

PRACTICAL CHEMISTRY-II

SC-120

Self Learning Material



Directorate of Distance Education

**SWAMI VIVEKANAND SUBHARTI UNIVERSITY
MEERUT-250 005
UTTAR PRADESH**

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PROPOSED SYLLABUS

B.Sc. (Part II) Chemistry PRACTICAL CHEMISTRY (SC-120)

[I] INORGANIC CHEMISTRY

Volumetric Analysis

- (i) Estimation of iron using
- (ii) Estimation of copper sulphate using sodium thiosulphate.
- (iii) Estimation of silver nitrate using ammonium thiocyanate or sodium chloride.

[II] ORGANIC ANALYSIS

(i) Qualitative Analysis

Identification of an aliphatic and aromatic organic compound (including N, S and halogen containing compounds) through the functional group analysis, determination of melting point/boiling point and preparation of suitable derivatives.

(ii) Paper Chromatography

- (1) To separate and identify the sugars present in the given mixture by the technique of paper chromatography and report the values.
- (2) To separate and identify amino acids (glycine, aspartic acid, glutamic acid and tyrosine in a mixture of amino acids with the help of paper chromatography)

[III] PHYSICAL CHEMISTRY

(i) Transition Temperature

- (1) Determination of the transition temperature of the given substance by thermometric method (e.g.,

(ii) Solubility

- (1) To determine the solubility of benzoic acid at 40°C and at a temperature lower than the room temperature by titration method.
- (2) To determine the solubility of in water at 30°, 40°, 50°, 60° and 70°C and thus plot a solubility curve also.

(iii) Adsorption

- (1) To study the adsorption of acetic acid on charcoal and prove the validity of Freundlich's adsorption isotherm.

(iv) Thermochemistry

- (1) To determine the enthalpy of neutralization of a strong acid versus strong base.

CHAPTER 1 VOLUMETRIC ANALYSIS

INTRODUCTION

The Volumetric Analysis involves the estimation of a substance in solution either by precipitation, neutralization, oxidation or reduction by means of solution of known strength. In this method the substance to be estimated is made to react with a reagent, the equation governing the reaction being known.

Volumetric analysis depends on the measurement of the volumes of solution of the interacting substances. In this analysis a measured volume of solution of substance A is allowed to react completely with the solution of definite strength of another substance B. The end point of the reaction is indicated by some marked change such as the appearance or disappearance of colour or formation of precipitate. Thus we know the volumes of the solutions used in the reaction and the strength of solution B, so the strength of the other solution A is computed.

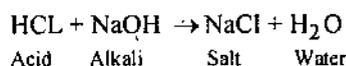
Unit of volume : The fundamental unit in the measurement of volume of liquids is the "litre" which is defined as the volume occupied by 1 kilogram of water of the temperature (4°C) of its maximum density and at the normal atmospheric pressure. One-thousandth part of this is termed the "millilitre".

The term "litre" was originally applied to a cubic decimetre and its thousandth part was the "Cubic centimetre" called c.c. The relation between millilitre and cubic centimetre is 1000 ml. = 1000.28 c.c. The difference between ml. and c.c. being very small, both the terms may be used. But the use of ml. should be preferred.

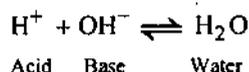
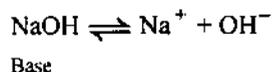
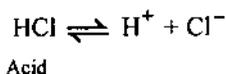
1 ml. is equal to 1.00028 c.c.

Classification of Volumetric Reactions

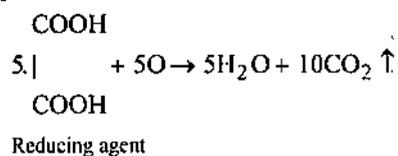
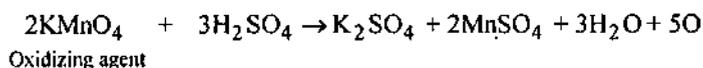
(1) Acidimetry and alkalimetry : Acid and alkali react with each other and become neutral.



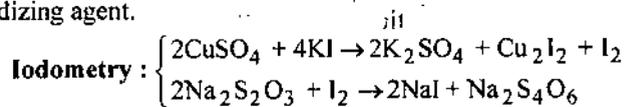
Actually these reactions are between H^+ ions (produced by acids) and OH^- ions (produced by bases).



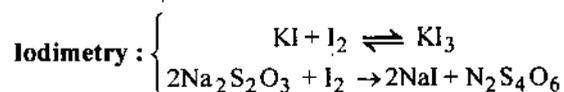
(2) Oxidation-reduction titration : In this type of titration a reducing agent is estimated by titrating it with a standard oxidizing agent and vice-versa. Generally the oxidizing agent is employed as standard. Such reactions are accompanied by a change in the valency of ions. In this type of reaction oxidation and reduction take place simultaneously. If one substance is oxidized then the other is reduced.



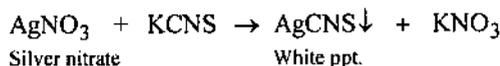
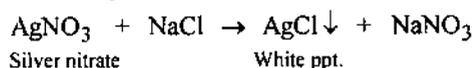
(3) **Iodometry and iodimetry** : In iodometry titrations iodine liberated from KI solution by the chemical reaction is used for oxidation. While in iodimetry titrations a solution of iodine in KI solution is used as an oxidizing agent.



Sodium tetrathionate



(4) **Precipitation titration** : In this type of titration the strength of a solution is determined by its complete precipitation with the help of known (standard) solution of another substance.



Advantages of Volumetric Analysis over Gravimetric Analysis

(i) **Simplicity** : Volumetric analysis require simple apparatus and can be conveniently carried out with greater ease.

(ii) **Rapidity** : Volumetric analysis can be carried out rapidly and the result can be submitted within 2 hrs. While gravimetric analysis is time consuming analysis.

(iii) **Accuracy** : Volumetric methods surpass gravimetric ones in accuracy.

(iv) **Applicability** : Volumetric analysis find a wider range of applicability than gravimetric ones.

Standard Solution and Standardisation

A standard solution is a solution of definite concentration. This term is very common in volumetric analysis. The solution of a known strength is termed as Standard Solution.

The strength of a standard solution can be expressed in the following two terms :

(i) In terms of normality.

(ii) In terms of gram per litre.

Normality : In order to understand it, we must first understand *Normal solution*.

A solution containing one gram equivalent weight of the substance in one litre is known as a normal solution of the substance and it is denoted by *N*. If one litre of solution contains $\frac{1}{2}$, $\frac{1}{10}$ or $\frac{1}{100}$ th etc. of the

gram equivalent, it is called a semi normal $\left(\frac{N}{2}\right)$, decinormal $\left(\frac{N}{10}\right)$ or a centinormal $\left(\frac{N}{100}\right)$ solution and so on.

Hence the fraction of the gm. equivalent of a substance dissolved in one litre of the solution determines the 'Normality' of the solution. If $\frac{1}{20}$ th of the gram equivalent weight of a substance is dissolved in 1 litre

then, the normality of the solution so prepared will be $\left(\frac{N}{20}\right)$.

In grams per litre : It is the amount of the active substance in grams which is dissolved in one litre of water.

The process whereby the concentration of a standard solution is determined by titration of a primary standard is called standardisation.

Relation between Normality and Strength (grams per litre).

Mathematically, Normality is represented as

$$\text{Normality} = \frac{\text{Strength in grams per litre}}{\text{Equivalent weight}}$$

Strength in grams per litre = Normality \times Equivalent weight

$$S = N \times E$$

Molarity and molar concentration : The molarity of the solution is defined as the number of gram molecular weights of the substance dissolved in one litre of it is called a molar solution. A solution which contains one gram-molecular weight of the substance dissolved in one litre of it is called a molar solution. Thus molar solution of sodium carbonate, oxalic acid, sulphuric acid contain 106 g, 126 g and 98 g of the substance respectively in 1000 ml. of solution. This is known as M-solution.

But titrations are generally carried out in terms of Normality.

Equivalent Weight

Equivalent weight of a substance is the weight of that substance which is chemically equivalent to one gram atom of hydrogen, $\frac{1}{2}$ gm. atom of oxygen or one gram atom of chlorine. When it is expressed in grams,

it is known as the **gram equivalent weight**.

(i) Equivalent weight of an acid :

Equivalent weight of an acid

$$= \frac{\text{Molecular weight of an acid}}{\text{The number of replaceable hydrogen atoms in a molecule of an acid}}$$

$$= \frac{\text{Molecular weight of an acid}}{\text{Basicity of an acid}}$$

(ii) Equivalent weight of a base :

Equivalent weight of a base

$$= \frac{\text{Molecular weight of base}}{\text{The number of replaceable hydroxyl (OH}^- \text{) groups present in one molecule of a base.}}$$

$$= \frac{\text{Molecular weight of a base}}{\text{Acidity of a base}}$$

(iii) Equivalent weight of a salt :

$$= \frac{\text{Molecular weight of a salt}}{\text{The total number of positive or negative valencies of its radicals}}$$

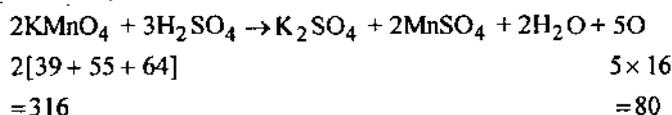
Equivalent weights of some important acids, bases and salts

Acid/Base	Mol. Wt.	Basicity/ Acidity	Equi. Wt.	Salt	Mol Wt.	Valency	Equi. Wt.
HCl	36.5	1	36.5	N ₂ Cl	58.5	1	58.5
HNO ₃	63.00	1	63.00	Na ₂ CO ₃	106.00	2	53.00
CH ₃ COOH	60.00	1	60.00	CaCO ₃	100.00	2	50.00
HCOOH	46.00	1	46.00	NaHCO ₃	84.00	1	84.00
H ₂ SO ₄	98.00	2	49.00	KHCO ₃	100.00	1	100.00
H ₂ C ₂ O ₄ .2H ₂ O	126.00	2	63.00	Ca(HCO ₃) ₂	162.00	2	81.00
H ₃ PO ₄	98.00	3	32.7	BaCl ₂ .2H ₂ O	244.5	2	122.25
NaOH	40.00	1	40.00	Na ₂ B ₄ O ₇ .10H ₂ O	381.5	2	190.75
KOH	56.00	1	56.00				
Ba(OH) ₂ .8H ₂ O	315.00	2	157.5				
Ca(OH) ₂	74.00	2	37.00				

(iv) **Equivalent weight of an oxidising or reducing agent** : Equivalent weight of an oxidising agent is its weight which can supply for reaction 8 parts by weight of oxygen or react with one part by weight of hydrogen.

Similarly equivalent weight of reducing agent is its weight which can supply for reaction 1 part by weight of hydrogen or react with 8 parts by weight of oxygen.

For example KMnO_4 in acid medium behaves as



Since 316 parts by weight of KMnO_4 give 80 parts by weight of oxygen hence 31.6 parts by weight of KMnO_4 give 8 parts by weight of oxygen.

Hence the equivalent weight of KMnO_4 in acidic medium is 31.6.

Thus the equivalent weight of an oxidizing agent

$$= \frac{\text{Molecular weight of the substance}}{2 \times \text{the number of oxygen atoms available}}$$

In case of KMnO_4 its equivalent weight will be

$$= \frac{316}{2 \times 5} = 31.6$$

Similarly equivalent weight of $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
= 392.1

Primary standard substance

A primary standard substance possess the following characteristics :

- It must be obtained in a high degree of purity.
- It should be stable and unaffected by the atmosphere.
- It should not be deliquescent or efflorescent.
- It should be readily soluble in water.
- Its solution in distilled water should keep well on keeping.

Crystalline oxalic acid, anhydrous sodium carbonate, NaCl , KCl , AgNO_3 , $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ etc. are some of the common primary standard substances; which are used in the laboratory.

A substance which does not possess the above characteristics is called a secondary standard substance e.g. HCl , H_2SO_4 , HNO_3 , NaOH , KOH , KMnO_4 etc.

Calculation of Strength Based on Normality

The strength of a unknown solution can be found out through normality by titration. *We know that equivalent weight of an acid will neutralize equivalent weight of a base.*

When solution of different normalities react with one another, their interacting volumes will inversely proportional to their normalities. In other words, we may say that the *normalities of two solutions are inversely proportional to their interacting volumes*. Let the normality of an unknown solution be N_1 . V_1 c.c. of this solution required V_2 c.c. of another solution of normality N_2 for complete reaction.

$$V_1 \propto \frac{1}{N_1}$$

or

$$V_1 = \frac{k}{N_1} \qquad \dots(i)$$

where k is a constant.

$$V_2 \propto \frac{k}{N_2}$$

$$\text{or } V_2 = \frac{k}{N_2} \quad \dots(ii)$$

where k is a constant.

Dividing (i) by (ii),

$$\frac{V_1}{V_2} = \frac{N_2}{N_1}$$

$$\text{or, } N_1 V_1 = N_2 V_2$$

Normality \times Volume of one soln. = Normality \times Volume of other soln.

This equation is known as **Normality Equation**. By using this equation the normality of an unknown solution can be calculated, since we know the volumes of the two solutions (taken by pipette and used by burette) and the normality or the strength of one solution. If we know the equivalent weight of the substance, then the strength of the solution may be found out in grams/litre by the following relation :

$$\text{Strength of the soln. in grams/litre} = \text{Normality} \times \text{Gram Equivalent Weight.}$$

Importance of Indicator

Indicator plays an important role in the volumetric analysis. The success of volumetric exercise depends upon the indicator. When the reaction between two solutions is completed, then the slight excess of one solution is revealed by the colour change in the solution. This stage of reaction is known as **end point**.

Indicator indicates the end point generally by a change of colour of the solution. Indicator is that substance which indicates the physico-chemical condition of a chemical reaction.

We have three kinds of titrations with respect to the use of indicators.

- (a) Internal Indicator.
- (b) External Indicator.
- (c) Self Indicator.

Internal indicator : These are chemical substance which are added to the volumetric flask in which the titration is carried out e.g., phenolphthalein, methyl orange, starch etc.

External indicator : These indicators can not be added to the volumetric flask in which the titration is carried out e.g., potassium ferricyanide in the titration of potassium dichromate with ferrous ammonium sulphate. External indicators are very few.

Self indicator : If the reagent is strongly coloured and is decolourized by the substance that is being determined or if it is converted into slightly coloured compounds, the end point is marked by the colour of a slight excess of the reagent. This is well illustrated by **potassium permanganate**.

Internal indicator : They are further divided according to the types of reactions in which they are used :

- (i) Acid base indicators.
- (ii) Precipitation indicators.
- (iii) Redox indicators.
- (iv) Adsorption indicators.

Preparation of Standard Solution

Weighing should be done very carefully because incorrect weighing will spoil the complete analysis.

First of all check your chemical balance and observe, whether the pointer moves equally on both the sides of the zero point, if not then adjust it with the help of **adjusting screws**.

First of all rough weight of the weighing tube is taken without using rider (weight of rider is 10 mg. i.e., 0.001 gm). Then to this weight is added the amount of substance to be weighed and the total weights are placed on the pan. The substance to be weighed is then taken in the weighing tube and placed on the left pan. Increase or decrease the amount of the substance till the pointer starts moving on the scale. Now take the accurate weight of the weighing tube containing the substance with the help of rider. Note down this weight.

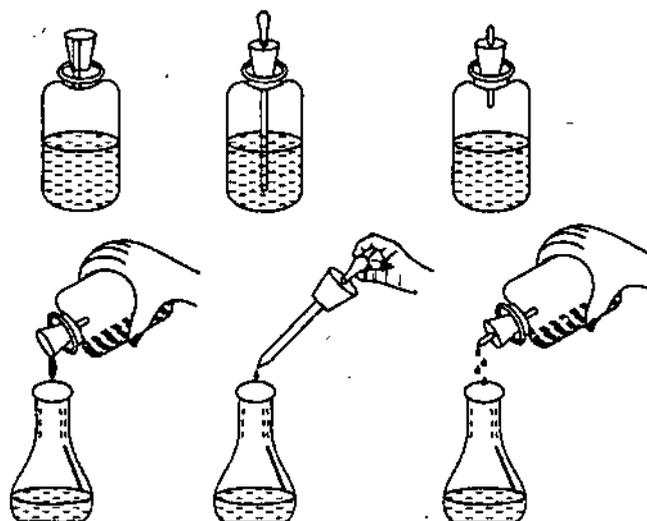
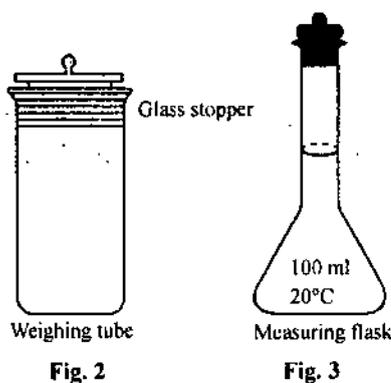


Fig. 1. Various forms of indicators dropping bottles (top) and the way they are used (bottom)



Calculation of weights for preparing standard solution in terms of normality or molarity.

In terms of normality :

$$\frac{\text{Capacity of measuring flask in ml.}}{1000} \times \text{Eq. wt. of the solution} \times \text{normality of the solution to be prepared.}$$

In terms of molarity :

$$\frac{\text{Capacity of measuring flask in ml.}}{1000} \times \text{mol. wt. of the substance} \times \text{molarity of the solution to be prepared.}$$

Now a dry funnel is placed in the neck of measuring flask (of required capacity) washed previously with distilled water and then weighing tube with the substances is carefully inverted over it and tapped. The substance comes in the flask through the funnel. Do not allow any particle of the substance to fall out of the funnel. The weighing tube is again weighed accurately. The difference of the last two weights gives the weight of the substance which has been actually placed in the measuring flask. Distilled water is slowly poured on the funnel so that any particle of the substance sticking on it goes inside the flask. Remove the funnel from the flask and dissolve the substance taken. Let a clear solution be prepared. Now add water and make up to the mark carefully. Keep this solution for sometime so that it may become homogeneous. The flask should be shaken well before use.

Calculations : Weight of weighing tube

$$\text{(First reading)} = 10.20 \text{ gms.}$$

Weight of weighing tube + weight of Na_2CO_3 (required)

$$\text{(Second reading)} = 11.2650 \text{ gms.}$$

Accurate weight of empty weighing tube

$$\text{(Third reading)} = 10.2150 \text{ gms}$$

∴ Weight of Na_2CO_3 taken = 1.05 gms.

200 c.c. solution contains = 1.05 gms. of Na_2CO_3

∴ 1000 c.c. solution contains = $\frac{1.05}{200} \times 1000 = 5.25$ gms.

Hence the strength of the solution = 5.25 gms/litre

∴ The normality of the solution = $\frac{\text{Strength gms / litre}}{\text{Equivalent weight}} = \frac{5.25}{53} \text{ N}$

The normality of the solution may also be calculated directly from the formula.

$$\text{Normality} = \frac{\text{Weight taken}}{\text{Eq. weight}} \times \frac{1000}{\text{Capacity of Measuring flask}}$$

Note : One of the most important tools of the analytical Chemist is the balance. It is therefore essential that the student should have a proper understanding of its construction, use and care. It is really very delicate instrument and thus requires very careful handling. Least count of balance is 0.0002 gm.

