the washings also to the volumetric flask and make the volume upto the mark by adding distilled water.

2.   Standardization of Versenate Solution:

Take 50 ml of standard $CaCl_2$ solution in a conical flask. Add 3-4 drops of indicator (EBT) and 10ml of buffer solution containing ($NH_4OH + NH_4Cl$) to hold the pH around 10. Titrate it against EDTA solution (0.01M) till colour just changes from wine red to sky blue and note down the burette readings.

3. Determination of Hardness:

i. Total hardness: Take 50ml of water sample in the conical flask. Add 3-4 of the indicator (EBT) and 10ml of buffer solution to hold the pH around 10, the colour of the solution will be wine red if any hardness is present. Now add the reagent (EDTA solution) from the burette until the wine red colour just changes to sky blue.

ii. Permanent Hardness: Take 50ml of the hard water sample in a beaker, boil it to reduce its volume to approximately less than half (to ensure that the temporary hardness is completely removed), cool and filter into a conical flask rinsed with distilled water. Wash the beaker with distilled water two or three times and filter the washing also in the same flask to ensure that no permanent hardness producing salts are left in the beaker. Make up the volume upto 50ml. Add 10ml buffer solution and 3-4 drops of indicator to it. Titrate the filter with the versenate solution and note down the end point when the colour changes from wine red to sky blue.

Observations:

Weight of empty watch glass $= W_1$……..g

Weight of watch glass + $CaCO_3$ $= W_2$……..g

Weight of $CaCO_3$ $= W_2 – W_1$=…….g

1. Standardization of EDTA solution:

S.N.	Volume of $CaCl_2$ solution taken	Burette reading		Volume of EDTA Used
		Initial	Final	
1	50 ml			
2	50ml			Xml
3	50ml			

Volume of 50ml of standard $CaCl_2$ solution = Xml EDTA solution used

2. Determination of total hardness:

S.N.	Volume of hard water solution taken	Burette reading		Volume of EDTA Used
		Initial	Final	
1	50 ml			

| 2 | 50ml | | | Yml |
| 3 | 50ml | | | |

Volume of 50ml of hard water = Yml EDTA solution used

3. Determination of permanent hardness water:

S.N.	Volume of boiled hard water solution taken	Burette reading		Volume of EDTA Used
		Initial	Final	
1	50 ml			
2	50ml			Zml
3	50ml			

Volume of 50ml of boiled hard water = Zml EDTA solution used

Calculation:

Now

250 ml of $CaCl_2$ solution contains = 0.05g of $CaCO_3$

1ml of $CaCl_2$ solution contains = 0.05g/ 250ml of $CaCl_2$ ($CaCO_3 = CaCl_2$)

50 ml of $CaCl_2$ solution contains = $\dfrac{0.05 \times 50}{250}$ = 0.01g of $CaCl_2$

Xml of EDTA solution = 0.01 g of $CaCl_2$

1ml of EDTA solution = $\dfrac{0.01g}{X}$ of $CaCl_2$

Total Hardness:

So

Yml of EDTA solution used for 50ml of hard water = $\dfrac{0.01 \times Y}{X}$ g of $CaCl_2$

EDTA solution which is used for 1ml hard water sample = $\dfrac{0.01}{X} \times \dfrac{Y}{50}$ g of $CaCl_2$

10^6 ml of hard water = $\dfrac{0.01 \times Y}{X} \times \dfrac{10^6}{50}$ g of $CaCO_3$

Total hardness of given water sample = -------------ppm

Permanent Hardness :

Similarly for permanent hardness

Zml of EDTA solution used for 50ml boiled hard water = $\dfrac{0.01 \times Z}{X}$ g of $CaCO_3$

EDTA solution which is used for 1 ml boiled hard water = $0.01 \times \dfrac{Y}{X} \dfrac{}{50}$ of $CaCl_2$

10^6 ml of hard water = $0.01 \times \dfrac{Z}{X} \times \dfrac{10^6}{50}$ g of $CaCl_2$

Result:-

1) Total hardness _____ppm
2) Permanent hardness_____ppm
3) Temporary hardness_____(1 – 2)ppm

Standard result of hardness can be classified on the basis of their hardness value

S. No.	Classification	mg/l or ppm	grains/gal
1.	Soft Water	0 – 17.1	0 -1
2.	Slightly Hard	17.1 – 60	1 – 3.5
3.	Moderately Hard	60 – 120	3.5 – 7.0
4.	Hard	120 – 180	7.0 – 10.5
5.	Very Hard	180 & above	10.5& above]

Multiple Choice Questions:

1. A water sample contains 222 ppm of calcium chloride. The hardness in term of calcium carbonate will be
   1)400ppm ii) 20°F iii)40°F iv).400mg/l

2. Titraion of hardwater against EDTA involved

   i)Redox titration ii) Complexometric titration

   iii)Neutralisation titration iv) Precipitation titration

3. EBT has following linkage in its structure
   i)-COOH ii) -C≡N iii)-N=C iv)-N=N-

4. The color of metal –EDTA complex is
   i)Blue ii)Wine red iii)Yellow iv) Colorless

EXPERIMENT NO. 5

Object: Determination of alkalinity in the given water sample.

Apparatus: Burette, Conical Flask, Pipette.

Theory: The alkalinity of water may be defined as its capacity to neutralize acids. It is due to the presence of HCO3-, CO32-and OH- of Na+, K+, Ca2+ & Mg2+ . Some of the salts not all which causes alkalinity also causes hardness. However presence of otheer bases such as borates, silicates phosphates can also contributes to alkalinity through to a smaller extent.

The alkalinity of water can be considered to be mainly due to

Caustic alkalinity (due to OH- and CO32- ions)

Bicarbonate alkalinty also called temporary hardness (due to HCO3- ions)

Highly alkaline waters may lead to caustic embrittlement and also may cause deposition of precipitates and sludges in the boiler tubes and pipes. Bicarbonates of calcium and magnesium induces temporary hardnesss in water, which if untreated, causes scale formation in boilers. The possible combinations of ions causing alkalinity in water are:

OH⁻ only or

CO_3^{2-} only or

HCO_3^{-}only or

OH⁻ & CO_3^{2-}together or

HCO_3^{-}& CO_3^{2-} together

The possibility of OH⁻ and HCO_3^{-} ions together is ruled out, because they combine instantaneously to form CO32- ions.

$$OH^- + HCO_3^- \longrightarrow CO_3^{2-} + H_2O$$

$$NaOH +| NaHCO_3 \longrightarrow Na_2CO_3 + H_2O$$
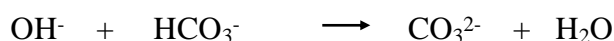
Thus OH⁻ and HCO_3^{-} ions cannot exist together in water. On the basis of same reasoning, all the three (OH⁻, CO_3^{2-}, HCO_3^{-}) cannot exist together.

