B.Sc. CHEMISTRY LAB MANUAL

6th Semester

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Chemistry

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[Choice Based Credit System]

SEMESTER-VI

C13P: Inorganic Chemistry Lab

ANALYSIS always does not mean breaking of substance into its ultimate constituents. Finding out the nature of substance and identity of its constituents is also analysis and is known as qualitative analysis. Qualitative analysis of inorganic salts means the identification of cations and anions present in the salt or a mixture of salts. Inorganic salts may be obtained by complete or partial neutralization of acid with base or vice-versa. In the formation of a salt, the part contributed by the acid is called anion and the part contributed by the base is called cation. For example, in the salts $CuSO_4$ and NaCl, Cu^{2+} and Na^+ ions are cations and SO_4^{2-} and Cl^- ions are anions. Qualitative analysis is carried out on various scales. Amount of substance employed in these is different. In macro analysis, 0.1 to 0.5 g of substance and about 20 mL of solution is used. For semimicro analysis, 0.05 g substance and 1 mL solution is needed while for micro analysis amount required is very small. Qualitative analysis is carried out through the reactions which are easily perceptible to our senses such as sight and smell.

Such reactions involve:

(a) Formation of a precipitate

(b) Change in colour

(c) Evolution of gas etc.

Systematic analysis of an inorganic salt involves the following steps:

(i) Preliminary examination of solid salt and its solution.

(ii) Determination of anions by reactions carried out in solution (wet tests) and confirmatory tests.

(iii) Determination of cations by reactions carried out in solution (wet tests) and confirmatory tests.

Preliminary examination of a salt often furnishes important information, which simplifies further course of analysis. Although these tests are not conclusive but sometimes they give quite important clues for the presence of certain anions or cations. These tests can be performed within 10-15 minutes. These involve noting the general appearance and physical properties, such as colour, smell, solubility etc. of the salt. These are named as dry tests.

Heating of dry salt, blow pipe test, flame tests, borax bead test, sodium carbonate bead test, charcoal cavity test etc. come under dry tests. Some of these tests are given later in this unit. Solubility of a salt in water and the pH of aqueous solutions give important information about the nature of ions present in the salt. If a solution of the salt is acidic or basic in nature, this means that it is being hydrolysed in water. If the solution is basic in nature then salt may be some carbonate or sulphide etc. If the solution shows acidic nature then it may be an acid salt or salt of weak base and strong acid. In this case it is best to neutralise the solution with sodium carbonate before testing it for anions. Gases evolved in the preliminary tests with dil. H_2SO_4/dil. HCl and conc. H_2SO_4 also give good indication about the presence of acid radicals (See Tables 1and 3). Preliminary tests should always be performed before starting the confirmatory tests for the ions.

EXPERIMENT -1:

Aim

To detect one cation and one anion in the given salt from the following ions:

Cations - Pb^{2+}, Cu^{2+}, As^{3+}, Al^{3+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+}, NH_4^+.

Anions – CO_3^{2-}, NO_3^-, SO_4^{-}, NO_2^-, $S_2O_3^{2-}$, S^{2-}, Cl^-, Br^-, I^-, PO_4^{3-}, CH_3COO^-, $C_2O_4^{2-}$

(Insoluble salts to be excluded)

Theory

Two basic principles of great use in the analysis are:

(i) The Solubility product; and

(ii) The Common ion effect.

When ionic product of a salt exceeds its solubility product, precipitation takes place. Ionic product of salt is controlled by making use of common ion effect which you have studied in the textbook of chemistry.

Material Required

- Boiling tube : As per need
- Test tube stand : One
- Test tube holder : One
- Corks : As per need
- Reagents : As per need
- Test tubes : As per requirement
- Measuring cylinder : One
- Delivery tube : One
- Filter paper : As per need

SYSTEMATIC ANALYSIS OF ANIONS

Step - I: Preliminary Test with Dilute Sulphuric Acid

In this test the action of dilute sulphuric acid (procedure is given below) on the salt is noted at room temperature and on warming. Carbonate (CO_3^{2-}), sulphide (S^{2-}), sulphite (SO_3^{2-}), nitrite

(NO_2^-) and acetate (CH_3COO^-) react with dilute sulphuric acid to evolve different gases. Study of the characteristics of the gases evolved gives information about the anions. Summary of characteristic properties of gases is given in Table 1 below.

Procedure

(a) Take 0.1 g of the salt in a test tube and add 1–2 mL of dilute sulphuric acid. Observe the change, if any, at room temperature. If no gas is evolved, warm the content of the test tube. If gas is evolved test it by using the apparatus shown in Fig.7.1 and identify the gas evolved (See Table 1).

Table 1: Preliminary test with dilute sulphuric acid

Observations	Inference	
	Gas Evolved Possible Anion	Gas Evolved Possible Anion
A colourless, odourless gas is evolved with brisk effervescence, which turns lime water milky.	CO_2	Carbonate (CO_3^{2-})
Colourless gas with the smell of rotten eggs is evolved which turns lead acetate paper black.	H_2S	Sulphide (S^{2-})
Colourless gas with a pungent smell, like burning sulphur which turns acidified potassium dichromate solution green.	SO_2	Sulphite (SO_3^{2-})
Brown fumes which turn acidified potassium iodide solution containing starch solution blue.	NO_2	Nitrite (NO_2^-)
Colourless vapours with smell of vinegar. Vapours turn blue litmus red.	CH_3COOH vapours	Acetate, (CH_3COO^-)

Confirmatory tests for CO_3^{2-} S^{2-}, SO_3^{2-}, NO_2^- and CH_3COO^-

Confirmatory (wet) tests for anions are performed by using **water extract** when salt is soluble in water and by using sodium carbonate extract when salt is insoluble in water. Confirmation of CO_3^{2-} is done by using aqueous solution of the salt or by using solid salt as such because sodium carbonate extract contains carbonate ions. Water extract is made by dissolving salt in water. Preparation of sodium carbonate extract is given below.

Preparation of sodium carbonate extract

Take 1 g of salt in a porcelain dish or boiling tube. Mix about 3 g of solid sodium carbonate and add 15 mL of distilled water to it. Stir and boil the content for about 10 minutes. Cool, filter and collect the filtrate in a test tube and label it as sodium carbonate extract. Confirmatory tests for acid radicals, which react with dilute sulphuric acid are given below in Table 2.

Table 2: Confirmatory tests for CO_3^{2-} S^{2-}, SO_3^{2-}, NO_2^- and CH_3COO^-

Anion	Confirmatory Test
Carbonate (CO_3^{2-})	Take 0.1 g of salt in a test tube, add dilute sulphuric acid. CO_2 gas is evolved with brisk effervescence which turns lime water milky. On passing the gas for some more time, milkiness disappears.
Sulphide (S^{2-})	Take 1 mL of water extract and make it alkaline by addingammonium hydroxide or sodium carbonate extract. Add a drop of sodium nitroprusside solution. Purple or violet colouration appears.
*Sulphite (SO_3^{2-})	(a) Take 1 mL of water extract or sodium carbonate extract in a test tube and add barium chloride solution. A white precipitate is formed which dissolves in dilute hydrochloric acid and sulphur dioxide gas is also evolved. (b) Take the precipitate of step (a) in a test tube and add a few drops of potassium permanganate solution acidified with dil. H_2SO_4. Colour of potassium permanganate solution gets discharged.
Nitrite (NO_2^-)	(a) Take 1 mL of water extract in a test tube. Add a few drops of potassium iodide solution and a few drops of starch solution, acidify with acetic acid. Blue colour appears. (b) Acidify 1 mL of water extract with acetic acid. Add 2-3 drops of sulphanilic acid solution followed by 2-3 drops of 1-naphthylamine reagent. Appearance of red colour indicates the presence of nitrite ion.
Acetate (CH_3COO^-)	(a) Take 0.1 g of salt in a china dish. Add 1 mL of ethanol and 0.2 mL conc. H_2SO_4 and heat. Fruity odour confirms the presence of acetate ion. (b) Take 0.1 g of salt in a test tube, add 1-2 mL distilled water, shake well filter if necessary. Add 1 to 2 mL neutral** ferric chloride solution to the filtrate. Deep red colour appears which disappears on boiling and a brown-red precipitate is formed.

* Like CO_2 sulphur dioxide also turns lime water milky. But CO_2 is odourless gas and SO_2 has a characteristic smell.
** Prepareation of neutral Ferric Chloride: Add dilute NaOH solution to ferric chloride solution drop by drop with shaking until a small but permanent precipitate of ferric hydroxide is obtained. Filter the precipitate and use the filtrate for analysis.

Step-II: Preliminary Test with Concentrated Sulphuric Acid

If no positive result is obtained from dil. H_2SO_4 test, take 0.1 g of salt in a test tube and 3-4 drops of conc. H_2SO_4. Observe the change in the reaction mixture in cold and then warm it. Identify the gas evolved on heating (see Table 3).

Table 3: Preliminary examination with concentrated sulphuric acid

Observations	Inference	
	Gas/Vapours Evolved	**Possible Anions**
A colourless gas with pungent smell, which gives dense white fumes when a rod dipped in ammonium hydroxide is brought near the mouth of the test tube.	**HCl**	Chloride, (**Cl^-**)
Reddish brown gas with a pungent odour is evolved. Intensity of reddish gas increases on heating the reaction mixture after addition of solid MnO_2 to the reaction mixture. Solution also acquires red colour.	**Br_2** vapours	Bromide, (**Br^-**)
Violet vapours, which turn starch paper blue and a layer of violet sublimate is formed on the sides of the tube. Fumes become dense on adding MnO_2 to the reaction mixture.	**I_2** vapours	Iodide, (**I^-**)
Brown fumes evolve which become dense upon heating the reaction mixture after addition of copper turnings and the solution acquires blue colour.	**NO_2**	Nitrate, (**NO_3^-**)
Colourless, odourless gas is evolved which turns lime water milky and the	**CO** and **CO_2**	Oxalate, (**$C_2O_4^{2-}$**)

gas coming out of lime water burns with a blue flame, if ignited.		

Confirmatory tests for the anions which react with concentrated sulphuric acid are given in Table 4.

Table 4: Confirmatory tests for Cl^-, Br^-, I^-, NO_3^- and $C_2O_4^{2-}$

Anion	Confirmatory Test
Chloride (Cl^-)	(a) Take 0.1 g of salt in a test tube, add a pinch of manganese dioxide and 3-4 drops of conc. Sulphuric acid. Heat the reaction mixture. Greenish yellow chlorine gas is evolved which is detected by its pungent odour and bleaching action. (b) Take 1 mL of sodium carbonate extract in a test tube, acidfy it with dil. HNO_3 or take water extract and add silver nitrate solution. A curdy white precipitate is obtained which is soluble in ammonium hydroxide solution. (c) Take 0.1 g salt and a pinch of solid potassium dichromate in a test tube, add conc. H_2SO_4, heat and pass the gas evolved through sodium hydroxide solution. It becomes yellow. Divide the solution into two parts. Acidify one part with acetic acid and add lead acetate solution. A yellow precipitate is formed. Acidify the second part with dilute sulphuric acid and add 1 mL of amyl alcohol followed by 1 mL of 10% hydrogen peroxide. After gentle shaking the organic layer turns blue.
Bromide (Br^-)	(a) Take 0.1 g of salt and a pinch of MnO2 in a test tube. Add 3-4 drops conc.sulphuric acid and heat. Intense brown fumes are evolved. (b) Neutralise 1 mL of sodium carbonate extract with hydrochloric acid (or take the water extract). Add 1 mL carbon tetrachloride (CCl_4)/chloroform ($CHCl_3$)/ carbon disulphide. Now add an excess of chlorine water dropwise and shake the test tube. A brown colouration in the organic layer confirms the presence of bromide ion. (c) Acidify 1 mL of sodium carbonate extract with dil. HNO3 (or take 1 mL water extract) and add silver nitrate solution. A pale yellow

	precipitate soluble with difficulty in ammonium hydroxide solution is obtained.
Iodide (I^-)	(a) Take 1 mL of salt solution neutralised with HCl and add 1 mL chloroform/carbon tetrachloride/carbon disulphide. Now add an excess of chlorine water drop wise and shake the test tube. A violet colour appears in the organic layer. (b) Take 1 mL of sodium carbonate extract acidify it with dil. HNO3 (or take water extract). Add, silver nitrate solution. A yellow precipitate insoluble in NH4OH solution is obtained.
*Nitrate (NO_3^-)	Take 1 mL of salt solution in water in a test tube. Add 2 mL conc. of H2SO4 and mix thoroughly. Cool the mixture under the tap. Add freshly prepared ferrous sulphate along the sides of the test tube without shaking. A dark brown ring is formed at the junction of the two solutions.
Oxalate ($C_2O_4^{2-}$)	(a) Take 1 mL of water extract or sodium carbonate extract acidified with acetic acid and add calcium chloride solution. A white precipitate insoluble in ammonium oxalate and oxalic acid solution but soluble in dilute hydrochloric acid and dilute nitric acid is formed. (b) Take the precipitate from test (a) and dissolve it in dilute H2SO4. Add very dilute solution of KMnO4 and warm. Colour of KMnO4 solution is discharged. Pass the gas coming out through lime water. The lime water turns milky.

Chemistry of Confirmatory Tests

1. Test for Chloride ion [Cl^-]

(a) If on treatment with warm conc. H_2SO_4 the salt gives a colourless gas with pungent smell or and if the gas which gives dense white fumes with ammonia solution, then the salt may contain Cl^- ions and the following reaction occurs.

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$

$$HCl + NH_3 \rightarrow NH_4Cl \quad \text{(Ammonium chloride white fumes)}$$

Step-III : Test for Sulphate and Phosphate

If no positive test is obtained in Steps-I and II, then tests for the presence of sulphate and phosphate ions are performed. These tests are summarised in Table 5.

Table 5: Confirmatory tests for Sulphate and Phosphate

Ion	Confirmatory Test

Sulphate (SO_4^{2-})	(a) Take 1 mL water extract of the salt in water or sodium carbonate and after acidifying with dilute hydrochloric acid add $BaCl_2$ solution. White precipitate insoluble in conc. HCl or conc. HNO_3 is obtained. (b) Acidify the aqueous solution or sodium carbonate extract with acetic acid and add lead acetate solution. Appearance of white precipitate confirms the presence of SO_4^{2-} ion.
Phosphate (PO_4^{3-})	(a) Acidify sodium carbonate extract or the solution of the salt in water with conc. HNO_3 and add ammonium molybdate solution and heat to boiling. A canary yellow precipitate is formed.

The tests for cations may be carried out according to the following scheme.

Step - I: Preliminary Examination of the Salt for Identification of Cation

1. Colour Test

Observe the colour of the salt carefully, which may provide useful information about the cations. Table 7.6 gives the characteristic colours of the salts of some cations.

Table 6: Characteristic colours of some metal ions

Colour	Cations Indicated
Light green, Yellow, Brown	Fe^{2+}, Fe^{3+}
Blue	Cu^{2+}
Bright green	Ni^{2+}
Blue, Red, Violet, Pink	Co^{2+}
Light pink	Mn^{2+}

2. Dry Heating Test

(i) Take about 0.1 g of the dry salt in a clean and dry test tube.

(ii) Heat the above test tube for about one minute and observe the colour of the residue when it is hot and also when it becomes cold. Observation of changes gives indications about the presence of cations, which may not be taken as conclusive evidence (see Table 7).

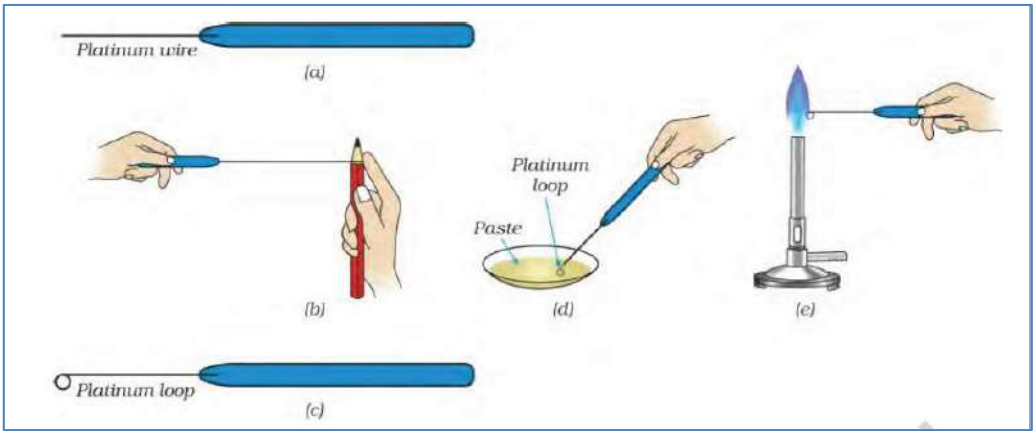
Table 7: Inferences from the colour of the salt in cold and on heating

Colour when cold	Colour when hot	Inference
Blue	White	Cu^{2+}
Green	Dirty white or yellow	Fe^{2+}
White	Yellow	Zn^{2+}
Pink	Blue	Co^{2+}

3. Flame Test

The chlorides of several metals impart characteristic colour to the flame because they are volatile in non-luminous flame. This test is performed with the help of a platinum wire as follows:

(i) Make a tiny loop at one end of a platinum wire.
(ii) To clean the loop dip it into concentrated hydrochloric acid and hold it in a non-luminous flame.
(iii) Repeat step (ii) until the wire imparts no colour to the flame.
(iv) Put 2-3 drops of concentrated hydrochloric acid on a clean watch glass and make a paste of a small quantity of the salt in it.
(v) Dip the clean loop of the platinum wire in this paste and introduce the loop in the non-luminous (oxidising) flame (Fig. 7.3).
(vi) Observe the colour of the flame first with the naked eye and then through a blue glass and identify the metal ion with the help of Table 8.



Performing flame test

Table 8: Inference from the flame test

Colour of the flame observed by naked eye	Colour of the flame observed through blue glass	Inference
Green flame with blue centre	Same colour as observed without glass	Cu^{2+}
Crimson red	Purple	Sr^{2+}
Apple green	Bluish green	Ba^{2+}
Brick red	Green	Ca^{2+}

4. Borax Bead Test

This test is employed only for coloured salts because borax reacts with metal salts to form metal borates or metals, which have characteristic colours.
(i) To perform this test make a loop at the end of the platinum wire and heat it in a flame till it is red hot.
(ii) Dip the hot loop into borax powder and heat it again until borax forms a colourless transparent bead on the loop. Before dipping the borax bead in the test salt or mixture, confirm that the bead is transparent and colourless. If it is coloured this means that, the platinum wire is not clean. Then make a fresh bead after cleaning the wire.
(iii) Dip the bead in a small quantity of the dry salt and again hold it in the flame.
(iv) Observe the colour imparted to the bead in the non - luminous flame as well as in the luminous flame while it is hot and when it is cold.
(v) To remove the bead from the platinum wire, heat it to redness and tap the platinum wire with your finger.

On heating, borax loses its water of crystallisation and decomposes to give sodium metaborate and boric anhydride.

$$Na_2B_4O_7 .10H_2O \longrightarrow Na_2B_4O_7 + 10H_2O$$

Borax

$$Na_2B_4O_7 \longrightarrow \underset{\text{Sodium metaborate}}{2NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}$$

On treatment with metal salt, boric anhydride forms metaborate of the metal which gives different colours in oxidising and reducing flame. For example, in the case of copper sulphate, following reactions occur.

$$CuSO_4 + B_2O_3 \xrightarrow{\text{Non-luminous flame}} \underset{\substack{\text{Cupric metaborate}\\ \text{Blue-green}}}{Cu(BO_2)_2} + SO_3$$

Two reactions may take place in the reducing flame:

(i) The blue $Cu(BO_2)_2$ is reduced to colourless cuprous metaborate as follows:

$$2Cu(BO_2)_2 + 2NaBO_2 + C \xrightarrow{\text{Luminous flame}} 2CuBO_2 + Na_2B_4O_7 + CO$$

or (ii) Cupric metaborate may be reduced to metallic copper and the bead appears red and opaque.

$$2Cu(BO_2)_2 + 4NaBO_2 + 2C \xrightarrow{\text{Luminous flame}} 2Cu + 2Na_2B_4O_7 + 2CO$$

Table 9: Inference from the borax bead test

Heating in oxidising (non-luminous) flame		Heating in reducing (luminous) flame		Inference
Colour of the salt bead		Colour of the salt bead		
In cold	In hot	In cold	In hot	
Blue	Green	Red opaque	Colourless	Cu^{2+}
Reddish brown	Violet	Grey	Grey	Ni^{2+}
Light violet	Light violet	Colourless	Colourless	Mn^{2+}
Yellow	Yellowish brown	Green	Green	Fe^{3+}

5. Charcoal Cavity Test

Metallic carbonate when heated in a charcoal cavity decomposes to give corresponding oxide. The oxide appears as a coloured residue in the cavity. Sometimes oxide may be reduced to metal by the carbon of the charcoal cavity. The test may be performed as follows:

(i) Make a small cavity in a charcoal block with the help of a charcoal borer. Do not apply pressure otherwise it will crack [Fig.7.6 (a)].

(ii) Fill the cavity with about 0.2 g of the salt and about 0.5 g of anhydrous sodium carbonate.

(iii) Moisten the salt in the cavity with one or two drops of water, otherwise salt/mixture will blow away.

(iv) Use a blowpipe to heat the salt in a luminous (reducing) flame and observe the colour of oxide/ metallic bead formed in the cavity both when hot and cold [Fig. (7.6 b)]. Obtain oxidising and reducing flame as shown in Fig. 7.7 a and b.

(v) Always bore a fresh cavity for testing the new salt.

When test is performed with $CuSO_4$, the following change occurs.

$$CuSO_4 + Na_2CO_3 \xrightarrow{Heat} CuCO_3 + Na_2SO_4$$

$$CuCO_3 \xrightarrow{Heat} CuO + CO_2$$

$$CuO + C \xrightarrow{Heat} \underset{\text{Red colour}}{Cu} + CO$$

In case of $ZnSO_4$:

$$ZnSO_4 + Na_2CO_3 \xrightarrow{Heat} ZnCO_3 + Na_2SO_4$$

$$ZnCO_3 \xrightarrow{Heat} ZnO + CO_2$$

Yellow when hot,
White when cold

The metal ion can be inferred from Table 10.

Observations	Inference
Yellow residue when hot and grey metal when cold	Pb^{2+}
White residue with the odour of garlic	As^{3+}
Brown residue	Cd^{2+}
Yellow residue when hot and white when cold	Zn^{2+}

6. Cobalt Nitrate Test

If the residue in the charcoal cavity is white, cobalt nitrate test is performed.

(i) Treat the residue with two or three drops of cobalt nitrate solution.

(ii) Heat it strongly in non-luminous flame with the help of a blow pipe and observe the colour of the residue. On heating, cobalt nitrate decomposes into cobalt (II) oxide, which gives a characteristic colour with metal oxide present in the cavity. Thus, with ZnO, Al_2O_3 and MgO, the following reactions occur.

Step-II : Wet Tests for Identification of Cations

The cations indicated by the preliminary tests given above are confirmed by systematic analysis given below. The first essential step is to prepare a clear and transparent solution of the salt. This is called original solution. It is prepared as follows:

Preparation of Original Solution (O.S.)

To prepare the original solution, following steps are followed one after the other in a systematic order. In case the salt does not dissolve in a particular solvent even on heating, try the next solvent.

The following solvents are tried:

1. Take a little amount of the salt in a clean boiling tube and add a few mL of distilled water and shake it. If the salt does not dissolved, heat the content of the boiling tube till the salt completely dissolves.
2. If the salt is insoluble in water as detailed above, take fresh salt in a clean boiling tube and add a few mL of dil.HCl to it. If the salt is insoluble in cold, heat the boiling tube till the salt is completely dissolved.
3. If the salt does not dissolve either in water or in dilute HCl even on heating, try to dissolve it in a few mL of conc. HCl by heating.
4. If salt does not dissolve in conc. HCl, then dissolve it in dilute nitric acid.

5. If salt does not dissolve even in nitric acid then a mixture of conc. HCl and conc. HNO3 in the ratio 3:1 is tried. This mixture is called aquaregia. A salt not soluble in aqua regia is considered to be an insoluble salt.

Group Analysis

(I) Analysis of Zero group cation (NH_4^+ ion)

(a) Take 0.1 g of salt in a test tube and add 1-2 mL of NaOH solution to it and heat. If there is a smell of ammonia, this indicates the presence of ammonium ions. Bring a glass rod dipped in hydrochloric acid near the mouth of the test tube. White fumes are observed.

(b) Pass the gas through Nessler's reagent. Brown precipitate is obtained. Chemistry of Confirmatory Tests for NH_4^+ ion

(a) Ammonia gas evolved by the action of sodium hydroxide on ammonium salts reacts with hydrochloric acid to give ammonium chloride, which is visible as dense white fume.