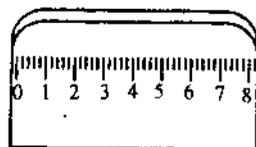
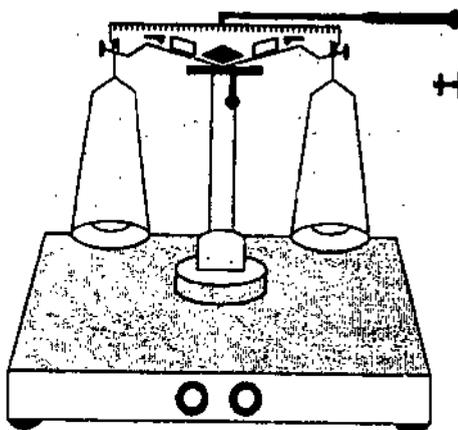
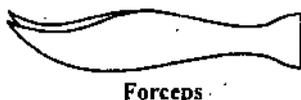


Fig. 4. Chemical balance and its scale



Forceps

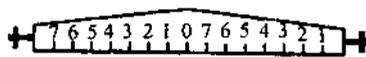


Fig. 5. Scale of balance

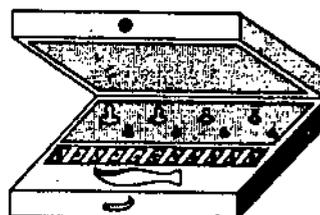


Fig. 6. Weight box

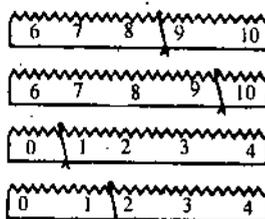


Fig. 7. Way of using rider and its reading

- (1) The balance should be placed upon a firm foundation which is free from mechanical vibrations as far as possible.
- (2) The door of the balance should be kept closed.
- (3) Weights and the object to be weighted should always be placed in the centres of the respective pans.
- (4) You have to use your own balance and weight box allotted to you.
- (5) Substances must be weighed in suitable containers such as small beakers, weighing tubes, crucibles or upon watch glasses.
- (6) Do not add or remove anything from the pans when the knob is raised.
- (7) The balance must not be overloaded.
- (8) Rider and weights should be handled only with the forceps provided with box.

(9) The knob of the balance should always be raised and lowered very gently and try to avoid jerks as far as possible.

(10) Nothing must be left on the pans when the weighing has been completed.

(11) Always try to use the rider on the right arm or on the side of the weights.

(12) Always use the windows of the balance for keeping and removing objects and weights.

(13) Note down all the weights separately and correctly when weighing is completed.

(14) Keep your balance neat and clean.

(15) While weighing nothing should fall on the pans.

(16) Close the balance before leaving the balance room.

(a) *The strength in gms/litre of the unknown solution*

$$= 4 \times \text{Weight of the substance in 250 ml. measuring flask} \\ \times \frac{\text{Volume of intermediate soln. used with unknown soln.}}{\text{Volume of intermediate soln. used with known soln.}}$$

(b) *The strength in gms/litre of the unknown solution*

$$= 5 \times \text{weight of the substance in 200 ml. measuring flask} \\ \times \frac{\text{Volume of intermediate soln. used with unknown soln.}}{\text{Volume of intermediate soln. used with known soln.}}$$

(c) *The strength in gms/litre of the unknown solution*

$$= 10 \times \text{weight of the substance in 100 ml. measuring flask} \\ \times \frac{\text{Volume of intermediate soln. used with unknown soln.}}{\text{Volume of intermediate soln. used with known soln.}}$$

(d) *The strength of unknown solution in gms/litre*

$$= \frac{1000 \times W \times V_2}{x \times V_1}$$

where,

W = Weight of the substance taken in the measuring flask.

x = Volume or capacity of the measuring flask.

V₁ = Volume of intermediate soln. used with known soln.

V₂ = Volume of intermediate soln. used with unknown soln.

(e) *Strength of unknown solution in gm/litre*

$$= \frac{1000 \times W \times V_1}{x \times V_2}$$

(When intermediate soln. is taken in conical flask.)

where,

W = Weight of the substance taken in the measuring flask.

x = Capacity of the measuring flask.

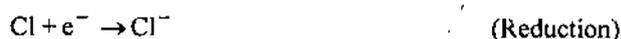
V₁ = Volume of prepared solution used.

V₂ = Volume of the supplied (unknown) solution used.

OXIDATION-REDUCTION OR REDOX TITRATIONS

Many substances in solution can be estimated by oxidation-reduction reactions. In these methods an oxidizing or reducing agent reacts with another reducing or oxidizing agents respectively.

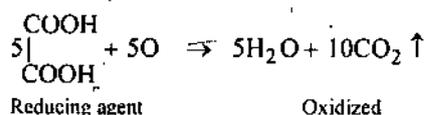
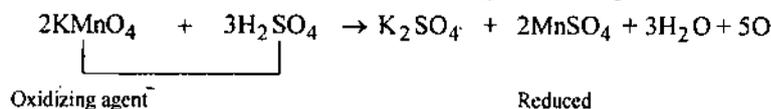
Oxidation-reduction reactions are characterised by the transfer of electrons in the reactions. Oxidation is a process in which electrons are furnished e.g., Reduction is a process in which electrons are accepted.



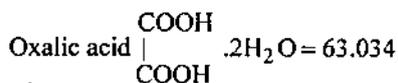
The titrations involving the solutions of oxidizing and reducing agent substances are known as oxidation-reduction titrations or redox titrations.

The solutions of oxidizing and reducing agents react together and destroy the oxidizing and reducing properties of each other.

Actually oxidation and reduction are complementary to one another and take place simultaneously, while one substance is being oxidized, the other one is being reduced e.g.,



Equivalent weights :

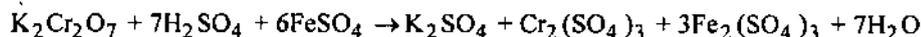
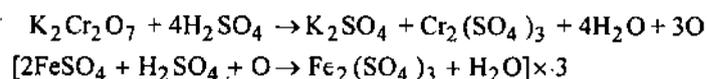


Potassium permanganate (KMnO_4) = 31.6.

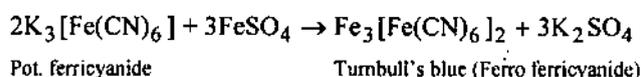
[ESTIMATION OF IRON USING $\text{K}_2\text{Cr}_2\text{O}_7$] FERROUS AMMONIUM SULPHATE- $\text{K}_2\text{Cr}_2\text{O}_7$ TITRATION (EXTERNAL INDICATOR)

Experiment 1. Prepare $\frac{N}{30}$ ferrous ammonium sulphate standard solution and find the strength of supplied ferrous ammonium sulphate solution using $\text{K}_2\text{Cr}_2\text{O}_7$ soln. as an intermediate solution.

Reaction : Ferrous sulphate is the active constituent of ferrous amm. sulphate. It is oxidized to ferric sulphate by acidified potassium dichromate as follows :



Potassium ferricyanide gives a blue coloured ppt. with ferrous ions only and no reaction takes place with ferric salt.



Indicator : *Potassium ferricyanide (External).

End point : No green colour by the reaction mixture with the indicator (No change in colour of the indicator).

*It should be freshly prepared because its solution does not keep well for a long time.

Equivalent weights :

Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) = 49.03.

Ferrous ammonium sulphate [$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$] = 392.10.

Amount of ferrous ammonium sulphate $\left(\frac{N}{30}\right)$ to be dissolved in 100 ml. measuring flask = $\frac{392.10}{30} \times \frac{100}{1000} = 1.3060$ gm

Amount of ferrous ammonium sulphate $\left(\frac{M}{30}\right)$ to be dissolved in 100 ml. measuring flask = $\frac{392.10}{30} \times \frac{100}{1000} = 1.3060$ gm

In pipette : (Conical flask) Ferrous ammonium sulphate solution.

In burette : $K_2Cr_2O_7$ solution.

Procedure : Prepare standard solution of ferrous amm. sulphate $\left\{ \text{Approx. } \frac{N}{30} \right\}$. Nearly 10 ml. of dil.

H_2SO_4 are added before making the volume up to mark in the measuring flask. Dissolve 1.3060 g of ferrous ammonium sulphate in a 100 ml. measuring flask with distilled water.

Take 20 ml. of ferrous amm. sulphate solution in a conical flask and add about one full test tube (20 ml.) of dil. H_2SO_4 in it. Now run in the dichromate solution from a burette and add nearly 10 ml. of the dichromate solution in the conical flask without taking out any drop from it. Now remove a drop of the solution from the titration flask by means by a glass rod, and touch it with a drop of ferricyanide on the tile or white paper. If a blue colour is produced it shows the presence of ferrous ions in the solution that is being titrated. Continue the addition of dichromate, until a drop of the solution in the titration flask ceases to give any colour with the ferricyanide indicator. The glass rod must be washed each time before used for withdrawing a drop from the titration flask.

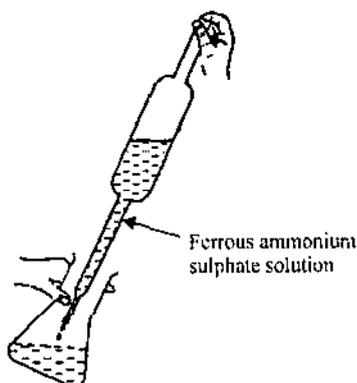


Fig. 8. Method of pipetting solution

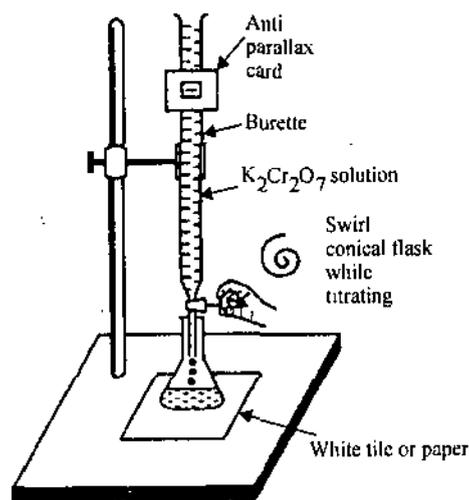


Fig. 9. Method of titration

After the first titration, which obviously is a rough one, the dichromate solution is run into the ferrous amm. sulphate solution without testing, to within half a ml. of the rough reading.

[Rough reading is low because a number of drops have been removed from the titration flask]. As far as possible least number of drops of reaction mixture should be taken out. The minimum the number of drops taken out, greater will be accuracy.

Then it is run dropwise, the solution being tested after the addition of each drop.

The first few titrations will not give accurate results but will a little accuracy and practice burette readings will be obtained in the subsequent titrations.

Now wash the pipette with water and rinse it with supplied (unknown) ferrous amm. sulphate solution and pipette out 20 ml. of this solution in a clean conical flask. Repeat the titration, using the same $K_2Cr_2O_7$ solution in the burette as usual.

Observations and Calculations :

- (1) Weight (approx.) of empty weighing tube = 10.20 g
- (2) Weight of weighing tube + Ferr. amm. sulphate = 11.5186 g
- (3) Weight of empty weighing tube = 10.2126 g

Note : Series of smallest possible drops of the indicator solution should be placed on dry white tile or paper by means of a thin glass rod.

Hence weight of ferrous ammonium sulphate dissolved in 100 ml measuring flask.

$$= 115186 - 102126 = 13060 \text{ g}$$

$$\text{Weight of } \text{FeSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O} = 1.3060 \times 10 = 13.06 \text{ g L}^{-1}$$

\(\therefore\) Normality of $\text{FeSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$ (prepared)

$$= \frac{\text{Strength (g L}^{-1}\text{)}}{\text{Equivalent weight}} = \frac{13.06}{392.10} \text{ N}$$

(i) Volume of $\text{K}_2\text{Cr}_2\text{O}_7$ used with 10 ml of known (prepared) ferrous ammonium sulphate solution.

S. No.	Volume of ferrous amm. sulphate taken	Initial reading of burette	Final reading of burette	Volume of $\text{K}_2\text{Cr}_2\text{O}_7$ used
1	10 ml	0 ml	11.0 ml	11.0 ml
2	10 ml	0 ml	11.5 ml	11.5 ml
3	10 ml	0 ml	11.7 ml	11.7 ml
4	10 ml	0 ml	11.7 ml	11.7 ml

} Concurrent reading

Concordant reading = 11.7 ml

Volume of $\text{K}_2\text{Cr}_2\text{O}_7$ used with 10 ml of unknown (supplied) ferrous ammonium sulphate solution

S. No.	Volume of ferrous amm. sulphate taken	Initial reading of burette	Final reading of burette	Volume of $\text{K}_2\text{Cr}_2\text{O}_7$ used
1	10 ml	0 ml	10.0 ml	10.0 ml
2	10 ml	0 ml	10.5 ml	10.5 ml
3	10 ml	0 ml	10.2 ml	10.2 ml
4	10 ml	0 ml	10.2 ml	10.2 ml

} Concurrent reading

Concordant reading = 10.2 ml

For the titration using standard ferrous ammonium sulphate solution

$$N_1 V_1 = N_2 V_2$$

(ferrous amm. sulphate) ($\text{K}_2\text{Cr}_2\text{O}_7$)

$$\frac{13.06}{392.1} \times 10 = N_2 \times 11.7$$

or Normality of $\text{K}_2\text{Cr}_2\text{O}_7$, $N_2 = \frac{13.06 \times 10}{392.1 \times 11.7} \text{ N}$

For the titration using supplied ferrous ammonium sulphate solution,

$$N_3 V_3 = N_4 V_4$$

(ferrous amm. sulphate) ($\text{K}_2\text{Cr}_2\text{O}_7$)

$$N_3 \times 10 = \frac{130.6}{392.1 \times 11.7} \times 10.2$$

\(\therefore\) Normality of ferrous ammonium sulphate solution,

$$N_3 = \frac{130.6 \times 10.2}{392.1 \times 11.7 \times 10} \text{ N}$$

\(\therefore\) Strength of ferrous ammonium sulphate (g L^{-1})

$$= \text{Normality} \times \text{Eq. wt.}$$

$$= \frac{130.6 \times 10.2}{392.1 \times 11.7 \times 100} \times 392.1$$

$$= 11.3856 \text{ gL}^{-1}$$

Alternate Method of Calculation

Strength of ferr. amm. sulphate (gL^{-1})

$$= \frac{10 \times \text{wt. of ferrous amm. sulph.} \times \text{Vol. of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ with supplied soln.}}{\text{Vol. of } \text{K}_2\text{Cr}_2\text{O}_7 \text{ with prepared soln.}}$$

$$= \frac{10 \times 1.3060 \times 10.2}{11.7}$$

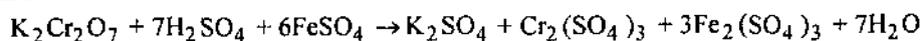
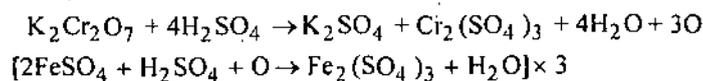
$$= 11.3856 \text{ gL}^{-1}$$

Result : The strength of the supplied ferr. amm. sulphate solution is 11.3856 gL^{-1} .

**$\text{FeSO}_4 \cdot (\text{NH}_2)_2\text{SO}_4 \cdot 6\text{H}_2\text{O} - \text{K}_2\text{Cr}_2\text{O}_7$ TITRATION
(INTERNAL INDICATOR)**

Experiment 2. Prepare $\frac{N}{30}$ ferrous ammonium sulphate standard solution and find out the strength of supplied ferrous ammonium sulphate solution using $\text{K}_2\text{Cr}_2\text{O}_7$ solution as an intermediate solution (internal indicator).

Reaction : Ferrous sulphate is the active constituent of ferrous amm. sulphate. It is oxidized to ferric sulphate by acidified potassium dichromate as follows :



Diphenylamine is used as an internal indicator. So long as ferrous ions are present, it is not oxidised but the moment, the dichromate is present in slight excess, the diphenylamine is oxidized by dichromate and a bluish violet or purple colour appears.

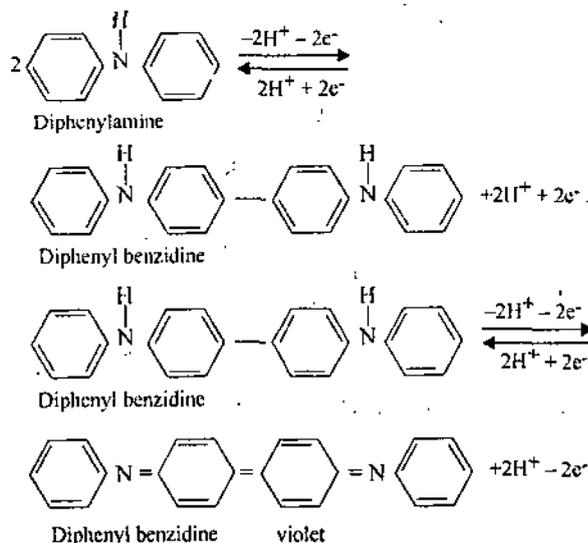
Indicator : Diphenylamine.

End point : Appearance of bluish violet or purple colour.

In pipette (Conical flask) : Ferrous ammonium sulphate solution.

In burette : $\text{K}_2\text{Cr}_2\text{O}_7$ solution.

Indicator solution : It is prepared by dissolving 1 gm. of diphenylamine in 20 ml. of concentrated sulphuric acid.



Procedure : Take 20 ml. of standard ferrous ammonium sulphate solution in a conical flask and about 35 ml. of a mixture of sulphuric and phosphoric acids. (It is prepared by adding 10 ml. of syrup phosphoric acid and 10 ml. of concentrated sulphuric acid to 50 ml. of water and dilute to 100 ml.). Add 3 – 4 drops of the indicator and 10 ml. of (1 : 2) H_2SO_4 . Now run in the dichromate solution from a burette.

At the end point colour change is from green to bluish violet or purple. Repeat the titration till two consecutive readings are the same.

Now wash the pipette with distilled water and rinse it with the supplied (unknown) ferrous ammonium sulphate solution and pipette out 20 ml. of this solution in a clean conical flask. Repeat the titrations, using the same $K_2Cr_2O_7$ solution in the burette, as usual.

Calculate the result as explained in experiment 1.

Note 1. In this titration, we can also take potassium dichromate in titration flask and ferrous ammonium sulphate in the burette. Indicator, phosphoric acid, sulphuric acid in the requisite amount are added to titration flask containing potassium dichromate. The colour of the mixture is bluish violet at this stage. Ferrous ammonium sulphate solution is run in from the burette till the colour changes to green. This is the end point.

$K_2Cr_2O_7$ —FERROUS AMMONIUM SULPHATE TITRATION

Experiment 3. Prepare $\frac{N}{30}$ potassium dichromate standard solution and find the strength of supplied potassium dichromate solution using ferrous ammonium sulphate as an intermediate solution.

Reaction : Same as in experiment 1.

Indicator : Same as in experiment 1.

In pipette (conical flask) : Ferrous Amm. Sulphate solution.

In burette : $K_2Cr_2O_7$ soln.

Procedure : Prepare a standard solution of $K_2Cr_2O_7$ * $\left(\text{Approx. } \frac{N}{30} \right)$. Dissolve 0.1633 gms. of potassium dichromate in a 100 ml. measuring flask with distilled water. Rinse the burette with it and fill up to zero mark. Take 20 ml. of ferrous amm. sulphate soln. in a conical flask, and add about one full test tube (20 ml.) of dil. H_2SO_4 in it. Titrate by the same method as explained in experiment 1.

Now rinse the burette with the supplied $K_2Cr_2O_7$ solution and fill with it. Repeat the titration with the supplied $K_2Cr_2O_7$ solution taking the same ferrous ammonium sulphate solution by means of a pipette.

Record the observations as explained in experiment 1. In this experiment calculation is done as follows :

Strength of the $K_2Cr_2O_7$ solution in gms/litre

$$= \frac{1000 \times W \times V_1}{x \times V_2}$$

where, W = Wt. of the substance taken in the measuring flask.

x = Capacity of the measuring flask.

V_1 = Volume of the prepared solution used.

V_2 = Volume of the supplied solution used.