The type and extent of alkalinity present in the water sample can be determined by titration an aliquot of the sample against a standard acid, using phenolphthalein and methyl orange as indicators. The determination is based on the following reactions:

1) $[OH^-] + [H^+] \longrightarrow H_2O$

2) $[CO_3^-] + [H+] \longrightarrow [HCO_3^-]$

3) $[HCO_3^-] + [H+] \longrightarrow H_2O + CO_2$
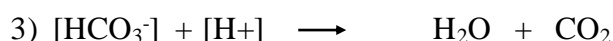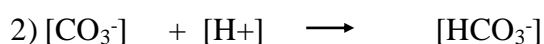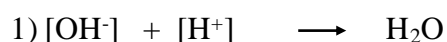
**Action of Indicator (Modern Quinoid Theory) :**

Phenolphthalein: (pH 8- 9.6) It possesses a benzenoid structure in acidic medium, where as it changes to pink coloured quinoid in alkaline medium having quinoid form.

Phenolphthalein

Colourless, benzenoid form
(in acid)

Red, Quinoidform
(in alkali)
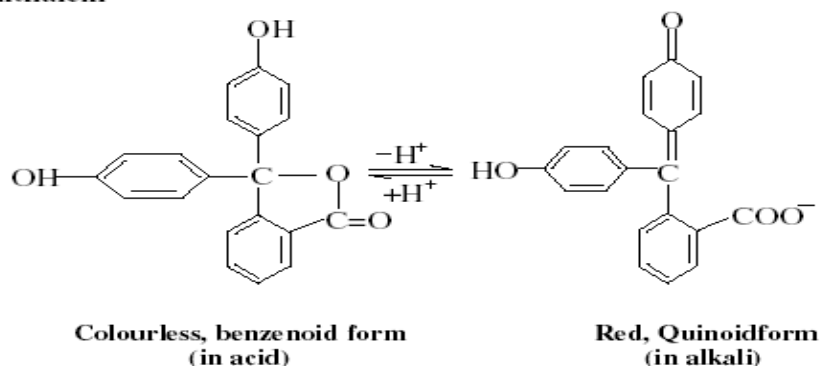
Methyl Ornage: (pH 3.1-4.4) It also exists in two aromatic forms. In alkaline solution it exists in benzzenoid form and is yellow in colour. In acidic solution it exists in red colour having quinoid structure.

Methyl Orange

Yellow Benzenoid form (in bases)

Red Quinoid form (in acids)
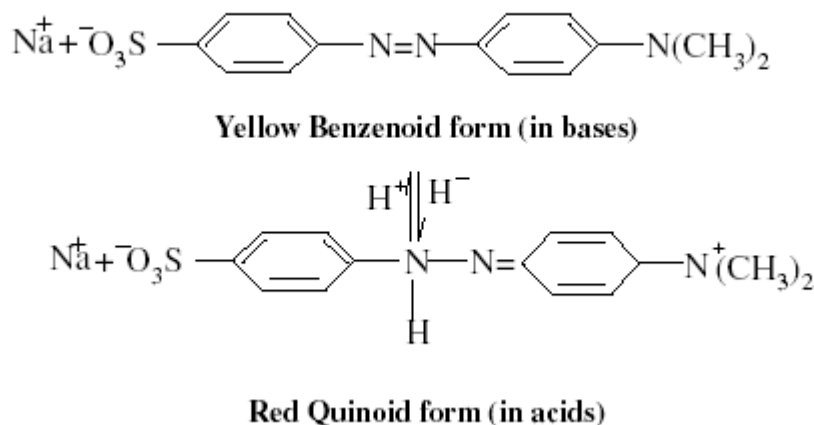
The titration of the water sample against a standard acid up to phenolphthalein end point marks the completion of reaction (1) and (2) i.e. complete neutralization of OH- ions and neutralization of CO_3^{2-} up to HCO_3^- stage (half neutralization of CO_3^{2-} ions). On the other hand the volume of acid used up to methyl orange end-point marks the completion of reaction (1), (2) and (3). Hence, the amount of acid used after the phenolphthalein end point corresponds to one-half of normal carbonate plus all the bicarbonates while the total amount of acid used represents the total alkalinity (due to OH^-, HCO_3^-, CO_3^{2-})

Table I represents various forms of alkalinity present in water sample

Alkalinity	OH- (ppm)	CO32- (ppm)	HCO3- (ppm)

P=0	NIL	NIL	M
P=1/2M	NIL	2P	NIL
P<1/2M	NIL	2P	(M-2P)
P>1/2M	(2P-M)	2(M-2P)	NIL
P=M	P=M	NIL	NIL

P= Phenolphthalein end-point , M= Methyl orange end-point

Procedure:

Transfer 50 ml of the water sample into a conical flask and add 1 ml of phenolphthalein indicator. Titrate the sample with the standard HCl until the pink colour just disappears. Note the titrate vaulue as the phenolphthalein end-point, (P). Add 1ml of methyl orange indicator to the same solution and continue the titration until a sharp colour change from yellow to red takes place. Note the titrate value from the beginning of the experiment as methyl orange end-point (M)

Observations:

S.N.	Vol. of the water sample taken	Burette Reading	Volume of N/50 HCl rundown	
		Initial	[P] Xml	[M] Yml
1	50	0		
2	50	0		
3	50	0		

Calculations:

$$\text{Now [P] = X mL} \qquad\qquad \text{[M] = Y mL}$$

Since [P] < ½ [M] the sample should contain only CO_3^{2-} and HCO_3^- and it does not contain OH^- further

Similarly 2[P] should correspond to CO_3^{2-} thus volume of N/50 HCl is equivalent to

$CO_3^{2-} = 2[P] = 2$ X ml

Similarly 2[P] should correspond to HCO_3^- So volume of N/50 HCl equivalent to

$HCO_3^- = [M – 2P] = [Y-2X]$ mL

<u>Now for CO_3^{2-}</u>

$N_1 V_1 = N_2 V_2$

N_1 = Normality of water sample

V_1 = Volume of water sample taken

N_2 = Normality of HCl

V_2 = Volume of HCl used

$$N_1 \times 50 = \frac{N_2 \times 2P}{50} \qquad [\ \{2P\}= XmL \ ]$$

$$\text{Or} \quad N1 = \frac{N_2 \times 2X}{50 \quad 50} = \frac{2X}{2500}$$

The Strength of CO_3^{2-} = $N_1 \times 30$ g/L   [equivalent weight of CO_3^{2-} = 30]