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2H_2O$$

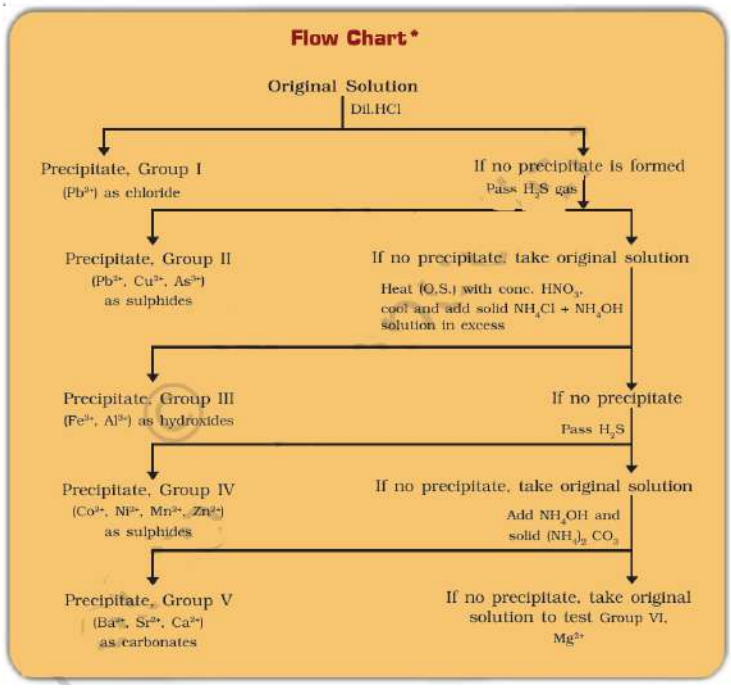
$$NH_3 + HCl \rightarrow NH_4Cl$$

On passing the gas through Nessler's reagent, a brown colouration or a precipitate of basic mercury(II) amido-iodine is formed.

$$2K_2HgI_4 + NH_3 + 3KOH \longrightarrow \underset{\substack{\text{Basic mercury (II)}\\ \text{amido-iodine}\\ \text{(Brown precipitate)}}}{HgO.Hg(NH_2)I} + 7KI + 2H_2O$$

For the analysis of cations belonging to group's I-VI, the cations are precipitated from the original solution by using the group reagents (see Table 7.11) according to the scheme shown in the flow chart given below:

The separation of all the six groups is represented as below:



This flow chart is for the detection of one cation only. For detection of more than one cation modification will be required.

Table 11: Group reagents for precipitating ions

Group	Cations*	Group Reagent
Group zero	NH_4^+	None
Group-I	Pb^{2+}	Dilute HCl
Group-II	Pb^{2+}, Cu^{2+}, As^{3+}	H_2S gas in presence of dil. HCl
Group-III	Al^{3+}, Fe^{3+}	NH_4OH in presence of NH_4Cl
Group-IV	Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}	H_2S in presence of NH_4OH
Group-V	Ba^{2+}, Sr^{2+}, Ca^{2+}	$(NH_4)_2CO_3$ in presence of NH_4OH
Group-VI	Mg^{2+}	None

(II) Analysis of Group-I cations

Take a small amount of original solution (if prepared in hot conc. HCl) in a test tube and add cold water to it and cool the test tube under tap water. If a white precipitate appears, this indicates the presence of Pb^{2+} ions in group –I. On the other hand, if the original solution is prepared in water and on addition of dil. HCl, a white precipitate appears, this may also be Pb^{2+}. Confirmatory tests are described below in Table 12.

Table 12: Confirmatory tests for Group-I cation (Pb^{2+})

Experiment	Observation
Dissolve the precipitate in hot water and divide the hot solution into three parts.	
1. Add potassium iodide solution to the first part.	A yellow precipitate is obtained.
2. To the second part add potassium chromate solution.	A yellow precipitate is obtained which is soluble in NaOH and insoluble in ammonium acetate solution.
3. To the third part of the hot solution add few drops of alcohol and dilute sulphuric acid.	A white precipitate is obtained which is soluble in ammonium acetate solution.

Chemistry of the Confirmatory Tests of Pb^{2+} ions

Lead is precipitated as lead chloride in the first group. The precipitate is soluble in hot water.
1. On adding potassium iodide (KI) solution, a yellow precipitate of lead iodide is obtained which confirms the presence of ions.

This yellow precipitate (PbI_2) is soluble in boiling water and reappears on cooling as shining crystals.

$$\underset{\text{(Hot solution)}}{PbCl_2} + 2KI \longrightarrow \underset{\text{Yellow precipitate}}{PbI_2} + 2KCl$$

3. A white precipitate of lead sulphate (PbSO4) is formed on addition of alcohol followed by dil. H_2SO_4.

$$PbCl_2 + H_2SO_4 \longrightarrow \underset{\text{(White precipitate)}}{\underset{\text{Lead sulphate}}{PbSO4}} + 2\,HCl$$

Lead sulphate is soluble in ammonium acetate solution due to the formation of tetraacetoplumbate(II) ions. This reaction may be promoted by addition of few drops of acetic acid.

$$PbSO_4 + 4\ CH_3COONH_4 \longrightarrow (NH_4)_2\ [Pb(CH_3COO)_4] + (NH_4)_2SO_4$$

Ammonium tetraacetoplumbate(II)

(III) Analysis of Group–II cations

If group-I is absent, add excess of water to the same test tube. Warm the solution and pass H_2S gas for 1-2 minutes. Shake the test tube. If a precipitate appears, this indicates the presence of group-II cations. Pass more H2S gas through the solution to ensure complete precipitation and separate the precipitate. If the colour of the precipitate is black, it indicates the presence of Cu^{2+} or Pb^{2+} ions. If it is yellow in colour, then presence of As^{3+} ions is indicated. Take the precipitate of group-II in a test tube and add excess of yellow ammonium sulphide solution to it. Shake the test tube. If the precipitate is insoluble, group II-A (copper group) is present. If the precipitate is soluble, this indicates the presence of group-II B (arsenic group). Confirmatory tests for the groups II A and II B are given in Table 13.

Table 13: Confirmatory tests for Group-II A and II B cations

<table>
<tr><td colspan="2">Black precipitate of Group II A ions (Pb^{2+}, Cu^{2+}) insoluble in yellow ammonium sulphide is formed.</td><td>If a yellow precipitate soluble in yellow ammonium sulphide is formed then As^{3+} ion is present.</td></tr>
<tr><td colspan="2">Boil the precipitate of Group II A with dilute nitric acid and add a few drops of alcohol and dil. H_2SO_4.</td><td rowspan="2">Acidify this solution with dilute HCl. A yellow precipitate is formed. Heat the precipitate with concentrated nitric acid and add ammonium molybdate solution. A canary yellow precipitate is formed.</td></tr>
<tr><td>White precipitate confirms the presence of Pb^{2+} ions. Dissolve the precipitate in ammonium acetate solution. Acidify with acetic acid and divide the solution into two parts.
(i) To the first part add potassium chromate solution, a yellow precipitate is formed.
(ii) To the second part, add potassium iodide solution, a yellow precipitate is formed.</td><td>If no precipitate is formed, add excess of ammonium hydroxide solution. A blue solution is obtained, acidify it with acetic acid and add potassium ferrocyanide solution. A chocolate brown precipitate is formed.</td></tr>
</table>

(IV) Analysis of Group–III cations

If group-II is absent, take original solution and add 2-3 drops of conc. HNO_3 to oxidise Fe^{2+} ions to Fe^{3+} ions. Heat the solution for a few minutes. After cooling add a small amount of solid ammonium chloride (NH_4Cl) and an excess of ammonium hydroxide (NH_4OH) solution till it smells of ammonia. Shake the test tube. If a brown or white precipitate is formed, this indicates the presence of group-III cations. Confirmatory tests of group-III cations are summarised in Table 14. Observe the colour and the nature of the precipitate. A gelatinous

white precipitate indicates the presence of aluminium ion ($A1^{3+}$). If the precipitate is brown in colour, this indicates the presence of ferric ions (Fe^{3+}).

Table 14 : Confirmatory test for Group-III cations

Brown precipitate Fe^{3+}	White precipitate Al^{3+}
Dissolve the precipitate in dilute HCl and divide the solution into two parts. (a) To the first part add potassium ferrocyanide solution [Potasium hexacyanoferrate (II)]. A blue precipitate/colouration appears. (b) To the second part add potassium thiocyanate solution. A blood red colouration appears.	Dissolve the white precipitate in dilute HCl and divide into two parts. (a) To the first part add sodium hydroxide solution and warm. A white gelatinous precipitate soluble in excess of sodium hydroxide solution. (b) To the second part first add blue litmus solution and then ammonium hydroxide solution drop by drop along the sides of the test tube. A blue floating mass in the colourless solution is obtained.

Group IIIA:-Cations:- Fe^{3+},Al^{3+} Cr^{3+}.
Group reagents:- NH_4Cl & NH_4OH
Precipitation reactions:-

$$1)\ Fe^{3+} + 3NH_4OH \xrightarrow{NH_4Cl} Fe(OH)_3 + 3NH_4^+$$

$$2)\ Al^{3+} + 3NH_4OH \xrightarrow{NH4Cl} Al(OH)_3 + 3NH_4^+$$

The hydroxide precipitates of IIIrd A group cations are having lower Solubility product (KSP) value while further group cation hydroxides are having higher KSP values hence hydroxides of IIIrd group get precipitated while hydroxides of further group cations remains in solution.
As hydroxide precipitate of IIIrd A group cation are having low Solubility product (KSP) Values, amount of hydroxide ions required for the precipitation of these cations are very less. Hence ionization of NH4OH is carried out in presence of NH_4Cl which gives NH_4^+ common ion in solution. Due to common ion effect of NH_4^+ ion from NH_4Cl the ionization of NH4OH get suppressed by which limited OH^- ions will be produced which will be enough for complete precipitation of IIIrd Agroup cations.

NH_4^+(common ion fromNH_4Cl suppresses ionization of (NH_4OH)

NH_4OH=========$NH_4^+ + OH^-$

Group IIIB:- Cations :- Co^{2+},Ni^{2+}, Mn^{2+}, Zn^{2+}.
Group reagents:- $NH_4Cl + NH_4OH$ & H_2S gas
Precipitation reactions

$$1)\ Zn^{2+} + H_2S \xrightarrow{NH_4Cl+NH_4OH} ZnS + 2H^+$$

The cations of IIIrd B get precipitated as sulphide in alkaline medium. The Ksp values of sulphides of IIIrdB group cations being relatively high hence amount of sulphide ions required for precipitation of cations are very high. If the precipitation of IIIrdB group is carried out with H2S in presence of NH4Cl and NH4OH the OH- ion from NH4OH combines with H^+ ion from H2S and gives undissociated water molecule as

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$, $H_2S \rightleftharpoons 2H^+ + S^{--}$,

$H^+ + OH^- \rightarrow HOH$ (unionized)

As H^+ ions are removed from H_2S, free ionization of H_2S takes place by which excess H^+ ions produces in solution which are enough for complete precipitation of IIIrdB group cations In above solution NH4Cl added suppresses ionization of NH4OH by common ion effect due to which excess OH- ions may not produces by which hydroxide precipitation of further group cations may be avoided

Group IV: - Cations:- Ca^{2+}, Ba^{2+}, Sr^{2+}.

Group reagents:-NH_4OH+NH_4Cl and $(NH_4)_2CO_3$

Precipitation reactions :-

$$1)\ Ca^{2+} + (NH_4)_2CO_3 \xrightarrow{NH_4Cl+NH_4OH} CaCO_3 + 2NH_4^+$$

$$2)\ Ba^{2+} + (NH_4)_2CO_3 \xrightarrow{NH_4Cl+NH_4OH} BaCO3 + 2NH_4^+$$

The K_{SP} values of carbonate precipitate of IVth group cations are low. Hence for the precipitation of of IVth group cation limited CO_3^{2-} ions are required. If the precipitation of IVth group cations is carried out in presence of NH_4OHandNH_4Cl , NH_4^+ common ions of NH_4OH suppresses ionization of $(NH_4)_2CO_3$ by which limited CO_3^{2-} ions produces which are inough for precipitation of IVth group cations. The NH_4Cl added suppresses ionization of NH_4OH by common ion effect unless hydroxide precipitation of Vthgroup cation(Mg^{++})takes place along with IVth group carbonate precipitate.

Group V:- Cation :-Mg^{2+}

Group reagents :-NH_4Cl + NH_4OH and Na_2HPO_4

Precipitation reaction :-

$$Mg^{2+} + Na_2HPO_4 \xrightarrow{NH_4Cl + NH_4OH} MgHPO_4 + 2Na^+$$

Mg^{2+}gives white precipitate of $MgHPO_4$ with Na_2HPO_4 in presence of NH4Cl and NH_4OH . Here use of NH_4Cl prevent hydroxide precipitation of Mg2+ While the buffer (NH_4Cl + NH_4OH) provides optimum pH (pH=10)for effective precipitation of Mg^{2+} as $MgHPO_4$

Group VI:- Cations :-Na^+,NH_4^+,K^+

Group Reagents:-There is no specific reagent for this group. These cations gives their water soluble salts with the reagents Cations of this group are detected and confirmed by their individual characteristic tests.

Complex formation:-

The addition product or a complex compound in which number of ligands (equal to coordination number of central metal ion) binds with central metal ion by strong coordinate bonding and produces a compound called as addition product or a complex compound. If it bears any charge then it is known as complex ion. It plays an important role in detection separation and confirmation of most of acidic and basic radicals in Inorganic semi-micro qualitative analysis. The formation of complex ion in solution experiences sudden change in colour, sudden change in solubility and dramatic change in chemical properties.

Applications of complex formation:-There are several applications of complex formation in qualitative analysis some of them are

1) Separation of IInd group in to IIA and IIB

2)Separation of Cu^{2+} from Cd^{2+}as a cyano complex

3) Separation of $Co^{2+}$from Ni^{2+}

4) Separation of Cl- from Br^- and I^-

5)Detection of NO^{2-} and NO^{3-} (Brown ring test)

1)Separation of IInd group in to IIA and IIB:-

The IIA group or Copper group cations are Cu^{++}, Cd^{++}, Hg^{++}, Pb^{++}, Bi^{+3}. While the IIB Group or Tin group cations are Sn^{+2}, Sn^{+4}, Sb^{+3} Sb^{+5}, As^{+3}, As^{+5}.The mixture containing IIA and IIB group cations dissolved in suitable mineral acid solution or in distilled water and its solution can be prepared Aqueous solution of IIA and IIB group cations treated with dilute HCl and excess of H_2S gas. A sulphide precipitate of IIA and IIB group cations produces.

$$Cu^{2+} + H_2S \xrightarrow{HCl} CuS\downarrow + 2H^+, \qquad Sn^{2+} + H_2S \xrightarrow{HCl} SnS\downarrow + 2H^+$$

The sulphide precipitate of IIA and IIB group cations treated with yellow ammonium sulphide ($(NH_4)_2S_x$) after gentle worming IIB group precipitate dissolves in($(NH_4)_2S_x$) while IIA group precipitate remains as it is hence both can be separated from each other by filtration. The precipitate of IIB group cations dissolves in ($(NH_4)_2S_x$) and gives clear solution of cations by following reactions

1) $Sb_2S_3+3(NH_4)_2S \rightarrow 2(NH_4)_3[SbS_3]$ (Ammonium thio antimonite)

2) $As_2S_3+3(NH_4)_2S \rightarrow 2(NH_4)_3[AsS_3]$ (Ammonium thio arsinite)

3) $Sb_2S_5+3(NH_4)_2S \rightarrow 2(NH_4)_3[SbS_4]$ (Ammonium thio antimonate)

4) $As_2S_5+3(NH_4)_2S \rightarrow 2(NH_4)_3[AsS_4]$ (Ammonium thio arsinate)

5) $SnS+(NH_4)_2S_2 \rightarrow (NH_4)_2[SnS_3]$ (Ammonium thio stannate)

6) $SnS_2+(NH_4)_2S \rightarrow (NH_4)_2[SnS_3]$

All these thioantimonite ,thioarsinite, thioantimonate, thioarsenate and thiostannate salts are water soluble salts which gives clear solution of respective cations used for their confirmatory tests.

2) Separation of Cu^{2+} from Cd^{2+}:-

Both the cations are IIA group or copper group cations Aqueous solution containing $Cu^{2+}$and Cd^{2+} cations treated with dilute HCl and excess of H_2S gas. A sulphide precipitate CuS and CdS produces as

$$Cu^{2+} + H_2S \xrightarrow{HCl} CuS + 2H^+, \qquad Cd^{2+} + H_2S \xrightarrow{HCl} CdS + 2H^+$$

The sulphide precipitate of $Cu^{2+}$and Cd^{2+}digested with concentrated Nitric acid (HNO_3) and a clear solution of Cu $(NO_3)_2$ and $Cd(NO_3)_2$ produces by following reactions

$CuS + 2HNO_3 \rightarrow Cu(NO_3)_2 + H_2S$, $CdS + 2HNO_3 \rightarrow Cd(NO_3)_2 + H_2S$

When aqueous solution of Cu $(NO_3)_2$ and $Cd(NO_3)_2$ treated with excess potassium cyanide (KCN) solution Cd^{2+} ion gives precipitate of cyanide first while Cu^{2+}ion remains in solution because the $Cu(NO_3)_2$ react with KCN and gives unstable $Cu(CN)_2$as

$$Cu(NO_3)_2 + 2KCN \rightarrow Cu(CN)_2 + 2KNO_3$$

$$2Cu(CN)_2 \rightarrow Cu_2(CN)_2 + (CN)_2\uparrow \text{ (cynogen gas)}$$

$$Cu_2(CN)_2 + 6\,KCN \rightarrow 2K_3[Cu(CN)_4] \text{ (unstable complex)}$$

$$K_3[Cu(CN)_4] \rightleftharpoons 3K^+ + [Cu(CN)_4]^{-} \text{(unstable complex ion)}$$

$$[Cu(CN)_4]^{-3} \rightleftharpoons Cu^+ + 4CN^- \text{----------(I)}$$

By applying law of mass action to the above reaction (I) we get

$$K_{inst} = [Cu+]\,[CN-]^4 / [Cu(CN)4]^{-3} = 5.00\times10^{-28}$$

When $Cd(NO_3)_2$ reacts with excess KCN gives very weak cyano complex

$$Cd(NO_3)_2 + 2KCN \rightarrow Cd(CN)_2 + 2KNO_3$$

$$Cd(CN)_2 + 2KCN \rightarrow K_2[Cd(CN)_4]$$

$$K_2[Cd(CN)_4] \rightleftharpoons 2K^+ + [Cd(CN_4)]^{-2}$$

$$[Cd(CN_4)]^{-2} \rightleftharpoons Cd^{++} + 4CN^- \text{----------(II)}$$

By applying law of mass action to the above reaction (II) we get

$$K_{inst} = [Cd^+]\,[CN-]^4 / [Cu(CN)_4]^{-2} = 1.4\times10^{-17}$$

The ionization constant value for $[Cd(CN_4)]^{-2}$is higher than $[Cu(CN)_4]^{-3}$due to which excess Cd^{++} ions remains free in solution than Cu^{++}ions Hence free Cd^{++} Ion from solution precipitated first with H_2S gas than Cu^{++} ions .

3) Separation of Co^{2+} from Ni^{2+}:-

Both the cations are IIIrdB cations Aqueous solution containing $Co^{2+}$and Ni^{2+} cations treated with NH_4OH and$NH_4Cl$and excess of H_2S gas black precipitate of CoS and NiS produces as

1) $Co^{++} + H_2S \xrightarrow{NH_4Cl+NH_4OH} CoS + 2H^+$ 2) $Ni^{++} + H_2S \xrightarrow{NH_4Cl+NH_4OH} NiS + 2H^+$

Wash the residue of CoS and NiS with distilled water and treat it with aquargia ($HCl+HNO_3$= 1:3) in a evaporating dish. Evaporate the solution to dryness cool it add littlie distilled water stir well and filter. Clear solution of $CoCl_2$ and $NiCl_2$ produces as

$$3HCl + HNO_3 \rightarrow 2H_2O + 3Cl + NO$$

1) $CoS + 2Cl \rightarrow CoCl_2 + S$

2) $NiS + 2Cl \rightarrow NiCl_2 + S$

Divide the above solution in to two parts and take test for Co^{2+} and Ni^{2+}

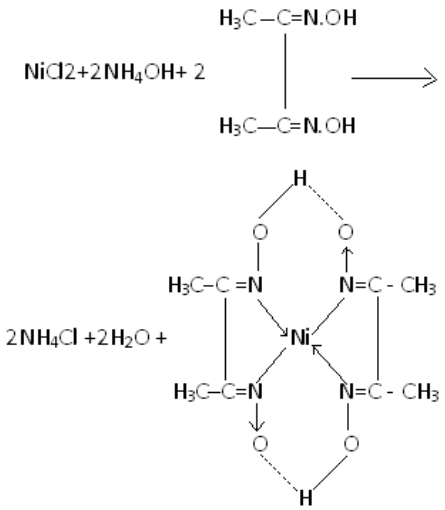
Test for Co^{2+}:-Treate one poartion of above solution with little amyl alcohol, add few crystals of NH4CNS,A shake well. Deep blue coloured alcohol layer produces indicates presence of Co^{2+}

$$Co^{2+} + 4NCS^- \rightarrow [Co(NCS)_4]^{2-}$$

In above test use of water must be avoided because if water is used , pink colored $[Co(H_2O)_6]$ complex ion produces instead of deep blue or green $[Co(NCS)_4]^{2-}$ complex ion

NI2+present in the solution does not form colored complex with NCS^- ion. Hence Co^{2+} is detected in presence of Ni^{2+}

Test for Ni^{2+}:- To another portion of test solution add excess NH4OH till alkaline and enough alcoholic dimethyl glyoxime solution the scarlet red colored precipitate of $[Ni(Dmg)_2]$produces indicates confirmation of Ni^{2+} Dimethyl glyoxime is specific reagent for Ni^{2+} it gives scarlet red precipitate for Ni^{2+} in alkaline medium but it does not gives such a precipitate for Co^{2+}.



Scarlet red coloured complex of $Ni(Dmg)_2$

Detection and separation of acidic radicles (byComplex formation)

1)Separation of Cl^- from $Br^-$and I^-:-

All the halides are similar in properties the group reagent for halides is silver nitrate ($AgNO_3$) which gives halide precipitate as AgCl(white),AgBr(pale yellow) and AgI (yellow) which all are insoluble in dilute HNO_3

$$MX + AgNO_3 \rightarrow AgX\downarrow + MNO_3$$

Where X=Cl-, Br- or I- and M = Na^+ or K^+

Cl- can be separated from Br- and I- as, the precipitate of AgCl, AgBr and AgI treated with aqueous ammonium carbonate solution .Silver chloride gives clear solution of amine complex while AgBr and AgI are sparingly soluble in ammonia solution hence remains undissolved the solution is centrifuged .The centrifugate containing Cl- acidified with dilute HNO_3. AgCl get reprecipitated as a result of decomposition of ammine complex.

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

$$AgCl\downarrow + (NH_4)_2CO_3 \rightarrow [Ag(NH_3)_2]Cl + H_2O + CO_2$$

$$[Ag(NH_3)_2]Cl + 2HNO_3 \rightarrow AgCl\downarrow + 2NH_4NO_3$$

In this way Cl-ion detected and separated from the mixture containing Cl-, Br- and I-.NH4OH is not used in the above reactions because AgBr is partially soluble in ammonia

2) Detection of aNO_2^- and NO_3^-(By Brown ring test)

If the given mixture contain both NO_2^- and NO_3^- together both can be detected by Brown ring test as follows

a) Detection and confirmation of NO_2-:-Treat the aqueous solution of a mixture containing NO_2^- and NO_3^- with cold, fresh and saturated solution of $FeSO_4$ in a clean test tube to it add dilute CH_3COOH solution from the side wall of test tube till solution becomes acidic, brown ring of $[FeNO]SO_4$ complex(or brown coloured solution) produces at the junction of liqude layers indicate conformation of NO_2^- ion .The brown ring of $[FeNO]SO_4$ produces by following reactions

$$NO_2^- + CH_3COOH \rightarrow CH_3COO^- + HNO_2$$

$$3HNO_2 \rightarrow H_2O + HNO_3 + 2NO\uparrow$$

$$Fe^{2+} + SO_4^{2-} + NO \rightarrow [FeNO]SO_4$$

For detection of NO_2^- the aqueous solution used must be free from Br- and I- which gives colored complexes with Fe^{2+}.

b) Detection and conformation of NO_3^-:-Treat the aqueous solution of mixture containing NO3- ion (free from NO2- Br- and I-) with enough concentrated H2SO4 shake well cool under tap water. To it add cold, fresh and saturated FeSO4 solution from the side wall of test tube.Brown ring at the junction of two liquid layers indicates the conformation of NO3- ion

The brown ring of [FeNO]2+complex ion produces by following reactions

2NO3-+H2SO4 →2HNO3+SO42-

2HNO3 → H2O+2NO+3[O]

2Fe2++2H++[O] → H2O+2Fe3+

Fe2++NO → [FeNO]2+

The aqueous solution used for confirmation of NO3-must be free from NO2- , Br- and I- ions.