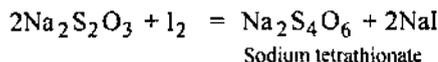
IODIMETRY AND IODOMETRY TITRATIONS

The branch of volumetric analysis based upon the use of iodine as an oxidizing agent is called Iodimetry or Iodometry. Iodimetry, as the word implies, is concerned with titrations using standard solution of iodine

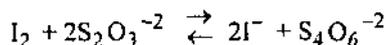
* Amount of potassium dichromate $\left\{ \frac{N}{30} \right\}$ to be dissolved in 100 ml. measuring flask = $\frac{49.03}{30} \times \frac{100}{1000} = 0.1633$ gm.

while Iodometry deals with the titrations of iodine liberated in chemical reactions. Iodine is no doubt a much weaker oxidizing agent than potassium permanganate and dichromate.

The usefulness of iodine in volumetric analysis depends largely upon its reaction with sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$. The reaction between iodine solution and $\text{Na}_2\text{S}_2\text{O}_3$ is represented by the equation.



Or



Sodium tetrathionate and sodium iodide being formed. By this reaction iodine can be estimated in any solution when in the free state. This is useful reaction and provides a means of estimating oxidising and reducing agents, since iodine is liberated from acidified potassium iodide by oxidising agents.

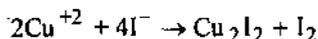
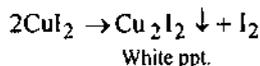
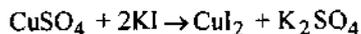
Important : In these titrations a standard solution of hypo can not be prepared as it is hygroscopic. Therefore hypo is always used as the intermediate solution and is always taken in the burette. The solution of iodine (solution or liberated) is always taken in the conical flask.

[ESTIMATION OF COPPER USING SODIUM THIOSULPHATE]

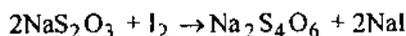
$\text{CuSO}_4 - \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ TITRATION

Experiment 4. Prepare $\frac{N}{30}$ copper sulphate standard solution and find the strength of supplied copper sulphate solution using sodium thiosulphate as an intermediate solution.

Reaction : Copper sulphate reacts with KI forming cupric iodide which is unstable and gives cuprous iodide.



Iodine so liberated gets dissolved in KI forming brown solution. This liberated iodine is titrated against sodium thiosulphate solution.



Indicator : Starch solution.

End point : Disappearance of blackish-blue colour.

In pipette (conical flask) : CuSO_4 solution.

In burette : Hypo solution.

Procedure : Prepare standard solution of CuSO_4 . Dissolve 0.8333 gms. of copper sulphate (N/30) in a 100 ml. measuring flask with distilled water. Add nearly one full test tube of acetic acid in this solution before making it up to the mark in the measuring flask. Pipette out 20 ml. of this solution in a conical flask and add 1 gm. of solid KI and shake it. **Dark yellow colour** will be developed due to the liberated of iodine

Equivalent weights :

Copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) = 249.71

Sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) = 248.20.

Amount of copper sulphate (N/30) to be dissolved in 100 ml. measuring flask

$$= \frac{249.71}{30} \times \frac{100}{1000} = 0.8333 \text{ gm}$$

Amount of copper sulphate (M/30) to be dissolved in 100 ml. measuring flask

$$= \frac{249.71}{30} \times \frac{100}{1000} = 0.8333 \text{ gm}$$

and its dissolution in excess of KI (solution of iodine in KI is dark yellow). Run down from the burette the solution of sodium thiosulphate until a pale yellow colour appears. Add 1 c.c. freshly prepared starch solution—a bluish-blue colour is developed. Continue addition of thiosulphate drop by drop with constant shaking until the bluish-blue colour just disappears. Repeat the process till concurrent readings are obtained.

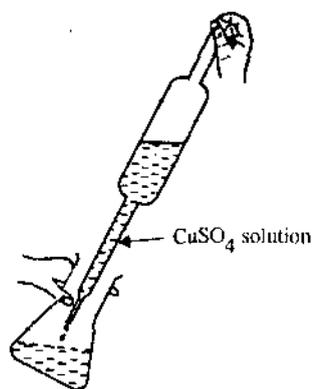


Fig. 10

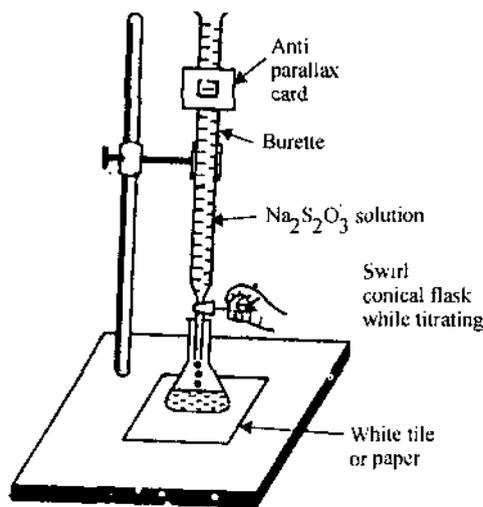


Fig. 11

Proceed exactly in the same manner with the solution of CuSO_4 of unknown strength.

Record the observations as explained in Experiment 1.

Calculate the results as explained in experiment 1.

Note :

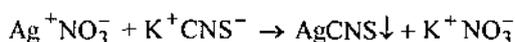
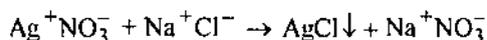
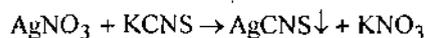
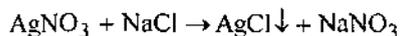
(i) The amounts of KI and starch solution should almost be equal in each titration.

(ii) CuSO_4 solution must be free from any acid except a little acetic acid which checks the hydrolysis of copper sulphate.

(iii) Cu_2I_2 is insoluble in acetic acid, hence its presence is not harmful in this titration. It is dirty pink in colour due to adsorption of iodine. This precipitate releases adsorbed iodine very slowly to the solution for reaction with hypo. Addition of little KCNS or NH_4CNS , a little before the end point serves to displace the adsorbed iodine very quickly and thus will serve to give a better end point.

PRECIPITATION TITRATIONS

Precipitation process of volumetric analysis is based upon the formation of insoluble precipitates when the reacting solutions are brought together. Thus when a solution of AgNO_3 is treated with a solution of NaCl or KCNS, we get a white ppt. of silver chloride (AgCl) or silver thiocyanate (AgCNS).



This allows volumetric estimation of silver by titrating against NaCl or KCNS, using a suitable indicator. In the titration with NaCl, a neutral solution of K_2CrO_4 is used as indicator (**Mohr's method**) and in the titration with KCNS, an acidic solution (HNO_3) of ferric alum is used as an indicator (**Volhard's method**).

For efficient precipitation titrations, the following conditions must be fulfilled :

(a) The substance (precipitated) must be formed quickly.

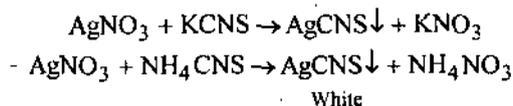
(b) The substance precipitated should be relatively insoluble substance and should be the only substance to precipitate on adding the reagent.

(c) A detectable change at the end point should be observable in the reaction.

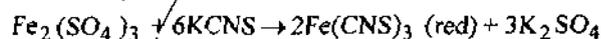
**[ESTIMATION OF SILVER USING AMMONIUM THIOCYANATE
OR SODIUM CHLORIDE]
AgNO₃ – NH₄CNS TITRATION**

Experiment 5. Prepare $\frac{N}{30}$ AgNO₃ standard soln. and find out the strength of supplied AgNO₃ solution using potassium or amm. thiocyanate as an intermediate solution.

Reaction : When AgNO₃ is treated with KCNS or NH₄ CNS solution a white ppt. of AgCNS is formed.



Slight excess of KCNS or NH₄ CNS gives blood red tinge with ferric salt.



Indicator : Ferric alum solution.

End point : Appearance of light red colour or tinge.

In pipette : (Conical flask) : AgNO₃ solution.

In burette : NH₄ CNS solution.

Procedure : Prepare (N/30) AgNO₃ standard solution. Dissolve 0.5663 g. of silver nitrate in 100 ml. measuring flask with distilled water. Now rinse and fill the burette with the given intermediate solution (KCNS or NH₄ CNS). Pipette out 20 ml. of the standard AgNO₃ solution in the conical flask. Add 5 c.c. of the purified HNO₃* and 1 c.c. of the ferric alum indicator solution. The thiocyanate solution is then run from the burette. At first a white ppt. of AgCNS is obtained. Each drop of thiocyanate added gives a red colour which disappears on slight shaking. Near the end point the ppt. flocculates and settles. **Finally a faint red colour is obtained by adding a drop or two of thiocyanate solution.**

This is the end point. Repeat titration till concurrent readings are obtained.

Repeat the titration exactly in the same manner with the solution of AgNO₃ of unknown strength.

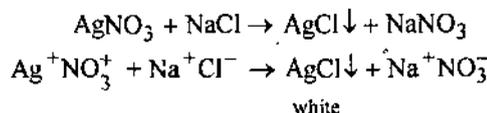
Record the observations as explained in experiment 1.

Calculate the result as explained in experiment 1.

NaCl – AgNO₃ TITRATION

Experiment 6. Prepare $\frac{N}{30}$ sodium chloride standard solution and find out the strength of supplied sodium chloride solution using silver nitrate as an intermediate solution.

Reaction : Silver nitrate reacts with sodium chloride to give a white ppt. AgCl.



Equivalent weights :

Silver nitrate (AgNO₃) = 169.89

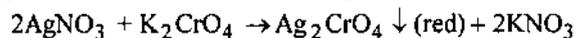
Ammonium thiocyanate (NH₄CNS) = 76.00.

*It is colourless and free from lower oxides of nitrogen. It is prepared by boiling conc. nitric acid and water (4 : 1 until the solution becomes colourless).

Amount of silver nitrate (N/30) to be dissolved in 100 ml. measuring flask

$$= \frac{169.89}{30} \times \frac{100}{1000} = 0.5663 \text{ gm.}$$

Slight excess of AgNO_3 gives a brick red ppt. with K_2CrO_4 .



Indicator : Potassium chromate solution.

End point : Appearance of brick red precipitate.

In pipette (Conical flask) : NaCl solution.

In burett : AgNO_3 solution.

Procedure : Prepare a standard solution (N/30) of sodium chloride. Dissolve 0.1933 gms. of sodium chloride in a 100 ml. measuring flask with distilled water. Take 20 ml. of this solution in the conical flask with the help of pipette and add 4-5 drops K_2CrO_4 solution. Titrate it with the AgNO_3 solution taken in the burette. Go on adding AgNO_3 solution with continuous shaking drop by drop from the burette till a permanent faint red colouration is imparted to the precipitate.

Repeat this process till two concurrent readings are obtained.

Perform the titration exactly in the similar manner with the given sodium chloride solution of unknown strength.

Record the observations as explained in experiment 1.

Calculate the result as explained in experiment 1.



Equivalent weights :

Silver nitrate (AgNO_3) = 160.89

Sodium chloride (NaCl) = 58.46

Ammonium thiocyanate (NH_4CNS) = 76.00

Amount of sodium chloride (N/30) to be dissolved in 100 ml. measuring flask

$$= \frac{58.46}{30} \times \frac{100}{1000} = 0.1933$$

Amount of sodium chloride (M/30) to be dissolved in 100 ml. measuring flask

$$= \frac{58.46}{30} \times \frac{100}{1000} = 0.1933$$

CHAPTER

2

TEST YOURSELF IN VIVA VOCE FOR PRACTICE

You should know the answer of the following questions during practical examination :

1. What do you understand by the term titration ?
2. Why does titration known as volumetric analysis ?
3. What is gram equivalent ?
4. What is standard solution ?
5. What is normal solution ?
6. What do you understand by the strength and normality of the solution ?
7. What is end point ?
8. How is end point known ?
9. What is indicator ?
10. How many types of indicators do you know ?
11. Can you differentiate internal indicators ?
12. What are oxidation-reduction reactions ?
13. What is oxidation ?
14. What is reduction ?
15. What is oxidising agent ?
16. What is reducing agent ?
17. What do you know about equivalent weight of oxidising agent ? Determine the equivalent weight of KMnO_4 in acidic medium.
18. Does the equivalent weight of the substance depend upon the chemical reaction ?
19. Determine the equivalent weight of potassium dichromate in acidic medium.
20. Why do you prepare standard solution in distilled water ?
21. If you add some water in the conical flask, after taking the solution from pipette. Is there any effect on the titration ?
22. How many types of titrations do you know ?
23. Why do you use potassium ferricyanide as an external indicator in the titration of ferrous ammonium sulphate and potassium dichromate ?
24. Write down the chemical equation taking place in ferrous ammonium sulphate and potassium dichromate titration.
25. The molecular weight of ferrous ammonium sulphate is $392.1 \text{ g mole}^{-1}$. What is the equivalent weight ?
26. Why do you use dil. H_2SO_4 in the preparation of standard solution of ferrous ammonium sulphate ?
27. What are iodine titration ?
28. How do iodine liberate in iodometric titrations ?

29. What happens when hypo solution is added in $\text{CuSO}_4 + \text{KI}$ solution ?
30. Why do you use freshly prepared starch solution ?
31. Why do you add starch solution near the end point ?
32. Why should the solution of copper sulphate be neutral in the iodometric titration ?
33. What do you mean by precipitation titration ?
34. Why do you add nitric acid in the titration of silver nitrate by Volhard's method ?
35. Can you prepare standard solution of ammonium thiocyanate ?
36. Is the excess of acid in Volhard's method harmful ?
37. Which type of end point develops in Volhard's method ?
38. Why should the reaction mixture be stirred in Volhard's method ?
39. Can Volhard's method be used in the titration of chloride salts ?
40. What is Mohr's salt ? Why do you prefer it in place of ferrous sulphate ?
41. Why do you use ferric alum as internal indicator in the titration of silver nitrate-potassium sulphocyanide ?

□

CHAPTER

3

ORGANIC ANALYSIS

The analysis of organic compound is fundamentally different from that of the inorganic salts. The analysis of inorganic salt consists of the detection of acidic and basic radicals which are relatively few in number and give quickly precipitates with the group reagents. The scheme of their analysis is, therefore, very systematic and concise. Organic compounds, on the other hand, give very slow and often indistinct reactions. Further-more, the number of groups in organic compounds is too much large and their reactions vary from compound to compound, depending on the molecular structure. It is thus evident that organic analysis is greatly complicated and no hard and fast rules can be laid down for the same.

Therefore, in order to affect a quick and correct identification, the sequence of the following operations should be strictly adopted.

1. Preliminary observations.
2. Heating effect.
3. Solubility determination.
4. Detection of elements.
5. Determination of melting point or boiling point.
6. Detection of functional groups.
7. Confirmation of functional groups.
8. Classification of compounds.
9. Identification of compounds.
10. Preparation of derivatives.
11. Method of recording the result.

1. Preliminary Observations

The observations are of immense importance for the identification of the organic substances. They include physical state, colour, odour, appearance etc. which are described below :

(a) Physical state : The knowledge of the physical state of the given compound is very essential. Whether the given compound is crystalline or amorphous, solid or liquid, viscous or mobile, all the facts should be carefully recorded.

As a matter of fact the compounds belonging to the same class (i.e., homologous series) are liquids when their molecular weights are low and solid when higher. Many of the lower alcohols, aldehydes, ketones, monobasic acid and their esters etc. are liquids, while the aliphatic dibasic acids, aromatic acids, amides etc. are solids.

Phthalic acid has needle shape crystals and benzoic acid is prismatic crystalline solid. Some compounds (i.e., osazones) have characteristic crystalline structure if examined under microscope.

Glycerol is very viscous. Benzene and toluene being lighter therefore form the upper layer with water. While chloroform, carbon tetrachloride and chlorobenzene being heavier and form the lower layer with water.

(b) Colour : The colour of the substance also gives a little information regarding the chemical nature of the compound.

A majority of the compounds containing carbon and hydrogen with or without oxygen and halogens are usually colourless. Some of these which contain chromophoric groups are coloured (e.g., benzoquinone).

Many compounds containing nitrogen such as nitro phenols, azo-benzene etc. are coloured (colour usually ranging from pale white to brown red). A few are colourless when pure but darken on exposure to air such as aniline.

The characteristic colour of few compounds are as given below :

Pale yellow ...	Nitrobenzene (liquid)
Brownish yellow ...	Aniline (liquid)
Pinkish ...	β -Naphthol (Solid)

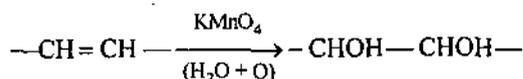
(c) **Odour** : The odour of some of the compounds is much more suggestive than any other physical characteristic. The characteristic odours of the various compounds are as below :

Carbolic smell ...	Naphthols and their homologues
Fishy smell ...	Aromatic amines
Winous or spirituous smell ...	Alcohols
Pleasant smell ...	Acetophenone
Mouse like smell ...	Acetamide
Smell of bitter almonds ...	Benzaldehyde, nitro-benzene
Characteristic ...	nitro-toluenes
Aromatic smell ...	Benzene and toluene
Smell of moth balls ...	Naphthalene
Characteristic smell ...	<i>p</i> -Dichloro benzene

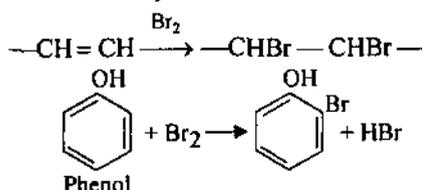
But they are not quite certain for the sense of smell as it varies greatly with the individual, and moreover substance of different constitutions may have similar odours.

(d) **Saturation and unsaturation** : It is necessary to investigate whether the given compound is saturated or unsaturated. It can be judged as follows :

(i) Shake the given compound in the form of solution with 2 or 3 drops of Baeyer reagent *i.e.*, 1% alkaline KMnO_4 solution. If the pink colour is discharged, the given compound is unsaturated in character or otherwise it is saturated.



(ii) Similar test can be performed with the solution of bromine water. The decolorisation of bromine water shows the unsaturation of the compound.



Note : Students are advised to be well acquainted with the characteristic residues. Sometimes they give very important information. A few characteristics are given below :

- White glistening plates—*Benzoic and salicylic acids.*
- Transparent sticky—*Cane sugar, tartaric acid, citric acid.*
- Reddish or brownish—*Impure glucose, resorcinol, aniline salts.*
- Naphthalene*, may volatilise with steam and not leave any solid residue.
- Aniline, nitro benzene and benzaldehyde* may volatilise with steam and leave no liquid residue.
- Solid, white with blister—*Acetanilide.*

(2) Heating Effect

The nature of the vapours evolved on heating a substance and the type of flame obtained on ignition gives, in most of the cases, a fair indication of general class to which the compound belongs. In actual practice, 0.1 gm of the solid or 3-4 drops of the liquid is taken on the nickel spatula and heated at first gently and then strongly. The following facts are then observed whether it :

- (i) is inflammable,
- (ii) melts and then vapourises or chars,
- (iii) sublimes,
- (iv) does not melt but chars,
- (v) emits vapours of characteristic odour.
- (vi) leaves a residue.

On burning the compound, the copious smoke and the colour of the flame should also be noted.

(a) If it burns with smoky flame.

—Aromatic*

Certain aliphatic compounds e.g., chloroform, chloral hydrate etc. also give smoky flame.

(b) If it burns without smoke.

—Aliphatic*

Certain aromatic alcohol e.g., benzyl alcohol does not burn with smoky flame.

If the compound gives yellow colour solution on boiling with conc. nitric acid, the compound is aromatic, otherwise aliphatic.