Or strength of CO_3^{2-} = $N_1 \times 30 \times 1000$ mg/L

[30g of CO_3^{2-} = 50g of $CaCO_3$]

Strength of CO_3^{2-} in term of $CaCO_3$ = Strength of CO_3^{2-} $\times \dfrac{50}{30}$ m/L

For HCO$_3^-$:

N_3 = Normality of water sample

V_3 = Volume of water sample taken

N_4 = Normality of HCl

V_4 = Volume of used HCl

$$N_4 \ V_4 = N_3 \ V_3$$

$$N_3 \times 50 = \frac{N}{50} \times [\ M - 2P \ ] \qquad [\ \{P\} = X \ mL, \quad \{M\} = YmL \ ]$$

$$N_3 \times 50 = \frac{N}{50} \times [\ Y - 2X \ ] = \frac{N}{50} \times \frac{[\ Y - 2X \ ]}{50}$$

The strength of HCO_3^- = $N_3 \times 61$ g/L   [61 of HCO_3^- = 50g of $CaCO_3$]

Or strength of HCO_3^- = $N_3 \times 61 \times 1000$ mg/L

[61g of HCO_3^- = 50g of $CaCO_3$]

Strength of HCO_3^- in term of $CaCO_3$ = Strength of HCO_3^- $\times \dfrac{50}{61}$ g/L

Result:

Alkalinity with respect to CO_3^{2-} = ……. mg/L

Alkalinity with respect ot HCO_3^- = …… mg/L

Total Alkalinity   =………….. [1+2] mg/L

Multiple Choice Questions:

1. Which of the following cannot exist together in water with OH$^-$
i) CO_3^{2-} ii) HCO_3^- iii)both of the above   iv) none of the above

2. Which of the following are draw backs of highly alkaline water
i)Carcinogenic disease formation   ii)Deposition of sludges
 iii)Caustic embrittlement   iv)All the above

3. Which of the chromo groups is present in methyl orange
    i)Azo group   ii) keto group iii)Imino group iv) benzyne group

 4. Which of the chromophoric group is present in phenolpthalein indicator

   i) keto group ii) Azo group iii) imino group iv)none of the above

EXPERIMENT NO. 6

Object: Determination of available chlorine in bleaching powder.

Apparatus: Burette, pipette , conical flask, Pestle mortar, Volumetric flask

Theory and significance: The available chlorine is the amount of chlorine liberated by the action of dilute mineral acids on bleaching powder and it expressed in terms of percentage weight of bleaching powder. Commercially Bleaching powder contains 36 – 40% available chlorine and it deteriorates on storage due to continuous decomposition, so available chlorine is determined as soon as the sample is prepared.

Bleaching powder is a mixture of many constituents. The main constituents of bleaching powder are calcium hypochlorite $Ca(OCl)_2$, basic calcium chloride $[CaCl_2.Ca(OH)_2.H_2O]$, calcium hydroxide $[Ca(OH)_2]$ and some free slaked lime. The active constituent is Calcium hypochlorite, which on treatment with HCl generates Hypochlorous acid, which is mainly responsible for the disinfecting and bleaching action.

$$CaOCl_2 + HCl \longrightarrow CaCl_2 + H_2O + Cl_2 \uparrow$$
$$\text{(Available chlorine)}$$

$$Cl_2 \uparrow + H_2O \longrightarrow HCl + HOCl$$
$$\text{(Hypochlorous acid)}$$
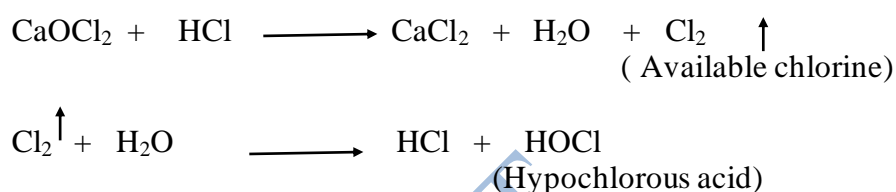
The disinfecting action of HOCl, take place by direct chemical reaction of HOCl with the enzymes in the cell of microorganisms. The effectiveness of HOCl is supported by Chlorine concentration and pH. pH should be greater than 8 for the efficient working of HOCl. At lower pH, HOCl will be dissociated into hypochlorite ion, which is less effective than HOCl in disinfecting action.

If pH<8 then $HOCl \longrightarrow H^+ + OCl^-$
$$\text{(hypochlorite ion)}$$

The available chlorine is estimated by Bunsen's method. In this method, a suspension of bleaching powder is treated with dilute acetic acid in presence of KI solution. The liberated chlorine from bleaching powder reacts with KI to form an equivalent amount of Iodine, which is titrated against sodium thiosulphate solution using starch as an indicator

$$CaOCl_2 + CH_3COOH \longrightarrow (CH_3COO)_2Ca + H_2O + Cl_2 \uparrow$$

$$Cl_2 \uparrow + 2KI \longrightarrow 2KCl + I_2$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$
$$\text{(Sodium tetrathionate)}$$
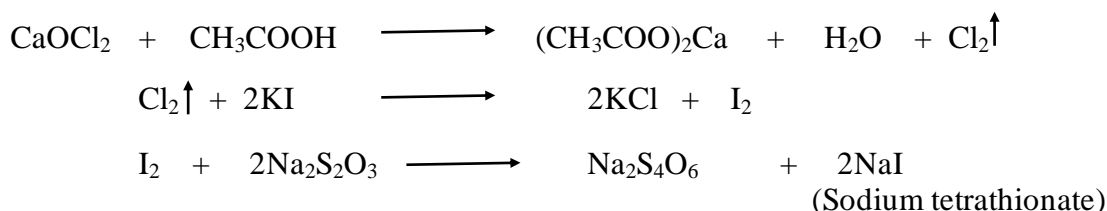
Procedure:
The following solutions are supplied

1. Standard N/20 Iodine solution.

2. Sodium thiosulphate solution (to be standardized)

(a) Standardization of Sodium thiosulphate solution (Iodimetric titration)

Take the given Sodium thiosulphate solution in a burette. Pipette out 10ml of standard iodine solution in a conical flask. Add about 3ml of HCl to it, the solution turns brown due to the liberation of iodine since reaction is not instantaneous hence 4-5minutes must be allowed for the complete liberation of iodine. Titrate it against Sodium thiosulphate to a light yellow colour. Add 5-6 drops of starch indicator when yellow colour turns to blue. Continue the addition of Sodium thiosulphate drop-wise till the blue colour disappears. Note down the volume of the sodium thiosulphate used.