Applications of oxidation-reduction:- In qualitative analysis many cation and anaions are detected by means of their behavior towards oxidising or reducing agents

1)Separation of Cl- ,Br –and I-:- The Cl- ,Br –and I- are separated from each other by two probable methods

Method –I:-Use of potassium per sulphate (K2S2O8) The oxidation potential of K2 S2O8is very high (2.05V) so used for separation of Cl- ,Br –and I-

a)Detection , confirmation and removal of I- :-To the mixture of Cl-, Br– and I- little (K2S2O8) is added and mixture is warmed, evolution of violet fumes indicates detection and confirmation of I- in solution.

$$2KI+K_2S_2O_8 \xrightarrow{\text{Heat}} 2K_2SO_4+I_2\uparrow$$

Add slight excess K2S2O8 and warm it gently till violet fumes disappears completely (avoid over heating) - I- completely removed. Here per sulphate oxidizes I- to I2 and itself get reduced to SO42-

b)Detection , confirmation and removal of Br-:-Take solution from above test free from I- to it add dilute H2SO4and worm the solution gently. Evolution of brown vapors indicates detection and confirmation of Br-.

$$2KBr+K_2S_2O_8+2H_2SO_4 \xrightarrow{\text{Heat}} 4KHSO_4+Br_2\uparrow$$

Add slight excess K2S2O8 and heat the solution gently till brown vapors completely removed (avoid over heating). Br- completely removed. Here per sulphate oxidizes Br- to Br2

c) Detection and confirmation of Cl-:- Take solution from above test free from I- and Br- to it add enough AgNO3 white precipitate of AgCl produces which dissolves completely in ammonia and then reprecipitated with dilute HNO3 confirms presence of Cl- ion in solution

Cl- +Ag+ →AgCl↓

AgCl +2NH4OH→[Ag(NH3)2]Cl+H2O

[Ag(NH3)2]Cl+2HNO3→AgCl↓+2NH4NO3

Method II:- Use of chlorine water:-

a) To the aqueous solution of a mixture containing Cl-, Br– and I- add enough chlorine water and chloroform .Shake well the solution and allow to separate two layers. Violet colour to lower organic layer indicate presence of I-in the given solution. Take upper aqueous layer in a test tube to it add excess chlorine water and chloroform shek well repeat the same till violet colour to lower organic layer does not produces. Here I- get removed completely in this test the Cl2 itself under goes reduction and oxidizes I- to iodine this iodine dissolves in organic layer (chloroform) and gives violet colour to organic layer

$2NaI+Cl2 \rightarrow 2NaCl+I2$

Or $[2I^-+Cl2 \rightarrow 2Cl^-+I2]$

b) To the aqueous layer from above step(free from I-) add enough chlorine water and chloroform .Shake well the solution and allow to separate two layers yellow colour to lower organic layer indicate presence of Br- in the given solution. Take upper aqueous layer to it add excess chlorine water and chloroform shake well repeat the same till yellow colour to lower organic layer does not produces. Here Br- get removed completely

in this test the chlorine it self under goes reduction and oxidizes Br- to Br2 which dissolves in organic layer (chloroform) and gives yellow colour to organic layer

$2NaBr+Cl2 \rightarrow 2NaCl+Br2$

Or $[2Br^-+Cl2 \rightarrow 2Cl^-+Br2]$

c)The aqueous layer from above step (completely free from I-,Br- and organic layer) or aqueous solution containing Cl- ,Br –and I- used for confirmation of Cl- which can be treated with AgNO3 solution. A white precipitate of AgCl produces. It can be treated with aqueous ammonium carbonate solution .AgCl gives clear solution of amine complex. If the solution is treated with dilute HNO3 Ci-ion get reprecipitated as AgCl . Hence Cl-ion detected and confirmed .

$Ag^++Cl^- \rightarrow AgCl\downarrow$

$AgCl+(NH4)2CO3 \rightarrow [Ag(NH3)2]Cl +H2O+CO2$

$[Ag(NH3)2]Cl+2HNO3 \rightarrow AgCl\downarrow+2NH4NO3$

2)Separation of $NO2^-$ and $NO3^-$:-

a) Detection of $NO2^-$:-The aqueous solution containing NO-2 and NO-3 acidified with H2SO4and treated with very dilute KMnO4 solution. Decolouration of KMnO4 solution confirms the presence of $NO2^-$ here KMnO4 is reduced by HNO2 to MnSO4 where as HNO2is oxidized to HNO3

$2KMnO4+3\ H2SO4 \rightarrow K2SO4+2MnSO4+3H2O+5(O)$

$2KNO2 + H2SO4 \rightarrow K2SO4+2HNO2$

$HNO2+ (O) \rightarrow HNO3$

Nitrate present in the solution does not interferes in the above test.

b) Removal of $NO2^-$:-Under specific conditions nitrite can be reduced to nitrogen and separated from nitrate. To the solution containing$NO2^-$ an excess of solid NH4Cl is added and the solution is boiled to expel out $NO2^-$ as N2 gas.

$$NaNO2 + NH4Cl \xrightarrow{\text{Boil}} NH4NO2+NaCl$$

$$NH4NO2 \xrightarrow{\text{Boil}} N2\uparrow+H2O$$

c) Detection of $NO3^-$:-After the removal of $NO2^-$, $NO3^-$can be tested by following tests :-

1)Solution is warmed with Cu foil and conc. H2SO4.Brown gas evolves that turns starch iodide paper black indicates confirmation of $NO3^-$.

$2NaNO3+ H2SO4 \rightarrow Na2SO4+2HNO3$

$Cu+ 4HNO3 \rightarrow Cu(NO3)2+2NO2\uparrow+2H2O$

2) Brown ring test:-[Please refer the brown ring test for $NO3^-$]

Spot tests

Scientist F.Fiegl and his colleges developed a advanced analytical technique in 1918 for detection and confirmation of basic radicals called as Spot tests analysis. The technique is most superior technique than Inorganic semi micro qualitative analysis because of following advantages

Advantages

1) Very simple equipments are required.
2) Very less space is required.
3) Less number of labors are required.
4) Very very small quantity of sample and reagents are required.
5) Very fast technique, less time can be consumed.
6) It is more economical.
7) Simple to operate.
8) Pollution free technique.
9) Carried out even at micro level.

The spot test analysis is a simple technique for which one or two drops of sample solution of a high purity material is required. One drop of reagent solution is required. The equipments required are filter paper strips or a spot plate, reagent bottles, sample solution containers, dryer and etc.

Experimental procedure for spot test analysis :- Take a drop of sample solution on a paper strip, dry it with the dryer apply a drop of a reagent on it , intense colour develops on a paper strip indicates confirmation of the cation. Spot tests also may be carried on spot plate.

Requirements:-The basic requirements of spot test analysis are, High purity (A.R. Grade) inorganic salts and reagents, suitable experimental conditions and cleanliness of equipments and working place are required

The technique has some limitations like the reagents required for the analysis must be of higher quality, which are costly. The sample solution must be free from quantamination, prepared by using A.R. grade inorganic salts. The organometallic complex formation or chelation reactions which proceids in spot test analysis may not be clearly understood.

Table 15: Detection of some cations by spot test analysis

Test	Observation Colour of the spot	Inference
1)Rubeanic acid test:-take a drop of original solution(O.S.) on a paper strip + a drop of reagent-expose to NH_3 gas	a)Olive green b)Blue c)Brown	Cu^{2+}present Ni^{2+} present Co^{2+}present
2)Dimethyl glyoxime test:- take a drop of O.S. on a paper strip + adropof reagent-expose toNH_3 gas	Scarlet red colour	Ni^{2+} present and confirmed
3)Potassium ferrocyanide test:- take a drop of O.S. on a spot plate + a drop of reagent	Intence blue colour	Fe^{3+} present and confirmed

C14P: Physical Chemistry Lab

Experiment 1: Determination of surface tension of a liquid using Stalagmometer.

Theory:

At a particular temperature surface tension of a liquid can be defined as the force acting tangentially to the surface and perpendicularly to any line of unit length drawn on it. The unit of surface tension is dyne cm^{-1} (CGS) or N m^{-1} (SI).Surface tension originates due to unbalanced force of attraction acting on the interface between two phases in contact and hence can truly be termed as interfacial tension.

The magnitude of surface tension of a liquid decreases with increase in temperature because of decrease in intermolecular attractive forces among the molecules with rise in temperature.

By drop counting method, the measurement of surface tension is carried out using a Stalagmometer where the liquid is allowed to form a complete drop slowly from the flat end of a capillary tube of exactly circular opening under the action of gravity. Just before detachment the drop becomes cylindrical having radius equal to the outer radius ® of the capillary end. The radius of curvature of the drop head is also equal to the radius of the liquid cylinder. Under this condition, just at the point of detachment of the drop, upward force due to surface tension (λ) is balanced by the downward force due to weight of the drop (mg) and the force due to excess pressure.

Generalized expression for excess pressure is given as,

$P_{excess} = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2}\right)$, for curved liquid surface (like cylindrical surface) having one liquid-air interface with two different radii of curvatures r_1 and r_2.

For the cylindrical surface, $r_1 = \propto$ and $r_2 = r$, $P_{excess} = \gamma/r$

Therefore total downward force = $mg + \pi r^2 . \gamma / r = mg + \pi r \gamma$

So, at the moment of detachment, $2 \pi r \gamma = mg + \pi r \gamma$ or, $\pi r \gamma = mg$

Or, $\pi r \gamma = mg$

Since the volume of the drop that actually separates from the flat end of a capillary tube is smaller than the volume of the pendant drop at the moment of detachment, Harkins and Brown modified this expression by introducing a correction factor ∅ [a function of (v/r^3), where v is the volume of a drop] as follows;

$mg = \pi r \gamma \emptyset$

If two liquids forming drops of very similar volume are used in the same instrument ($\emptyset_1 = \emptyset_2$) then from equation (i), we get

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2} = \frac{v_1 d_1}{v_2 d_2} = \frac{\left(\frac{V}{n_1}\right) d_1}{\left(\frac{V}{n_2}\right) d_2} = \frac{n_2 d_1}{n_1 d_1} \qquad \ldots\ldots\ldots\ldots\ldots \text{(ii}$$

Here, d_1 and d_2 are the densities of the liquids, v_1 and v_2 are the drop volumes, V is the same volume of two liquids, which generates n_1 and n_2 number of drops. Thus by counting the number of drops of each liquid for a fixed volume of both and determining the ratio of densities, one can compare the surface tension of two liquids. If liquid 2 be water then the equation (ii) becomes

$\frac{\gamma_1}{\gamma_2} = \frac{n_w d_1}{n_1 d_w} = \frac{n_w}{n_1} s_1$, where w stands for water and s_1 stands for the specific gravity of the liquid 1.

Apparatus required:

1) 100ml beaker -2
2) Sp. Gravity bottle (10ml) -1
3) Stalagmometer (fitted with rubber tube), (No. of drops should be 10-15 drops per minute use pinchcock if necessary).

Chemicals required:

Acetic acid/ ethanol.

Procedure:

1) Clean the Stalagmometer with chromic acid and wash thoroughly with distilled water. Make sure that the Stalagmometer is clamped vertically [view from front and at right angle to make it vertical] in a stand. Suck in water and allow water to flow from one fixed mark to another and count the number of drops.
2) Remove water completely from the Stalagmometer, rinse it with a small amount of experimental liquid and count the number of drops for the same volume of solution as before. For each of the liquids (water, experimental liquid) count the number of drops at least twice.

3) Use a clean dry 10ml specific gravity bottle to determine the specific gravity of the given experimental liquid at room temperature. Record the experimental temperature.
4) Calculate λ_1/λ_w.

Experimental result:

1) Room temperature:
2) Determination of specific gravity of experimental liquid:

Weight of empty sp. Gravity bottle (w_1g)	Weight of sp. Gravity bottle+ water (w_2g)	Weight of sp. Gravity bottle + expt. Solution (w_3g)	Sp. Gravity of the experimental solution $S_1=(w_3-w_1)/(w_2-w_1)$

3) Determination of relative surface tension of experimental liquid :

Liquid	No. of drops	Mean no. of drops
Water	i) ii) iii)	n_w=
Experimental Liquid	i) ii) iii)	n_1=

Calculation: $\lambda_1/\lambda_w = n_w/n_1.s_1$=……..

Therefore relative surface tension of experimental liquid w.r.t water = …at …. 0^0C.

Precautions and suggestions

1) The Stalagmometer should be cleaned and dried before use.
2) While sucking the liquid into the Stalagmometer, no air bubble should be formed.
3) Stalagmometer should be held in a vertical position throughout the drop counting process.
4) Drop formation should be adjusted at a slower rate and should not exceed fifteen drops per minute.

Experiment 2: Determination of CMC from surface tension measurements

Theory:

A detergent is a surfactant or a mixture of surfactant or a mixture of surfactants with cleaning properties in dilute solutions. Surfactants are water-soluble amphiphilic molecules that consist of a non-polar hydrophobic part (tail) and a polar hydrophilic part (head group). The hydrophilic head group can be nonionic, anionic, cationic, or zwitterionic. The balance between hydrophobic and hydrophilic parts gives special properties to surfactants, e.g. high affinity to absorb at interfaces and association in solution to form micelles.

The concentration at which surfactants in solution start to form micelles is called critical micelle concentration (C.M.C.). Each surfactant has a characteristic C.M.C. at a given temperature and salt concentration. The C.M.C. of a surfactant can be obtained by different techniques, based on the measurement of a physical property that shows an abrupt change at C.M.C. Some of the techniques in determining C.M.C. include surface tension, conductivity, spectrophotometry etc.

Due to the adsorption of surfactant molecules at the air/ water interface the surface tension of an aqueous solution of surfactant decreases with increasing surfactant concentration upto C.M.C. when the surfactant starts to form micelles in solution (at C.M.C.) the surface tension remains virtually constant. Therefore, the C>M>C. can be determined from surface tension measurements at different surfactant concentrations. The break in graphs of surface tension versus logarithm of surfactant concentration gives the C.M.C. Du Nouy ring method is used to measure the surface tension of air/water interface of an aqueous surfactant solution.

Apparatus Required:

1) Surface tensiometer.
2) Variable volume micropipette (50 µl - 1000µl) -1
3) 50 ml volumetric flask -2
4) 10 ml pipette -1

Chemicals required: SDS(sodium Dodecyl Sulphate)

Procedure:

1) Clean properly the vessel with chromic acid wash thoroughly with deionized water. Wash the Du Nouy ring with PET ether and burn the ring only in oxidizing flame of a Bunsen burner to remove any impurity. Do not overheat; otherwise the ring may be deformed.
2) Add 30 ml of deionized water using a pipette to the vessel and place it on the stage of the tensiometer.. Hang the clean ring from the balance hook over the vessel.
3) For manual tensiometer after calibration, set the instrument at 0 mN/m when the ring is hung in the air. Lift the vessel stage with the screw and immerse the ring in the water. Turn the scale knob and lower the sample table at the same time keeping the index zero. Write down the scale reading as the value of surface tension just at the breaking point of the water film.
4) Prepare 50ml 120 mM solutions of SDS(MW_{SDS} =288.37 g/mol). Repeat the process of surface tension measurement after adding different volumes of the SDS solutions to the water in the vessel according to the following table:

Volume of SDS solution added to the vessel	Total volume in the vessel (ml)
0	30
100 µL of 120 mM SDS	30.1
Plus 50 µL of 120 mM SDS	30.15
Plus 100 µL of 120mM SDS	30.25
Plus 150 µL of 120 mM SDS	30.40
Plus 100 µL of 120mM SDS	30.50
Plus 150 µL of 120 mM SDS	30.65
Plus 150 µL of 120mM SDS	30.80
Plus 200 µL of 120mM SDS	31.00
Plus 300 µL of 120mM SDS	31.30
Plus 350 µL of 120mM SDS	31.65
Plus 500 µL of 120mM SDS	32.15
Plus 500 µL of 120 mM SDS	32.65
Plus 1ml of 120 mM SDS	33.65
Plus 1ml of 120mM SDS	34.65
Plus 2ml of 120 mM SDS	36.65
Plus 4ml of 120mM SDS	40.65

5) Plot the experimental data of surface tension versus logarithm of surfactant concentration. Determine the C.M.C. of SDS from the graph.

Experimental result:

1) Room temperature:
2) Determination of surface tension:

SDS concentration in the vessel (mM)	Log (SDS conc.)	Surface tension (mN/m)

SDS concentration = $\frac{\text{Volume of prepared SDS solution(ml)} \times \text{its strength (mM)}}{\text{Total volume of solution in the vessel (ml)}}$

Conclusion: From the break in the curve on plotting the experimental data of surface tension versus logarithm of surfactant concentration, C.M.C. of surfactant is found to be …..mM at ….^{0}C.

Experiment 3: Verification of Beer and Lambert's Law for KMnO4 and K2Cr2O7 solution .

Theory:

Lambert's law deals with the effect of thickness f a medium on the intensity of any monochromatic light passing through it and is given by,

$$I = I_0 e^{-\alpha l} \qquad \text{……. (1)}$$

Where I_0 is the intensity of the incident light, I that of emergent light, l is the thickness of the absorber and α is a constant for a given absorber for fixed wavelength of the light used temperature. This constant 'α' is called absorption coefficient.

Equation (1) may be expressed as,

$I = I_0 10^{-0.4343\alpha l} = I_0 10^{-kl}$, where $k = 0.4343\alpha$ is called extinction coefficient.

Or, $\log \frac{I_0}{I} = kl$

$\log \frac{I_0}{I}$ is called optical density or absorbance (A) of the sample and (I_0/I) is called transmittance.

Beer developed the equation for the effect of concentration of the light absorbing species present in the medium. According to him the decrease in intensity of any monochromatic light passing through an absorbing medium is given by,

$$I = I = I_0 e^{-\alpha' cl} \quad \ldots\ldots\ldots\ldots\ldots (2)$$

Where 'c' is the concentration of the absorbing species and 'α' is called molar absorption coefficient of absorbing species which depends on the wavelength of the light, the solvent and the temperature.

Equation (2) may be expressed as,

$$I = I_0 10^{-0.4343\alpha' cl} = I_0 10^{-\epsilon cl} \quad \ldots\ldots\ldots\ldots\ldots (3)$$

Where $\epsilon = 0.4343\alpha'$ is called molar extinction coefficient or molar absorptivity.

Equation (3) may be expressed as,

$$\log \frac{I_0}{I} = A = \epsilon\, cl$$

Molar extinction coefficient(ϵ) is normally cited in units of $M^{-1}cm^{-1}$or L $mol^{-1}cm^{-1}$.

'ϵ' of any species if not known, can be determined by measuring transmittance I/I_0 of its solution of known concentrations in the same cell of length 'l' and plotting absorbance ($A = \log \frac{I_0}{I}$) vs 'c'. From the slope (ϵ l) of the straight line thus obtained, ϵ can be calculated;

Apparatus required:

1) 100ml volumetric flask -5
2) 250ml glass bottle -1
3) 250ml conical flask -2
4) Test tube -18

Chemicals required:

Oxalic acid, $KMnO_4$, H_2SO_4, $K_2Cr_2O_7$

Procedure:

1) Prepare 100ml (N/10) oxalic acid solution by accurate weighing.
2) Prepare 100ml ~ (M/100) $KMnO_4$ solution.
3) Standardize the prepare (M/100) $KMnO_4$ solution with the standard oxalic acid solution following the procedure given below-

   Pipette out 10ml of the standard oxalic acid solution in a 250ml conical flask. Add 30ml of (4N) H_2SO_4, followed by addition of 20ml of water. Heat the solution to 70^0C- 80^0C .Titrate in hot condition with the prepared $KMnO_4$. Note the end point of the titration when the faint pink colour persists for 30 sec.

4) Prepare 100ml (M/100) $KMnO_4$ solution by quantitative dilution of standardized 10ml of supplied (M/100)$KMnO_4$ solution using distilled water.
5) From the (M/1000) $KMnO_4$ solution, prepare 100ml exact 10^{-4} (M) $KMnO_4$solution by exact dilution with distilled water.

6) Prepare the following set of solutions in suitably labeled test-tubes:

Vol (ml) of 10^{-4}(M) $KMno_4$	5	5.5	6	6.5	7	7.5	8	8.5	9	10
Vol (ml) of distilled water	5	4.5	4	3.5	3	2.5	2	1.5	1	0

7) In the colorimeter instrument, set the wavelength at around 530 nm (peak) ; adjust the instrument and measure the transmittance (T) with all the solutions prepared in step(6).
8) Calculate the absorbance (A) from Transmittance (T) and plot 'A' vs concentration to verify Lambert-Beer's law. Estimate '$\in$' assuming l=1cm
9) Prepare 100ml exact (M/100) $K_2Cr_2O_7$ solution by accurate weighing with 1(N) H_2SO_4.
10) Prepare 100ml of exact 10^{-3} (M) $K_2Cr_2O_7$ solution from the prepare exact (M/100) $K_2Cr_2O_7$ solution by exact dilution with 1(N) H_2SO_4.
11) Prepare the following set of solutions in suitably labeled test-tubes with the exact (M/1000) $K_2Cr_2O_7$ by exact dilution with 1(N) H_2SO_4.

Vol (ml) of 10^{-3}(M) $K_2Cr_2O_7$	3	4	5	6	7	8	9	10
Vol (ml) of 1 (N) H_2SO_4	7	6	5	4	3	2	1	0

12) Set the wave length in the colorimeter at around 475 nm (peak). Note transmittance (T) for all these solutions.
13) Calculate the absorbance (A) from Transmittance (T) and plot 'A' vs concentration to verify Lambert-Beer's law. Estimate '$\in$' assuming l=1cm.
14) Measure the transmittance (T) for the solution of $K_2Cr_2O_7$ of unknown strength and calculate its absorbance (A). From the calibration curve for $K_2Cr_2O_7$, determine the concentration of this solution.

Experimental result:

1) Room temperature:
2) Preparation of 100ml 0.1 (N) Oxalic acid.
3) Preparation of 100ml ~ (M/100) $KMnO_4$ solution.
4) Standardization of the prepared $KMnO_4$ solution:

Volume of 0.1(N) oxalic acid (ml)	Burette reading		Volume of $KMnO_4$ used (ml)	Average volume of $KMnO_4$ (ml)
	Initial(ml)	Final(ml)		
10				
10				

Strength of $KMnO_4$: ……..

5) Preparation of 100ml (M/1000) $KMnO_4$ solution by quantitative dilution of standardized 10ml of prepared (M/100) $KMnO_4$ solution using distilled water.

6) Preparation of 100ml exact 10^{-4}(M) $KMnO_4$ solution:

Required volume of ~ 10^{-3}(M)$KMnO_4$ solution = $\frac{100\times10^{-4}}{strength\ of\ \sim10^{-3}\text{KMnO4 solution}}$ ml

…..ml prepared ~ 10^{-3}(M)$KMnO_4$ solution was taken in a 100ml volumetric flask and rest of the volume was made by adding deionized water up to the mark.

7) Preparation of sets for $KMnO_4$ solutions:

Test tube no.	1	2	3	4	5	6	7	8	9	10
Vol(ml) of 10^{-4} (M) $KMnO_4$	5	5.5	6	6.5	7	7.5	8	8.5	9	10
Vol(ml) of distilled water	5	4.5	4	3.5	3	2.5	2	1.5	1	0

8) Measurement of absorbance (A) for $KMno_4$ solutions (at wavelength 530nm):

Test tube no.	Concentration of $KMnO_4$ solution	% Transmittance(T)	Absorbance(A)
1	0.5×10^{-4} (M)		
2	0.55×10^{-4} (M)		
3	0.6×10^{-4} (M)		
4	0.65×10^{-4} (M)		
5	0.7×10^{-4} (M)		
6	0.75×10^{-4} (M)		
7	0.8×10^{-4} (M)		
8	0.85×10^{-4} (M)		
9	0.9×10^{-4} (M)		
10	1.0×10^{-4} (M)		

9) Preparation of 100ml exact (M/100) $K_2Cr_2O_7$ solution.

10) Preparation of 100ml exact (M/1000) $K_2Cr_2O_7$ solution.

11) Preparation of sets for $K_2Cr_2O_7$ solutions:

Test tube no.	1	2	3	4	5	6	7	8
Vol(ml)of 10^{-3} $K_2Cr_2O_7$	3	4	5	6	7	8	9	10
Vol(ml)of 1(N) H_2SO_4	7	6	5	4	3	2	1	0

12) Measurement of absorbance (A) for $K_2Cr_2O_7$ solutions (at around wavelength 475 nm):

Test tube no.	Concentration of $K_2Cr_2O_7$ solution	% Transmittance(T)	Absorbance (A)=2-logT
1	0.3×10^{-3} (M)		
2	0.4×10^{-3} (M)		
3	0.5×10^{-3} (M)		
4	0.6×10^{-3} (M)		
5	0.7×10^{-3} (M)		

6	0.8×10^{-3} (M)		
7	0.9×10^{-3} (M)		
8	1.0×10^{-3} (M)		

13) Plot absorbance (A) vs Concentration (C) for both $KMnO_4$ and $K_2Cr_2O_7$ solutions respectively in separate graph paper and from the respective straight line thus obtained (which verifies the Lambert- Beer's law) '$\in$' (for $KMnO_4$ and $K_2Cr_2O_7$) can be calculated from the slope of the respective straight line (assuming l= 1cm).