(3) Solubility Determination

The solubility of the organic compounds in various solvents also give valuable information about the chemical nature of the compound. For example, acids are usually soluble in hot water, or alcohol but sparingly soluble in cold water. Hydrocarbons are, on the other hand, quite insoluble in water but soluble in ether and benzene.

The solubility of the substance in the solvent is determined by vigorous shaking of 0.1 gm. of solid or 3-4 drops of liquid in 3 c.c. of the solvent taken in test tube. The transparent solution so obtained, clearly indicates the solubility of that particular solvent.

The solubility of the substance is determined successively in

- (i) water
- (ii) 5% aqueous sodium hydroxide,
- (iii) 5% aqueous sodium bicarbonate,
- (iv) 5% dilute hydrochloric acid and,
- (v) conc. sulphuric acid.

The classification of the organic compounds based upon the solubility is given as follows :

Soluble in cold water	Insoluble in cold water					
	Soluble in 5% aq. NaOH		Insoluble in 5% aq. NaOH			
	Also soluble in 5% aq. NaHCO ₃	Insoluble in 5% aq. NaHCO ₃	Soluble in 5% aq. HCl	Insoluble in 5% aq. HCl		
				Compounds containing N or S or both	Compounds not containing N or S	
			Soluble in conc. H ₂ SO ₄		Insoluble in conc. H ₂ SO ₄	
Group I	Group III	Group III	Group IV	Group V	Group VI	Group VII

*Aromatic compounds contain a high percentage of carbon as such they burn with smoky flame.

**Aliphatic compounds contain a low percentage of carbon as such they burn without smoky flame.

Following are the lists of various possible compounds which have been placed in different groups on the basis of their solubility behaviour.

Group I

Compounds soluble in cold water

Alcohols	...	Methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl alcohol, glycol, glycerol.
Aldehydes	...	Formaldehyde, acetaldehyde.
Ketones	...	Acetone, methyl ethyl ketone.
Acids	...	Formic, acetic, propionic acid, oxalic, malonic, succinic acid, malic, tartaric, citric acid.
Esters	...	Methyl, ethyl acetate; methyl, ethyl oxalates
Sugars	...	Glucose, fructose, sucrose.
Phenols	...	Phenol, resorcinol, pyrogallol, hydroquinone
Chloroaldehydes	...	Chloral hydrate.
Sulphonic Acids	...	Benzene sulphonic acid.
Amides	...	Formamide, acetamide, urea.
Amines	...	Hexamine, benzaldehyde, simple aliphatic amines.

Group II

Compounds insoluble in cold water but soluble in 5% aq. NaOH and 5% aq. NaHCO₃ both

Acids	...	Benzoic, salicylic, cinnamic and phthalic acid.
Amino acids	...	Anthranilic and <i>p</i> -aminobenzoic acids.
Halogeno	...	Bromo benzoic and chlorobenzoic acids
Substituted acids	...	(<i>o</i> , <i>m</i> -or <i>p</i> -)
Amino sulphonic acid	...	Sulphonic acid.
Nitro phenols	...	<i>o</i> -and <i>p</i> -Nitrophenols, picric acid.
Halogeno phenols	...	2 : 4 : 6-Trichlorophenol.
	...	2 : 4 : 6 Tribromophenol.

Group III

Compounds insoluble in cold water, soluble in 5% aq. NaOH but insoluble in 5% aq. NaHCO₃

Phenols	...	Phenol, <i>o</i> -, <i>m</i> -and <i>p</i> -cresols; α -and β -naphthols.
Halogeno	...	Chlorophenols (<i>o</i> -, <i>m</i> -, <i>p</i> -)
Substituted Phenols	...	Bromophenols (<i>o</i> -, <i>m</i> -, <i>p</i> -)

Group IV

Compounds insoluble in cold water and soluble in 5% aq. HCl but insoluble in 5% aq. NaOH.

Primary amines	...	Aniline, <i>o</i> -, <i>m</i> - and <i>p</i> -toluidines, α - and β -naphthylamines
Secondary amines	...	Methyl aniline, ethyl aniline
Tertiary amines	...	Dimethyl aniline, diethyl aniline
Nitro amines	...	<i>o</i> -nitro, <i>p</i> -nitro and <i>m</i> -nitro aniline
Halogeno amines	...	<i>p</i> -chloro and <i>m</i> -chloro aniline.
	...	<i>p</i> -bromo and <i>m</i> -bromo aniline.

Group V

Compounds containing N or S with or without halogens; insoluble in water, 5% aq. NaOH, 5% aq. NaHCO₃ and 5% aq. HCl.

Nitro compounds	...	Nitrobenzene; <i>o</i> -, <i>m</i> - and <i>p</i> -nitrotoluene, 2 : 4-dinitrobenzene, <i>o</i> -nitronaphthalene
Secondary amines	...	Diphenyl aniline

Nitro amines	...	<i>o</i> -Nitroaniline, 2 : 4 dinitroaniline
Halogeno aromatic	...	2 : 4 : 6-Tribromoaniline
Amines	...	2 : 4 : 6-Trichloroaniline
Higher amides	...	Benzamide
Substituted amines	...	Acetamide.

Group VI

Compounds insoluble in cold water, 5% aq. NaOH, 5% aq. NaHCO₃ and 5% aq. dil. HCl but soluble in conc. H₂SO₄.

Higher aldehydes	...	Benzaldehyde, paraldehyde.
Higher ketones	...	Acetophenone, benzophenone.
Higher esters	...	Ethyl oxalate, phenyl acetate, phenyl benzoate, ethyl benzoate
Ether	...	Dimethyl ether, diethyl ether.

Group VII

Compounds insoluble in cold water, 5% aq. NaOH, 5% aq. NaHCO₃ and 5% aq. dil. HCl and even in conc. H₂SO₄.

Hydrocarbons	...	Hexane, cyclohexane, benzene, toluene, naphthalene.
Chloro hydrocarbons	...	Chlorobenzene, <i>p</i> -dichlorobenzene, benzyl chloride, α -chloronaphthalene
Bromo hydrocarbons	...	Ethyl bromide, bromobenzene, <i>p</i> -dibromo naphthalene, α -bromonaphthalene.
Iodo hydrocarbons	...	Iodobenzene.

A better clue for the classification of the compounds regarding the solubility of solid with cold or hot water is, however, as follows :

(I) Aliphatic solid, soluble in cold water : Citric, oxalic and succinic acid (sparingly soluble), tartaric acid, glucose, cane sugar, urea, acetamide and chloral hydrate.

(II) Aromatic solid, soluble in cold water : Resorcinol, pyrogallol, hydroquinone.

(III) Aliphatic solid, soluble in hot water : Methyl oxalate.

(IV) Aromatic solid, soluble in hot water : Benzoic, phthalic and salicylic acids, phenol, α -naphthol, β -naphthol, nitrophenols, benzamide.

(V) Aliphatic liquid, miscible with cold water : Formic, acetic acids, methyl, ethyl and *n*-propyl alcohols, glycol, glycerol acetaldehyde, formaldehyde (formalin), acetone, methyl ethyl ketone, ethyl oxalate.

(VI) Aromatic liquid, non-miscible with water : Cresols.

(VII) Aliphatic liquid, non-miscible with cold water (floating over water) : *n*-Butyl alcohol, ethyl acetate.

(VIII) Aromatic liquid, non-miscible with cold water (floating over water) : Benzene, toluene, dimethyl aniline, *m*-toluidine.

(IX) Aliphatic liquid, non-miscible with water (forming layer below water) ; Chloroform, carbon tetrachloride, ethylene dichloride, ethyl bromide.

(X) Aromatic liquid, non-miscible with water (forming layer below water) : Benzyl alcohol, phenyl acetate, ethyl benzoate, methyl salicylate, benzaldehyde, acetophenone, aniline, *o*-toluidine, nitro benzene, nitro-toluenes, chlorobenzene, bromo-benzene, phenol.

(4) Detection of Elements

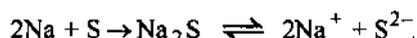
(Nitrogen, Sulphur and Halogens)

In an organic compound the most commonly occurring elements are nitrogen, sulphur and halogens along with carbon, hydrogen and oxygen. The organic compound is subjected for the detection of these elements before the functional groups are to be looked for. In order to identify these elements in organic

compounds, they are converted into ionisable inorganic substances. This may be accomplished by fusing the substance with metallic sodium, thus converting nitrogen, sulphur and halogens to ionisable sodium cyanide, sulphide and halides respectively. This process is known as **Lessaigne's test**.

(I) Lessaigne's Test

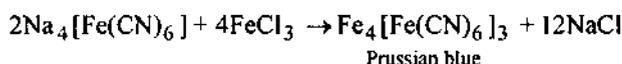
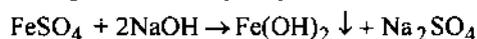
Dry a piece of metallic sodium between a piece of filter paper. Introduce it into a clean ignition tube and then cover it with the given substance and heat gently in the flame holding the tube by means of a pair of tongs. Take the ignition tube away from flame, again heat and repeat this process, three to four times when reaction begins. Wait for some time and heat strongly until the bottom of the tube becomes red hot. Then plunge the tube while hot, into a small beaker or porcelain dish containing 15 ml of distilled water. Stir the contents and allow the remaining sodium to react with water. Boil the mixture for five minutes and filter. This filtrate known as **Sodium Extract** (Lessaigne's solution) should be clear, colourless and transparent, if not repeat the fusion using a larger piece of sodium.



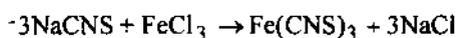
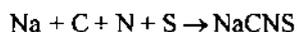
(where, X = Cl, Br, I)

(II) Detection of Nitrogen

Treat 2 c.c. of sodium extract with 2-3 drops of fresh and saturated solution of FeSO_4 followed by 2 drops of NaOH . Boil the contents for 1-2 minutes. Cool it and add 1 c.c. conc. HCl or 2 c.c. dil. H_2SO_4 to dissolve the precipitate of ferrous hydroxide and make the solution acidic. Then add 2 drops of FeCl_3 . Formation of a **prussian blue or greenish blue** precipitate or colouration indicates the presence of nitrogen.



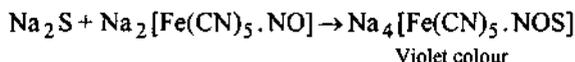
In the presence of sulphur and nitrogen both, it gives blood red colour with the drops of FeCl_3 .



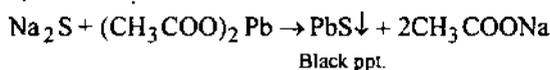
Ferric sulphocyanide
(Blood red)

(III) Detection of Sulphur

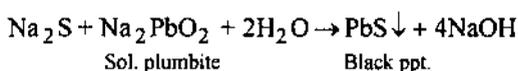
(i) Add 2-3 c.c. of freshly prepared sodium nitroprusside (colourless) to 1 c.c. of sodium extract. A **voilet or purple** colouration confirms the presence of sulphur.



(ii) Alternatively add lead acetate to the sodium extract acidified with acetic acid. A **black** precipitate indicates the presence of sulphur.



(iii) Treat sodium extract (1 c.c.) with 1 or 2 drops of sodium plumbite. Formation of a black colour or precipitate confirms sulphur.

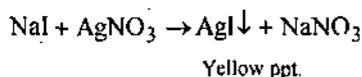
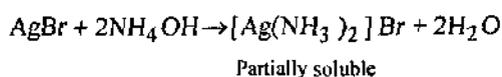
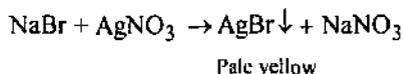
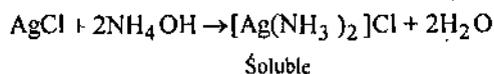
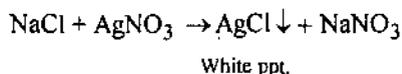


(IV) Detection of Halogens

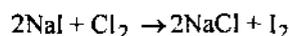
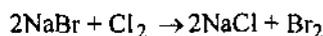
(a) **Silver Nitrate Test** : Boil 2 c.c. of sodium extract with 1 c.c. conc. HNO_3 and then add AgNO_3 .

Note that :

- (i) **White curdy precipitate** soluble in NH_4OH —Cl present.
 (ii) **Pale yellow precipitate** partially soluble in NH_4OH —Br present.
 (iii) **Yellow precipitate** insoluble in NH_4OH —I present.



(b) **Chloroform test** : Acidify the sodium extract with dil. HNO_3 , add 2 drops of chloroform (or CS_2 or CCl_4) and shake vigorously with chlorine water. If chloroform layer turns **pale-brown**, **bromine** is present; but if it turns **violet** then **iodine** is present.



(c) **Beilstein's test for halogens** : This test, is of course, very sensitive for detecting even the traces of halogens. Heat a copper wire at one end in a non-luminous flame till it ceases to impart green colour to the flame. Take a little substance to be tested on the copper wire. Again heat, a green or **bluish green** flame identifies the presence of **halogen**.

This test should not be employed in the presence of urea or thiourea, as they also give green colouration on heating with flame.

(5) Determination of Melting and Boiling Point

The melting point of solid or boiling point of liquid should always be determined because of its immense significance in the identification of particular substance.

(a) **Determination of melting point** : It can be conveniently determined by the apparatus shown in the figure. It consists of 50 c.c. flask half filled with conc. sulphuric acid in which a loosely fitting test tube is so dipped with conc. sulphuric acid in which a loosely fitting test tube is so dipped that it remains about 1 cm above the bottom. This test tube also contains

Note : The following facts should be known that :

(a) If aliphatic solid does not contain strong characteristic smell-Halogen absent. And if it does not evolve NH_3 on heating with NaOH —Nitrogen absent.

(b) Aliphatic liquids never contain **Nitrogen** : If they give sweet smell and are non-miscible and heavier than water. —Halogen definitely present.

(c) If aromatic compounds are soluble in cold water. —Nitrogen and halogen absent.

conc. H_2SO_4 sufficient to cover the bulb of thermometer inserted in it.

In actual practice, a small quantity of the organic substance is finely powdered between the pieces of filter paper and introduce it in a glass capillary closed at one end. The material is picked by gentle tapping the capillary on the table. This capillary is then dropped into the test tube of the bath, along the side of thermometer, with its sealed end down. The open end of the capillary should remain above the surface of sulphuric acid in this inner tube. The flask is gently heated and from time to time the burner is removed so

that the slow steady rise of temperature is maintained. The temperature at which the substance melts and becomes almost transparent is noted. This is melting point.

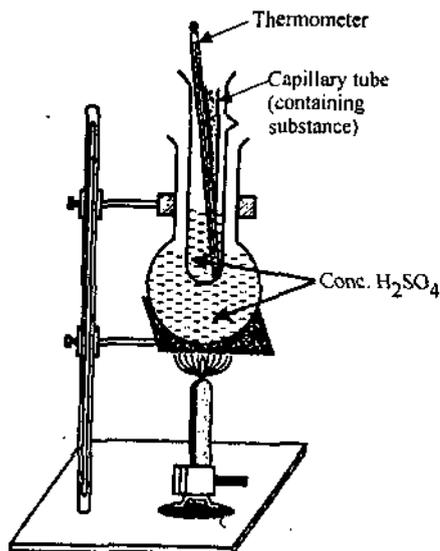


Fig. 1. Determination of melting point.

Traces of moisture or impurities considerably lower the melting point. The substance for the determination of the melting point should, therefore, be dry and pure.

Mixed Melting Point

The mixed melting point is determined to establish the purity of known organic compounds. A small amount of the compound under investigation is mixed with a little of some pure compound (should be arranged from the laboratory). The melting point of such a mixture is determined in the usual manner. If the value of the melting point of the mixture is the same as that of the pure compound then the compound under investigation is pure but if the value of melting point is lower than that of the pure compound then the compound under investigation is impure. Therefore this technique not only helps in the identification of organic compound but also in establishing the purity of known compound.

(b) **Determination of boiling point** : A simple apparatus for the determination of boiling point is shown in the figure. It consists of a hard glass tube. It is fitted with a cork having two holes for the thermometer and a bent tube.

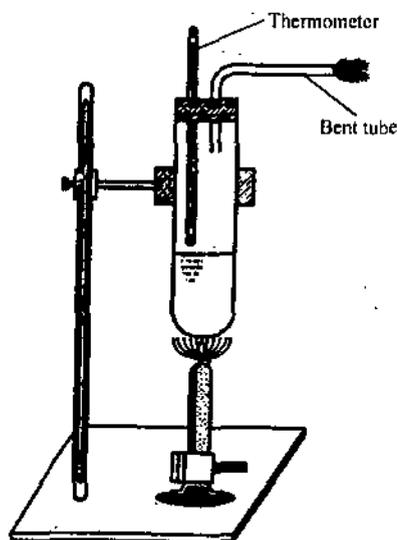


Fig. 2. Determination of boiling point.

The liquid, whose boiling point is to be determined, is taken in this tube and the bulb of thermometer is adjusted about one cm. above its surface. The tube is very gently heated. Heating must be very carefully regulated so that the temperature rises slowly and boiling takes place gently. A rapid stream of bubbles starts issuing from the liquid and the temperature in the thermometer ceases to increase and becomes constant. This temperature is the boiling point of the liquid.

To ensure a constant heating and to stop the bumping the glass chips may be added in the test tube.

Calibration of Thermometer

Although the thermometers used by the students are calibrated, even then it may be checked by the determination of the melting point or boiling point of pure substance. Accordingly we may modify the given values. For this purpose the following compounds may be used.

Naphthalene (80-82°C); Acetanilide (113.5 – 114°C)

Urea (132.5 – 133°C); Distilled water (100°C)

Crystallisation

Procedure : The given impure organic compound is powdered and mixed with a just sufficient quantity of the suitable solvent in a beaker. The mixture is heated on a water bath until the compound gets dissolved. The hot saturated solution obtained is then filtered through a filter paper placed in a glass funnel.

If the organic compound crystallises during filtration, a hot water funnel is used. This funnel is enclosed with a hot water jacket. The hot water keeps the solution hot and prevents crystallisation during filtration. The insoluble and suspended impurities remain on the filter paper and a clear solution gets collected in the beaker placed below the funnel.

The hot filtrate is now allowed to cool undisturbed in a beaker. After sometime, crystals of the substance are obtained in the beaker. Now the crystals are separated from the mother liquor by filtration with the help of a *Buchner funnel* and a *suction pump*. (as shown in figure). When whole the mother liquor has been drained into the filtration flask crystals present in the Buchner funnels are washed two or three times with small quantities of the pure solvent to remove the impurities if adhered on their surface.

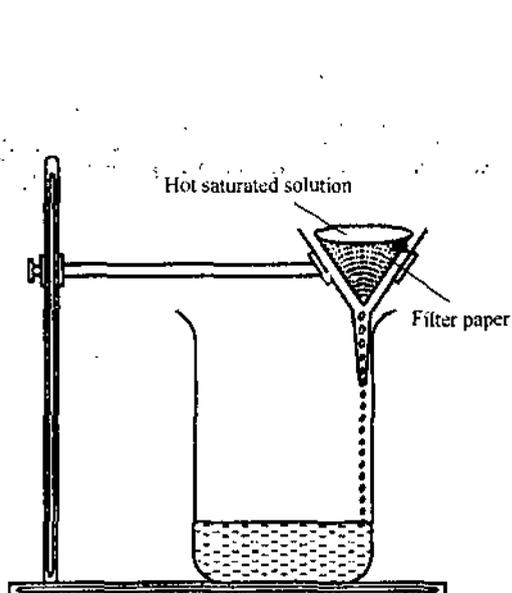


Fig. 3. Filtration with the help of ordinary funnel.