(b). Determination of available chlorine (Iodometric titration)

Weight out accurately 1.0g of bleaching powder in watch glass and transfer it to a mortar. Add a few ml of distilled water. Grind it to a smooth thick paste and dilute it with more distilled water. Transfer the suspension completely to 100ml volumetric flask with small portions of distilled water and make the volume up to the mark. Shake it vigorously and pipette out 10ml of homogeneous suspension in a conical flask. Add about 1 g of solid KI and about 5ml of glacial acetic acid. Titrate the liberated iodine against Sodium thiosulphate as above. Note down the volume of Sodium thiosulphate used.

Observations:

Weight of empty watch glass $\qquad = \qquad W_1$ g

Weight of watch glass + bleaching powder $= \qquad W_2$ g

Weight of bleaching powder $\qquad = \qquad W_2 - W_1 = W$ g

Standardization of sodium thiosulphate solution:

S.N.	Volume of Iodine (V_2)	Burette reading		Volume of sodium thiousulphate Used (V_1)
		Initial	Final	
1	10	0		
2	10	0		
3	10	0		

Determination of Available chlorine:

S.N.	Volume of bleaching powder solution (V_4)	Burette reading		Volume of sodium thiousulphate Used (V_1)
		Initial	Final	
1	10	0		
2	10	0		
3	10	0		

Calculation:

According to normality equation,

$N_1 V_1 = N_2 V_2$

N_1 = Normality of Sodium thiosulphate.

V_1 = Volume of Sodium thiosulphate solution used.

N_2 = Normality of iodine solution.

V_2 = Volume of iodine solution taken.

$$N_1 = \frac{N_2 V_2}{V_1} = \frac{N}{20} \times \frac{10}{V_1} = \frac{2N}{4V_1}$$

Let the weight of Bleaching powder dissolved in 100ml = ...W g (W=1.0 g)

Strength of bleaching powder = 10 x W g/L

Let V_3 ml be the volume of 2N ($N_1=N_3$) Sodium thiosulphate required for 10ml

$$\overline{4V_1}$$

(V_4) bleaching powder suspension and N_4 be the normality of Iodine liberated by bleaching powder.

Now according to normality equation,

$$N_3 V_3 = N_4 V_4$$

N_3 = Normality of Sodium thiosulphate which is equal to N_1

V_3 = Volume of Sodium thiosulphate solution used.

N_4 = Normality of bleaching powder solution.

V_4 = Volume of bleaching powder solution taken.

$$N_3 V_3 = N_4 V_4$$

Or $N_4 = \dfrac{N_3 V_3}{V_4} = \dfrac{2N}{4V_1} \times \dfrac{V_3}{V_4}$ $\left[N_1 = N_3 = \dfrac{2N}{4V_1} \right]$

Thus normality of chlorine = $\dfrac{2N}{4V_1} \times \dfrac{V_3}{V_4}$ [Normality of Iodine = Normality of available chlorine]

Strength of available chlorine = $\dfrac{2N}{4V_1} \times \dfrac{V_3}{V_4} \times 35.5$ g/L

$$= \frac{2N}{4V_1} \times \frac{V_3}{V_4} \times 35.5 \times \frac{100}{1000}$$

% of available chlorine $= \left[\frac{2N}{4V_1} \times \frac{V_3}{V_4} \times 35.5 \times \frac{100 \times 100}{W \times 1000} \right]$

[W = 1.0 g]

Result: - The given bleaching powder sample contains….……… % available chlorine.

Precautions:

1. The suspension of bleaching powder is very unstable and hence should be titrated immediately after its preparation.

2. The solution should not be sucked in to the pipette with mouth as chlorine vapours are harmful.

Multiple Choice Questions:

1. The indicator used in Iodometric titration is
   i) Starch   ii) $K_3Fe(CN)_6$ iii) K_2CrO_4 iv) $Na_2S_2O_3$

2. In the titration of bleaching powder with hypo solution, what is the role of glacial acetic acid……………….…….

3. The yellow color of solution in iodometric titration is due to
   i)low concentration of I_2 ii)Liberation of I_2
   iii)Formation of Starch-Iodide complex   iv)None of the above

4. The bleaching action of HOCl depends on
   i)pH   ii) concentration of I_2 iii)Mineral acids   iv) Conc. of Hypochlorite ion

EXPERIMENT NO. 7

Object: Determination of coefficient of viscosity of the given liquid by Ostwald's Viscometer method.

Apparatus: Ostwald's viscometer, stop watch, specific gravity bottle, pipette, distilled water, rubber tubing.

Theory:

(i) Ostwald's Viscometer: It consists of a capillary tube connected at its upper end with a bulb B and its lower end with a U-tube provided with bulb A. Bulb A is of larger size than B (Fig. 1) Marks C and D are etched on the capillary tube above and below the bulb B. The bulbs are necessary to maintain the hydrostatic pressure during flow of liquid. Through the capillary the liquid flows with a measurable speed.

Fig. 1:- Ostwald Viscometer
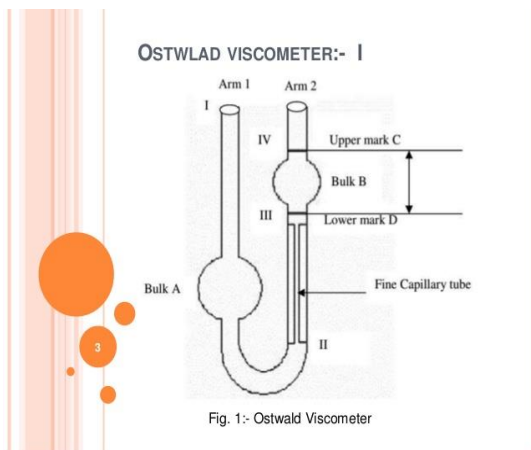
(ii) Relative Density Bottle: The density of liquid is conveniently measured by means of a relative density bottle or specific gravity bottle. It is a round bottomed glass vessel, fitted with a glass cork containing a fine capillary Fig. 2.

The Ostwald's Viscometer method is based on poiseuille's equation. This related the rate of flow of a liquid through a capillary tube with the coefficient of viscosity and is expressed by the equation,

$$n = \frac{\pi r^4 tP}{8Vl}$$

V= Volume of the liquid of viscosity n flowing in time t, through a capillary tube of radius r and length l

P= Hydrostatic pressure of the liquid.

Thus the determination of the absolute viscosity by means by Poiseuille's expression involves the determination of V, r, t, l, and P.