14) The % transmittance (T) for the solution of $K_2Cr_2O_7$ of unknown strength was measured and its absorbance (A) was calculated. From the calibration curve for $K_2Cr_2O_7$ concentration of this solution was found to be…….

Experiment 4: Study of kinetics of K2S2O8 + KI reaction, spectrophotometrically

APPARATUS REQUIRED:

(a) 100 ml vol. flask-4
(b) 250 ml conical flask-2
(c) 100 ml beaker-1
(d) 500 ml conical flask-1
(e) Burette-1
(f) Pipette 10 mL-1
(g) Watch glass-2
(h) Glass bottle-2

CHEMICALS:

$K_2Cr_2O_7$, $K_2S_2O_8$, KI, $Na_2S_2O_3$, Starch, Glacial acetic acid.

PROCEDURE:

(1) Prepare 100 ml of standard (N/10) $K_2Cr_2O_7$ solution by accurate weighing.

(2) Prepare 250 ml (N/10) sodium thiosulphate solution.

(3) Standardize the (N/10) sodium thiosulphate solution idometrically sing starch solution as indicator. Take 10 ml of standard (N/10) $K_2Cr_2O_7$ solution solution in a 500 ml conical flask. Add about 15 ml (one test tube) of 105 KI solution and 20mL of 4(N) HCl solution. Cover the conical flask with watch glass and keep in dark for about 5 minutes. Add 150 ml of deionized water and titrate the liberated iodine with sodium thiosulphate solution using starch as indicator.

(4) Prepare 250 ml $K_2S_2O_8$ solution [of strength> (N/10)].

(5) Standardize the prepared $K_2S_2O_8$ solution [of strength> (N/10)] using the following procedure:

Take 10 ml of the prepared $K_2S_2O_8$ solution in a 250 ml conical flask; add 20 ml of 10% KI solution and 2 ml of glacial acetic acid. Prepare two sets at the same time, cover the conical flask with watch glass and keep the mixture in dark for about 45 minutes. Add 50 ml of water and titrate the liberated iodine against the standard thiosulphate solution using starch solution as indicator.

(6) Prepare an exact (N/10) $K_2S_2O_8$ solution from the standardize $K_2S_2O_8$ solution by quantitative dilution (total volume 100 ml).

(7) Prepare 100 ml of a standard KI solution of strength greater than (N/10) by accurate weighing. From this prepare 100 ml of an exact (N/10) KI solution. Set up the colorimeter and adjust properly the SET 0 and SET 100 controls, using the filter at 525 nm.[peak wavelength].

(8) Pipette out 100mL of the exact (N/10) $K_2S_2O_8$ solution in a clean dry 100 ml beaker. Add 10 ml of the exact (N/10) KI solution to this solution by the same pipette and note the half discharge time as t= 0.Mix the solution carefully.

(9) Note the absorbance (A) of the reaction mixture at 525 nm (peak) wavelength at an interval of 1 minute for 15 readings.

(10) Plot $(1/A_t)$ versus (1/t) for the reaction mixture and calculate the rate constant from the graph.

Experimental Data:

1) Rom temperature,

2) Preparation of 100 mL (N/10) $K_2Cr_2O_7$ solution by accurate weighing:

3) Preparation of the prepared sodium thiosulphate solution:

4) Standardization of the prepared sodium thiosulphate solution:

Vol. of 0.1N $K_2Cr_2O_7$ (mL)	**Burette reading**		**Vol. of $Na_2S_2O_3$ used (mL)**	**Average vol. of $Na_2S_2O_3$ (mL)**
	Initial(mL)	**Final(mL)**		
10				
10				

Strength of $Na_2S_2O_3$ solution:

5) Preparation of 250 ml $K_2S_2O_8$ solution [of strength > (N/10)]:

6) Standardization of the prepared $K_2S_2O_8$ solution:

	Burette reading	**Vol. of $Na_2S_2O_3$**	

Vol. of $K_2S_2O_8$ solution(ml)	Initial(ml)	Final(ml)	used (ml)	Average vol. of $Na_2S_2O_3$ (ml)

Strength of $K_2S_2O_8$ solution:

7) Preparation of 100 ml exact (N/10) $K_2S_2O_8$ solution:

Required volume of prepared $K_2S_2O_8$ solution = $\frac{100\times0.1}{strength\ of\ \mathbf{K2S2O8\ solution}}$ **ml**

…. ml prepared $K_2S_2O_8$ solution was taken (using burette) in a 100 mL volumetric flask and rest of the volume was made by adding deionized water up to the mark.

8) Preparation of 100 ml of a standard KI solution of strength slightly greater than (N/10) by accurate weighing:

9) Preparation of 100 ml of an exact (N/10) KI solution:

10) Measurement of absorbance (A_t) at different times:

Time	Time in Sec(t)	% Transmittance(T)	Absorbance(A_t)=2-logT

Conclusion:

A straight line is obtained on plotting (1/t) with

Intercept, $(1/A_\infty)$ = …… Slope = $(1/ak' A_\infty)$

So, $k' = \frac{\mathbf{intercept}}{\mathbf{a\times slope}}$, where a= initial concentration of $S_2O_8^-$ =N/20 or (M/40).

Experiment 5: Determination of pH of unknown solution (buffer), by color matching method:

Theory:

P^H of a solution is defined as the negative logarithm of its H^+ ion activity i.e,

$$P^H = -\log a_{H^+}$$

In case of solution of low ionic strength

$$P^H = -\log c_{H^+}$$

The solution having applicable capacity to resist the change in its P^H due to addition of acid or base are called buffer solutions. Usually they consist of a mixture of a weak acid or base and its salt.

In case of a mixture of a weak acid and its salt [provided the solution is not very acidic (P^H>4)]. P^H of the solution can be expressed as

$$P^H = pK_a + \log \frac{[Salt]}{[acid]}$$

And I case of a mixture of weak base and its salt [provided the solution is not very basic (P^H<10)].

$$P^H = pK_b + \log \frac{[salt]}{[base]}$$

Both the equations are known as Henderson equation for weak acid and weak base respectively and will be valid only within the P^H range 4 to10.

As indicator is a substance which can indicate, generally by colour change, the specific physic-chemical condition of a chemical system.

The acid-base indicator or neutralization indicators are substance which exhibit different colours according to the hydrogen ion concentration of their environment. It is therefore possible to obtain a idea of the P^H of a given solution by adding a little of a suitable indicator to the same. Colour changes are believed to be due to some structural changes. In solution the acidic form (In_A) and the basic (In_B) of an indicator will be in equilibrium.

$$In_A \rightleftharpoons H^+ + In_B$$

The equilibrium constant called indicator constant (K_{In}) corresponding to this equilibrium is

$$K_{In} = a_{In}a_{H^+}/a_{InA} = [H^+][In_B]/[In_A], \text{ in solution of low ionic strength}$$

$$\text{Or, } P^H = pK_{In} + \log \frac{[InB]}{[InA]}$$

The colour of the indicator as perceived by the eye is determined by the ratio of the concentrations of the acid and alkaline forms i.e, by $[In_B]/[In_A]$

The value of $[In_B]/[In_A]$ determines the actual shade of colour as a mixture of two colours (predominant colours in acidic and basic medium). Thus by changing the P^H of the solution one can developed by an indicator. If a solution of known P^H exhibits a particular shade of colour, with a definite amount of indicator, then another solution (of unknown P^H) which exhibits the same shade of colour, with the same amount of indicator, must also posses the same P^H.

Apparatus required:

1. 100 ml volumetric flask-3
2. 500 ml bottle-2
3. Burette-1
4. 10 ml pipette-1
5. 250 ml conical flask-1
6. Hard glass test tubes of equal diameter-10

Procedure:

1) Prepare 100 ml standard 0.5(N) oxalic acid solution in a volumetric flask by accurate weighing.
2) Prepare 250 ml~0.5(N) NaOH solution.
3) Standardize the prepare NaOH solution against the 0.5(N) oxalic acid solution, taking 10 ml of the acid as aliquot and using phenolphthalein as indicator.
4) Determine the strength of the alkali: Prepare 100 ml of exact 0.4(N) NaOH solution by proper dilution.
5) Prepare 250 ml 0.5(N) CH_3COOH solution and Standardize it against prepared ~ 0.5(N) NaOH solution.
6) Determine the strength of CH_3COOH solution. Prepare 100 ml of exact 0.4(N) CH_3COOH solution by proper dilution.
7) Take 10 hard glass test tubes by approximately equal diameter, lebel them from 1 to 9 and prepare the following buffer solutions by proper mixing of exact 0.4(N) NaOH and 0.4(N) CH_3COOH.

Test tube No.	**Volume of CH_3COOH(ml)**	**Volume of NaOH(ml)**	**Volume of H_2O(ml)**	**Total volume(ml)**	**P^H**

8) In the remaining test tube pipette out exactly 10 ml of the unknown buffer. To each of these test tubes add 5 drops of the indicator. Mix thoroughly to develop uniform colour in each test tube. Identify the p^H of the buffer solution by colour matching.

Experimental Result:

1) Room temperature
2) **Preparation of 100 mL 0.5(N) oxalic acid:**
   Required weight (3.15 gm) of oxalic acid was taken in a 100 mL volumetric flask and volume was made up to the mark by deionized water.
3) **Preparation of 250 ml approximately 0.5(N) NaOH solution:**
   5 gm NaOH solid was taken in a glass bottle and~250 mL deionized water was added (using measuring cylinder) to make 250 mL~0.5(N) NaOH solution.
4) **Standardization of the prepared NaOH solution:**

Volume of 0.5(N) Oxalic acid (ml)	**Burette reading**		**Volume of NaOH(ml)**	**Average volume of NaOH(ml)**
	Initial(ml)	**Final(ml)**		

5) **Preparation of 100 ml exact 0.4(N) NaOH solution:**
   Required volume of prepared NaOH solution = $\frac{100\times0.4}{\text{strength of NaOH solution}}$ mL
   …… ml prepared NaOH solution was taken (using burette) in a 100 ml volumetric flask and rest of the volume was made by adding deionized water up to the mark.
6) **Preparation of 250 ml 0.5(N) acetic acid:**
   7.4 ml of the acetic acid was taken in a glass bottle and~250 ml deionized water was added (using measuring cylinder) to make 250 ml~0.5(N) CH_3COOH solution.
7) **Standardization of the prepared CH_3COOH solution:**

Vol. of~0.5(N) acetic acid (ml)	**Burette reading**		**Vol. of standardization NaOH solution used (ml)**	**Average vol. of NaOH (ml)**
	Initial(ml)	**Final(ml)**		

Strength of CH_3COOH solution:

8) Preparation of 100 ml exact 0.4(N) CH_3COOH solution:

Required volume of prepared CH_3COOH solution= $\frac{100\times0.4}{Strength\ of\ CH3COOH\ solution}$ **ml.**

…..mL prepared CH_3COOH solution was taken (using burette) in a 100 mL volumetric flask and rest of the volume was made by adding deionized water up to the mark.

9) Preparation of buffer solution:

Test Tube No.	Volume of CH_3COOH(mL)	Volume of NaOH(mL)	Volume of H_2O (mL)	Total volume (mL)	P^H
1	0.5	0.5	4.5	10.0	3.72
2	0.5	1.0	4.0	10.0	4.05
3	0.5	1.5	3.5	10.0	4.27
4	0.5	2.0	3.0	10.0	4.45
5	0.5	2.5	2.5	10.0	4.63
6	0.5	3.0	2.0	10.0	4.80
7	0.5	3.5	1.5	10.0	4.99
8	0.5	4.0	1.0	10.0	5.23
9	0.5	4.5	0.5	10.0	5.57

Conclusion:

The colour of the test tube containing unknown buffer matched with the colour of the test tube no …… having p^H …… Therefore p^H of the unknown buffer solution is……

Experiment 6: Spectrophotometric determination of CMC.

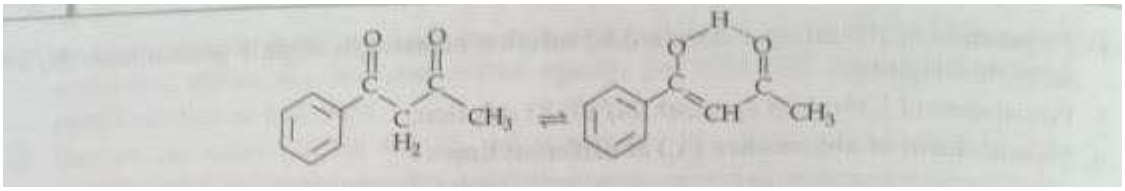
Theory:

Surfactants are water-soluble amphiphilic molecules that consist of a non-polar hydrophobic part (tail) and a polar hydrophilic part (head group). The hydrophilic head group can be nonionic, anionic, cationic, or zwitterionic. Due to this dual character, the surfactant molecules in polar solvent like water have high affinity to be adsorbed at interfaces and arrange themselves into organized molecular assemblies known as micelles.

The concentration at which surfactants in solution start to form micelles is called critical micelle concentration (C.M.C.).Each surfactant has a characteristic C.M.C. at a given temperature and salt concentration. Various physic- chemical properties of surfactant solution, such as surface tension, conductivity, fluorescene, UV absorption etc., change due to the formation of micellar aggregates. Therefore, C>M.C. can be determined from the position of

the breaking point in the concentration dependence of the selected physical or chemical property of the surfactant solution.

Determination of C.M.C. of sodium Dodecyl sulphate (SDS) by UV-absorption spectroscopy: In this method solvent dependent keto-enol tautomerism of benzoylacetone or 1-phenyl-1,3- butadiene (MW-162.18 g/mol) is used to determine the C.M.C. of sodium Dodecyl Sulphate (SDS). In solution benzoylacetone enolizes exclusively to cis-enolic form due to its stabilization by intramolecular hydrogen bonding and remains in equilibrium with its keto form.



In nonpolar solvent the proportion of enol form is much greater than that in polar solvent like water. In water above CMC, SDS molecules form aggregates (micelles) with hydrophobic core and polar head groups at the micelle water interface. When SDS solution is added to an aqueous solution of benzoylacetone below CMC no changes are observed in the absorption band centered at 312 nm increases and the absorption band at 250nm decreases with increase in surfactant concentration above CMC. The concentration corresponding to the breaking point of the curve of absorbance vs concentration of SDS represents CMC of SDS (approx value: ~ 8 mili molar at 25 ^{0}C.

Apparatus required:

1) UV- Vis spectrophotometer.
2) Variable volume micropipette (50 µl – 1000 µl).
3) 25 ml volumetric flask -2
4) 50ml volumetric flask -1
5) 10ml graduated pipette -1

Chemicals required:

SDS (Sodium Dodecyl Sulphate), Benzoylacetone, Dioxane.

Procedure:

1) Prepare 25 ml ~ 0.05 M benzoylacetone solution in Dioxane. [Dissolve 0.2027 g benzoylacetone in Dioxane in a 25ml volumetric flask.]
2) Pipette out 1ml of the benzoylacetone stock solution in a 25ml volumetric flask add deionized water up to the mark to prepare ~ 0.002 M solution.
3) Prepared 100ml 80 mM SDS solution in deionized water by accurate weighing in a volumetric flask. [Required weight of SDS = 2.307 g].

4) Following sets were prepared in clean and dry test tubes for determination of CMC of SDS spectroscopically :

Set No.	Volume of ~ 0.002M solution of benzoylacetone	Volume of water	Volume of SDS solution (80 mM)	Total volume
1	300µl	9.7ml	0ml	10ml
2	300µl	9.6ml	0.1ml	10ml
3	300µl	9.5ml	0.2ml	10ml
4	300µl	9.4ml	0.3ml	10ml
5	300µl	9.3ml	0.4ml	10ml
6	300µl	9.1ml	0.6ml	10ml
7	300µl	8.9ml	0.8ml	10ml
8	300µl	8.7ml	1.0ml	10ml
9	300µl	8.5ml	1.2ml	10ml
10	300µl	8.3ml	1.4ml	10ml
11	300µl	8.1ml	1.6ml	10ml
12	300µl	7.9ml	1.8ml	10ml
13	300µl	7.7ml	2.0ml	10ml

5) Prepare reference for each set containing same concentration of SDS without solution of benzoylacetone .
6) Record UV-Vis spectrum of benzoylacetone in presence of varying concentration of SDS. Determine the absorbance values at 312 nm and 250nm and plot against concentration of SDS. Determine CMC from the breaking point of the curve.

Experimental data:

1) Experimental temperature:
2) Determination of absorbance at 250nm and 312 nm:

Set no.	SDS concentration (mM)	Absorbance at 250nm	Absorbance at 312 nm
1	0		
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			

13			

$$SDS\ concentration = \frac{\text{Volume of prepared SDS solution (ml)added} \times \text{strength of SDS solution (mM)}}{\text{Total volume of solution inthe test tube (ml)}}$$

Conclusions:

From the break in the curve on plotting the experimental data of absorbance at 250 nm/312nm versus surfactant concentration, CMC of SDS solution is found to be …… mM at ……^{0}C.

DSE3: Lab

1. Safer starting materials

• Preparation and characterization of nanoparticles of gold using tea leaves.

❖ **Materials required:**

1) Sodium Chloroaurate
2) Tea leaves
3) Double distilled water

❖ **Procedure:**

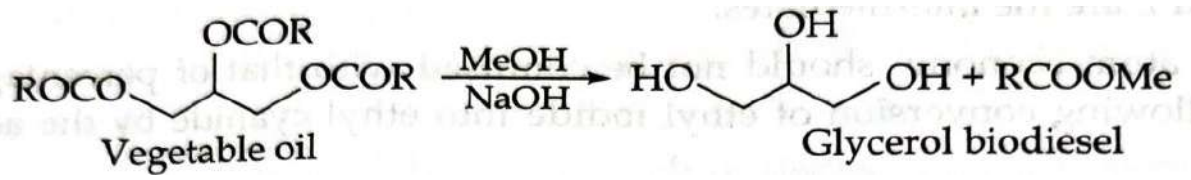
Tear~100 mg of tea leaves into fine pieces and add it to10 ml of double distilled water taken in clean vial. Stir the mixture vigorously at room temperature for 15-20 minutes. Dissolve 3.61 mg of sodium Chloroaurate in 100 µl of double distilled water. Add the Chloroaurate solution to the tea extract with continuous stirring. The reaction mixture will change colour from pale yellow to purple red within 5 minutes which indicates the formation of gold nanoparticles. Shake the reaction mixture for a further period of 15 minutes. Filter the gold nanoparticles from tea leaves using a 5µ filter. Characterise the gold nanoparticles by UV-Vis absorption spectroscopy (λ_{max}~550 nm).

❖ **Green Context:**

1) Use of renewable feedstock (tea leaves)
2) Use of innocuous solvent water
3) Use of safer chemicals
4) Use of a reaction that can be carried out easily.

2. Using renewable resources

• Preparation of biodiesel from vegetable/ waste cooking oil.



❖ **Chemicals required:**

1) Vegetable oil
2) Methanol
3) Sodium hydroxide

❖ **Procedure:**

Finely grind 3-4 pellets of anhydrous NaOH in a clean and dry mortar with a pastle. Add this sodium hydroxide to 20ml of pure (99% or higher purity) methanol in a 250 ml Erienmeyer flask and stir vigorously until the sodium hydroxide dissolves completely (methoxide solution). Warm 100 ml of pure vegetable oil (coconut oil may be used) to about 40ºC in a 250 ml beaker. Pour the warmed up oil in to the methoxide solution with continuous stirring. At first mixture would become cloudy, but soon it will separate into two layers. Stir the mixture for 15-20 minutes. Transfer the contents of the flask into a 250 ml separatory funnel. Allow the mixture to separate into two layers. The lower layer contains glycerol, sodium salt of long chain fatty acids and the upper layer consists of the methyl ester (biodiesel). Allow the mixture to stand for an hour. Drain out the lower layer into a small beaker. Gently stir the biodiesel layer with a little water to remove methanol, glycerol, sodium hydroxide and the sodium salts of fatty acid taking care that an emulsion is not formed. Drain the lower aqueous into a beaker. Filter the biodiesel layer under suction. Add 1-1.5 g of anhydrous sodium sulfate or magnesium sulfate to the filtrate for removal of the traces of water. Decant in a clean and dry beaker. The ratio of the weight of biodiesel produced to that of vegetable oil taken multiplied by 100 gives the % of conversion from vegetable oil.

❖ **Green context:**

1) Use of renewable feedstock (vegetable oil)
2) Catalysis by NaOH
3) Design for degradation

3. Avoiding waste

Principle of atom economy

• Use of molecular model kit to stimulate the reaction to investigate how the atom economy can illustrate Green Chemistry.

Atom economy, an important concept of green chemistry, first introduced by B.M.Trost in early 1991 refers to the percentage of conversion of all the atoms in the reactants into the desired product. Atom economy can be expressed as

Atom economy (%) =

(Molecular weight of desired product/Molecular weight of all the reactants) ×100

For a multistep reaction in which the intermediates are formed in one step and used up in the successive steps: **A+B= C; C+D= E; E+F= G** (Final product)

The % atom economy can be expressed as

Atom economy (%) =

(Molecular weight of G/ Sum of molecular weight of A, B, D and F) × 100

Where C and E are the intermediates.

The concept of atom economy should not be confused with that of percentage yield. Let as consider the following conversion of ethyl iodide into ethyl cyanide by the action of sodium cyanide.

$$MeCH_2I + NaCN = MeCH_2CN + NaI$$

Molecular weight: 156 49 55

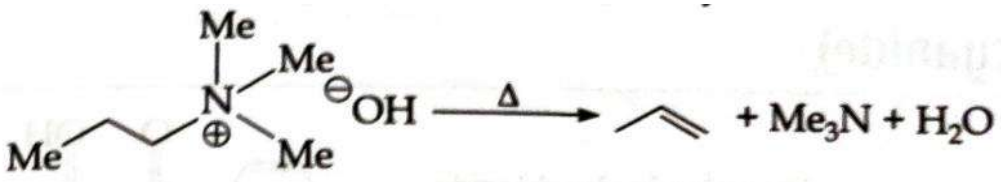
If 1 mole i.e, 55g of ethyl cyanide is obtained from 1 mole i.e, 156g of ethyl iodide yield of the reaction is 100% yield 0.55 g of ethyl cyanide should be obtained from 1.56 g of ethyl iodide. Actually 0.48g of ethyl cyanide is produced from 1.56g of ethyl iodide. Thus yield of the reaction becomes (0.48/0.55) × 100 = 87.27%. But atom economy of the reaction will be [55/(156+49)} × 100 = 26.83%.

Thus a high yielding reaction may easily be associated with very poor atom economy. Improvement of atom economy demands designing of reaction that involves formation of minimum amount of wasteful side products and if possible, recycling of the side product. Proper choice of starting materials and catalyst system may serve the purpose.

❖ Calculation of atom economy:

1) **Elimination reaction:** Propene can be prepared by Hofmann elimination of trymethyl propyl ammonium hydroxide and acid catalysed dehydration of propanoyl.

Hofmann elimination of trimethyl propyl ammonium hydroxide



Molecular weight: 119 42

So atom economy (%) = (Molecular weight of desired product / Molecular weight of all the reactants) × 100 = (42/119) × 100 = 35.29%

2) **Acid catalysed dehydration of propanoyl:**

$$MeCH_2CH_2OH + H_2SO_4 = MeCH{=}\ CH_2 + H_2O$$

Molecular weight: 60 40

Here sulfuric acid is not incorporated into the desired product and so its molecular weight needed not be considered.

Hence atom economy (%) = **(Molecular weight of desired product/Molecular weight of all the reactants) ×100 = (42/60) ×100 = 70%**

Thus, dehydration of propanoyl is more atom economical than Hofmann elimination of trimethyl propyl ammonium hydroxide for the formation of propene.

3) **Substitution reaction:**
Let us consider the hydrolysis of propyl bromide with aqueous sodium hydroxide.

$MeCH_2CH_2Br + NaOH = MeCH_2CH_2OH + NaBr$

Molecular weight: 123 40 60

Hence atom economy: = (Molecular weight of desired product / Molecular weight of all the reactants) × 100

= (60/123+40) × 100= 36.81%

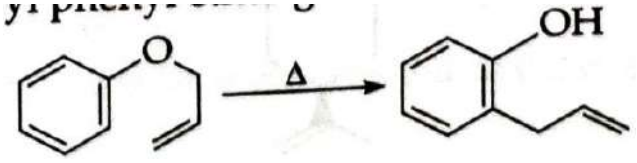
4) Addition reaction: Addition of bromine to a C=C leads to incorporation of all the bromine into the substrate. So that atom economy of the reaction becomes 100%.

$MeCH= CHMe + Br_2 = MeCH(Br)CH(Br)Me$

Molecular weight: 56 160 216

Thus atom economy: = (Molecular weight of desired product / Molecular weight of all the reactants) × 100 = (216/56+160) × 100 = 100%

5) **Rearrangement reaction:** In rearrangement reactions mostly all the atoms in the substrate are included in the desired product So this type of reaction also enjoys 100% atom economy.
Claisen rearrangement of allyl phenyl ether gives 2-allyl phenol under thermal conditions.