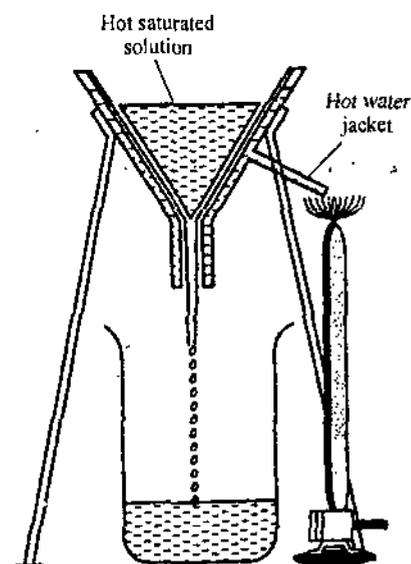


Fig. 4. Filtration with the help of hot water funnel.

The crystals are now dried by pressing between folds of filter paper. The crystals are finally dried over anhydrous calcium chloride in a vacuum desiccator.

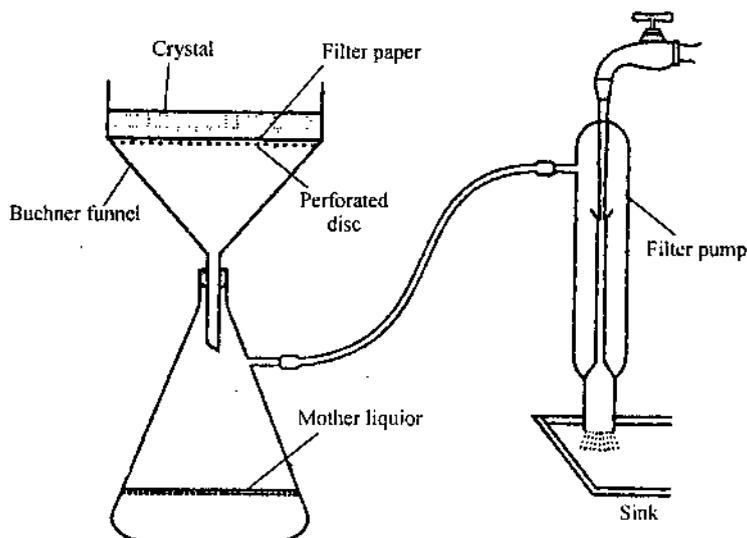


Fig. 5. Filtration with a Buchner funnel using a suction pump.

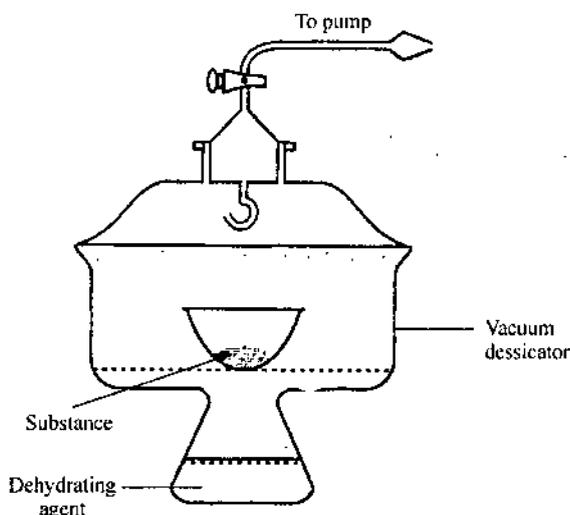


Fig. 6. Drying crystals in a vacuum desiccator.

Decolourisation

Procedure : Sometimes, the crystals obtained are slightly coloured due to the presence of traces of impurities in them. In such a case, the crystals are redissolved in a small quantity of the solvent and the solution is boiled with a small quantity of animal charcoal. The suspension is filtered and crystallised as described above to get the colourless crystals.

(6) Presence of Functional Groups

Organic compounds may be regarded as the derivatives of hydrocarbons having different functional groups in place of one or more of hydrogen atoms. Their characteristic properties and reactions are largely due to the functional groups present in their molecules. Correct detection of functional groups present in an organic compound leads to a very reasonable and accurate identification of that compound.

For the sake of convenience, all the compounds are divided into four types, depending upon the presence of elements N, S and halogens. After detecting the elements by Lessaigne's test, students are advised to perform only those tests under the type I, II and III whichever be suitable according to the presence of element in the compound. Once the possibility of the group determined they should then follow the instructions as given on the subsequent pages.

Type I
(Compounds containing C and H with or without O)

	Experiment	Observation	Inference
1.	Treat the compound with NaHCO ₃ solution	Brisk effervescence	Acids
	Treat the compound with blue litmus.	Blue litmus turns red	Acids
2.	Add ceric ammonium nitrate solution to the compound.	Red colouration	Alcohols
3.	(a) Add a drop of FeCl ₃ to an aqueous or alcoholic solution of compound.	Typical colour changes	Phenols
	(b) Perform phthalein test*	Positive	Phenols
4.	Heat the compound with Fehling's solution or Benedict's solution*	Red precipitate	Aldehydes or reducing sugars
5.	Test with Schiff's solution*	Pink colouration	Aldehydes
6.	Shake with sodium bisulphite solution	White precipitate	Aldehydes or ketones
7.	Treat with alkaline sodium nitroprusside solution	Red colouration	Methyl ketones
8.	Perform Molisch's test*	Positive	Sugars
9.	Heat with dil. NaOH solution containing a drop of phenolphthalein.	Pink colour slowly discharges	Esters
10.	Heat the compound with fuming H ₂ SO ₄	(i) Soluble (ii) Insoluble	Aromatic or unsaturated hydrocarbon Saturated aliphatic hydrocarbons or ethers

Type II
(Compounds containing C, H and halogens [Cl, Br, I] with or without O)

	Experiment	Observation	Inference
1.	Boil the compound with alcoholic AgNO ₃	White precipitate soluble in NH ₄ OH	Chloro-compounds
		Light yellow precipitate partially soluble in NH ₄ OH	Bromo-compounds
		Deep yellow precipitate insoluble in NH ₄ OH	Iodo-compounds
2.	Heat the compound with fuming H ₂ SO ₄	(i) Soluble (ii) Insoluble	Aromatic or unsaturated alkyl halides Saturated aliphatic alkyl halides

*See test given under heading confirmation of functional groups.

Type III
(Compounds containing C, H and N with or without O)

	Experiment	Observation	Inference
1.	Boil the compound with aq. NaOH	Smell of ammonia	Amides
2.	Treat the compound with dil. HCl followed by NaNO ₂ in cold.	(i) Brisk effervescence (ii) Brown or green ppt. (iii) Blue colouration	Amides, amino acids, primary amines or urea
3.	Treat the above content with alkaline β-naphthol solution.	Bright orange red dye	Aromatic primary amines
4.	Boil the compound with water	Yellow colouration	Nitro compounds or nitro phenols
5.	Boil the compound with zinc dust and aq. NH ₄ Cl, filter and treat the filtrate with Tollen's reagent.	Grey precipitate	Nitro compounds

Type IV
(A) (Compounds containing C, H, N and S with or without O)

	Experiment	Observation	Inference
1.	Add few drops of FeCl ₃ to aqueous solution of the substance.	Violet or red colour	Sulphonic acids of phenols or of hydrocarbons
2.	Mix equal quantities of the substance and animal charcoal and fill one-third of the ignition tube with it and heat.	Disagreeable garlic like odour of ethyl mercaptan	Sulphones

(B) (Compounds containing C, H, S and N with or without O)

	Experiment	Observation	Inference
1.	Add 2 c.c. of NaOH solution of a trace of the substance in a test tube, heat to boiling, cool and add 2 drops of aq. lead acetate.	Brown or black colour or ppt.	Thioureas
2.	Dissolve a trace of the substance by boiling in 2 c.c. of water in a test tube, introduce a piece of blue litmus paper.	If colour changes to red	Perform 'a' test also
		No change	Perform 'b' test also
(a)	Dissolve a trace of the substance in 3 c.c. of dil HCl, cool in ice cold water and add 3 c.c. of 2% sod. nitrate solution and then 4 c.c. of alkaline β-naphthol soln.	Red solution	Amino sulphonic acids
(b)	Add 5 drops of conc. H ₂ SO ₄ to a trace of substance and heat gently for few seconds, cool and dilute with 2 c.c. water. Add flakes of NaOH. Bring a piece of moistened red litmus paper near the mouth of the test tube.	Colour changes to definite blue and smell of NH ₃ .	Sulphonaide or Saccharin

(7) Confirmation of Functional Groups

(Including performance of some special tests)

In spite of the various efforts made for the detection of the functional groups, there is always the uncertainty of their presence. Therefore, when it is guessed, any way, is then confirmed by the performance of some following tests. Below is given a chart indicating reagents used for detecting the functional groups.

Type I

(Compounds containing C and H with or without O)

	Compounds (Functional groups)	Reagents or tests
1.	Carboxylic acids.	NaHCO ₃ solution, Distillation with NaOH, Blue litmus, Ceric ammonium nitrate solution.
2.	Alcohols.	Ceric ammonium nitrate solution.
3.	Phenols.	Ferric chloride solution, Bromine water, Phthalic anhydride.
4.	Aromatic aldehydes.	Schiff's solution, 2 : 4 dinitro phenyl hydrazine.
5.	Ketones.	2 : 4-dinitrophenol hydrazine, Sodium bisulphite solution, Alkaline sodium nitroprusside solution.
6.	Carbohydrates.	Molisch's test.
7.	Hydrocarbons.	Fuming sulphuric acid.

Type II

Compounds containing C, H and Halogens (Cl, Br, or I) with or without O

	Compounds (Functional groups)	Reagents or tests
8.	Halogen Compounds	Alc. AgNO ₃

Type III

(Compounds containing C, H and N with or without O)

	Compounds (Functional groups)	Reagents or tests
9.	Amides	Heating with NaOH, treatment with dil. HCl and NaNO ₃ .
10.	Anilides	Carbylamine test, Tafel's test
11.	Amines	Nitrous acid (HCl + NaNO ₂).
12.	Nitro compounds	Zn and alcoholic CaCl ₂ mixture.

Type IV

(Compounds containing C, H and S with or without N and O)

	Compounds (Functional groups)	Reagents or tests
13.	Sulphonic acid.	Sodium bicarbonate test, fusion test.

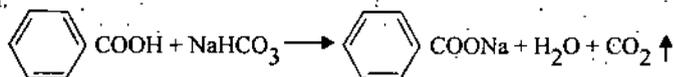
TYPE I

(Compounds containing C and H with or without O)

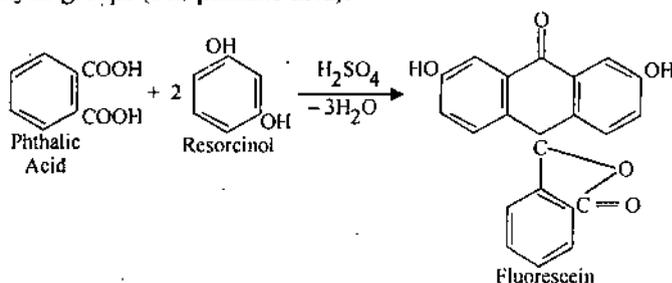
(1) CARBOXYLIC ACID (—COOH)

(i) **Sodium bicarbonate test** : Add a small amount of the compound to 3 c.c. of saturated sodium bicarbonate solution. Formation of brisk effervescence shows the presence of —COOH group.

(ii) **Litmus paper test** : Add the litmus paper or solution to the aqueous solution or suspension of the compound. It turns red.



(iii) **Fluorescence test** : Heat gently 0.2 gm of organic compound with 0.5 gm. of resorcinol and few drops of conc. H_2SO_4 in a hard test tube for two minutes. Cool and pour the contents into a beaker containing NaOH diluted largely with water. Formation of intense green fluorescence indicates the presence of 1, 2 or *ortho*-dicarboxylic groups (*i.e.*, phthalic acid).



(iv) **Ester formation** : Heat a small quantity of the substance with ethyl alcohol and a litre conc. H_2SO_4 . Cool the solution and pour in a tube containing water. A fruity smell due to the formation of an ester, indicates the presence of carboxylic groups.

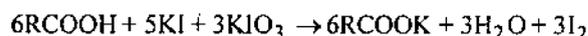
(v) **Ferric chloride test** : Neutralise 0.5 gm. of the acid with excess of ammonia in a boiling test tube. Boil the solution to remove excess of ammonia. Cool and add a few drops of neutral FeCl_3 solution. Note the colour produced.

Observation	Inference
Yellow ppt.	Cinnamic acid.
Reddish brown ppt.	Aliphatic carboxylic acid
Buff ppt.	Aromatic acids and certain dibasic acids.
Yellow colour	α -Hydroxy acids.
Red brown colour	<i>m</i> -or <i>p</i> -Hydroxy benzoic acids.
Violet colour	Aromatic hydroxy acids.

Note : Phenols and α -Naphthyl amine also produce characteristic colour with FeCl_3 .

(vi) **Iodate-iodide test** : This is very sensitive test for the detection of even weak carboxylic acids.

To a small quantity of the compound add two drops of 5% KI solution and two drops of 5% KIO_3 solution. Cork the tube and place it in a boiling water bath for two minutes. Cool the contents and add few drops of freshly prepared starch solution. Appearance of a blue colour shows the presence of carboxylic acid.



↓
Gives blue colour with starch

Note : Phenols, some aromatic amines and certain other compounds which are readily oxidised to coloured compounds, also give a green to brown ppt. with the reagent.

Quick Guess

(i) **Aliphatic solid** : Heat with conc. H_2SO_4

- (a) Turns black-Tartaric acid.
- (b) Turns brown after sometime-Citric acid.
- (c) Nothing taking place-Oxalic or succinic acid.

(ii) **Aliphatic liquid** : Warm with conc. H_2SO_4 and burn the gas evolving out.

- (a) Blue flame-Formic acid.
- (b) Does not burn-Acetic acid.

(iii) **Aromatic solid** : Add 2 drops of $FeCl_3$ to the aqueous solution or suspension.

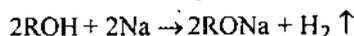
- (a) Violet colour-Salicylic acid.
- (b) No change in colour-Benzoic acid and phthalic acid.

Phthalic acid can be confirmed by performing fluorescence test.

(2) ALCOHOL (— OH)

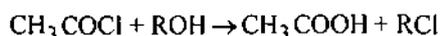
(i) **Ceric ammonium nitrate test** : Treat 2 drops of the organic substance with 0.5 c.c. of ceric ammonium nitrate solution and dilute it with 2 c.c. of water. A red colouration indicates alcoholic hydroxy group.

(ii) **Sodium test** : Take about 2 c.c. of the given liquid in a test tube and add a piece of anhydrous $CaCl_2$ to absorb any water if present. Transfer the clear liquid (free from water) to another dry test tube and add a dry piece of sodium. Effervescence indicates the liquid to be an alcohol.

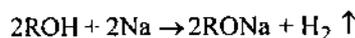


(iii) **Iodoform test** : To the ethyl alcohol add twice of iodine solution followed by dilute sodium hydroxide until the colour is pale yellow and warm gently. Formation of yellow precipitate indicates the presence of simple alcohol.

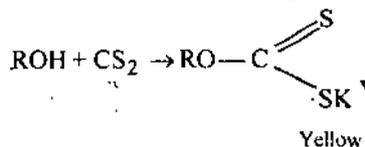
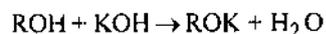
(iv) **Evolution of HCl and H_2** : In a completely dry test tube take about 2 ml of the compound and add a small amount of anhydrous $CaSO_4$. Filter the solution in another dry test tube and divide the filtrate in two parts. To first part add 2 drops of acetyl chloride very carefully and expose a moist blue litmus paper at the mouth of the test tube. If the compound contains an alcoholic group, the paper becomes red.



To second part, add a small piece of dry sodium. Effervescence indicates the compound to be an alcohol.



(v) **Xanthate test** : To one ml. of the conc. aq solution of the original compound add 2 pellets of KOH . Heat and cool. Then add 1 ml. of the ether followed by the addition of 2-3 drops of carbon disulphide. Formation of a yellow ppt. indicates the presence of alcoholic groups.



Filter the above solution and to 1 ml. of the filtrate add 0.5 ml. of ammonium molybdate solution and excess of dil. HCl . Production of a red or blue colour confirms the presence of alcoholic group in the original substance.

Distinction among Primary, Secondary and Tertiary Alcohols

Treat 2 ml. of the compound with about 8 ml. of Lucas reagent (Dissolve 32 gm. of anhydrous $ZnCl_2$ in 20 ml. of conc. HCl) and shake. Note the following observations. Separation of an insoluble layer at once \rightarrow Tertiary alcohol; Appearance of cloudiness within 4-5 minutes \rightarrow Secondary alcohol, solution remains clear Primary alcohol.

Quick Guess

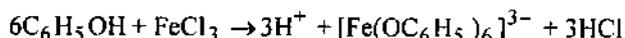
- (a) If liquid burns in flame—Methyl alcohol, ethyl alcohol, *n*-propyl alcohol.
- (b) If liquid does not burn in flame, shake it with water.
- (i) Soluble—Glycol.
- (ii) Floating on water—*n*-Butyl alcohol.
- (iii) Forming layer below water—Benzyl alcohol.

(3) PHENOL* (—OH)

(1) Ferric chloride test : Add 2 drops of ferric chloride to 2 c.c. of aqueous or alcoholic solution of the compound. Formation of green blue or violet colour shows the presence of phenols. Nitrophenols do not show this test.

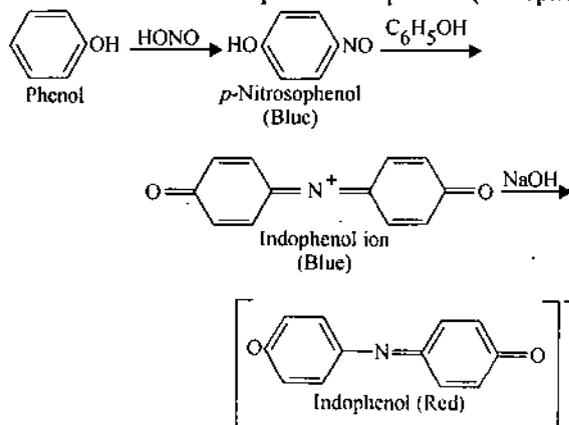
Violet colour	— Phenol, <i>o</i> -Cresol, Salicylic acid, Aspirin
Green colour	— Catechol
Blue changing to red	— Hydroquinone, Pyrogallol
White opalescence	— β -Naphthol
If on boiling with water blue-violet colour appears	— <i>m</i> - and <i>p</i> -Nitrophenol
White ppt.	— α -Naphthol
Bluish violet colour in alcoholic solution	— α -Naphthol
Green colour in alc. solution	— β -Naphthol; <i>o</i> , <i>m</i> , <i>p</i> -Cresols; Resorcinol

(Exceptions : α -Naphthylamine gives blue colour and benzoic acid gives buff ppt. with FeCl_3).



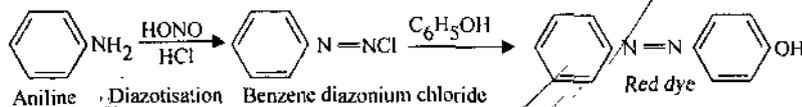
Violet

(2) Liebermann's reaction : Fuse the little amount of the compound with a crystal of sodium nitrite in a tube. Cool the mixture and add 1 c.c. conc. sulphuric acid. A deep green to blue solution is formed which turns red when poured in large excess of water. This red aqueous solution becomes again deep green or blue if made alkaline with NaOH. It indicates the presence of phenol. (Nitrophenols do not respond to this test).