The method is however tedious and laborious one. Hence, a simpler method is used wherein we compare the viscosities of the two liquids. If the coefficient of viscosity of one liquid is known, then that of the other can be calculated. If t_1 and t_2 are the flow times required to flow for equal volumes of two liquids through the same length of a capillary tube then from equation we have

$$\eta_1 = \pi P_1 r^4 \, t_1 / 8VI$$

$$\eta_2 = \pi P_2 \frac{r^4 \, t_2}{8VI}$$

$$\frac{\eta_1}{\eta_2} = \frac{P_1 \, t_1}{P_2 t_2}$$

P=hdg

Where h is the height of the liquid column (It is constant for all the liquids if taken for identical points and liquids are taken in equal volumes for a particular set of observations.)

g = acceleration due to gravity

d = density of the liquid

Since in this case for two liquids h and g are same hence,

$$\frac{\eta_1}{\eta_2} = \frac{d_1}{d_2} \frac{t_1}{t_2}$$

This will give us the relative viscosity of the given liquid. Relative viscosity has no units. The absolute viscosity $\eta = \frac{d1}{d2} \cdot \frac{t1}{t2} . \eta_1$

Procedure:

1. Clean the viscometer with chromic acid ($K_2 \, Cr_2 O_7 + Conc. H_2 SO_4$) and then wash it several times with distilled water. It is finally washed with alcohol and ether and then dried.

2. Attach a piece of clean rubber tube to the end C and clamp the viscometer vertically in air.

3. Now introduce a sufficient volume of the given liquid with the help of a pipette in bulb B so that the bend portion of the U-tube and more than half of bulb B are filled up.

4. Through the rubber tube, suck up the liquid until it rises above the mark X. Make sure that there is no air bubble inside the liquid.

5. Now, allow the liquid to fall freely through the capillary upto the mark X. Start the stop watch and note the time t_1 for the flow of the liquid from mark X to mark Y.

6. Repeat the experiment thrice. The values should be concordant.

7. Remove the liquid and clean and dry the viscometer again.

8. Repeat the experiment by taking the same volume fo the distilled water and note down the time taken t_2 for flow of water from mark X to Y. Repeat thrice.

9. Weigh the relative density bottle and note down its weight.

10. Fill it with the given liquid and weigh it again.

11. Remove the liquid. Wash it with chromic acid and then distilled water. Dry in the oven. Now fill it with the distilled water and weight it

Observations :

Room temperature =……….. °C

Observation Table:

S. No.	Given liquid		Water	
	Time of Flow	Mean (t_1)	Time of flow	Mean (t_2)
1.				
2.				
3.				

Weight of empty specific gravity bottle =…..$\omega_1\,g$

Weight of empty specific gravity bottle + given liquid =…..ω_{2g}

Weight of empty specific gravity bottle + distilled water =…..ω_{3g}

Calculation:

$$\frac{Density\ of\ solution}{Density\ of\ water} = \frac{d_1}{d_2} = \frac{\omega_2 - \omega_1}{\omega_3 - \omega_1}$$

Relative viscosity of the given liquid $= \dfrac{\eta_1}{\eta_2} = \dfrac{d_1}{d_2} X \dfrac{t_1}{t_2}$

Absolute Viscosity $= \dfrac{d_1}{d_2} X \dfrac{t_1}{t_2} X \eta_2$

Result: The relative viscosity of the given solution is ... at…………. °C

The absolute viscosity of the given solution is….…… Pas at ……..…°C

<u>Multiple Choice Questions:</u>

1. Which property measures the resistance of a liquid to flow?
   a) Density   b) Viscosity   c) Volume   d) Solubility

2. What is viscosity index?
   a. effect of pressure on changes in viscosity
   b. effect of temperature on changes in viscosity
   c. effect of resistance between two surfaces
   d. none of the above
3. What is coefficient of viscosity?
4. What is SI unit of Viscosity?

EXPERIMENT NO. 8

Object: To determine the surface tension of the given liquid at room temperature by stalagmometer using drop number method.

Apparatus: Stalagmometer, distilled water, unknown liquid, beaker, rubber tube with screw pinch cock, clamp stand, specific gravity bottle or pyknometer.

Theory: Surface tension is defined as the attractive force exerted upon the surface molecules of a liquid by the molecules beneath that tends to draw the surface molecules into the bulk of the liquid and makes the liquid assume the shape having the least surface area. It is a physical property of every liquid due to the intermolecular attraction among the molecules, which is equal to the amount of force per unit area.

$$\gamma = F/ L$$

Gamma represents surface tension, F represents force, and L represents the length along which the force is felt. Its SI unit is N/m and CGS unit is dyne /cm.

Surface tension forces are due to intermolecular forces between the liquid's molecules at the liquid's outer boundaries. The molecule in the interior of liquid attracted by surrounding molecules in all direction by cohesive forces and hence resultant force on that molecule is zero (Fig.1). However, the molecules at the surface do not have other like molecules on all sides around them and they are pulled inwards the liquid core by non-zero net force (Fig. 1) Consequently, they cohere more strongly to those associated with them directly on the surface and form a surface "film"(called Surface Strain or Stretching). Nevertheless, these surface molecules are in the energetically unfavourable state, which forces liquid to minimize the surface area. The geometrical requirement of smallest surface area at the fixed volume is satisfied by the sphere. It is the reason why the free drops of water form spherical droplets.
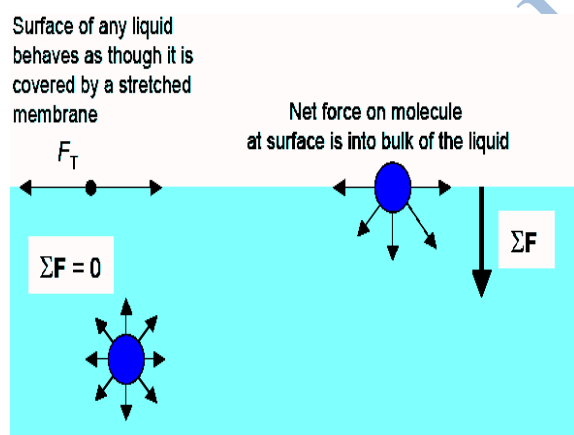
Figure 1: Forces on the Molecule

The surface tension of the given liquid is determined relative to water at the room-temperature by using stalagmometer. The no. of drops for the same volume of water and the given liquid are counted and let these be as $n1$ and $n2$ respectively. Now if $d1$ and $d2$ are densities of water and the given liquid at the room temperature as determined separately by using specific gravity bottle or pyknometer, then the surface-tension $y2$ of the given liquid can be calculated by using the simplified relationship as:

$$\frac{\gamma 1}{\gamma 2} = \frac{n2}{n1} \times \frac{d1}{d2}$$

Description of the apparatus: The stalagmometer consists of a bulbed dropping tube with a capillary. The lower end of capillary is well ground, polished and flattened in order to provide larger dropping surface. There are two marks **A** and **C** above and below the bulb **B**. The upper end of the apparatus is connected with a rubber tube with a screw pinch cock in order to control the rate of flow so that spherical drop may be formed. Hence by simply counting the number of drops for the given liquid and water and knowing their density, we can find the relative surface tension of the liquid. The drop-count method is a very convenient and quick process and can also be employed for determinations at different temperatures by placing the whole apparatus in a thermostat.