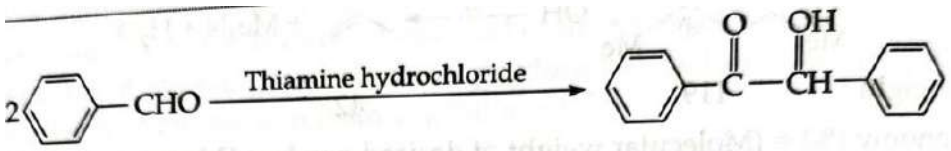


Molecular weight: 134 134

Thus atom economy: = (Molecular weight of desired product / Molecular weight of all the reactants) × 100 = (134/134) = 100%.

4. Use of enzymes as catalysts

• Benzoin condensation using Thiamine Hydrochloride as a catalyst instead of cyanide.



❖ Chemicals required:

1) Benzaldehyde
2) Thiamine hydrochloride
3) Ethanol

Dissolve 1.75 g of thiamine hydrochloride in~5 ml of water in a 100 ml round bottom flask. Add 15 ml of absolute ethanol and cool the solution in an water bath. Dissolve~400-500 mg of sodium hydroxide in 5 ml of water in a small conical flask and cool the solution in an ice bath. Add the sodium hydroxide solution drop wise to the thiamine hydrochloride solution over a period of 10 minutes. Then add 10 ml of freshly distilled Benzaldehyde (the Benzaldehyde must also be free from benzoic acid) to the reaction mixture. Heat the mixture gently on a water bath for about 90 min. Cool the mixture to room temperature and then in ice bath. Benzoin begins to crystallize out. If the product separated as oil, heat the mixture until it becomes homogeneous again. Then allow it to cool more slowly than before. Scratching of the inner wall of the flask with a glass rod may be induce crystallisation.

Yield = 6 g (30%)

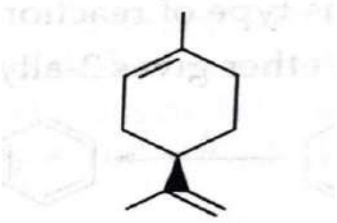
Literature melting point of benzoin is 134-36ºC.

❖ Green Context:

1) Deadly poisonous cyanide ion is replaced by thiamine hydrochloride
2) Reaction is carried out at a lower temperature.

5. Alternative Green solvents

• Extraction of D-limonene from orange peel using liquid CO2 prepared form dry ice.



D-Limonene

Principle: D(+)-Limestone, a water insoluble monocyclic monoterpene, is responsible for the fragrance of orange. This essential oil has traditionally been extracted by steam distillation or oraganic solvent extraction. During the past two decades, technical advances have been made in the industrial use of supercritical and liquid carbon dioxide instead of organic solvents. Noninflamability, nontoxicity and ready availability make CO_2 a useful green alternative.

❖ Materials required:

Orange peels, Zester, Dry ice, Copper wire, Centrifuge tube(with cap), Plastic measuring cylinder or beaker(250 ml)

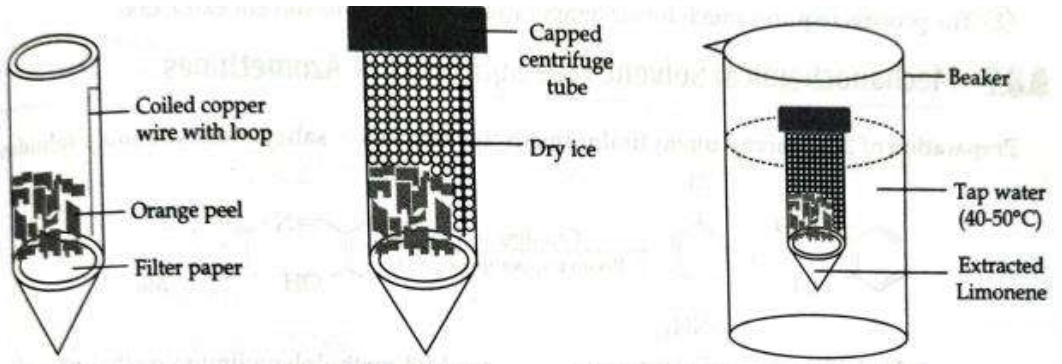


Figure 9.1 Limonene Extraction

❖ Procedure:

1) Grate 2.5 to 3.0 grams of orange peel from the outside coloured part of an orange with the smallest grating surface of the Zester.
2) Record the mass of a 15 mL centrifuge tube accurately.
3) Coil the end of a copper wire into a loop. Insert a small coffee filter paper into the loop. Put the copper wire into the tube in such a way that the loop reaches up to the top surface of the bottom conc. Of the tube. Ensure that no portion of the wire is left outside the tube. Record the mass of the tube with wire.
4) Add approximately 2.5 grams of grated orange peel to the test tube avoiding tight packing. Calculate the exact mass of orange peel added to the tube by subtracting the mass obtained in (3) from that obtained in (4).
5) Fill approximately two third of a 250 mL plastic graduated cylinder or a beaker with warm (40-50ºC) tap water.
6) Fill the rest portion of the centrifuge tube with crushed dry ice using a scoop and cap the tube tightly.
7) Immediately after capping, immerse the centrifuge tube, tapered end down, into the water in the cylinder or beaker (Figure.)
8) After~15 seconds, liquid CO_2 should appear.
9) After commencement of boiling the liquid should pass through the peel and reach the bottom of the tube.
10) After evaporation of the liquid and stoppage of gas evolution remove the tube from the cylinder (beaker) with tweezers and open the cap carefully.
11) Repeat the entire process three to four times with the same orange peel to obtain approximately 0.1 mL of D-limonene as a pale-yellow oil at the tip of the centrifuge tube.
    Calculate percentage recovery by multiplying the ratio of the mass of extracted oil to that of orange peel by 100.

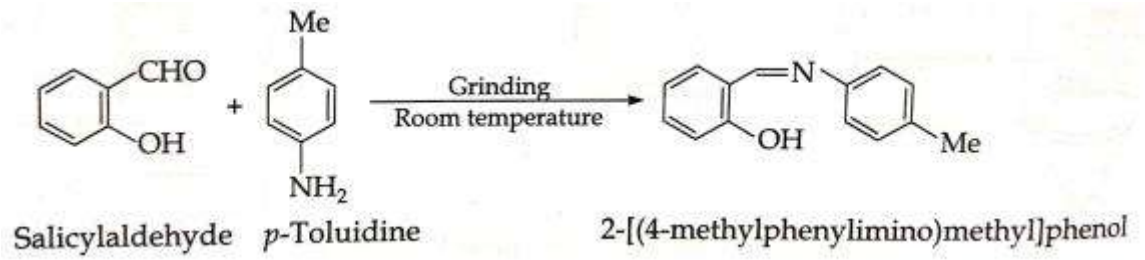
❖ Green context:

1) Omission of solvent in huge quantity.
2) The process requires much lower temperature compared to solvent extraction.

ii) Alternative Green solvents

Mechanochemical solvent free synthesis of azomethines.

Preparation of 2- [(4- methylphenylimino)methyl] phenol from salicylaldehyde and p-toluidine



❖ Chemicals Required:

Salicylaldehyde, p-toluidine, Ethanol

❖ Procedure:

Take 1.07 g of p-toluidine in a clean and dry mortar. Grind it with a pestle into a powdered form. Then add 1.22 g of salicylaldehyde to the powdered p-toluidine uniformly and grind the mixture thoroughly with a pestle for 5 minutes. Keep the reaction mixture at room temperature for 30- 35 minutes with a little grinding from time to time. A yellow mass will adhere to the inner surface of the mortar. Scrap off the yellow solid with the flat end of a small spatula. Record the weight of this solid. Recrystallise a portion of it from ethanol 2-[(4-methylphenylimino) methyl] Phenol appears as shinning yellow crystals.

Literature melting point of 2-[(4-methylphenylimino)methyl] phenol is 98-100 ^{0}C.

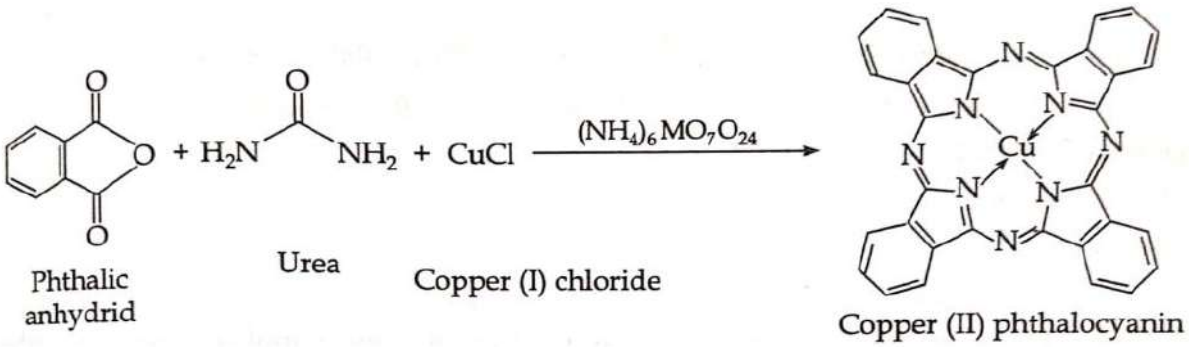
❖ Green Context:

1) Solvent- free conditions
2) Room temperature reaction

3) Easy product separation
4) Short reaction time.

6. Alternative sources of energy

i) Solvent free, microwave assisted one pot synthesis of phthalocyanine complex of copper (II).



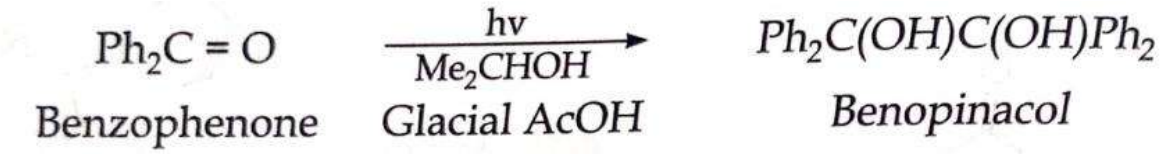
Chemicals Required	Apparatus required
Urea	Microwave system ETHOS 1600
Phthalic anhydride	Glass tube (40 cm, NS29)
Copper (I) chloride	100ml two-neck flask
Ammonium heptamolybdate	Magnetic stirrer
Conc. Hydrochloric acid (32%)	Magnetic sir bar
Ethanol	Reflux condenser
	Adapter with ground- glass joint and hose coupling

- **Procedure:** Fill the reaction flask with a mixture of 5.53 g (92.0 mmol) urea, 2.67 g (18.0 mmol) pthalic anhydride, 500mg (5.00 mmol) copper (i) chloride and 75 mg (0.061 mmol) ammonium heptamolybdate. Add two drops of water to the reaction mixture. Then install the reaction apparatus in the microwave system with the glass tube. Irradiate the reaction mixture for 10 minutes at a temperature restriction of 250 ^{0}C with 1000w. The melt will solidify to a porous violet mass.

Cool the solid to room temperature and break the lumbs in the reaction flask. Then add 50 ml water and 5 ml conc. Hydrochloric acid and install the flask in the microwave system with magnetic stirrer bar, temperature sensor and reflux condenser. Heat the mixture under stirring with 800 w for 10 minutes at 102 $^{0}_{C,}$ when excessive or unreacted substances are extracted from the solid. Cool the mixture and filter. Wash the solid with 50ml water, then with little ethanol, and dry. Crude yield: 2.40 g, violet solid. Take this violet solid with 50 ml ethanol in the two neck flask and install in the microwave system with magnetic stirrer bar, temperature sensor and reflux condenser. Heat with a radiation of 500 W under stirring at 80 ^{0}C for 10 minutes, whilst the side product dihydrophthalocyanine should be extracted from the solid. Cool the mixture to 50 ^{0}C, filter, wash the solid with 20 ml ethanol and dry in a desicator at reduced pressure.

- **Yield:** 2.15 g (3.73 mol, 83 %). For a pure product no melting or decomposition can be noticed blow 200 ^{0}C. The side product dihydrophthalocyanine melts with decomposition 195 – 197 ^{0}C.
- **Green Context:**
  1) Use of alternative energy source for heating purpose.
  2) Omission of hazardous organic solvent (trichlorobenzene).

ii) Photo reduction of benzophenone to benzopinacol in the presence of sunlight.



- **Chemicals required:**

Benzophenone, Isopropanol, Glacial acetic Acid

- **Procedure:**

Dissolve 2.5 g of benzophenone in 10ml of Isopropanol in a dry test tub. Add one drop of glacial acetic acid to it. Fill the test tube with Isopropanol (to exclude air from the reaction vessel) and plug it tightly. Place the reaction mixture in bright sun light. After 5-6 h colorless crystals of benzopinacol will start to deposit along the sides of the test tube. Expose the reaction mixture to bright sun light for 4-5 days for completion of the reaction. Filter of the white crystalline solid and dry it in air. Record the yield of isolated benzopinacol.

Literature melting point of benzopinacol is 182 ^{0}C.

❖ **Green Context:**

1) Use of safe chemicals and reaction conditions.
2) Use of solar energy as renewable source of energy.
3) The product benzopinacol may be used in pinacol – pinacolone rearrangement to obtain Benzopinacolone.

DSE4P: Lab

1. Free radical solution polymerization of styrene / methyl methacrylate (MMA) / methyl acrylate (MA) / Acrylic acid (AA)

Polystyrene:

Plastics are widely used in modern society because of its low cost, strength, durability and versatile properties. One such plastic material, polystyrene finds many applications from thermal insulator to food packaging materials. Polymers are generally classified into thermoplastics and thermosetting based on their properties at different temperature. Thermoplastics are preferred over thermosetting polymers because of its low processing cost. Polystyrene is an aromatic polymer and there are two groups. General purpose polystyrene (GPPS) and high impact polystyrene (HIPS). The environmental degradation and impact caused by polymers can lowered by using recycled polymers.

Polystyrene is a polymer obtained from monomer styrene, which is a hydrocarbon obtained from petroleum. Polystyrene is used in solid form and it is naturally transparent material, however it can be coloured by adding colourants. Being thermoplastic polymer, polystyrene is in solid form at room temperature but flows if heated above 100°C (its glass transition temperature). It gets solidified again when it is cooled. There are many methods available for

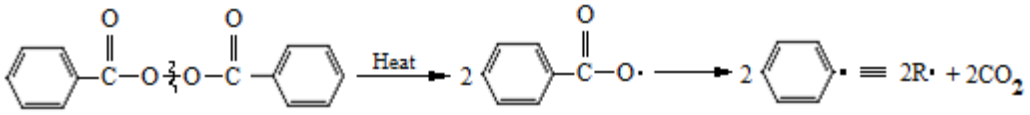
the preparation of polymers by radical means. Polystyrene can undergo copolymerisation easily with monomers such as, vinyl chloride, butadiene, acrylonitrile, acrylates among others giving products with unique properties. The thermal and mechanical properties of modified polystryene finds many applications in industries which improves the elasticity and performance of materials.

Materials and methods:

Styrene monomer and Benzol peroxide initiator was purchased from SRL, India. The boiling point of the styrene monomer is around 145°C. Benzoyl peroxide decomposes with the cleavage of its oxygen-oxygen bond at a temperature between 80 and 90°C. First 200 mg of benzoyl peroxide initiator was weighed accurately and transferred to a 100ml glass beaker. Then 15 ml of styrene was poured into beaker and stirred using magnetic stirrer until all the benzoyl peroxide get dissolved. The beaker was placed on heating mantle and heated between 80oC to 90oC. The beaker was continuously stirred till the polymerisation process gets over. After few minutes, the beaker started bubbling with emanation of white smoke. Also volume in the beaker decreased overtime with the increase in the viscosity of solution. To determine completeness of the polymerisation process, a small amount of the solution was extracted using a glassrod and a fibrous string was observed. Then the polymer was poured into a petridish to cool down and solidify. Polystyrene solidifies in the beaker itself while pouring and was difficult to remove. The solidified polystyrene was broken into pieces and used for characterization.

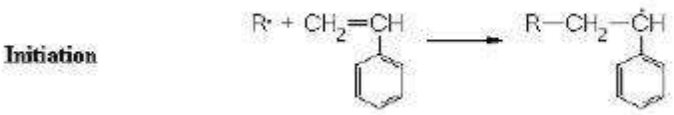
Mechanism:

Styrene is polymerized by a free-radical polymerisation mechanism. In this polymerization process the initiator benzoyl peroxide decomposes at 80-90oC with the cleavage Oxygen-Oxygen bond to give two benzoyloxy radicals, which then losses CO_2 to form two benzyl radicals

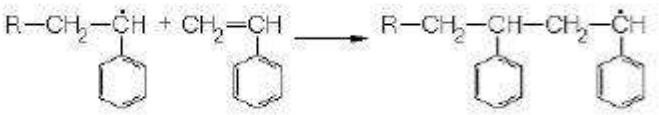


Benzoyl peroxide

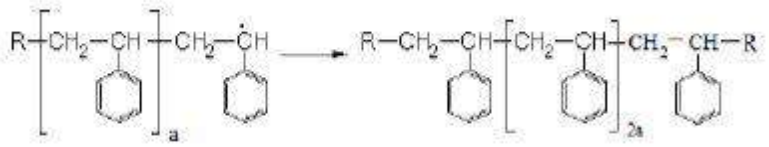
The initiator radicals (R*) add to the C=C bond of styrene to produce a new, benzyl-type free-radical, as shown below.



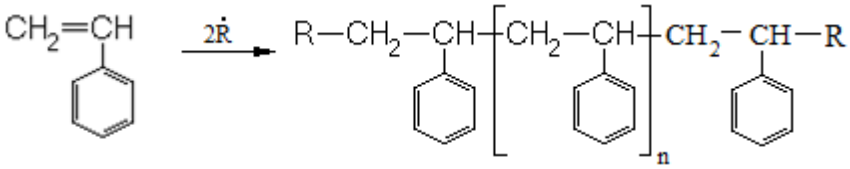
This radical then adds to another molecule of styrene, and the process continuous during which the polymer chain starts to grow

Propagation 

There is a possibility of addition of 5000 monomer units before the chain is terminated. The contribution to the molecular weight by radical is negligible (0.02%). At last growth of polymer chain is terminated by the combination of two radicals (either both polymer radicals or one polymer radical and one initiator radical).

Termination 2 

The overall equation for the polymerization process is as follows

(n+2) 

Result and discussion

The polystyrene was characterized by FTIR (Figure 1). The absorption bands at 3500-3000 cm^{-1} are assigned to =C-H aromatic stretching vibration. The peaks at 2900 cm^{-1} and 2800 cm^{-1} are assigned to $-CH_2$ and –CH aliphatic stretching vibration. The bands at 1630 cm^{-1} and 1550 cm^{-1} indicates deformation vibration of C-H in benzene ring. The bands at 750 cm^{-1} and 699 cm^{-1} can be attributed to C-H out of plane bending vibration of benzene ring.

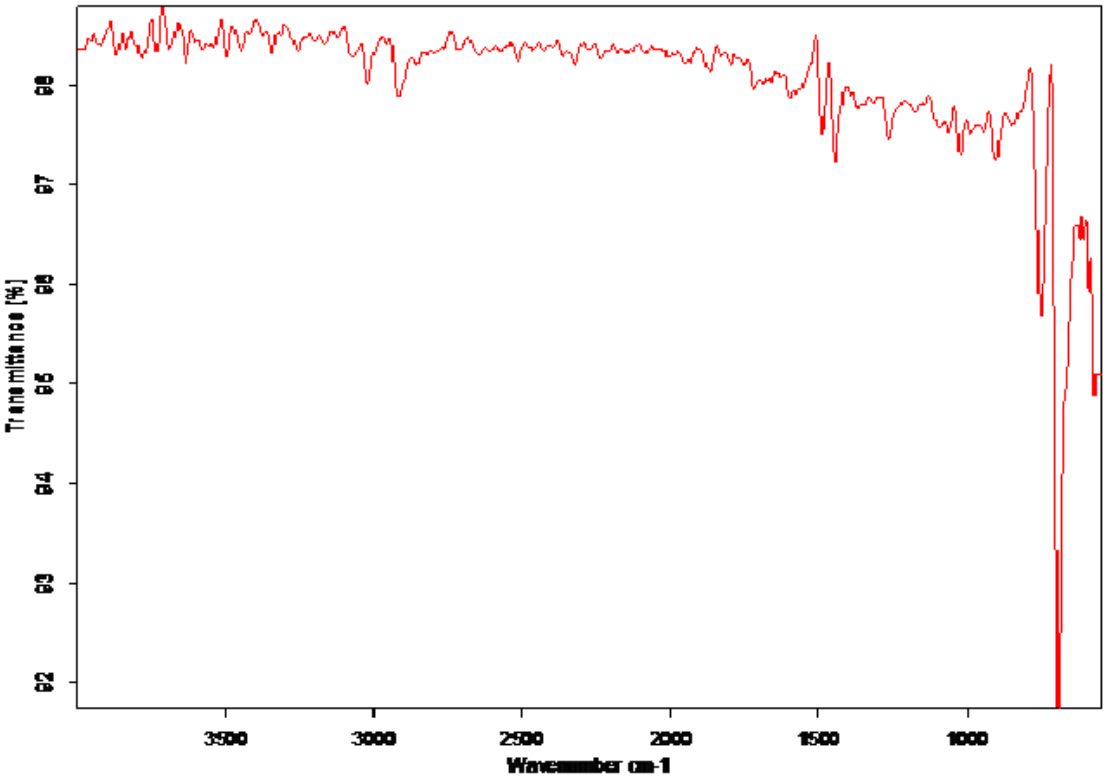
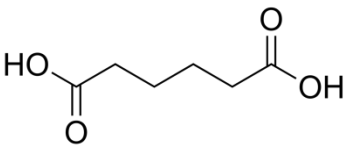


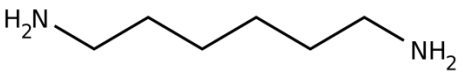
Figure 1. FTIR Spectrum of Polystyrene

2. Preparation of Nylon 66

Nylon 66 is a polyamide obtained by condensation polymerisation. The monomers of nylon 66, are adipic acid and hexamethylene diamine . Adipic acid is a dicarboxylic acid with six carbon atoms while hexamethylenediamine is a diamine with same number of carbon atoms.

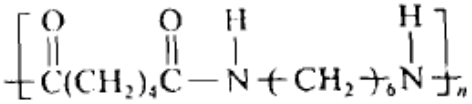


Adipic acid



Hexamethylene diamine

The resulting dimer has got two functional groups one carboxylic acid and the other amino group. This dimer can further combine with diamine and diacid on the acidic and amino functional group respectively or with another dimer molecule. This process continues to generate the polymer.



Nylon 66

Materials required:

Adipic acid

Hexamethylene diamine

Thionyl chloride

Dimethyl formamide

Carbon tetrachloride

Sodium hydroxide

Alcohol

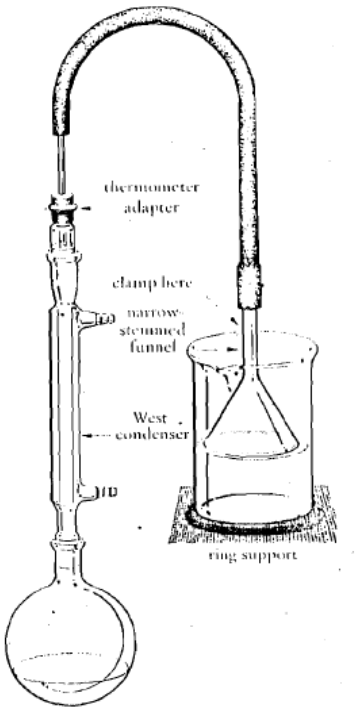
Round bottom flask 50 cm^3

Air condenser

Beaker 100 cm^3

Beaker 400 cm^3

Procedure:



Preparation of adipoyl chloride:

1. Set up the apparatus as shown in the figure. For this take a 50 cm^3 round bottom flask and fit an air condenser on to it. Take a glass funnel and inset its stem into a piece of rubber tubing. In sent a glass tube in the other end of the rubber tube and fit it on the air condenser as shown in the Fig. Put the inverted funnel into a beaker containing water or NaOH solution.

2. Take l g of adipic acid and 3-4 drops of dimethyl formamide in the flask and add 1 cm^3 of thionyl chloride dropwise with constant stirring.

3. Heat the flask on water bath for about 15 minutes. By this the evolution of gas ceased and the solid will disappear.

4. Allow the flask to cool a little and then add about 30cm^3 of $CC1_4$ to it. Mix thoroughly to dissolve the product obtained.

5. Transfer this solution to a 100 cm^3 beaker. Wash the flask thoroughly with additional 20 cm^3 of CCl_4, and transfer the washings to the beaker.

6. In a separate 100 cm^3 beaker take 1.1 g of hexamethylene diamine and 0.75 g of NaOH in 25 cm^3 of water and mix to dissolve them.