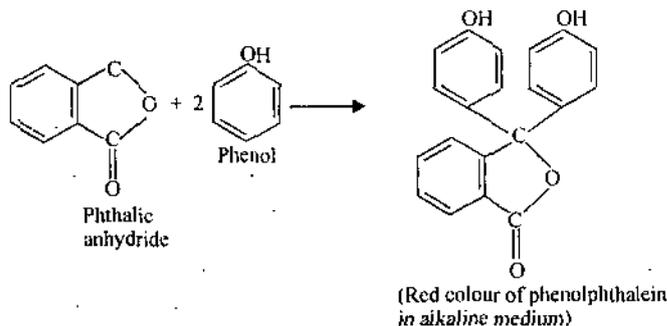


(3) Azo-dye formation : Treat a drop of aniline in a test tube with 0.5 c.c. conc. HCl, dilute it with water and cool in a freezing bath and add dilute NaNO_2 solution while shaking. Pour this diazotised solution to that of phenol in excess of 2N — NaOH solution. Formation of a dye or orange or red colour indicates the presence of phenolic group.

*Almost all phenols on exposure to air and light acquire darker colours. Some phenols even become dark-brown or black in colour. Hence the colour of phenols should not be given any importance when identifying them.



(4) **Phthalein test** : Heat 0.5 gm of compound with 1 gm. phthalic anhydride and a drop of conc. H_2SO_4 for one minute. Cool and make it alkaline liquid with dil. NaOH solution. Pour few drops of the alkaline liquid in 20 c.c. of water. Characteristic colour shows the presence of phenol.

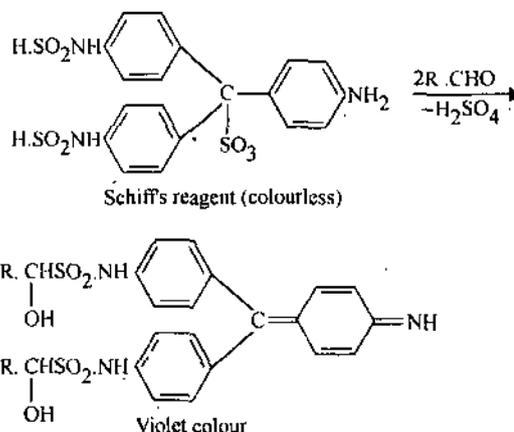


Red colour	—	Phenol, <i>o</i> -Cresol
Blue colour	—	Catechol, <i>m</i> -Cresol
Fluorescent green	—	Resorcinol
No coloration	—	<i>p</i> -Cresol
Deep blue	—	Hydroquinone.
Green	—	α -Naphthol.
Light green	—	β -Naphthol.

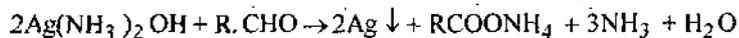
(5) **Ceric ammonium nitrate reagent** : Add 3-4 drops of the substance or its concentrated solution in water to 0.2 c.c. of the reagent, dilute with 2 c.c. of distilled water and shake. A brown to green precipitate is obtained in case of phenol.

(4) ALDEHYDE (— CHO)

(1) **Schiff's reagent** : Add 5-6 drops of liquid or 0.1 gm of solid compound to 2 c.c. of the reagent, shake vigorously and wait for 1-2 minutes. A deep red or violet colour indicates the presence of an aldehydic group. It is not to be heated here.

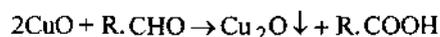


(2) **Tollen's reagent** : Add 0.1 gm. of solid or 0.1 c.c. of liquid compound to 2 c.c. to Tollen's reagent, warm and allow the contents to stand for 2-3 minutes. The formation of silver mirror or a grey ppt. (if the test tube is not clean) confirms the presence of aldehyde.



Silver mirror or
grey ppt.

(3) **Fehling's solution** : Add 0.1 gm of solid or 0.2 c.c. of liquid compound to 5 c.c. of Fehling's solution and boil the mixture. Formation of red ppt. shows the presence of aldehyde.



Red ppt.

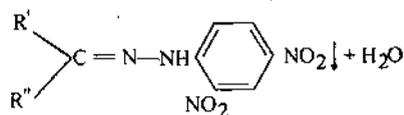
(4) **Benedict's solution** : Boil 0.1 gm of the compound with 2-3 c.c. of Benedict's solution for few minutes. Appearance of a red yellow precipitate confirms its presence.

Quick Guess

- (a) Smell of bitter almonds – Benzaldehyde.
 (b) If bad pungent odour, add NaOH to the liquid compound and shake—
 (i) brown resin formed—Acetaldehyde.
 (ii) no such change—Formaldehyde.

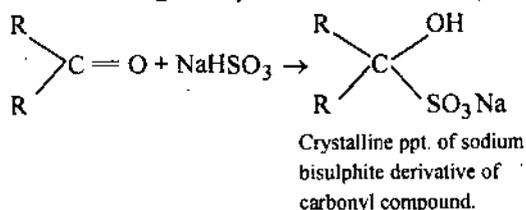
(5) KETONE (>C = O)

(1) **2 : 4-Dinitrophenyl hydrazine test** : Add 1 or 2 drops (0.05 gm) of the substance to about 2 c.c. of the reagent solution. Shake vigorously and heat, if necessary. A yellow or orange red precipitate separates out in case of ketone.



Yellow or orange red coloured crystalline derivative of 2 : 4 dinitrophenyl hydrazine of carbonyl compound.

(2) **Sodium bisulphite test** : Add 0.2 gm. (0.3 c.c.) of the compound to 1 c.c. of saturated sodium bisulphite solution and shake vigorously. Formation of white precipitate shows the presence of ketone.



(3) **Sodium nitroprusside test** : Add 0.1 gm. of solid or 0.2 c.c. of liquid compound to 2 c.c. of aq. sodium nitroprusside solution and then make it alkaline with 2-3 drops of sodium hydroxide. A red or purple colour indicates the presence of ketone (benzophenone does not give this test).

Note : The first two tests are given by aldehydes. Therefore to differentiate between aldehydes and ketones it should be known that ketone do not give any test with Tollen's reagent, Schiff's solution, Fehling's solution and Benedict's solution.

Quick Guess

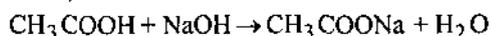
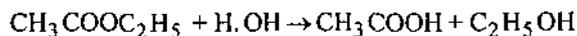
- (a) All the ketones are sweet smelling.
 (b) Burns with smoky flame—Acetophenone.

(6) ESTER (RCOOR')

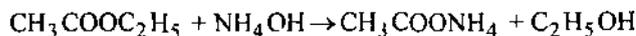
(1) **Smell** : All the esters possess fruity smell.

(2) **Phenolphthalein test** : To 3 c.c. of the compound add 2-3 drops of very dilute NaOH solution followed by a drop of phenolphthalein and heat gently. The pink colour is gradually discharged in case of ester.

It is due to the hydrolysis of ester.



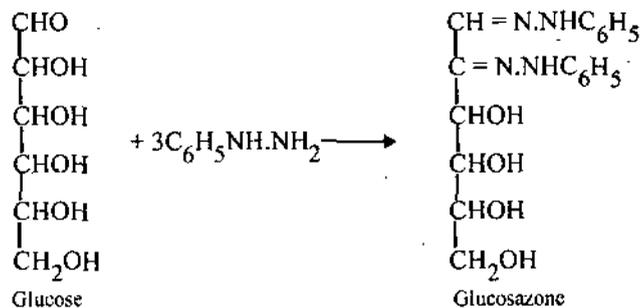
(3) **Feigl test** : To 0.5 c.c. of anormal solution of hydroxylamine hydrochloride in methanol, add one drop or a small crystal of the compound followed by 0.5 c.c. of 2N -KOH solution in methanol. Boil for one minute, cool and just acidify the solution with dil. HCl. Now add 1-2 drops of FeCl_3 . The appearance of red-violet coloration indicates the presence of an ester group.



(7) CARBOHYDRATE

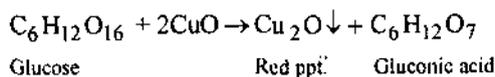
(1) **Molisch's Test** : Add 2 drops of 10% alcoholic solution of α -naphthol in 1 c.c. aqueous suspension of compound and shake well. Now add carefully 2 c.c. of conc. H_2SO_4 along the side of test tube. Formation of a reddish violet ring at the junction of two layers indicates the presence of carbohydrate.

(2) **Osazone formation** : Add 0.5 g of phenyl hydrazine hydrochloride to a 3% aq. sodium acetate and shake well till a clear solution is obtained. Now add 0.3 gm of the compound followed by 1 c.c. alcohol and heat the contents for about 10 minutes. On concentrating the solution, yellow crystalline osazone separates out. It clearly shows the presence of sugar.



(3) **Sulphuric acid test** : Treat a small amount of the powdered compound with 1 c.c. cold conc. H_2SO_4 . Formation of colour varying between yellow, brown and black indicates carbohydrates.

(4) **Fehling's solution** : Boil the mixture of 1 c.c. of solution of the compound and 2 c.c. of Fehling's solution for two minutes. Formation of red precipitate clearly indicates the presence of reducing sugar.



(5) **Benedict's solution** : Boil 1 c.c. of the aqueous solution of the compound with 2 c.c. of Benedict's solution for two minutes. It gives a red ppt. which shows the presence of reducing sugar.

If the mixture in the above case, remains blue and only slightly yellowish turbidity appears then sucrose is confirmed.

(6) **Tollen's reagent** : Add 0.1 gm of the compound to 2 c.c. of Tollen's reagent and heat gently. A silver mirror is obtained inside the wall of the vessel in case of carbohydrates.

(7) **Furfural test** : In the Molisch test add 8 ml. conc. HCl instead of conc. H_2SO_4 and boil the solution. Production of a violet colour immediately after the boiling starts shows the compound to be a fructose or sucrose. Glucose produces this colour only after 1-2 minutes of continuous shaking.

(8) **Barfoed's reagent test** : This test is used in differentiating mono saccharide from oligosaccharides. Take a little quantity of the compound in a test tube and add 2 ml. of the freshly prepared Barfoed's reagent. Shake and heat the contents for 2-3 minutes. Allow to stand. Formation of a yellow or orange red ppt. indicates the presence of a monosaccharide (glucose, fructose or galactose). On the other hand if a red ppt. is formed only after a prolonged heating indicates the presence of an oligosaccharide (sucrose or inulin).

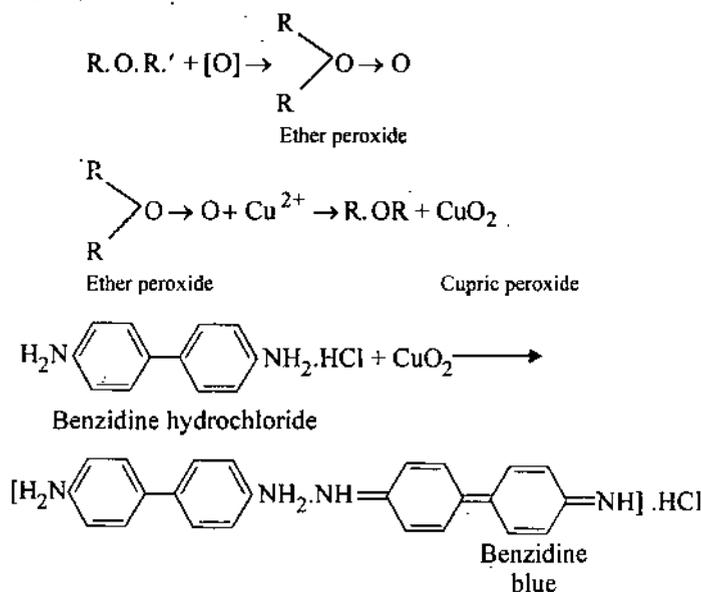
Quick Guess

- (a) Soluble in cold water—Glucose, sucrose.
 (b) Insoluble in cold water—Starch (gives blue colour with iodine).
 (c) Blue coloration with Benedict's solution—Sucrose.

(8) HYDROCARBON AND ETHER

If the compound does not respond to any above tests, it may be suspected to be either a hydrocarbon or an ether. Ethers are, however, soluble in syrupy phosphoric acid while, hydrocarbons are rendered insoluble. All ethers are sweet smelling. Liquid benzene and toluene have got characteristic sweet petrol like odour. They can be detected and confirmed by making the reference to the table.

Feigl's test for ethers : Take 1-2 ml. of ether in a boiling tube and cover the mouth of the tube with a filter paper moistened with a mixture of cupric acetate and benzidine hydrochloride solution. On heating to boiling point, a deep blue colour appears on filter paper due to the formation of benzidine blue, confirming the presence of ether group.



Following tests may however be applied to detect ethers and if these tests are also negative then compound will be a hydrocarbon.

(a) To 0.5 ml of the compound add 1 ml. of iodine solution in CS₂ and shake well. If purple colour of CS₂ layer changes then the compound is an ether.

(b) Mix 1 ml. compound, 4 ml. of glacial acetic acid and 1 ml. conc. H₂SO₄. Heat the mixture under reflux for about 5 minutes. Cool well and extract with benzene. Purple colour indicates ether.

(Note—This test can be applied only when ester group is found to be absent).

TYPE II**[Compounds containing C, H and halogens (Cl, Br or I) with or without O]****(9) HALOGENO COMPOUND**

(1) **Alc. silver nitrate test :** Heat the little amount of the compound with 2 c.c. alcoholic silver nitrate for a few minutes and note :

(a) Formation of a precipitate with silver nitrate indicates the presence of aliphatic or reactive halogen.

(b) No precipitate indicates the presence of halogen atom attached to benzene nucleus.

(Exception : 1-Chloro-2, 4-dinitrobenzene does not respond to this test).

Quick Guess

(a) Aliphatic solid—colourless and crystalline containing—CHO —Chlorohydrate.

(b) Aromatic solid—colourless crystalline containing —Cl with a characteristic smell—

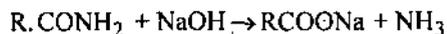
—*p*-dichloro benzene.

TYPE III

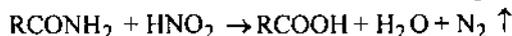
[Compounds containing C, H and N with or without O]

(10) AMIDE (– CONH₂)

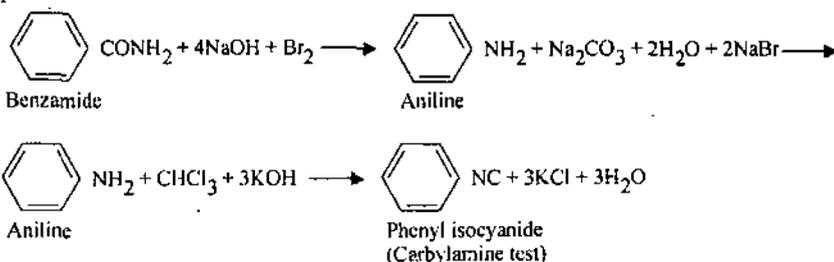
(1) **Sodium hydroxide test** : Heat 0.2 gm. of the substance, with 4 c.c. aq. NaOH. Evolution of ammonia indicates the presence of amino group.



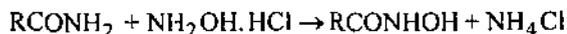
(2) **Nitrous acid test** : To 0.2 gm. of substance, add 2 c.c. of dil. HCl followed by 2 c.c. of 2% aq. NaNO₂ and shake. Brisk effervescence due to the evolution of nitrogen indicates an acid amide.



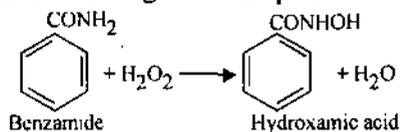
(3) **Hofmann's test** : Dissolve few drops of the liquid bromine in an ice cooled solution of caustic soda and shake it with 0.5 gm of the substance. Cool with stirring for few minutes. Now add a piece of solid caustic soda and stir for few minutes. An ammoniacal smell is obtained due to the evolution of an amine. This ammoniacal smell turns to a very offensive smell of carbonylamine on the addition of chloroform in case of aromatic compounds.



(4) **Hydroxylamine hydrochloride test** : In a test tube take 0.2 gm. of the compound, 0.2 gm. of hydroxylamine HCl and 2 ml. ethyl alcohol. Boil for five minutes. Cool and add few drops of FeCl₃. Formation of a blue-red colour indicates the presence of aliphatic amide.



(5) To the aqueous solution of the compound add about 7-8 drops of 6% H₂O₂ and heat the contents to nearly boiling. Cool and add 1-2 drops of 5% FeCl₃ solution. Formation of bluish red colour in cold within 2 minutes or a brown colour on warming shows the presence of an aromatic amide.



(Note : The result should not be applied in presence of phenolic group).

Quick Guess

- (a) All amides are solids.
- (b) Dissolve the compound in water by heating, cool and add 1 c.c. conc. HNO₃ :
 - (i) Crystalline ppt.—Urea.
 - (ii) No ppt.—Acetamide (burns with non-smoky flame)
—Benzamide (burns with smoky flame).

(11) ANILIDE (– NHCOR)

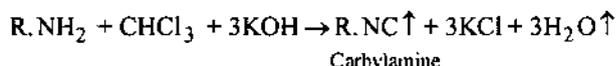
(1) **Dye test** : Boil 0.1 gm. of the substance with 5 c.c. dil. HCl cool and filter. Treat the filtrate with 4 c.c. aq. NaNO₂ and pour all this content into a beaker containing 10% alkaline β-naphthol. Formation of a bright orange red dye shows the presence of anilide.

(2) **Carbonylamine test** : Boil 0.1 gm. of the substance with 3 c.c. alc. KOH, cool and add a few drops of CHCl₃. On boiling this mixture, offensive vapours of intolerable smell are obtained.

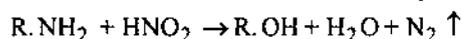
(3) **Tafel's test** : Add 4 c.c. conc. H₂SO₄ to about 0.5 gm. of the compound in a dry test tube, shake and then add a little of powdered potassium dichromate. Red or violet colour changing to green on heating, confirms acetanilide.

(12) AMINE ($-NH_2, NH, >N$)**(A) Primary Amine**

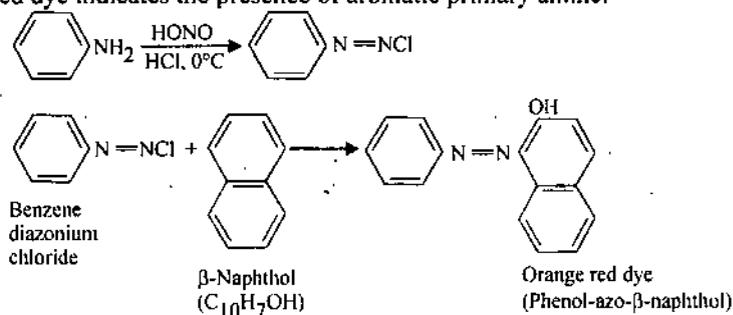
(1) **Carbylamine test** : Boil a mixture of 2 drops of the compound, 2 drops of chloroform and 2 c.c. of alcoholic caustic potash. An intolerable offensive odour of a carbylamine indicates the presence of a primary amine.



(2) **Nitrous acid test** : Dissolve about 0.2 gm of the compound in 10 c.c. dil. HCl and cool. Now add 10% aq. $NaNO_2$. Formation of brisk effervescence indicates the presence of aliphatic primary amine.



(3) **Diazotisation test** : Dissolve about 0.2 gm. of the compound in dil. HCl, and cool. Now add 10% aq. $NaNO_2$. Pour all this content into a beaker containing 10% alkaline β -naphthol. The appearance of a bright orange red dye indicates the presence of aromatic primary amine.



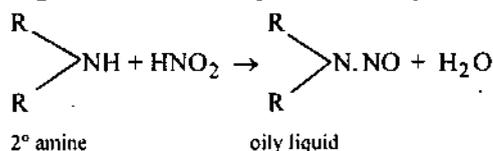
(4) **Rimini Test** : To about 0.3 gm of the compound taken in a test tube add 5 ml. of water, 1 ml acetone and few drops of sodium nitroprusside. Allow to stand for 2 minutes. Formation of a violet red colour shows the presence of aliphatic primary amine.