Figure 2: Stalagmometer

Procedure:

1. Clean the stalagmometer, a specific gravity bottle or pyknometer thoroughly first with chromic acid solution, then wash with distilled water and finally dry in electric oven.

2. By immersing lower end in a beaker containing distilled water, suck up water until it rises above the mark A and tighten the screw of the screwpinch.

3. Now loosen the screw of the screw-pinch care-fully so that the liquid drops start falling at an interval of about 2-3 seconds in successive drops. Counting of drops is started when the water meniscus just reaches the upper mark A, and stopped when the meniscus just passes the lower mark C. Repeat to get three readings and take the mean value.

4. Clean the stalagmometer and dry it. Fill it with liquid until it rises above the upper mark A and count the number of drops as before.

5. Clean and dry the specific gravity bottle or pyknometer and measure the density of liquid.

Observations:

Room Temp. = ... $^\circ C$.

Density of water at room temp. = $d1$

Weight of empty specific gravity bottle or pyknometer = $w_1 g$

Weight of specific gravity bottle or pyknometer with water = $w_2 g$

Weight of specific gravity bottle or pyknometer with liquid for the same volume as that of water = $w_3 g$

Weight of water = $(w2 - w1) = m_1 g$ (say)

33

Weight of liquid $= (w3 - w1) = m_2 g$

Liquids	No. of drops			Mean value
	(1)	(2)	(3)	
Water				$n1$
Given Liquid				$n2$

Calculations:

Density of the given liquid relative to water at room temperature.

$$\frac{m_2}{m_1} = d_2$$

Also

$$\frac{\gamma_1}{\gamma_2} = \frac{n_2}{n_1} \times \frac{d_1}{d_2}$$

$$\gamma_2 = Y_1 \times \frac{n_1}{n_2} \times \frac{d_2}{d_1}$$

Where γ_1 = surface tension of water at room temp. (say 72 dynes/cm at 25°C)

Substituting the values of γ_1, n_1, n_2, d_1 and d_2, the surface-tension of the given liquid at room temperature thus becomes known

Result: The relative surface tension of liquid with respect to water at room temperature is.........

Precautions:

1. The stalagmometer and specific gravity bottle or pyknometer should be cleaned properly and dried before use.

2. Fit the stalagmometer vertically.

3. The rate of the fall of drops should be adjusted in a way of having interval of at least 2-3 second in successive drops. The number of drops per minute must be in between 15-20.

4. The drops should fall from the tip of the stalagmometer under their own weight rather than pushing them by force.

5. Wash and dry the stalagmometer after use.

Multiple Choice Questions:

1. At the boiling point , what is its surface tension of water?
i) zero   ii) one   iii) three   iv) ten

2. What is the surface of water in contact with glass wall?
i) Concave   ii) Convex   iii) flat

3..What is the surface of mercury in contact with glass wall?
i) Convex   i) Concave   iii) flat

4.. How does soap affect the surface tension of water?

EXPERIMENT NO. 9

**Object**: To determine pH of acidic solution using a pH meter and titration of such a solution pH-metrically.

Materials: pH meter, Glass electrode HCl, 0.05 N NaOH.

Theory: The concept of pH was first introduced by Danish chemist Søren Peder Lauritz Sørensen at the Carlsberg Laboratory in 1909. pH is a measure of the acidity or basicity of an aqueous solution. pH is defined as a negative decimal logarithm of the hydrogen ion activity in a solution.

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

Pure water is said to be neutral, with a pH close to 7.0 at 25 °C. Solutions with a pH less than 7 are said to be acidic and solutions with a pH greater than 7 are basic or alkaline.

In this method, we use combined electrode (a device having two electrodes together). In combined electrode, glass electrode has balloon shaped structure at bottom made up of very thin glass. This thin glass has a property to from a gel layer when it comes in contact of an aq. medium
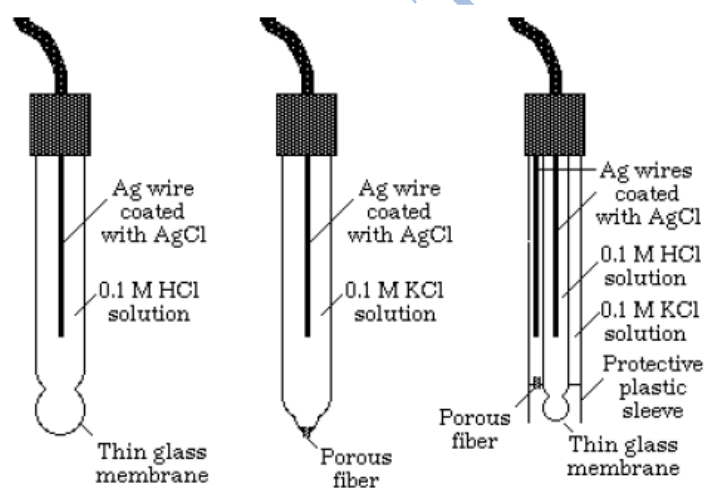

Functioning: When we dip the electrode in unknown solution, thin glass forms the inner gel layer (due to standard HCl solution) and outer gel layer (due to unknown solution). These two gel layers have two different potentials (Inner potential and outer potential). The potential difference indicates the value of pH. On titration, the outer potential changes hence difference between two potentials also gets changed, which gives a new pH value.

In case of strong acid and strong base titration, the equivalence point is at pH equal to 7. From sigmoid curve (Obtained in the case of strong acid – strong base titration) we can calculate the volume of NaOH used to neutralize the unknown HCl.

When an alkali is added to an acid solution the pH of solution increases slowly, but at the vicinity of the equivalence point, the rate of change of pH of the solution is very rapid. From the sharp break in the curve, we can read the equivalence point using sigmoidal curve, through which the strength can be calculated by using normality equation.

Strength of HCl can be determined by titrating it with a standard NaOH solution (Acid-Base titration). This determination can be done by pH-metric titration.

Nature of Graph:

Vol. of NaOH
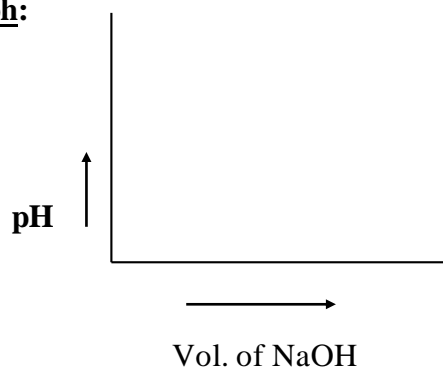
pH- metric titration is different from ordinary acid-base titration as we do not use indicators hence it is based on equivalence point not on end point.