7. Carefully transfer the aqueous solution of hexa methylene diamine to the beaker containing.adipoyl chloride.

8. You will observe the formation of a film of nylon 66, at the interface of the two liquids. Carefully insert a glass rod or a copper wire into the solution and pull out the polymer formed. a forshape can be used to do so.

9. Wrap the polymer around a clean test tube. Rotate the test tube to pull more and more of nylon.

CAUTION ! Avoid handling the polymer with hands. At this stage because the reactants specially adipoyl chloride and the solvent ($CC1_4$) both are harmful.

Do not pour the unreacted polymerization mixture in the sink. Stir it with a glass rod till there is no more polymerization. You may recover this crop of the polymer also and discard the rest of the solvent as usual.

10. Wash the polymer thoroughly with water. For this place the test tube, with polymer wrapped around, under the running tap water for about 5 minutes. Alternatively you may first wash the polymer with 50 % aqueous alcohol (alcohol:H_2O : 1:1) followed by tap water.

11. Dry the polymer in air or in the folds of filter paper. Weigh it and report the yield.

12. Submit a sample of the polymer so prepared to your examiner.

Result:

..... g of nylon 66 was obtained from ..... g of adipic acid.

3. Interfacial polymerization, preparation of polyester from isophthaloyl chloride (IPC) and phenolpthaelin:

Materials required:

Phenolphthalein

Sodium hydroxide

Tetraethylammonium chloride

Terephthaloyl chloride

1,2-dichloroethane

Hexane

Interfacial method:

1. Dissolve Phenolphthalein (0.01 mol, 3.18 g), 0.80 g of sodium hydroxide, and 1.0 g of tetraethylammonium chloride in 100 ml of water in a 1 qt blender jar. Cover the top of the jar with aluminum foil and raise a corner temporarily to permit introduction of the acid chloride.
2. Start the blender at an intermediate speed controlled by a variable transformer.
3. Introduce a solution of 2.03 g (0.01 mol) of terephthaloyl chloride in 30 ml of distilled 1,2-dichloroethane (Caution! Many halogenated solvents are toxic and should be used with care.) contained in a 50 ml Erlenmeyer flask, into the blender jar rapidly and smoothly and simultaneously increase the stirring speed near to maximum. Close the top at once and continue the stirring for a minimum of 5 min.
4. The initial blood-red color fades rapidly and should reduce to a tinge of pink.
5. Add hexane (250 ml) to precipitate the polymer, collect on a medium-porosity sintered-glass funnel and wash repeatedly with distilled water by stirring vigorously in the blender and filter.
6. Dry the washed granular polymer in a vacuum oven in a shallow glass dish at 60-80°C for 15-20 h.
7. Weigh and report the yield of polymer.
8. Submit a sample of the polymer so prepared to your examiner.

Result:

..... g of polyester was obtained.

Redox polymerization of acrylamide:

Materials required:

Acrylamide

Ferrous ammonium sulfate (Mohr's salt)

Hydrogen peroxide

Conc. HCl

Distilled water

Procedure:

1. The first step involves dissolving acrylamide in water. This can be done in 3 different concentrations. (all beakers contain 50 ml water)

a. In beaker 1, dissolve 1 gm of acrylamide.

b. In beaker 2, dissolve 3 gm of acrylamide.

c. In beaker 3, dissolve 8-10 gm of acrylamide.

[NOTE: The dissolution process is endothermic. You will notice the beakers getting cold as the acrylamide is dissolved.]

2. Add 0.08 g of Mohr's salt (or 0.06 g of $FeSO_4.7H_2O$) to the beaker and dissolve it by stirring.

3. Add 5ml of H_2O_2 to the solution while stirring. Stir for a few seconds then let the beaker rest.

[NOTE: Ferrous (Fe^{2+} salts are green in color. Adding H_2O_2 oxidizes the ferrous ions to Ferric (Fe^{3+}) ions which cause the solution to have a rusty color. The reaction produces $OH^{\cdot}$ radical which initiate the polymerization reaction of acrylamide. The polymerization process is exothermic and you will see a sharp increase in the temperature of the beaker. With time you will observe that the rusty color of the solution becomes lighter. This may be because the free Fe^{3+} ions combine with free OH^{-} ions to form hydroxides which are usually lighter in color.

CAUTION: There is chance of the beaker with highest concentrations to overflow because the heat released during reaction can cause the water in the solution to boil. Add more water to cool the reaction if this is needed.]

4. The highest concentration will turn viscous first. (Beaker 3 > Beaker 2 >Beaker 1)

5. After 25-30 mins, take a 200 ml beaker (with a magnetic stirring rod) and add 100 ml of isopropyl alcohol. Add a few drops of conc. HCl to this beaker and place the beaker on a magnetic stirrer.

6. With vigorous agitation (ensuring no spillage), add the poly-acrylamide reaction mixture from beaker 3 drop wise to the 200ml beaker. Decant and display the polymer formed. Follow the same process for beakers 2 and 1.

7. Collect the polymer and dry in an oven.

8. Weigh and calculate the yield.

Result:

..... g of polyacrylamide was obtained from …… g of acrylamide.

SAFETY:

Acrylamide is toxic. It is a known neurotoxin in high concentration and for long exposure times. Hence proceed with caution while conducting the experiment. Wear gloves, goggles and lab coat. Please read the wiki page of acrylamide and poly-acryalmide for more information. Acrylamide is present in cigarette smoke, pickles, coffee, fried, baked and microwaved foods, olives, prunes, dried pears, beef jerky. It is a product of browning during cooking apparently. In any case, wash your hands after this demo before you eat or smoke to be on the safe side.

Precipitation polymerization of acrylonitrile:

Materials required:

Acrylonitrile

$Na_2S_2O_5$ solution (5% in water)

$FeSO_4.7H_2O$

H_2S0_4

$K_2S_2O_8$

Procedure:

1. Into 250 ml round-bottomed flask, 175 ml water is added and nitrogen is bubbled for about 1/2 h.
2. 15 ml acrylonitrile, 0.5 ml of $Na_2S_2O_5$ solution (5% in water) and 2.5 ml of $FeSO_4.7H_2O$, solution (10 mg in 100 ml water+2 ml conc. H_2S0_4) are introduced and subsequently 2.5 ml of $K_2S_2O_8$ solution (5% in water) is added and mixed briefly at 20°C.
3. The mixture is stirred at 20°C for about 1 h.
4. The precipitated polymer is filtered, washed with water then with methanol and dried at 50°C in vacuum.
5. Measure the weight and calculate the yield.

Result:

..... g of polyacrylonitrile was obtained from …… g of acrylonitrile.

Preparation of urea-formaldehyde resin:

Chemical required:

Urea (2g)

40% aq formaldehyde solution or formalin (5 mL)

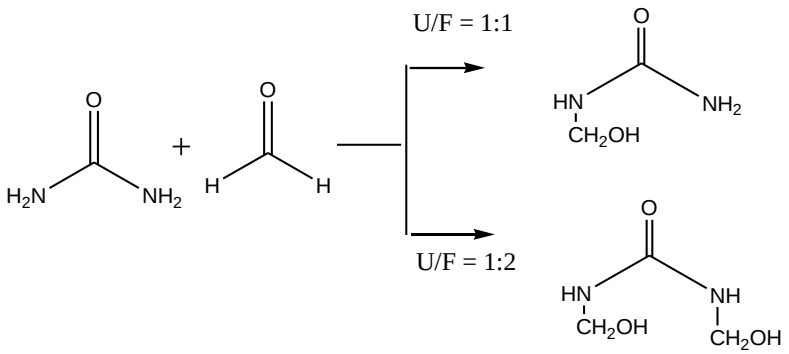
Conc. H_2SO_4 (3-4 drops)

Theory:

Urea formaldehyde resins are formed by condensation of urea and formaldehyde in acidic medium in following steps:

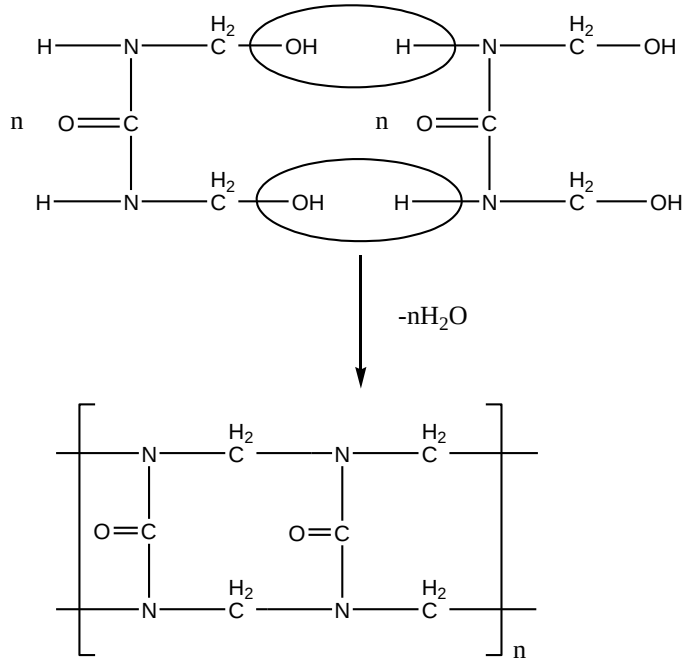
Step 1. Formation of methylol urea derivative:

Initially urea and formaldehyde react to form methylol urea derivatives depending upon formaldehyde (U/F ratio).



Step 2. Polymerization of methylol urea:

Several molecules of methylol urea derivatives condense with loss of water molecules to form a highly cross linked urea formaldehyde resin.



Procedure:

1. Take a 5 mL of 40% aqueous formaldehyde solution in a 100 mL beaker.
2. To this add 2 g urea powder. Stir with a glass rod to make a saturated solution.
3. Add a few drops of conc. H_2SO_4 and stir vigorously till a white solid mass is formed.
4. Filter the residue and wash it several times with distilled water to remove any acid.
5. Dry the residue in folds of filter paper or in an oven and weigh.
6. Report the yield of urea formaldehyde polymer formed.

Observation:

Weight of empty watch glass = W_1 g

Weight of watch glass + poymer formed = W_2 g

Weight of polymer formed = $W_2 - W_1$ g

Result:

Weight of urea formaldehyde resin = W g

Preparation of novalac resin/resole resin:

Chemicals required:

Phenol (2g)

40% aq formaldehyde solution or formalin (2.5 cc)

glacial acetic acid (5 ml)

Conc. HCl (8ml).

Theory:

Phenol formaldehyde resin or P-F resin or phenolic resins (also called phenoplasts) are important class of polymers which are formed by condensation polymerization of phenol and formaldehyde in acidic or alkaline medium.

Procedure:

1. Place 5 ml of glacial acetic acid and 2.5 ml of 40 % aq formaldehyde solution in a 100 cc beaker. Add 2 g phenol safely.
2. Add conc. HCl drop wise with vigorous stirring (Preferably in a magnetic stirrer), and wrap it by a glass rod till a pink coloured gummy mass appears.
3. Wash the pink residue several times to make it free from acid.
4. Filter the product and weigh it after drying in folds of a filter or in an oven.
5. Report the yield of polymer formed.

Observation:

Weight of empty watch glass = W_1 g

Weight of watch glass +poymer formed = W_2 g

Weight of polymer formed = $W_2 - W_1$ g

Result:

Weight of phenol formaldehyde resin = W g

Resole resign:

1. Dissolve phenol crystals in formaldehyde (formaldehyde to phenol ~ 1.5 ratio) (4 gm phenol, 6-10 grams phenol formaldehyde)
2. Dissolve NaOH in water (concentrated). Add ~ 10ml.
3. Combine two solutions into a test tube and bring to a boil.

NOTE: Make sure you only have a little quantity of the solution in the test tube for safety reasons.

SAFETY: Be careful while boiling as there is a tendency for the boiling water to squirt out.

4. Solution will turn brown then orange. Finally a pink/white precipitate will form on the sides of the vessel.

5. Filter the product and weigh it after drying in folds of a filter or in an oven.

6. Report the yield of polymer formed.

Observation:

Weight of empty watch glass = W_1 g

Weight of watch glass +poymer formed = W_2 g

Weight of polymer formed = $W_2 - W_1$ g

Result:

Weight of phenol formaldehyde resin = W g

Polymer Characterization:

1. Determination of molecular weight by viscometry:

Polyacrylamide-aq $NaNO_2$ solution:

The measurement of the viscosity of polymer solutions is called viscometry and the apparatus used is called the viscometer. Study can be done using three viscometers: falling ball viscometer, capillary (Ubbelohde) viscometer and Couette viscometer.

Capillary viscometer, intrinsic viscosity, Mark-Houwink empirical correlation :

A capillary viscometer is used to get a measure of the viscosity of very dilute polymer solutions. The solution is allowed to flow through a capillary of known diameter under the action of a pressure drop as a fully developed laminar flow and the time taken to flow through a given length is measured. For a dilute solution, the measured time (t_c) at a given temperature is proportional to the viscosity of the solution (η_c) at that temperature. At the same temperature, the flow time (t_s) for the solvent through the same capillary is also measured. t_s is proportional to the viscosity of the solvent (η_s). Thus,

$$\frac{\eta_c}{\eta_s} = \frac{t_c}{t_s} \qquad \ldots(1)$$

Thus, capillary viscometery gives only a relative measure of the viscosity and not an absolute one. Let us define a couple of terms before proceeding

Specific viscosity = $\eta_{sp} = \frac{\eta_c}{\eta_s} - 1$ …(2)

Intrinsic viscosity = $[\eta] = \lim_{c\to 0} \frac{\eta_{sp}}{c} = \lim_{c\to 0} \frac{1}{c} \ln \frac{\eta_c}{\eta_s}$ …(3)

where, c is the concentration of the polymer solution. Thus, if the specific viscosity is determined experimentally for polymer solutions of different concentrations (but same molecular weight), then the intrinsic viscosity can be determined by extrapolating the plot of $\frac{\eta_{sp}}{c}$ vs. c or $\frac{1}{c} \ln \frac{\eta_c}{\eta_s}$ vs. c

This intrinsic viscosity can be used to determine the molecular weight by using a previously determined Mark-Houwink empirical correlation for that polymer in a given solvent and temperature. The general form of the Mark-Houwink relation is

$[\eta] = K'M^a$ …(4)

where, [η] is reported in cm^3/g and the molecular weight is obtained in units g/mol. The range of a is $0.5 \leq a \leq 0.8$. Consider some examples:

Polymer solution	K'	a
PAM in 0.05 M $NaNO_3$ at 30 C	0.0063	0.800
NaPAA in 0.05 M $NaNO_3$ at 30 C	0.0281	0.770
PEO in 0.05 M $NaNO_3$ at 30 C	0.0120	0.784

A short note on the $\frac{\eta_{sp}}{c}$ vs. c and $\frac{1}{c} \ln[\frac{\eta_c}{\eta_s}]$ vs. c plots: These plots are typically found to be linear and describable by the following Huggins' equations:

$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c$ …(5)

$\frac{1}{c} \ln[\frac{\eta_c}{\eta_s}] = [\eta] + k''[\eta]^2 c$ …(6)

k' and k'' are called the Huggins' constants.

Procedure:

A. Intrinsic viscosity determination by Ubbelhode viscometer:

1. Prepare 0.05 M $NaNO_3$ and 0.02% NaN_3. Prepare PAM solutions (C_o = 4%, 8% or 12%) to form diluted solutions of concentration Ci such that

$C_1 = 0.0010$ g/cm^3

$C_2 = 0.0015$ g/cm^3

$C_3 = 0.0020$ g/cm^3

$C_4 = 0.0025$ g/cm^3

2. Prepare the water bath such that the bath is at a uniform temperature of 30°C.

3. Use the Ubbelhode viscometer (as described below) to measure the flow time of the solvent (t_s). Repeat the measurement. The two measurements of the flow time should agree within 0.5 sec.

Using the Ubbelohde capillary viscometer:

This method is used for dilute solutions. We shall be using Ubblehode viscometer of size OC or OB. These sizes are used for solutions in the following viscosity ranges:

Size	η(cStokes)/ t (sec)	η range (cStokes)
OC	0.003	0.6 to 3
OB	0.005	1.0 to 5

Let us consider the case where a concentrated solution of C_o is diluted to concentration C_i by using a solvent and we are to determine the viscosity of the solution of concentration C_i. The procedure is as follows (Note: in the following the sample could be solvent or any of the solutions):

a) Clean the viscometer using suitable solvents (water, then ethanol) and dry by passing clean, dry filtered air through the instrument to remove the final traces of solvents.

b) Charge the viscometer by introducing the sample through tube G into the lower reservoir; introduce enough sample to bring the level between lines J and K (this is about 15 ml).

c) Place the viscometer into the holder, and insert it into the constant temperature bath. Vertically align the viscometer in the bath if a self-aligning holder has not been used.

d) Allow approximately 15-20 minutes for the sample to come to bath temperature.

e) With the side vent tube (B) closed (using a finger) use a suction bulb on tube A to pull liquid upward through the capillary measuring bulb (E) until it is above the top mark and half way into bulb C. Remove the suction bulb. Remove the finger from the side vent (B) and immediately place the finger over tube A until the sample drops away from the lower end of the capillary into bulb I. Then remove the finger and measure the efflux or flow time.

f) To measure the flow time, allow the liquid sample to flow freely down the mark D (start the stopwatch when the meniscus drops below this top mark) , measuring the time for the meniscus to pass from mark D to mark F (stop the stop watch when the meniscus drops below the bottom mark F).

g) Without recharging the viscometer, repeat the measurement of the flow time.

h) The flow times and concentrations are used to calculate the intrinsic viscosity.

4. Empty solvent from the viscometer and add 5ml of next PAM solution to be tested, swirl to collect drops of solvent and then drain the solution.

5. For each solution of concentration C_i: Use the Ubbelhode viscometer to measure the flow time (t_i) of the solution of concentration C_i. Repeat the measurement. The two measurements of the flow time should agree within 0.5 sec. The flow times for the solutions will be greater than that of the solvent.

Observations and Calculations:

1) Record the calculations for the dilutions in the lab notebook.

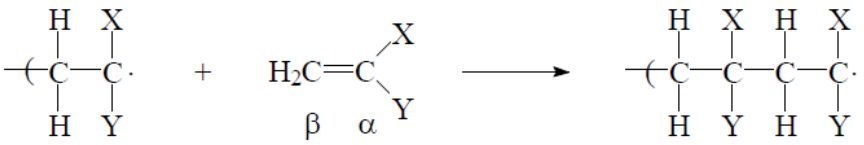
2) Tabulate the data for each run with the Ubbelhode viscometer. Use the equations in the section "Brief Background" to perform calculations.

3) Plot $\frac{\eta_{sp}}{c}$ vs. c and $\frac{1}{c}\ln\frac{\eta_c}{\eta_s}$ vs. c to calculate the intrinsic viscosity. Indicate on each plot your synthesis conditions (% acrylamide). Also calculate the Huggins constants.

4) Use equation 4 to calculate the molecular weight.

Determination of the viscosity average molecular weight of poly vinyl alcohol and the fraction of head to tail monomer linkages in the polymer:

PVOH is one of the few polymers that are water soluble. The solubility is strongly dependent on the degree of hydrolysis. A fully hydrolysed grade is soluble only in hot to boiling water, but remains soluble once the solution is cooled. However, partially hydrolysed grades (70% - 80%) are only soluble between 10°C - 40°C. The PVOH precipitates above 40°C. An interesting aside is that aqueous solutions of highly hydrolysed grades of PVOH increase in viscosity on storage. This does not occur in solutions of partially hydrolysed grades of PVOH. Typically, vinyl monomers add to the growing radical-ended polymer by the β-carbon of the vinyl group.

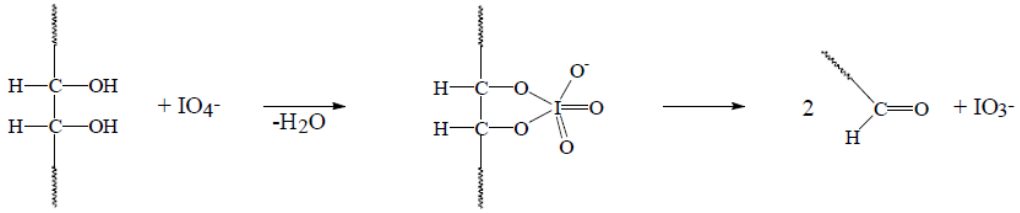


This is termed a "head-to-tail" addition. However, on occasion, a monomer unit will add through the α-carbon atom in a "head-to-head" fashion. In the case of PVOH, such a "head-to-head" linkage would yield a 1,2-diol in the polymer backbone as opposed to a 1,3-diol which is typically produced.

1,3-diol 1,2-diol

Head-to-tail addition is favoured over head-to-head addition on both steric and resonance grounds. From a steric stand point, approach of the vinyl group via the unsubstituted carbon (β-carbon) is sterically favoured over the a-carbon. On resonance grounds, the substituents on the α-carbon are able to stabilize the α-carbon radical, whereas they are not able to do this for the β-carbon radical. Therefore, for most vinyl polymers, especially poly(vinyl esters), there are typically fewer than 5% of head-to-head linkages.

For our purposes, the 1,2-diol linkages in PVOH are interesting in that they can be selectively cleaved by periodate ions.



The result, clearly, is that the polymer chain is broken into two shorter chains, and the molecular weight of the PVOH is decreased. It is this reduction in molecular weight that we will use to determine the number of head-to-head linkages in a commercial sample of PVOH.

The change in molecular weight of the PVOH upon cleavage of the 1,2-diol linkages will manifest itself in a reduction in the viscosity, of the polymer solution. We will employ a viscometer called an Ostwald viscometer (Figure 1) to determine this change in viscosity.

The time, t, taken for the meniscus of the solution to pass from mark a to mark b is measured, and the relative viscosity (η/η_o) is calculated from

$$\frac{\eta}{\eta_0} = \frac{t}{t_0} \qquad \ldots(1)$$

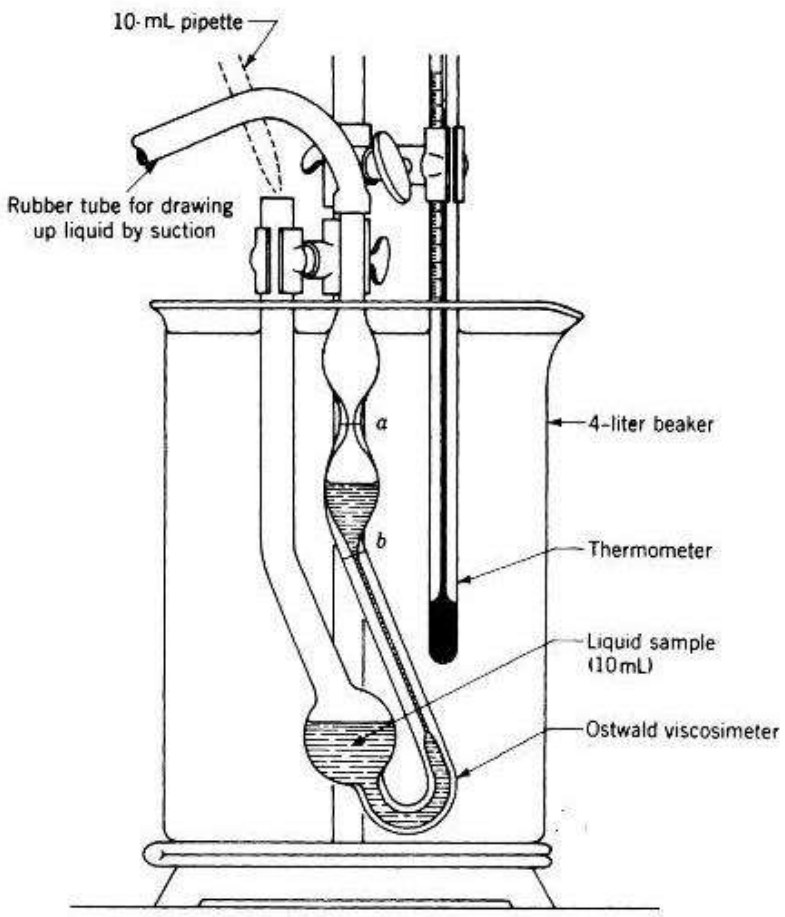
where t and to are the flow times in the viscometer for the solution and the solvent, respectively.