(5) **Hinsberg's test** : To about 0.2 gm. of the compound add 1 ml. of 5% NaOH and 3 ml. Pyridine. Shake well and add few drops of benzene sulphonyl chloride with continuous shaking. Formation of a yellow colour indicates the presence of a primary amine.

(Note—Naphthylamines do not respond to this test. Diamines give characteristic colour with $FeCl_3$)

(B) Secondary Amine

(1) **Nitrous acid test** : Prepare a solution of nitrous acid by adding ice cold dil. HCl to a solution of 1% aq. $NaNO_2$. Add gradually this solution or 0.2 gm. of the compound in dil. HCl (10 c.c.). An oily dark coloured liquid or low melting solid indicates the presence of aliphatic or aromatic secondary amine.



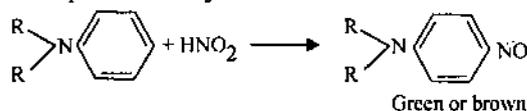
(2) **Libermann's nitroso reaction** : The nitroso compound, formed as in above reaction, is treated cautiously with 1 c.c. conc. H_2SO_4 . A blue coloration which changes to red on dilution with water and blue or green with aqueous alkali confirms the presence of secondary amine strongly.

(3) **Hinsberg test** : Repeat as on previous experiment \rightarrow Orange red colour.

(C) Tertiary amine

(1) **Nitrous acid test** : Prepare a solution of nitrous acid by adding ice cold dil. HCl to 1% aq. $NaNO_2$. Add gradually this solution to 0.2 gm of the compound in dil. HCl (10 c.c.) :

No reaction indicates aliphatic tertiary amine.



Production of green or brown coloured salt indicates aromatic tertiary amine.

(2) **Hinsberg test** : Proceed as in the Hinsberg's test for primary amines—Red or purple colour.

(3) **Ohkuma test** : Add about 5-6 drops of the citric acid and acetic anhydride reagent to the alcoholic solution of the compound, shake and heat in a boiling water bath. Development of a red or purple colour within 2-3 minutes, indicates the presence of tertiary amine.

Quick Guess

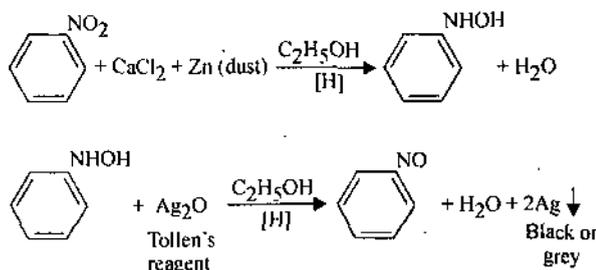
- (a) Aromatic solid—Naphthalamines, *p*-Toluidine.
- (b) Aromatic liquid, shake with water in a test tube.
 - (i) Floats on water—*m*-Toluidine, Dimethylamine.
 - (ii) Forms layer below water—*o*-toluidine, Aniline.

(13) NITRO COMPOUND (– NO₂)

(1) **Colour** : Almost all nitro compounds are light yellow or yellow in colour.

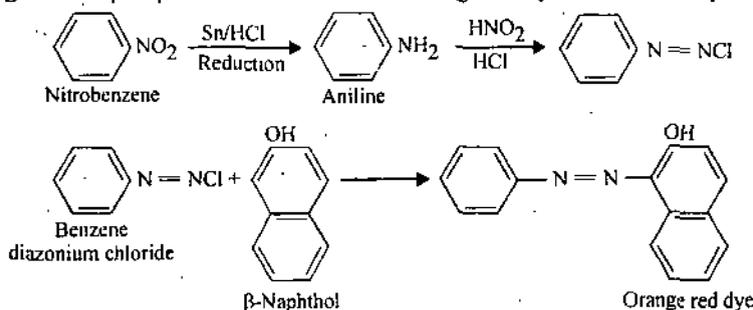
(2) **Sodium hydroxide test** : Shake a small quantity of the compound with 2 c.c. of NaOH solution. Production to yellow, intense yellow or orange colour shows the presence of a nitro group.

(3) **Mulliken test** : Dissolve 0.1 gm. of the compound in 3 c.c. alcohol and then add a few drops of 10% CaCl₂ solution followed by a pinch of zinc dust. Boil the mixture and set aside for five minutes to cool and filter directly in 2 c.c. of Tollen's reagent. On warming this content a grey or black precipitate is obtained which confirms the presence of a nitro group.



(4) **Zinc-ammonium chloride test** : Boil a small amount of the substance with 5 c.c. of 5% alcohol, 0.2 gm. each of NH₄Cl and zinc dust. Cool, filter and add 2 c.c. of Tollen's reagent to the filtrate. On heating, the formation of a black precipitate shows the presence of nitro group.

(5) **Azo dye formation** : Heat 0.1 gm of the substance with 0.5 c.c. of conc. HCl and 2-3 small piece of metallic tin for 3-4 minutes. Filter, cool and add 3 c.c. aqueous solution of NaNO₂. Pour this content into a beaker containing alkaline β-naphthol. Formation of an orange red dye identifies the presence of nitro group.



Quick Guess

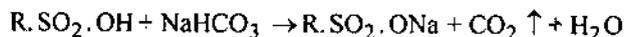
- (a) Solid if soluble in hot water—Nitrophenols.
- (b) Solid if insoluble in hot water—Nitronaphthalene, *m*-dinitrobenzene, *p*-nitrotoluene (bitter almond smell).
- (c) Liquid with smell of bitter almond—Nitrobenzene.

TYPE IV

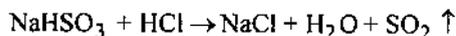
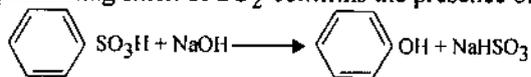
(Compounds containing C, H and S with or without N and O)

(14) SULPHONIC ACID (– SO₃H)

(1) **Sodium bicarbonate test** : Add little amount of the compound to few c.c. of aq. NaHCO₃ and stir the contents. Brisk effervescence of CO₂ confirms the presence of sulphonic acid group.



(2) **Fusion test** : Fuse the equal amount of the compound and solid caustic alkali, and the mixture with dilute mineral acid. A penetrating smell of SO_2 confirms the presence of sulphonic acid group.



Pass these vapours into acidic $K_2Cr_2O_7$ solution. Green colour is developed.

CLASSIFICATION OF COMPOUNDS

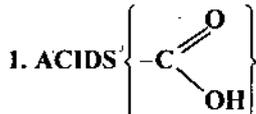
Below is given a list of large number of compounds included in University new syllabus. All these compounds are arranged groupwise in order of their increasing boiling points and melting points. It is advised to choose the probable compound in the following list (after finding out the m.p. or b.p. and functional group etc.) and then to confirm it with the help of more specific tests given in the chapter under "Identification of Organic Compounds".

For the sake to easiness all the compounds are classified into following four types :

TYPE I

(Compounds containing C and H with or without O)

(Acids, alcohols, phenols, aldehydes, ketones, esters, carbohydrates, hydrocarbons and ether)



Liquid (B.P.)

101° Formic Acid
140° Propionic acid

Solid (M.P.)

100° Citric acid
101° Oxalic acid
121° Benzoic acid
151° Adipic acid
153° Citric acid (anhydrous)
155° Salicylic acid
169° Tartaric acid
185° Succinic acid

Note : The compounds printed in dark black are aromatic.

2. ALCOHOLS (—OH)

Liquid (B.P.)

65° Methyl alcohol
78° Ethyl alcohol
83° *iso*-Propyl alcohol
83° *tert.* Butyl alcohol
97° Allyl alcohol
197° Glycol
205° Benzyl alcohol

3. PHENOLS (—OH)

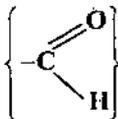
Liquid (B.P.)

181° Phenol
190° *o*-Cresol
201° *p*-Cresol
202° *m*-Cresol

Solid (M.P.)

31° *o*-Cresol
35° *p*-Cresol
42° Phenol
94° α -Naphthol
118° Resorcinol
122° β -Naphthol
133° Pyrogallol
169° Quinol (*Hydroquinone*)

4. ALDEHYDES



Liquid (B.P.)

21° Acetaldehyde
97° Acetaldehyde (aq. solution)
97-98° Formalin
(30° aq. formaldehyde)
179° Benzaldehyde

5. KETONES ($>C=O$)

Liquid (B.P.)

80° Methyl ethyl ketone
202° Acetophenone

Solid (M.P.)

6. Esters ($-COOR$)

Liquid (B.P.)

196° Phenyl acetate

213° Ethyl benzoate

Solid (M.P.)

68° Phenyl benzoate

Note : The compounds printed in dark black are aromatic.

7. CARBOHYDRATES

Solid (M.P.)

Glucose (hydrate)
146° *d*-Glucose
160° *d*-Sucrose (cane sugar)

Does not melt Starch

8. HYDROCARBONS

Liquid (B.P.)

80° Benzene
110° Toluene

Solid (M.P.)

80° Naphthalene

TYPE II

(Compounds containing C, H and Halogens with or without O)
(Chloro, bromo and iodo compounds)

1. CHLORO (Cl)

Liquid (B.P.)

61° Chloroform
77° Carbon tetrachloride
132° Chlorobenzene

Solid (M.P.)

53° *p*-Dichlorobenzene

2. BROMO (- Br)

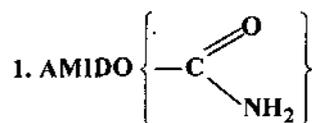
Liquid (B.P.)

155° Bromobenzene

TYPE III

(Compounds containing C, H and N with or without O)

(Amido, amino, nitro)



Solid (M.P.)

128° Benzamide



Solid (M.P.)

114° Acetanilide

3. Amines Primary (NH₂-)

Liquid (B.P.)

184° Aniline

198° *o*-Toluidine4. AMINES TERTIARY (\rightarrow N)

Liquid (B.P.)

192° Dimethyl aniline

5. NITRO (-NO₂)

Liquid (B.P.)

210° Nitrobenzene

Solid (M.P.)

54° *p*-Nitrotoluene90° *m*-Dinitrobenzene

□

CHAPTER

4

IDENTIFICATION OF COMPOUNDS

In this chapter various specific tests of organic compounds included in B.Sc. II Syllabus are discussed. Students are advised to consult the list after determining the solubility, the functional groups, the nature and the melting or boiling point of the compound. They should first choose two or three probable compounds from the list given in previous chapter and then should confirm the reality of one by performing specific tests and preparing derivatives of the compound.

TYPE I

1. IDENTIFICATION OF CARBOXYLIC ACIDS LIQUID

B.P.

100°. Formic acid : $\boxed{\text{HCOOH}}$

(i) Colourless, hygroscopic liquid very penetrating odour like SO_2 . Miscible with water, aliphatic. R.D. 1.245 (0°C). M.P. 8°C.

(ii) Gives white ppt. with HgCl_2 solution on heating.

(iii) Neutral aq. solution gives red coloration with FeCl_3 solution.

(iv) It gives black precipitate or silver mirror on heating with Tollen's reagent.

(v) CO is evolved on heating it with conc. H_2SO_4 . It burns with pale blue flame at the mouth of test tube.

(vi) Decolourises acidic KMnO_4 solution.

(vii) Gives yellow colour with conc. NaHSO_3 solution.

Derivative : Ammonium formate M.P. 114°, Anilide M.P. 47°.

140°. Propionic acid : $\boxed{\text{CH}_3\text{CH}_2\text{COOH}}$

(i) Characteristic smell. Miscible with water. Colourless liquid, aliphatic, density 0.996 (19°C).

(ii) *Neutral aq. solution gives red coloration with neutral FeCl_3 solution. Now add 1 ml. of amyl alcohol. Shake vigorously and allow the two layers to separate. Red brown colour goes to amyl alcohol layer.

(iii) It does not reduce Tollen's reagent:

Derivative : Anilide M.P. 103°, Amide M.P. 79°, Ammon. salt 54°C.

SOLID

M.P.

100°. Citric acid (hydrate) : $\boxed{\begin{array}{c} \text{CH}_2\text{COOH} \\ | \\ \text{C}(\text{OH})\text{COOH} \cdot \text{H}_2\text{O} \\ | \\ \text{CH}_2\text{COOH} \end{array}}$

(i) White crystalline solid, colourless, non-inflammable and readily soluble in water. Aliphatic.

* To 1 c.c. (1 gm.) of acid add NH_3 till it begins to smell. Now add 10 c.c. distilled water and heat till no smell of NH_3 is noticed. Add now 1 c.c. of NaOH . It is neutral aq. solution.

(ii) Loses water of crystallisation at 130° , forming anhydride, M.P. 153° .

(iii) Neutral solution gives no ppt. with CaCl_2 in cold, but on heating gives a white crystalline ppt. of Ca-citrate.

(iv) A blue colour is developed on adding β -naphthol solution in conc. sulphuric to nitric acid solution which does not change on heating.

(v) Gives no colour with Fenton's reagent.

(vi) To aq. solution of acid add AgNO_3 , a white ppt. is obtained. The ppt. is soluble in ammonia. Stand the test tube in boiling water, silver mirror is obtained.

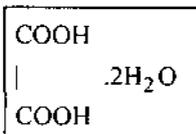
(vii) With iodine and NaOH solution it gives iodoform (yellow).

(viii) Gives yellow colour with conc. H_2SO_4 without charging which after neutralisation gives red colour with sodium nitroprusside and then turns violet after addition of acetic acid.

(ix) Heat 0.05 gm. of the O.S. in 2 c.c. of water with a drop of KMnO_4 solution, till the colour is discharged. On neutralising with NH_4OH it gives red coloration with sodium nitroprusside.

Derivative : Acetyl derivative M.P. 115° , Anilide M.P. 199° .

101° Oxalic acid (hydrated) :



(i) White or transparent crystalline solid. Soluble in 8 vols. of cold water. Odourless, aliphatic.

(ii) Neutral aq. solution gives a white ppt. of Ca-oxalate in cold, with CaCl_2 solution.

(iii) It decolourises the pink colour of acidified KMnO_4 .

(iv) On heating loses water of crystallisation.

Derivative : Anilide, M.P. 245° .

121° Benzoic acid : $\text{C}_6\text{H}_5\text{COOH}$

(i) White glistening scales, odourless, readily soluble in hot water. Aromatic.

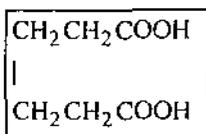
(ii) Neutral aq. solution gives buff ppt. with FeCl_3 solution.

(iii) On heating with a little alcohol in presence of conc. H_2SO_4 , gives a fruity smell of ethyl benzoate.

(iv) On heating with sodalime or solid NaOH gives benzene.

Derivative : Anilide M.P. 160° , Amide M.P. 128° .

151° Adipic acid :



(i) White solid, soluble in alcohol, sparingly soluble in cold water, aliphatic.

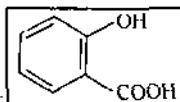
(ii) Gives red-violet fluorescein with resorcinol and trace of conc. H_2SO_4 .

Derivative : Amide (M.P. 220°), Anilide (M.P. 235°)

153° Citric acid : (Anhydrous)

Please see citric acid.

155° Salicylic acid : $\text{OHC}_6\text{H}_4\text{COOH (1:2)}$



(i) White shining crystals, needle shaped, odourless, hardly soluble in water, Aromatic.

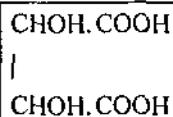
(ii) Aq. solution gives violet coloration with FeCl_3 .

(iii) On heating with soda lime yields phenol.

(iv) On heating with methyl alcohol in presence of conc. H_2SO_4 , it gives a characteristic smell of oil of winter green (methyl salicylate). (Smell of Iodex).

Derivative : Anilide M.P. 134° , with Br_2 in acetic acid yields Dibromo derivative M.P. 225° , Amide M.P. 139° .

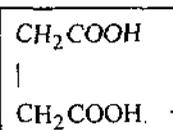
169°. Tartaric acid :



- (i) Colourless crystals like marble chips, odourless, soluble in water, aliphatic.
- (ii) Chars readily with hot and conc. H_2SO_4 and evolves CO_2 .
- (iii) Neutral aq. solution does not give a white precipitate with CaCl_2 on shaking.
- (iv) It gives water silver mirror with Tollen's reagent.
- (v) Aq. solution on treatment with solid FeSO_4 , H_2O_2 and NaOH gives deep violet colour. (Fenton's test)*.
- (vi) On warming with β -naphthol in conc. H_2SO_4 , gives green coloration which changes to orange on dilution.
- (vii) Take 2 c.c. of neutral aq. solution of compound. Add 0.5 gm. of cobalt nitrate and 3 c.c. of NaOH , heat – a blue solution which changes to colourless solution on cooling.

Derivative : Diacetyl M.P. 58° , Anilide M.P. 264° .

185°. Succinic acid :



- (i) White crystalline solid, odourless, soluble in water, aliphatic, B.P. 235° .
- (ii) Neutral aq. solution gives brownish red ppt. with FeCl_3 .
- (iii) Gives orange green fluorescence on heating with resorcinol and a drop of conc. H_2SO_4 and making the mixture alkaline.
- (iv) Amm. salt of the original solution on strong heating with zinc dust form pyrrole which turns pine wood splinter soaked in conc. HCl red.

Derivative : Anilide M.P. 226° , Anhydride M.P. 119° , Amide M.P. 242° .

2. IDENTIFICATION OF ALCOHOLS LIQUID

B.P.

65°. Methyl alcohol : CH_3OH

- (i) Colourless liquid, characteristic smell highly inflammable, miscible with water, aliphatic, R.D. 0.796 (20°C).
- (ii) Gives red coloration with ceric ammonium nitrate reagent.
- (iii) It gives odour of oil of Winter green (methyl salicylate) (smell of Iodex) when heated with salicylic acid in presence of a drop of conc. H_2SO_4 .
- (iv) Gives pungent smell of formaldehyde with red hot copper wire.
- (v) Gives formaldehyde with cold solution of $\text{K}_2\text{Cr}_2\text{O}_7$ and dil. H_2SO_4 . On adding resorcinol to this mixture, the ppt. is obtained which gives green fluorescence with dil. NaOH .

Derivative : 3 : 5-Dinitrobenzoate, M.P. 107° .

78°. Ethyl alcohol : $\text{C}_2\text{H}_5\text{OH}$

- (i) Colourless liquid, characteristic spirit like odour, inflammable, miscible with water, aliphatic. R.D. 0.798 (20°C).
- (ii) It gives characteristic strong smell of acetaldehyde on heating with copper wire.
- (iii) Iodoform test-positive. (See under the confirmation of functional group).
- (iv) On heating with $\text{K}_2\text{Cr}_2\text{O}_7$ and dil. H_2SO_4 gives strong smell of acetaldehyde.
- (v) Gives acetic acid with alkaline KMnO_4 .

*Fenton's test : To 2 c.c. aq. solution of original compound add a trace of powdered FeSO_4 . Shake to dissolve and add one drop of H_2O_2 . Add about 2 c.c. of NaOH solution. A deep violet colour is observed.

Derivative : 3 : 5-Dinitrobenzoate M.P. 92°, Iodo form M.P. 119°.

83°. Iso-Propyl alcohol : $(\text{CH}_3)_2\text{CHOH}$

- (i) Colourless liquid, characteristic spirit like smell, miscible with water, aliphatic.
- (ii) Iodoform test positive.
- (iii) Forms acetone when heated with a mixture of $\text{K}_2\text{Cr}_2\text{O}_7$ and dil. H_2SO_4 .
- (iv) On heating with conc. HCl , forms chloride salt which gives test of Cl^- radical.

Derivative : 3 : 5-Dinitrobenzoate M.P. 218°.