As in earlier stage of titration, strong acid is neutralized by small amount of strong base resulting in a slow change in pH. Then pH changes sharply near the equivalence point (at pH=7) and again there is a slow change in pH value on addition of NaOH as system has been changed into basic medium.

pH-metric titration is more accurate than an ordinary acid-base titration because it is based on equivalence point (the point when N_1V_1 is exact equal to N_2V_2) where as ordinary acid-base titration is based on end point calculation (point when mili equivalent of one compounds is slightly more than other).

Procedure:

Calibration of Electrodes:

The electrode should be calibrated before beginning measurements or when pH readings are suspect. Once the calibration has been carried out, do not change electrodes without further calibration.

Following procedure is adopted.

   a) Dip the combined electrode in a 4 pH buffer solution.
   b) Set the "TEMPERATURE C" control to the buffer solution temperature.
   c) Set the function selector switch to pH position and adjust "CALIBRATE" control until the meter displays the precise pH value of the buffer solution.
   d) Now set the function selector switch to STANDBY.

e) Remove the electrode from the buffer solution: wash with distilled or deionised water.
f) Dip the combined electrode into another buffer solution (says 9.2pH value).
g) Set the "TEMPERATURE C" control to the temperature of the selected buffer solution.
h) Set the function selector switch to pH position. Adjust the "SLOPE" correction control using a screwdriver, until the meter displays the pH value of the selected buffer solution. Check that the correct readings are obtained with both solutions without further adjustment.

pH Measurement:

To measure pH value of the solution, after calibrating the electrode proceed as follows:

a) Remove the electrode from the buffer solution, was with distilled or de-ionised water, and immerse in the solution under test (2).
b) Set the "TEMPERATURE C" control to the temperature of the test solution.
c) Set the function selector switch to the pH position.The meter will display pH value of the test solution.
d) Between measurements leave the electrode immersed in distilled water and function selector switch to "STANDBY" position.

In beaker (1) add sufficient water so that glass electrode as well as the reference electrode are completely dipped. In beaker (2) take 100 ml of HCl solution. Note the pH of pure acid solution. Now add 1ml of 0.05N NaOH from the burette in the beaker. Stir the content well and note the reading. Note the pH of the solution on each addition upto say 35ml of NaOH.

Volume of acid taken= 100ml (say)

Volume of Alkali added(ml)	00, 01, 02, 03, 04, 05, 06, 07, 08, 09, 10, 11, 12, 13, 14, 15, 16, 17, 18……..
pH	

Calculation:

A curve in plotted with pH values as ordinate and the voume of alkali added (ml) as abscicca.

Find out the end point suppose it is equivalent to x ml of NaOH.

From normality equation

$$N_1V_1 \qquad = \qquad N_2V_2$$

(Acid) \qquad\qquad (Alkali)

$$N_1 \ \text{x} \ 100 = \ 0.05 \ \text{x} \ X$$

Strength of HCl solution = $\dfrac{0.05 \text{ x } X \text{ x } 36.5}{100}$

Result: The strength of given acid solution is …………………..g/l.

Precautions:

1. The temperature control knob of the pH meter should be adjusted to the room temperature.
2. After addition of alkali, solution should be properly stirred.
3. The pH should be first standardized by taking the buffer of a known pH.
4. Soak the electrode in water for some hours (preferably over night before use).
5.

Quiz Questions:

1. The Reference electrode used in pH meter is
   i) Glass electrode   ii) Hydrogen electrode
   iii) Quinhydrone electrode   iv) Silver electrode

2. The least count of pH meter is
   i) 0.1   ii) 0.01   iii) 0.001   iv) none of the above

3. Why electrode is dipped in buffer solution before titration in pH metric titration?

4. Give the cell diagram of the electrode used.…………………..............................

EXPERIMENT NO. 10

Object: Preparation of Phenol – formaldehyde resin (Bakelite resin)

Apparatus requirement:
a). Beaker, glass rod, funnel and filter paper
b). Chemical. Phenol, Formaldehyde (40% of solution), conc. HCl and glacial acetic acid and hexa methylene tetramine.

Theory:
Phenol and formaldehyde react to form methylol derivate which act as monomers for subsequent polymerization.

Phenol — Monomethylol phenol — Dimethylol phenol — Trimethylol phenol
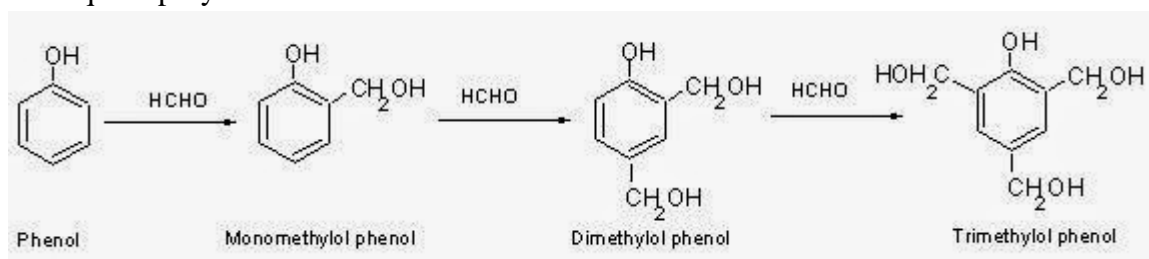
The nature of product depends on the nature of the catalyst (acidic or basic)

1) In presence of acid catalysts, the methylol derivatives condense with phenol to form the dihydroxy diphenyl methane. These on further condensation gives low molecular weight linear polymers which are fusible and soluble and are known as Novalacs.
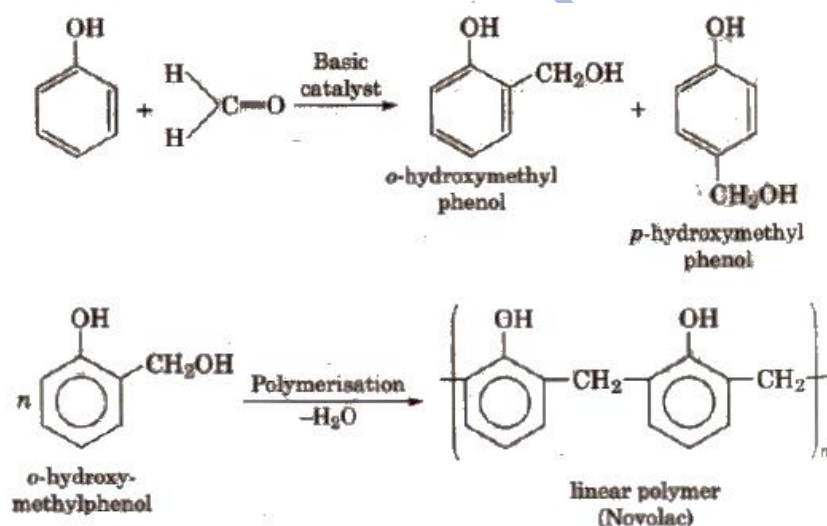
2) In presence of alkaline catalyst, methyl phenol can condense either through methylene linkages or through ether linkages to form Resols.