The intrinsic viscosity is defined as the ratio of the specific viscosity to the concentration, in the limit of zero concentration.

$$[\eta] = \lim_{c \to 0}\left[\frac{\eta_{sp}}{c}\right] = \lim_{c \to 0}\left[\frac{1}{c} \times \frac{\eta - \eta_o}{\eta_o}\right] \qquad (2)$$

A plots of η_{sp}/c against c yields a straight line at low concentrations, and can be used to determine [η].

$$[\eta] = K\overline{M}_V{}^a \qquad (3)$$



To calculate the ratio, Δ, of head-to-head linkages to the total number of monomer units. It is equal to the increase in the number of molecules present in the system, divided by the total number of monomer units represented by all molecules in the system.

$$\Delta = \frac{H-H\ linkages}{total\ monomer units} \qquad (4)$$

The total number of monomer units in a polymer chain is equal to $\overline{X_n}$, the total number of head-to-head linkages in a polymer chain is equal to the number of new segments formed $\frac{\overline{X_n}}{\overline{X_{n'}}}$ less one.

where $\overline{X_{n'}}$ is the total number of monomer units in the cleaved polymer chain; therefore, for all the molecules in the system (N_o), equation (4) becomes

$$\Delta = \frac{N_o\left(\frac{\overline{X}_n}{\overline{X'}_n} - 1\right)}{N_o\,\overline{X}_n} \qquad (5)$$

This simplifies to become

$$\Delta = \frac{\frac{\overline{X}_n}{\overline{X'}_n} - 1}{\overline{X}_n} \qquad (6)$$

which can be rewritten in terms of molecular weights, bearing in mind that

$$\overline{M}_n = \overline{X}_n M_o$$

$$\Delta = M_o \left[\frac{1}{\overline{M}_n} - \frac{1}{\overline{M'}_n} \right] \qquad (7)$$

where $\overline{M_n}$ and $\overline{M_n}$, are the number-average molecular weights before and after degradation, and M_o is the monomer weight (44 g/mol). Flory and Leutner also showed that $\bar{M}_v/\bar{M}_n$=1.89. Hence, we can write

$$\Delta = 83 \left[\frac{1}{\overline{M'}_v} - \frac{1}{\overline{M}_v} \right] \qquad (8)$$

which permits us to use viscosity average molecular weights directly.

Experiment:

Clean the viscometer with a chromic acid cleaning solution, rinse copiously with distilled water, and dry with acetone and air. Immerse in a 25°C bath to equilibrate. Place a small flask of distilled water (~100 mL) in the bath.

Preparation of the STOCK solution:

Weigh out accurately on a watch glass 4.0 to 4.5 g of the dry polymer. Add it slowly, with stirring (use a stir bar, and a stirrer/hotplate), to about 200 mL of distilled water in a beaker. When adding the polymer, carefully sift the powder onto the surface and stir gently so as not to entrain bubbles or produce foam. When all the polymer has been added, stir for an additional 10-15 minutes, and then increase the temperature to about 95°C to dissolve the

PVOH. Let the solution cool and transfer it carefully and quantitatively into a 250-mL volumetric flask. Avoid foaming as much as possible by letting the solution run down the side of the flask. Make the solution up to the mark and mix by slowly inverting a few times.

Pipette 50 mL of the stock solution into a 100-mL volumetric flask, and make up to the mark with distilled water. Mix, and place in the 25EC bath to equilibrate. Rinse the pipette very thoroughly with water and dry with acetone and air. Call this sample “UNCLEAVED A”. To cleave the polymer, pipette 100 mL of the STOCK solution into a 250-mL Erlenmeyer flask and add up 0.50 g of solid KIO4. Warm the flask to about 70 oC (on a hotplate), and stir until all the salt is dissolved. Clamp the flask in a thermostated bath and stir until the solution is at

25°C. Transfer quantitatively to a 100-mL volumetric flask. Place in the 25°C bath to equilibrate. Call this sample "CLEAVED A". (This operation can be carried out while viscosity measurements are carried out on the uncleaved polymer.)

At this point, two solutions have been prepared: 100 mL of each of two aqueous polymer solutions, one with a concentration of uncleaved polymer ~0.9 g/100 mL (UNCLEAVED A), and one with a concentration of ~1.8g/100mL of polymer cleaved with periodate (CLEAVED A). To obtain a second concentration of each material, pipette 50 mL of the "A" solutions into 100-mL volumetric flasks and make up to the mark with distilled water (UNCLEAVED B and CLEAVED B). And now make a third concentration of each polymer solution by pipetting 50 mL of the "B" solutions (~0.45 g/100 mL) into 100-mL volumetric flasks and make up to the mark with distilled water (UNCLEAVED C and CLEAVED C). Place all solutions in the thermostat bath to equilibrate. The viscosity of all three solutions of each polymer (six in total, uncleaved and cleaved) should be determined.

The recommended procedure for measuring the viscosity is as follows:

1. The viscometer should be mounted vertically in a constant-temperature bath so that both reference marks are visible below the water level. The temperature should be maintained within (25 ± 0.1)°C during a run.

2. Pipette the required amount of solution (or water) into the viscometer. Immediately rinse the pipette with copious amounts of distilled water, and dry it with acetone and air before using again.

3. Using a pipette bulb, draw the solution up to a point above the upper reference mark. Release the suction and measure the flow time between the upper and lower marks with a stopwatch. Obtain two or more runs with the same filling of the viscometer. Three runs agreeing within about 0.5second should suffice.

4. Each time the viscometer is emptied, rinse it very thoroughly with distilled water, then dry with acetone and air. Be sure to remove all polymer with water before adding acetone.

Calculations

For each of the polymer solutions studied, tabulate t/t_o and the concentration c in grams of polymer per 100 mL of solution. Then calculate η_{sp}/c. Plot η_{sp}/c versus c and extrapolate linearly to $c = 0$ to obtain $[\eta]$ for the original and degraded polymer.

Calculate Mv for both the original polymer and the degraded polymer, and obtain a value for Δ.

3. Determination of molecular weight by end group analysis: Polyethylene glycol:

Polymers are a special form of macromolecules They are compounds of high molecular weight formed by combining a large number of small molecules. The small molecules, called monomers, may all be of one type, as in the compound used in this experiment, or may be of different types.

The ends of PEG are alcohol groups, which may be analyzed by a reaction known as esterification. In an esterification the -OH reacts with an organic acid, or, more commonly, with a more reactive derivative of the acid. In this experiment the anhydride of 1,2,4,5-benzenetetracarboxylic acid, known commonly as pyromellitic dianhydride, or PMDA for short, will be used. The reaction must be conducted in a nonaqueous solvent, and, because of its low volatility and desirable solvating properties, N,N-dimethyl formamide, DMF, is a good choice. A catalyst is also required, and in many esterification procedures pyridine, a rather foul-smelling organic base, is used. However, for the reaction of alcohols with PMDA it has been found that imidazole, IMDA, a very soluble solid with no odor, has at least equal catalyzing power.

Procedure:

1. Weigh a sufficient quantity of PMDA (FW=218.12) to prepare 100 mL of 0.2 M solution, and dry at160°C for 2 hours. Dissolve the solid in 100 mL of DMF. Your glassware must be dry before you start. Do not add any water to this solution or to any of the samples until specified in the procedure. If it is necessary to store the solution for a week, obtain a small bottle from the stockroom and line the cap with aluminum foil.

2. Obtain a sample of PEG and accurately weigh 0.20-0.24 g samples into each of four dry 125 mL Erlenmeyer flasks. Note: With a viscous liquid sample it is not feasible to weigh by difference from a weighing bottle. Instead, weigh the dry flask, add the appropriate amount of polymer from a dropper (carefully, so as to deliver the sample to the bottom of the flask and not on the wall), and reweigh the flask. The top door of the analytical balance is very convenient for this weighing operation.

3. Pipet 10 mL aliquots of the 0.2 M PMDA into each of the Erlenmeyers. Wash any PEG on the flask wall to the bottom as the pipet drains. Avoid adding extra solvent, because the mixture may become too dilute for the reaction to go to completion.

4. Use a Mohr pipet to add one mL of 3 M IMDA (prepared ahead by the laboratory staff) to each flask.

5. Mix the contents and allow one-half hour for the reaction. While waiting, proceed to the PMDA standardization described below.

To standardize the PMDA solution pipet 10 mL aliquots into three Erlenmeyer flasks and add 1 mL of the IMDA solution to each. Add 30 mL deionized water and phenolphthalein to each (no waiting period required) and titrate with the standard 0.2 M NaOH. After waiting 30 minutes, add 30 mL deionized water to each flask. Add phenolphthalein indicator, and titrate with standard 0.2 M NaOH (prepared and standardized by laboratory staff).

Report:

For each standardization titration calculate and report the result as molarity of titratable hydrogens.

Calculate and report the average molarity and the standard deviation.

Calculate and report $\bar{M}_n$ for each aliquot of PEG, the average value of $\bar{M}_n$, and the standard deviation.

Some Notes on Calculations:

This experiment provides a good example of the usefulness of a back titration. The reaction between PEG and PMDA is slow. It would not be possible to titrate PEG end groups directly with PMDA. Adding an excess of PMDA and waiting 30 minutes drive the reaction to completion. The excess PMDA (actually the excess reactive hydrogens of pyromellitic acid) is then titrated with standard base. This reaction is rapid and thus suited to a titration with a visual end point.

4. Testing of mechanical property of polymer:

Stress–Strain behaviour:

The mechanical properties of polymers are specified with many of the same parameters that are used for metals—that is, modulus of elasticity, and yield and tensile strengths. For many polymeric materials, the simple stress–strain test is employed for the characterization of some of these mechanical parameters. The mechanical characteristics of polymers, for the most part, are highly sensitive to the rate of deformation (strain rate), the temperature, and the chemical nature of the environment (the presence of water, oxygen, organic solvents, etc.). Some modifications of the testing techniques and specimen configurations used for metals are necessary with polymers, especially for the highly elastic materials, such as rubbers.

Most thermoplastics (molten and solid) exhibit a non-Newtonian and viscoelastic behavior. The behavior is non-Newtonian (i.e., the stress and strain are not linearly related for most parts of the stress-strain curve). The viscoelastic behavior means when an external force is applied to a thermoplastic polymer, both elastic and plastic (or viscous) deformation occurs. The mechanical behavior is closely tied to the manner in which the polymer chains move

relative to one another under load. The deformation process depends on both time and the rate at which the load is applied.

Three typically different types of stress–strain behavior are found for polymeric materials, as represented in Figure 1. Curve A illustrates the stress–strain character for a brittle polymer, inasmuch as it fractures while deforming elastically. The behavior for a plastic material, curve B, is similar to that for many metallic materials; the initial deformation is elastic, which is followed by yielding and a region of plastic deformation. Finally, the deformation displayed by curve C is totally elastic; this rubber-like elasticity (large recoverable strains produced at low stress levels) is displayed by a class of polymers termed the elastomers.

Modulus of elasticity (termed tensile modulus or sometimes just modulus for polymers) and ductility in percent elongation are determined for polymers in same manner as for metals.

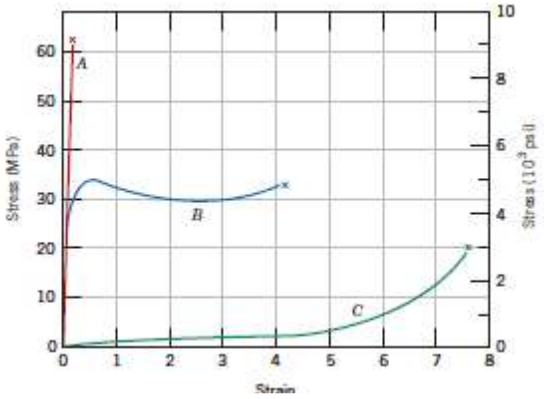


Figure.1. The stress–strain behavior for brittle (curve A), plastic (curve B), and highly elastic (elastomeric) (curve C) polymers

For plastic polymers (curve B, Figure 1), the yield point is taken as a maximum on the curve, which occurs just beyond the termination of the linear-elastic region (Figure 2). The stress at this maximum is the yield strength σ_y. Furthermore, tensile strength (TS) corresponds to the stress at which fracture occurs (Figure 2); TS may be greater than or less than Strength, for these plastic polymers, is normally taken as tensile strength.

Table 1 gives these mechanical properties for several polymeric materials;

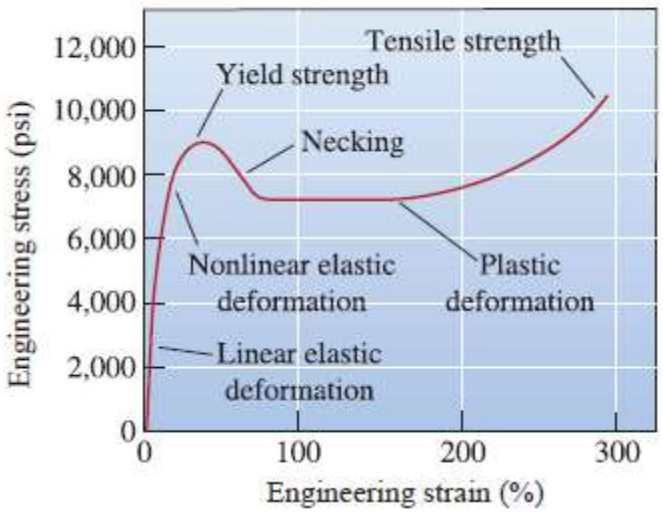


Figure.2 The stress–strain curve for a plastic polymer (6,6-nylon) showing how yield and tensile strengths are determined.

The strength of plastics materials is generally much lower than that of most other constructional materials. Nevertheless, plastics are light materials with a relative density between 0.9 and 2.0 so that when considered iii terms of strength/weight ratio they compare favourably with some metals and alloys. Figure 3 indicates the types of stress/strain relationship obtained for different groups of polymers.

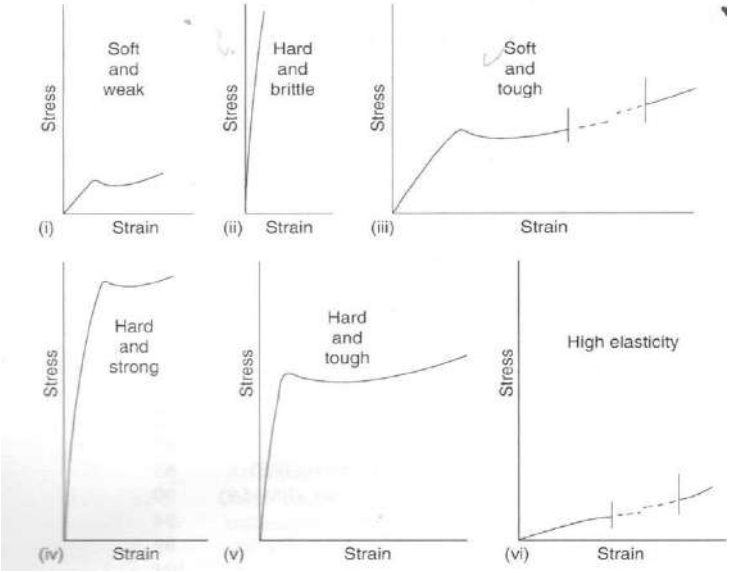


Figure 3 Types of stress-strain diagram for different polymer materials (after Carswell and Nason).

(i) Soft and weak :- Low elastic modulus,,..low yield stress, e.g. PVA and PTFE.

(ii) Hard and brittle :- High elastic modulus, low elongation, e.g. PF, PMMA and PS.

(iii) Soft and tough:- Low elastic modulus, low yield stress but high elongation and high stress at break, e.g. PE and plasticised PVC.

(iv) Hard and strong:- High elastic modulus, high yield stress, high tensile strength and low elongation, e.g. rigid PVC and modified PS.

(v) Hard and tough :- High elastic modulus, high yield stress, high tensile strength and high elongation, e.g. nylons and po!vcarbonates.

(vi) High elasticity :- Very low elastic modulus, low yield stress and low tensile strength but very high elastic elongation, e.g. natural rubber and other elastomers.

In addition, the mechanical characteristics of polymers are much more sensitive to temperature changes near room temperature. Consider the stress–strain behavior for poly (methyl methacrylate) (Plexiglas) at several temperatures between 4 and 60°C (Figure 3).

It should be noted that increasing the temperature produces:-

(1) a decrease in elastic modulus.

(2) a reduction in tensile strength, and

(3) an enhancement of ductility—at the material is totally brittle, while there is considerable plastic deformation at both 50 and 60 °C.

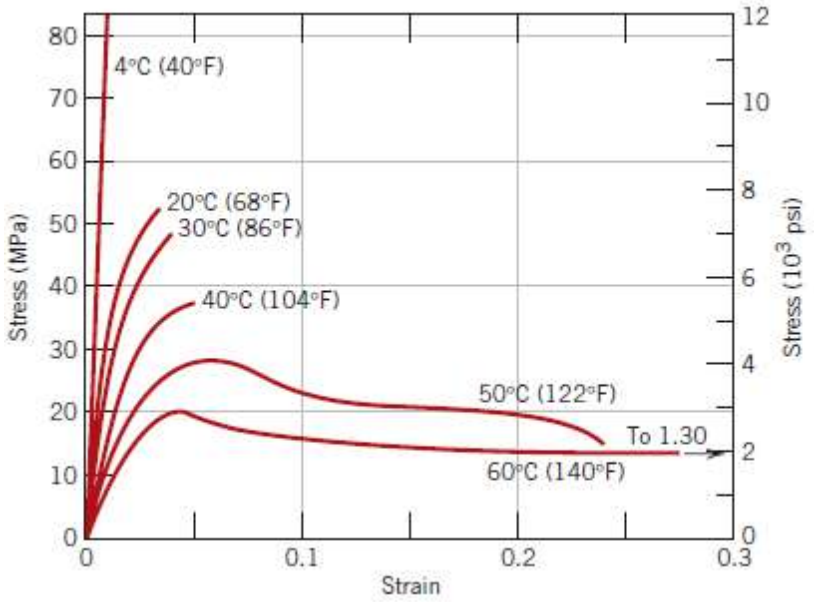


Figure.3 The influence of temperature on the stress–strain characteristics of poly(methyl methacrylate

The influence of strain rate on the mechanical behavior may also be important. In general, decreasing the rate of deformation has the same influence on the stress–strain characteristics as increasing the temperature; that is, the material becomes softer and more ductile.

Tensile testing:

Clearly if mechanical tests on plastics are to have any meaning, then a fixed testing temperature must be specified. Thus BS 2782 (Part 3) requires a testing temperature maintained at 23 ± 2°C with an atmospheric humidity of 50 ± 5 per cent for many thermoplastics materials; moreover, the test-pieces must be maintained under these conditions for 88 hours prior to the test. In some cases, for example thermosetting plastics, this conditioning is unnecessary since the permanent covalent bonds between the polymer chains render these materials much less temperature sensitive.

The rate of strain has a considerable effect on the recorded mechanical properties. Generally, as the strain rate increases so does the recorded yield stress and again BS 2782 (Part 3) lays down different conditions for different plastics as far as tensile testing is concerned. The speed of separation of the test-piece grips varies between 1 and 500 mm/min for different materials and forms of material.

The geometry of test-pieces also differs from that used in metals testing. Abrupt changes in shape cause stress concentrations which are likely to precipitate failure so tensile test-pieces are generally of the form shown in Figure 4

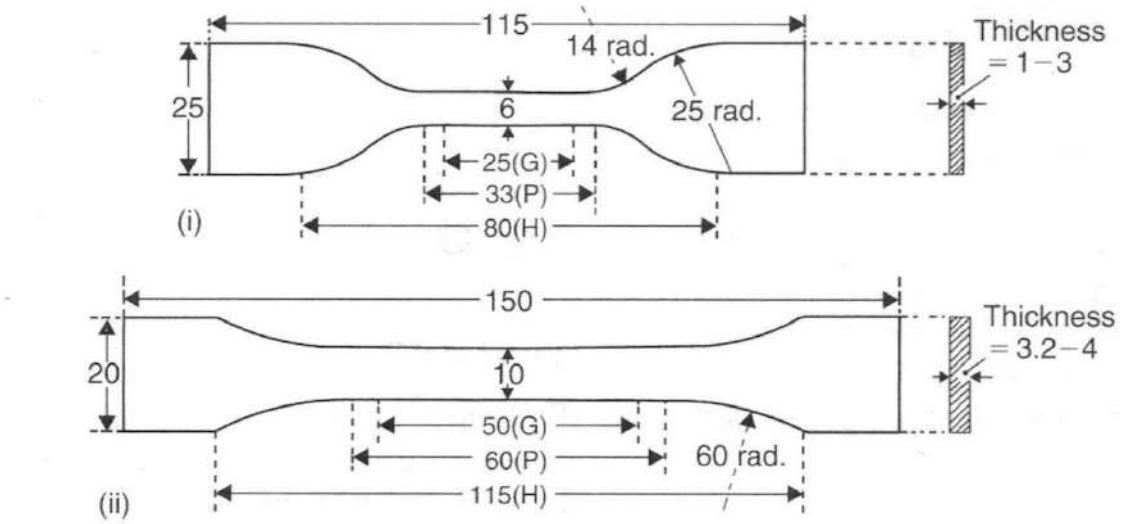


Figure 4. distance between grips H (measurements are in mm).

Many plastics do not obey Hooke's law as mentioned previously, i.e. elastic strain produced is not proportional to the stress applied, so that it becomes impossible to derive the tensile modulus of elasticity (Young's modulus) since this value applies only to materials with Hookean characteristics. As an alternative, it is usual to derive the secant modulus of the material. This is defined as the ratio of stress (nominal) to corresponding strain at some specific

point on the stress/strain curve. In Figure 5, the secant modulus associated with a strain of 0.2 per cent is shown and is, in fact, the slope of the line OS.

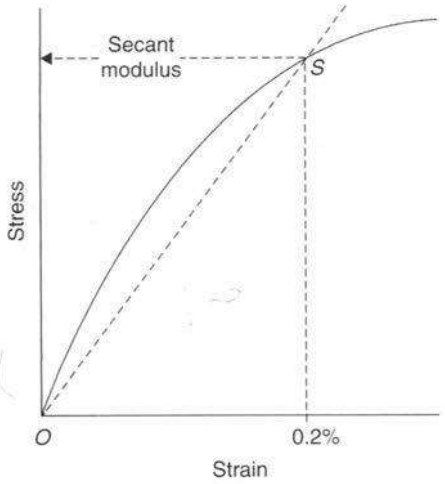


Figure 5. The secant modulus for non-Hookean polymer materials.

At the commencement of the tensile test, an initial force of w (usually about 10 per cent of the expected force necessary to produce 0.002 strain) is applied to 'take up slack' and straighten the test-piece. With this force applied the extensometer is set to zero. The force is then gradually increased (in accordance with the specified straining rate) until the necessary force W is reached to produce 0.2 per cent strain in the gauge length. The stress is then (W— w)/A, where A is the initial cross-sectional area of the test-piece at the gauge length used. Thus:

$$\text{secant modulus} = \frac{\text{stress}}{\text{strain}} = \frac{(W-w)/A}{0.002}$$

Other values of strain between 0.1 per cent and 2.0 per cent may be used depending upon the type of material. The strain value must therefore. be stated when quoting the secant modulus.

5. Determination of hydroxyl number of a polymer using colorimetric method.

The determination of hydroxyl number is a fundamental approach for polymer characterization. It is particularly used in quality control measurements for manufacturers and
users of polyols, and as a strategy for the chemical monitoring of polyesterification reaction between dicarboxylic acids and diols. According to the ASTM standard, the reference test for the determination of hydroxyl numbers in polyols is based on the esterification of the hydroxyl groups using a phthalic or acetic anhydride solution in pyridine with a final titration of the excess acid reagent by a previously standardized sodium hydroxide solution. However, this procedure requires a substantial period of time and promotes the exposure of the operator to some chemicals of documented toxicity, in particular the pyridine solution.

In the colorimetric-based method, Jones reagent addition provided a dark blue–green colour in the standard and the sample polymers vials. This result was based on the redox process between the chromic acid (acidified di- chromate, an oxidizing agent) and the hydroxyl end-groups (reducing agents) of these polymers.

Polymer analysis

1. Estimation of the amount of HCHO in the given solution by sodium sulphite method

Formaldehyde may be estimated in solution by oxidising it to formic acid by means of a known quantity (in excess) of iodine dissolved in an excess of NaOH solution (hypoiodite solution). The formic acid thus formed is neutralised by the alkali present. The unreacted hypoiodite is then acidified with HCI and the liberated iodine is titrated with standard sodium thiosulphate solution using starch as indicator.

$I_2 + 2NaOH \rightarrow NaOI + NaI + H_2O$

$HCHO + NaOI + NaOH \rightarrow HCOONa + NaI + H_2O$

$HCHO + I_2 + 3NaOH \rightarrow HCOONa + 2NaCI + I_2 + H_2O$

$NaOI + NaI + 2HCl \rightarrow 2NaCI + I_2 + H_2O$

$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_40_6 + 2NaI$

Solutions Provided:

i) Iodine solution. 0.1 M: Prepare iodine solution. (0.1M) of iodine by dissolving 3.17 g of it in 250 cm^3 volumetdc flask in distilled water. Standardise it by titrating against standard sodium thiosulphate (0.1M) solution.

ii) Sodium thiosulphale solution 0.1 M : It is prepared by dissolving 6.25 g sodium thiosulphate pentahydrate in distilled water in a 250 cm^3 volumetric flask.

iii) Sodium hydroxide solution 2M: It is prepared by dissolving 40 gm sodium hydroxide in 500 cm^3 volumetric flask with distilled water.

iv) Conc. hydrochloric acid. 2M: It is prepared by taking 45 cm^3 of Conc.HCl and making up to the mark with in 250 cm^3 volumetric flask.

v) Starch solution: Make a paste of 1.0g of starch with a little water and pour the suspension with constant stirring into 100 cm^3 of boiling water.