Further heating of novolac in the presence of a catalyst, Hexamethylene tetramine (it produces HCHO), induces three dimensional, cross – linked networked polymer, Bakelite, which is hard rigid and infusible solid.
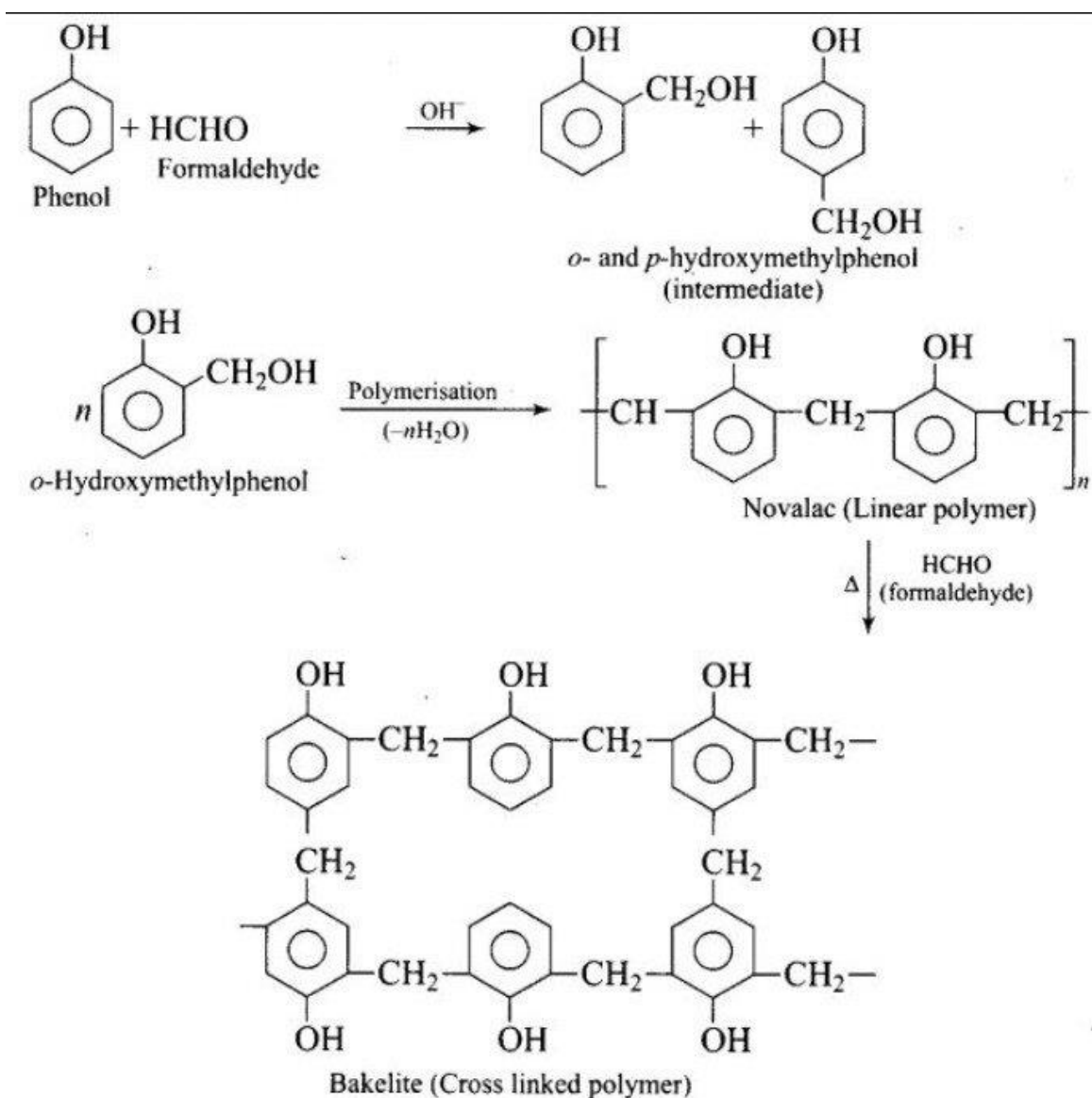
Bakelite is a hard, rigid, scratch resistant, infusible, water resistant solid. They possess excellent electrical insulating character.

Bakelite is used for making electric insulator parts like switches , plugs, heater handles etc. They are used for making moulded articles (like telephone parts etc.), as adhesive and in paints and varnishes.

Procedure:

a). Take 2 grams of phenol and 5 ml of glacial acetic acid in 250 ml beaker.
b). Add 2.5 ml of 40% formaldehyde solution into it.
c). Wrap a cloth loosely round the beaker.
d). Slowly add a few ml of conc. HCl into the mixture carefully and heat it slightly.
e) Formation of Novolac takes place which on further heating in presence of hexamethylene tetramine results in the formation of cross – linked, pink coloured polymer, Bakelite.
f). Wash the product, several times with distilled water.

g). Dry and measure the weight of this pink plastic.

h). Calculate the yield.

Precaution :

Add conc. HCl carefully for the formation of Bakelite as it is a vigorous reaction.

Multiple Choice Questions

1 The Catalyst used for formation of Bakelite is
   i)$(CH_2)_4N_4$ ii)$(CH_2)_6N_4$ iii)$(CH_2)_6N_3$ iv)$(CH_2)_6N_2$

2 Bakelite is a
   i)Phenol-Formaldeyde resin   ii) Cross linked polymer

   ii) Pink colored plastic   iv) All of the above

3 Thermoplastic product formed by the condensation of methylol derivative and phenol in presence of acid catalyst is
   i)Bakelite   ii)Resol   iii) Trimethylol phenol   iv) Novolac

4 Bakelite is said to be a cross linked polymer as
   i)Its combining monomer have one active site

   ii) Its combining monomer have two active site

   iii) Its combining monomer have more than two active site

   iv) Its combining monomer have 3- D structure