Procedure:

i) Formaiin solution: Weigh out accurately about 1.0 g of formalin solution, transfer it in a 250 cm^3 volumetric flask and make up to the mark with distilled water.

ii) Titration with Iodine solution (Blank titration): Pipette out 50 cm^3 of iodine solution in a 250 cm^3 conical flask. Titrate this solution with standard sodium thiosulphate solution. Sodium

thiosulphate solution can be standarised by titrating against dichoromate solution. Repeat the titration to get atleast two concordant readings. Record the observation in Observation Table-I.

iii) Titration with formaline Solution: Pipette out 25 cm^3 of unknown formalin solution in a 250 cm^3 conical flask and add 50 cm^3 of 0.1M iodine solution. Solution develops a dark-brown colour. Now add 2M NaOH solution from the burette into the conical flask until the solution becomes pale yellow in colour. Shake the contents of the flask and allow to stand for 15 minutes. Acidify with 40 cm^3 of 2M hydrochloric acid to liberate the remaining iodine. Titrate this solution with sodium thiosulphate solution (0.1M) using starch as indicator.

Observation:

Observation Table 1

Iodine Solution Vs Sodium Thiosulphate Solution

Sl no	Volume of iodine solution in cm^3	Burette reading		Volume of sodium thiosulphate in cm^3
		Initial	Final	
1	50			
2	50			
3	50			

Observation Table II

Formation of Iodine Solution Vs Sodium Thiosulphate Solution

Sl no	Volume of iodine solution added in cm^3	Burette reading		Volume of sodium thiosulphate in cm^3
		Initial	Final	
1	50			
2	50			
3	50			

Calculations:

(a) Volume of 0.1M iodine solution added = 50 cm^3

(b) Volume of 0.1M sodium thiosulphate solution used in titration = V cm^3

Since V cm^3 0.1M sodium thiosulphate = V cm^3 0.l M Iodine

Hence, the volume of 0.1M iodine used = (50-V) cm^3

According to the equation of the reaction

$HCHO + I_2 + 3NaOH \rightarrow HCOONa + 2NaI + H_2O$

From the above equation, it will be seen that 1 cm^3 of the M/10 iodine solution used in the oxidation is equivalent to 0.00150 g of formaldehyde.

Hence (50-V) cm^3 of 0.1M iodine solution = (50 - V) × 0.00150 g of HCHO

25 cm^3 of supplied solution contains = (50 - V) × 0.00150g of HCHO

Percentage of formaldehyde in the given solution = $\frac{(50-V)\times 0.00150\times 100}{25}$ = …%

Result:

Percentage of formaldehyde in the solutian - ..... %

Instrumental Techniques:

The focus of this is analysis and characterization of polymers and plastics. Analysis of polymeric systems is essentially a subtopic of the field of chemical analysis of organic materials. Because of this, spectroscopic techniques commonly used by organic chemists are at the heart of Polymer Analysis, e.g. infra-red (IR) spectroscopy, Raman spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and to some extent ultra-violet/visible (UV/Vis) spectroscopy. In addition, since most polymeric materials are used in the solid state, traditional characterization techniques aimed at the solid state are often encountered, x-ray diffraction, optical and electron microscopy as well as thermal analysis. Unique to polymeric materials are analytic techniques which focus on viscoelastic properties, specifically, dynamic mechanical testing. Additionally, techniques aimed at determination of colloidal scale structure such as chain structure and molecular weight for high molecular weight materials are somewhat unique to polymeric materials, i.e. gel permeation chromatography, small angle scattering (SAS) and various other techniques for the determination of colloidal scale structure.

IR studies of polymers:

Since 1945 infrared (IR) spectroscopy has become one of the most important methods for characterizing and studying the chemical and physical structure of compounds. Especially in the polymer field, IR spectroscopy and Raman spectroscopy have proved valuable for analytical and structural investigations. An IR spectrum of a polymer sample provides the following qualitative and quantitative information about the chemical and physical structure of the polymer under consideration:

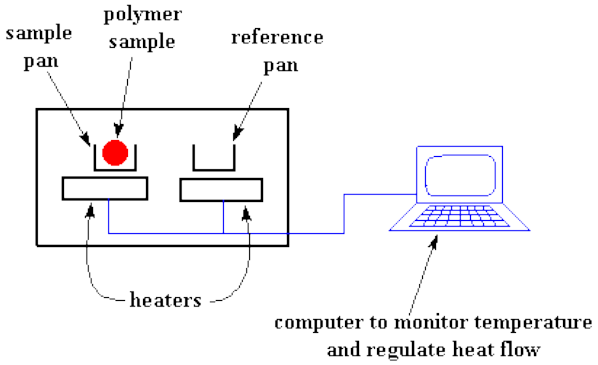
1. Chemical nature of the polymer: type and degree of branching,
2. Steric order: cis-trans isomerism, stereoregularity, etc.
3. Conformational order: physical arrangement of a polymer

4. Crystallinity: number of chains per unit cell, intermolecular forces etc.

There exist two basic approaches to the study and interpretation of the IR spectra of polymers. The empirical interpretation is based on the concept of nearly independently vibrating atomic groups in the macromolecule. It mainly collects information about the chemical nature of the polymer. The theoretical treatment focuses on the complete analysis of the IR spectrum in terms of vibrational behavior and intermolecular forces of the polymeric system. However, both methods have their limitations. The semiempirical treatment - a combination of these basic methods - uses the results of theoretical considerations and computations of simple and idealized polymers or monomers for the assignment and interpretation of the IR spectra of more complicated structures. As an example, we can consider the results of studies on polyethylene and higher alkanes which can often be used for elucidating steric and conformational order, and the crystallinity of polymers containing methylene sequences.

DSC analysis of polymers:

Differential scanning calorimetry is a technique used to study what happens to polymers when they're heated. We use it to study what we call the thermal transitions of a polymer. and what are thermal transitions? They're the changes that take place in a polymer when you heat it. The melting of a crystalline polymer is one example. The glass transition is also a thermal transition. So how do we study what happens to a polymer when we heat it? The first step would be to heat it, obviously. And that's what we do in differential scanning calorimetry, or DSC for short. We heat our polymer in a device that looks something like this:



It's pretty simple. There are two pans. In one pan, the sample pan, you put your polymer sample. The other one is the reference pan. You leave it empty. Each pan sits on top of a heater. Then you tell the nifty computer to turn on the heaters. So the computer turns on the heaters, and tells it to heat the two pans at a specific rate, usually something like 10°C per minute. The computer makes absolutely sure that the heating the rate stays exactly the same throughout the

experiment. But more importantly, it makes sure that the two separate pans, with their two separate heaters, heat at the same rate as each other.

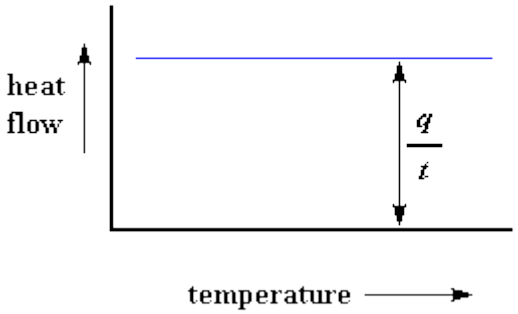
They would not heat at the same rate. The simple reason is that the two pans are different. One has polymer in it, and one doesn't. The polymer sample means there is extra material in the sample pan. Having extra material means that it will take more heat to keep the temperature of the sample pan increasing at the same rate as the reference pan.

So the heater underneath the sample pan has to work harder than the heater underneath the reference pan. It has to put out more heat. By measuring just how much more heat it has to put out is what we measure in a DSC experiment.

Specifically what we do is this: We make a plot as the temperature increases. On the X-axis we plot the temperature. On the y-axis we plot difference in heat output of the two heaters at a given temperature.

Heat Capacity:

We can learn a lot from this plot. Let's imagine we're heating a polymer. When we start heating our two pans, the computer will plot the difference in heat output of the two heaters against temperature. That is to say, we're plotting the heat absorbed by the polymer against temperature. The plot will look something like this at first.



The heat flow at a given temperature can tell us something. The heat flow is going to be shown in units of heat, q supplied per unit time, t. The heating rate is temperature increase T per unit time, t.

$$\frac{\text{heat}}{\text{time}} = \frac{q}{t} = \text{heat flow}$$

$$\frac{\text{temperature increase}}{\text{time}} = \frac{\Delta T}{t} = \text{heating rate}$$

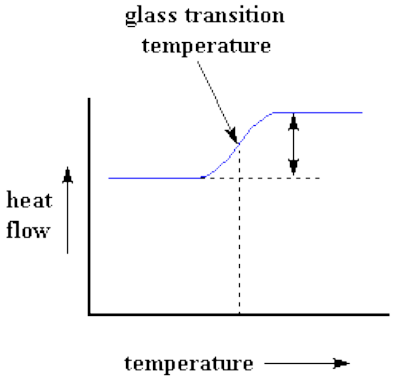
Let's say now that we divide the heat flow q/t by the heating rate T/t. We end up with heat supplied, divided by the temperature increase.

$$\frac{\frac{q}{t}}{\frac{\Delta T}{t}} = \frac{q}{\Delta T} = C_p = \text{heat capacity}$$

Remember from the glass transition page that when you put a certain amount of heat into something, its temperature will go up by a certain amount, and the amount of heat it takes to get a certain temperature increase is called the heat capacity, or C_p.

The Glass Transition Temperature:

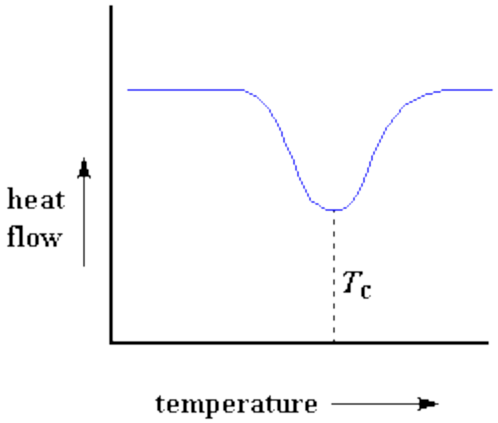
We can learn a lot more than just a polymer's heat capacity with DSC. Let's see what happens when we heat the polymer a little more. After a certain temperature, plot will shift upward suddenly, like this:



This means we're now getting more heat flow. This indicate an increase in the heat capacity of polymer. This happens because the polymer has just gone through the glass transition. As we know, polymers have a higher heat capacity above the glass transition temperature than they do below it. Because of this change in heat capacity that occurs at the glass transition, we can use DSC to measure a polymer's glass transition temperature. It may be noticed that the change doesn't occur suddenly, but takes place over a temperature range. This makes picking one discreet T_g kind of tricky, but we usually just take the middle of the incline to be the T_g.

Crystallization:

Above the glass transition, the polymers have a lot of mobility. They wiggle and squirm, and never stay in one position for very long. When they reach the right temperature, they will have gained enough energy to move into very ordered arrangements, which we call crystals. When polymers fall into these crystalline arrangements, they give off heat. When this heat is dumped out, it makes the little computer-controlled heater under the sample pan really happy. It's happy because it doesn't have to put out much heat to keep the temperature of the sample pan rising.

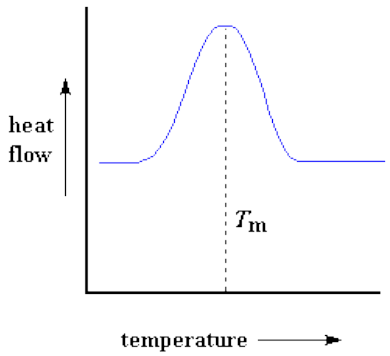


The temperature at the lowest point of the dip is usually considered to be the polymer's crystallization temperature, or Tc. Also, we can measure the area of the dip, and that will tell us the latent energy of crystallization for the polymer. But most importantly, this dip tells us that the polymer can in fact crystallize. If you analyzed a 100% amorphous polymer, like atactic polystyrene, you wouldn't get one of these dips, because such materials don't crystallize. Also, because the polymer gives off heat when it crystallizes, we call crystallization an exothermic transition.

Melting:

Heat may allow crystals to form in a polymer, but too much of it can be their undoing. If we keep heating our polymer past its T_c, eventually we'll reach another thermal transition, one called melting. When we reach the polymer's melting temperature, or T_m, those polymer crystals begin to fall apart, that is they melt. The chains come out of their ordered arrangements, and begin to move around freely. And in case you were wondering, we can spot this happening on a DSC plot.

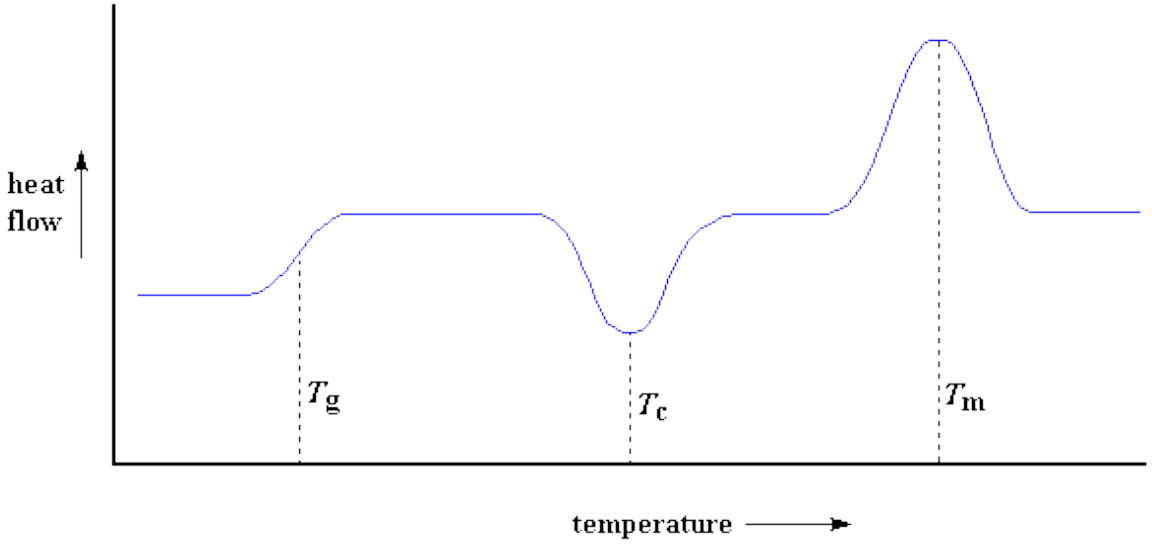
When we reach the T_m, there is a latent heat of melting as well as a latent heat of crystallization. When the polymer crystals melt, they must absorb heat in order to do so. Remember melting is a first order transition. This means that when you reach the melting temperature, the polymer's temperature won't rise until all the crystals have melted. This means that the little heater under the sample pan is going to have to put a lot of heat into the polymer in order to both melt the crystals and keep the temperature rising at the same rate as that of the reference pan. This extra heat flow during melting shows up as a big peak on our DSC plot, like this:



We can measure the latent heat of melting by measuring the area of this peak. And of course, we usually take the temperature at the top of the peak to be the polymer's melting temperature, T_m. Because we have to add energy to the polymer to make it melt, we call melting an endothermic transition.

Putting It All Together

We saw a step in the plot when the polymer was heated past its glass transition temperature. Then we saw a big dip when the polymer reached its crystallization temperature. Then finally we saw a big peak when the polymer reached its melting temperature. To put them all together, a whole plot will often look something like this:



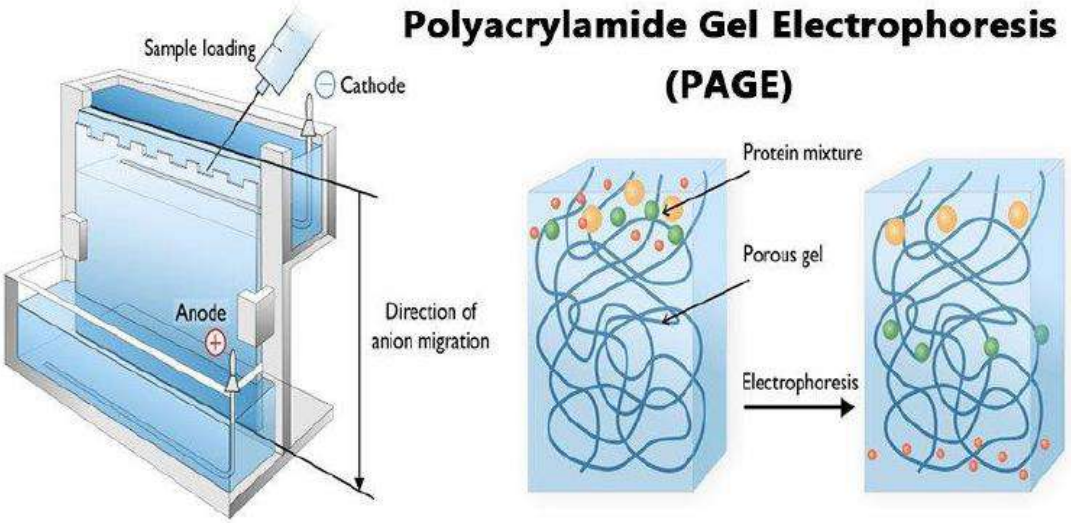
5. Preparation of polyacrylamide and its electrophoresis

Preparation:

Polyacrylamide is a chemically cross-linked gels produced as a result of the polymerization reaction between acrylamide and a cross linking agent, N,N'-methylene-bis-acrylamide (BIS). The reaction is a free radical polymerization, usually carried out with ammonium persulfate as the initiator and N,N,N',N'- tetramethylethylendiamine (TEMED) as the catalyst. The degree

of polymerization or crosslinking can be controlled by adjusting the concentration of acrylamide and BIS. The more the cross-linking the harder the gel.

Polyacrylamide gel electrophoresis (PAGE) is a powerful tool widely used in biochemistry, forensic chemistry, genetics, molecular biology and biotechnology to separate biological macromolecules, usually proteins or nucleic acids, according to their electrophoretic mobility. The most commonly used form of polyacrylamide gel electrophoresis is the Sodium dodecyl sulphate (SDS) Polyacrylamide gel electrophoresis (SDS- PAGE) used mostly for the separation of proteins. Polyacrylamide gel with small pores helps to examine smaller molecules better since the small molecules can enter the pores and travel through the gel while large molecules get trapped at the pore openings.



Principle of Polyacrylamide Gel Electrophoresis (PAGE):

SDS-PAGE (Polyacrylamide Gel Electrophoresis), is an analytical method used to separate components of a protein mixture based on their size. The technique is based upon the principle that a charged molecule will migrate in an electric field towards an electrode with opposite sign. The general electrophoresis techniques cannot be used to determine the molecular weight of biological molecules because the mobility of a substance in the gel depends on both charge and size. To overcome this, the biological samples need to be treated so that they acquire uniform charge, then the electrophoretic mobility depends primarily on size. For this, different protein molecules with different shapes and sizes, needs to be denatured (done with the aid of SDS) so that the proteins lose their secondary, tertiary or quaternary structure. Proteins being covered by SDS are negatively charged and when loaded onto a gel and placed in an electric field, it will migrate towards the anode (positively charged electrode), and will be separated by a molecular filtering effect based on size. After the visualization by a staining (protein-specific)

technique, the size of a protein can be calculated by comparing its migration distance with that of a known molecular weight ladder (marker).

Requirements for Polyacrylamide Gel Electrophoresis (PAGE):

• Acrylamide solutions (for resolving & stacking gels).

• Isopropanol / distilled water.

• Gel loading buffer.

• Running buffer.

• Staining, de- staining solutions.

• Protein samples

• Molecular weight markers.

The equipment and supplies necessary for conducting SDS-PAGE includes:

• An electrophoresis chamber and power supply.

• Glass plates (a short and a top plate).

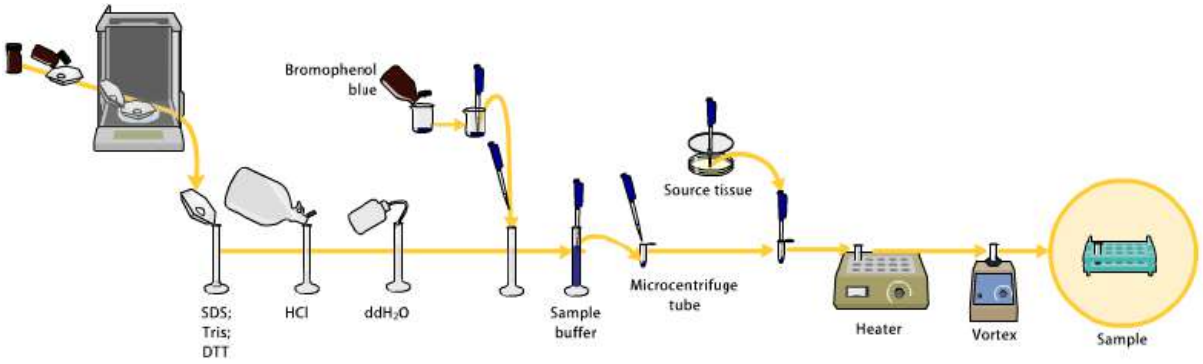
• Casting frame

• Casting stand

• Combs

Steps Involved in Polyacrylamide Gel Electrophoresis (PAGE):

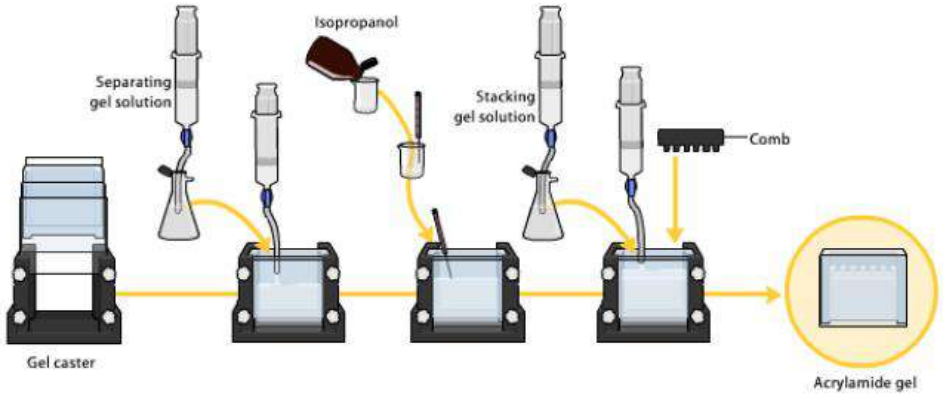
1. Sample preparation:



- Samples may be any material containing proteins or nucleic acids.
- The sample to analyze is optionally mixed with a chemical denaturant if so desired, usually SDS for proteins or urea for nucleic acids.
- SDS is an anionic detergent that denatures secondary and non–disulfide–linked tertiary structures, and additionally applies a negative charge to each protein in proportion to its mass. Urea breaks the hydrogen bonds between the base pairs of the nucleic acid, causing the constituent strands to anneal. Heating the samples to at least 60 -95° C further promotes denaturation.

- A tracking dye may be added to the solution. This typically has a higher electrophoretic mobility than the analytes to allow the experimenter to track the progress of the solution through the gel during the electrophoretic run.

2. Preparation of polyacrylamide gel



• The gels typically consist of acrylamide, bis acrylamide, the optional denaturant (SDS or urea), and a buffer with an adjusted pH.

• The ratio of bisacrylamide to acrylamide can be varied for special purposes, but is generally about 1 part in 35. The acrylamide concentration of the gel can also be varied, generally in the range from 5% to 25%.

• Lower percentage gels are better for resolving very high molecular weight molecules, while much higher percentages of acrylamide are needed to resolve smaller proteins,

• Gels are usually polymerized between two glass plates in a gel caster, with a comb inserted at the top to create the sample wells.

• After the gel is polymerized, the comb is removed and the gel is ready for electrophoresis.

3. Electrophoresis:

• Various buffer systems are used in PAGE depending on the nature of the sample and the experimental objective.

• The buffers used at the anode and cathode may be the same or different.

• An electric field is applied across the gel, causing the negatively charged proteins or nucleic acids to migrate across the gel away from the negative and towards the positive electrode (the anode).

• Depending on their size, each biomolecule moves differently through the gel matrix: small molecules more easily fit through the pores in the gel, while larger ones have more difficulty.

• The gel is run usually for a few hours, though this depends on the voltage applied across the gel.

• After the set amount of time, the biomolecules will have migrated different distances based on their size.

• Smaller biomolecules travel farther down the gel, while larger ones remain closer to the point of origin.

• Biomolecules may therefore be separated roughly according to size, which depends mainly on molecular weight under denaturing conditions, but also depends on higher-order conformation under native conditions.

4. Detection:

• Following electrophoresis, the gel may be stained (for proteins, most commonly with Coomassie Brilliant Blue or autoradiography; for nucleic acids, ethidium bromide; or for either, silver stain), allowing visualization of the separated proteins, or processed further (e.g., Western blot).

• After staining, different species biomolecules appear as distinct bands within the gel.

• It is common to run molecular weight (size) markers of known molecular weight in a separate lane in the gel to calibrate the gel and determine the approximate molecular mass of unknown biomolecules by comparing the distance travelled relative to the marker.