83°. tert-Butyl alcohol : $(\text{CH}_3)_3\text{COH}$

- (i) Colourless liquid, characteristic smell, soluble in water, aliphatic.
- (ii) Does not give iodoform test.
- (iii) Solidifies (M.P. 25°C) on cooling in a freezing mixture.

97°. Allyl alcohol : $\text{CH}_2 = \text{CH}-\text{CH}_2\text{OH}$

- (i) Colourless liquid, pungent smell, unsaturated, soluble in water, aliphatic.
- (ii) Decolourises bromine water immediately.
- (iii) On oxidation ($\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$) gives acrolein (B.P. 52°C) which has very pungent and of irritating odour.

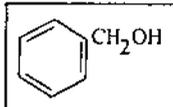
197°. Ethylene glycol (Glycol) :

$$\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$$

- (i) Colourless, sweet tasting viscous liquid. Miscible with water, aliphatic. R.D. 1.125.
- (ii) Gives red colouration with ceric ammonium nitrate solution.
- (iii) It oxidises to oxalic acid on heating with conc. HNO_3 .
- (iv) Take 10 drops of glycol in a dry test tube, add 10 drops of conc. H_2SO_4 and heat until mixture is deep brown in colour, cool and dilute with 5 c.c. water and then add solid NaOH with shaking until the mixture is alkaline, boil-characteristic disagreeable odour of aldehyde resin.

Derivative : Dibenzoate M.P. 73°.

205°. Benzyl alcohol : $\text{C}_6\text{H}_5 \cdot \text{CH}_2\text{OH}$



- (i) Soluble in 25 ml. cold water R.D. 1.043
- (ii) Colourless liquid, aromatic odour, non-inflammable, sparingly soluble in water, aromatic but burns without smoke.
- (iii) Forms a white resinous ppt. with conc. H_2SO_4 .
- (iv) Gives a smell of bitter almonds (benzaldehyde) on heating with KMnO_4 and dil. H_2SO_4 .
- (v) Forms chloride salt with alk. KMnO_4 .

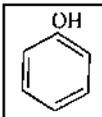
Derivative : Benzoic acid M.P. 121°, 3 : 5-Dinitro benzoate M.P. 113°.

3. Identification of Phenols

Liquid

B.P.

181°. Phenol : $\text{C}_6\text{H}_5\text{OH}$ (Carbolic acid)



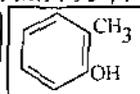
- (i) If solid M.P. 42°C.
- (ii) Characteristic smell. Miscible with 16 volumes of cold water. Colourless but turns to reddish brown, aromatic.
- (iii) Aq. solution gives violet coloration with FeCl_3 solution.
- (iv) Performs Liebermann's nitroso reaction.

(v) Phthalein test-positive. It forms phenolphthalein on heating with phthalic anhydride and conc. H_2SO_4 which gives red colour with alkalis.

(vi) Gives picric acid (M.P. $122^\circ C$) on heating with fuming HNO_3 .

Derivative : 2 : 4 : 6-Tribromophenol M.P. 93° , Phenyl benzoate M.P. 68° , Picrate M.P. 88° .

190°. o-Cresol : $CH_3C_6H_4OH$ (1 : 2)



(i) Colourless liquid, but turns reddish on standing. Phenolic odour, M.P. 31° . Insoluble in water, aromatic.

(ii) Aq. solution gives violet coloration with $FeCl_3$ solution.

(iii) On heating with phthalic anhydride and drop of conc. H_2SO_4 and then making it alkaline gives red colour.

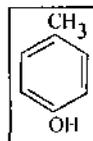
A red colour is also given by phenol, the two may be distinguished by the following test :

Take 0.5 c.c. of molten compound, add 2.5 c.c. of conc. NH_4OH and shake—If completely miscible—compound is phenol otherwise it is o-cresol.

(iv) Liebermann's nitroso reaction-positive.

Derivative : Picrate M.P. 88° , Dibromo derivative (56°).

201°. p-Cresol : $CH_3C_6H_4OH$ (1 : 4)



(i) Colourless in pure state, phenolic smell. Insoluble in water, aromatic.

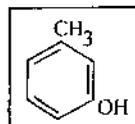
(ii) With $FeCl_3$ solution gives blue colour in water and green in alcohol.

(iii) Phthalein test-negative.

(iv) Take 0.5 gm. (0.5 c.c.) of compound in a dry test tube, add one or two crystals of $NaNO_2$ and 10 drops of conc. H_2SO_4 red colour.

Derivative : Tetra bromo dervt. M.P. 108° , Benzoate M.P. 71° . Forms no picrate.

202°. m-Cresol : $CH_3C_6H_4OH$ (1 : 3)



(i) Colourless liquid, phenolic smell. sinks in water, miscible with excess of water, aromatic.

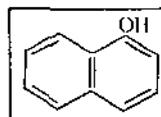
(ii) With $FeCl_3$ solution gives blue violet coloration in water, green in alcohol.

(iii) On fusing with phthalic anhydride in presence of conc. H_2SO_4 and making the product alkaline, blue coloration is obtained.

Derivative : Tribromo dervt. M.P. 84° , Picrate. M.P. 88° , Benzoate M.P. 54° .

SOLID

94°. α -Naphthol : $C_{10}H_7OH$ (I).



(i) Solid, yellow coloured shining plates but turns reddish brown on exposure, characteristic smell insoluble in water, aromatic, B.P. 278° .

(ii) No coloration with $FeCl_3$ solution but a white ppt. changing to red and finally to violet is obtained.

(iii) Alkaline solution on warming with Cu powder and CCl_4 gives the blue coloration (β -naphthol also gives blue colour but they can be distinguished as follows. Add 5 c.c. iodine and 5 c.c. aq. NaOH to 0.5 gm. of compound. If a violet colour rapidly darkens α -naphthol otherwise β -naphthol).

(iv) Alkaline solution on treatment with iodine gives violet colour which darkens and finally gives a ppt.

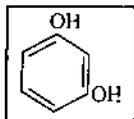
(v) Alkaline solution on boiling with few drops of chloroform gives blue coloration which changes to bluish green on standing.

(vi) Gives violet ppt. with NaBrO.

(vii) Gives green coloration with tannic acid in presence of conc. H_2SO_4 .

Derivative : Picrate orange yellow needles, M.P. 189°; Benzoate M.P. 56°, 2 : 4 Dinitro derivative M.P. 138°, Dibromo derivative M.P. 105°.

118°. Resorcinol : $C_6H_4(OH)_2$ (1 : 3)



(i) Pinkish white crystalline solid, odourless, aromatic, easily soluble in water, ether, alcohol, chloroform. B.P. 276°.

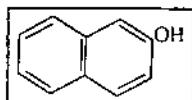
(ii) Aq. solution gives violet coloration with $FeCl_3$ while alc. solution gives green colour.

(iii) On heating with $CHCl_3$ and aq. NaOH gives red colour with green fluorescence.

(iv) On fusing with phthalic anhydride and a drop of conc. H_2SO_4 , it forms fluorescein which gives orange green fluorescence with alkali.

Derivative : Dibenzoate M.P. 117°, 2 : 4 : 6-tri-bromo resorcinol, M.P. 119°, Tri nitro derivatives 175°.

122°. β -Naphthol : $C_{10}H_7OH$ (2)



(i) White pinkish solid, phenolic smell, soluble in hot water, alcohol, ether, benzene, but insoluble in cold water, aromatic, B.P. 285°.

(ii) No colour change in aqueous solution but gives green coloration in alc. solution with $FeCl_3$.

(iii) Alkaline solution gives orange red dye with benzene diazonium chloride.

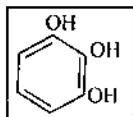
(iv) Its alkaline solution gives blue colour with $CHCl_3$. The colour disappears within few minutes.

(v) Gives yellow colour with NaBrO.

(vi) Gives red colour with tannic acid in presence of conc. H_2SO_4 .

Derivative : Picrate orange needles M.P. 156°. Benzoate M.P. 107°.

133°. Pyrogallol : 1 : 2 : 3 $C_6H_3(OH)_3$



(i) White solid crystals but turns grey on exposure, readily soluble in water, alcohol, ether etc. odourless and aromatic. B.P. 293°.

(ii) Aq. solution with traces of $FeSO_4$ gives blue coloration or blue ppt.

(iii) With $FeCl_3$ solution gives blue violet colour changing rapidly to dull red.

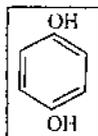
(iv) It reduces Tollen's reagent giving grey ppt. in cold.

(v) Alkaline solution turns brown on exposure to air.

(vi) To 2 c.c. of the aq. soln. of compound add 2 c.c. aq. lead acetate \rightarrow pale yellow emulsion changing to a heavy white ppt. in about 1 minute.

Derivative : Pyrogallol triacetate M.P. 161°, Tribenzoate M.P. 89°.

169°. Hydroquinone : (Quinol) $C_6H_4(OH)_2$ (1 : 4)



(i) White crystalline solid, odourless very easily soluble in water, alcohol and ether, but insoluble in benzene.

(ii) With $FeCl_3$ gives transient blue colour changing to reddish brown.

(iii) It gives grey or brown ppt. with Tollen's reagent in cold.

(iv) Take 0.5 gm. of the compound in a dry test tube, add 2 c.c. dil. H_2SO_4 warm until the solid is dissolved, cool and add a pinch of powdered $K_2Cr_2O_7$ immediate ppt. of quinhydrone consisting of green needles with a metallic lustre.

Derivative : Quinhydrone M.P. 171°, Diacetate M.P. 123°, Dibenzoate M.P. 199°.

4. IDENTIFICATION OF ALDEHYDES LIQUID

B.P.

21°. Acetaldehyde : CH_3CHO

(i) Colourless liquids, characteristic pungent suffocating smell. Miscible with water, aliphatic, R.D. 0.806 (0°C).

(ii) Gives red coloration with alkaline sodium nitroprusside.

(iii) On heating with few drops of 20% NaOH or KOH solution. It forms yellowish red resin having very unpleasant odour.

(iv) Gives wine red colour with Schiff's solution and a red ppt. with Benedict's solution.

(v) Its very dil. solution gives light yellow ppt. with Nessler's reagent, while conc. solution gives red ppt. which turns brown soon.

Derivative : 2 : 4-Dinitro phenylhydrazone, yellow prisms M.P. 162°, Iodoform M.P. 119°, Semicarbazone M.P. 162°.

97°. Acetaldehyde : (aq. solution)

See acetaldehyde.

97°-98°. Formalin : (37% aq. formaldehyde)

(i) Colourless liquid, very pungent odour, miscible with water, aliphatic.

(ii) Reduces tollen's reagent, Fehling's solution and Benedict's solution.

(iii) Gives pink colour with Schiff's reagent in cold which turns blue on addition of a drop of conc. HCl.

(iv) Add to it two drops of phenyl hydrazine, a drop of sodium nitroprusside and a few drops of aq. NaOH. Blue coloured precipitate which changes to green, brown and finally to red.

(v) Add to compound 2 c.c. of 5% phenyl hydrazine hydrochloride followed by 1 c.c. potassium ferrocyanide and 5 c.c. conc. HCl. A brilliant red colour is obtained.

(vi) To 2 c.c. of aq. solution add a pinch of resorcinol and pour 2 c.c. of conc. H_2SO_4 (contained in another test tube) carefully down the side of the test tube red ring at the junction of two liquids which changes to violet red in the aq. layer.

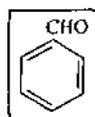
(vii) Gives white crystalline ppt. with semicarbazide hydrochloride.

(viii) No colour with sodium nitroprusside.

(ix) Its very dilute solution gives red brown ppt. with Nessler's reagent which becomes yellow-grey after sometime.

Derivative : 2 : 4 Dinitro phenylhydrazone, orange prisms M.P. 155°, Methylene di β -naphthyl ether M.P. 190°.

179°. Benzaldehyde : $\text{C}_6\text{H}_5\text{CHO}$



(i) Colourless liquid, smell of bitter almonds, turns light yellow on standing, immiscible and heavier than water soluble in alcohol, benzene, ether etc. aromatic. R.D. 1.050 (15°C).

(ii) Does not reduce Fehling's solution.

(iii) Reduces Tollen's reagent on heating.

(iv) Gives a white ppt. with conc. NaHSO_3 solution on shaking.

(v) On boiling with dil. KMnO_4 and then acidifying gives benzoic acid.

(vi) On heating with KOH forms benzoic acid and benzyl alcohol.

Derivative : 2-4-Dinitrophenyl hydrazone, orange needles M.P. 235°, Benzalanilide M.P. 54°; Benzoic acid M.P. 121°, Semi carbazone M.P. 214°.

5. IDENTIFICATION OF KETONES (Liquid)

B.P.

80°. Ethyl methyl ketone : $\text{CH}_3\text{COC}_2\text{H}_5$

- (i) Colourless liquid, characteristic pleasant smell. Miscible with water, aliphatic. R.D. 0.830 (0°C).
- (ii) With alkaline sodium nitroprusside solution gives red colour rapidly changing to yellow.
- (iii) Iodoform test positive.

Derivative : 2 : 4-Dinitro phenyl hydrazone, M.P. 115°. Semicarbazone M.P. 135°.

202°. Acetophenone : $\text{C}_6\text{H}_5\text{COCH}_3$

- (i) Colourless liquid, aromatic characteristic odour sparingly miscible with water, soluble in alcohol, benzene, ether, R.D. 1.023 (25°). M.P. 20°C.
- (ii) Gives an orange red ppt. with alk. solution of 2 : 4-dinitrophenyl hydrazine in presence of conc. H_2SO_4 .

(iii) Iodoform test-positive.

(iv) Gives wine red colour with alk. sodium nitroprusside which changes to blue by acetic acid.

(v) Gives benzoic acid (M.P. 121°C) with alk. KMnO_4 .

Derivative : 2 : 4-Dinitrophenyl hydrazone, orange red needles, M.P. 249°.

6. IDENTIFICATION OF ESTERS (LIQUID)

B.P.

196°. Phenyl acetate : $\text{CH}_3\text{COOC}_6\text{H}_5$

(i) Colourless liquid, pleasant smell, heavier than water, aromatic, R.D. 1.081 (15°C.).

(ii) Aq. solution gives violet colour on boiling with FeCl_3 .

(iii) Take 1 c.c. of the compound add 1 c.c. of NaOH solution of few pellets of solid NaOH, boil for few minutes and then acidify with dil. HCl smell of phenol and then acetic acid.

213°. Ethyl benzoate : $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$

(i) Pleasant smelling colourless liquid. Insoluble in water, aromatic R.D. 1.066 (0°C).

(ii) Decolorises pink colour of aq. NaOH containing a drop of phenolphthalein on boiling.

(iii) Take 1 c.c. of compound and boil it with 1 c.c. of NaOH for 5 minutes. Cool and acidify with dil. HCl-benzoic acid (M.P. 121°C) and ethyl alcohol are obtained.

(iv) Feigl test-positive.

(v) On adding conc. HNO_3 to its solution in cold and conc. H_2SO_4 , it forms ethyl-m-nitro benzoate M.P. 47°.

Derivative : Benzoic acid M.P. 121°.

SOLID

M.P.

68°. Phenyl benzoate : $\text{C}_6\text{H}_5\text{COOC}_6\text{H}_5$

(i) White crystalline solid, odourless, insoluble in water, aromatic, B.P. 299°C.

(ii) Take 0.5 gm. of compound and boil it with 1 c.c. of NaOH for 5 minutes. Cool and acidify with dil. HCl smell of phenol and a white ppt. of benzoic acid (M.P. 121°C) is obtained.

(iii) Phenolphthalein test-positive.

Derivative : Benzoic acid M.P. 121°.

7. IDENTIFICATION OF CARBOHYDRATES SOLID

M.P.

80-90°. Glucose : (Hydrated)

See glucose below.

146°. *d*-Glucose : (Grape sugar, Dextrose) $\text{CH}_2\text{OH} \cdot (\text{CHOH})_4 \cdot \text{CHO}$

- (i) White solid, odourless, sweet in taste, aliphatic, soluble in water.
- (ii) Performs Molisch's test.
- (iii) It gives red ppt. on heating with Fehling's solution or Benedict's solution.
- (iv) It gives silver mirror with Tollen's reagent.
- (v) Does not char with conc. H_2SO_4 in cold.
- (vi) Take 2 c.c. of the aq. solution of compound, and 0.5 gm solid lead acetate, heat to boiling then add 5 c.c. dil. NH_4OH , boil for 2 min. a rose pink colour.

Derivative : *Glucosazone* M.P. 205°, *Oxime* M.P. 137°.

160°. *d*-Sucrose : **(Cane sugar)** $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

- (i) Colourless crystalline solid, odourless, sweet in taste, soluble in water, aliphatic.
- (ii) Does not reduce Fehling's solution, Benedict's solution and Tollen's reagent.
- (iii) Chars with conc. H_2SO_4 .
- (iv) On heating with NiSO_4 saturated with NH_3 , in presence of HCl gives red colour.
- (v) On warming its aq. solution with CuSO_4 solution and NaOH, solution, a violet coloration is obtained.
- (vi) On warming its aq. solution with cobalt nitrate and NaOH solution, a violet coloration is obtained.
- (vii) Take 2 c.c. of aq. solution of compound add about 2 c.c. of conc. HCl and a pinch of resorcinol stand the test tube in boiling water for 5 minutes deep wine red colour with a ppt. (due to fructose, formed by hydrolysis).

Derivative : *Octa acetate* M.P. 67°, *Glucosazone* M.P. 205°.

Does not melt. *d*-Starch (Soluble) : $\text{C}_6\text{H}_{10}\text{O}_5)_n$

- (i) White tasteless, amorphous compound, odourless, insoluble in cold water but soluble in hot water, does not separate on cooling, aliphatic.
- (ii) Take a pinch of compound, add 5 c.c. water and heat to boiling, cool and fill the test tube with water and 1 drop of iodine solution. mix the contents a deep blue colour. On heating, the blue colour disappears which reappears on cooling again.

8. IDENTIFICATION OF HYDROCARBONS LIQUID

B.P.

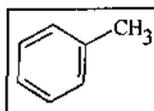
80°. Benzene. C_6H_6



- (i) Colourless liquid, characteristic odour, highly inflammable, floats on water, aromatic, R.D. 0.874 (20°C).
- (ii) Take 1 c.c. of compound add 1 c.c. mixture containing equal volumes of conc. H_2SO_4 and conc. HNO_3 . Shake and pour into 5 c.c. of cold water contained in a beaker-bitter almond odour due to the formation of nitrobenzene.
- (iii) Take 1 c.c. of compound add a mixture of 2 c.c. each of conc. H_2SO_4 and conc. HNO_3 . Heat to boiling then pour into 20 c.c. of cold water contained in a beaker → a pale yellow solid due to the formation of *m*-dinitrobenzene (M.P. 90°C).

Derivative : *m*-Dinitrobenzene M.P. 90°; *picrate* M.P. 84°.

110°. Toluene : $\text{C}_6\text{H}_5\text{CH}_3$



- (i) Colourless liquid, characteristic odour, insoluble in water, lighter than water and inflammable like benzene, aromatic.

(ii) Take 1 c.c. of compound and 2 c.c. each of conc. H_2SO_4 and conc. HNO_3 , warm and pour into 20 c.c. of cold water yellow crystals due to the formation of 2 : 4 dinitrotoluene (M.P. $70^\circ C$).

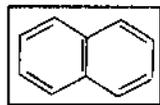
(iii) Take 1 c.c. of compound add a pinch of $K_2Cr_2O_7$ and 1 c.c. of conc. H_2SO_4 . Heat, cool and add 5 c.c. water a white ppt. due to the formation of benzoic acid (M.P. $121^\circ C$).

Derivative : 2 : 4-Dinitrotoluene M.P. 70° .

SOLID

M.P.

80°. Naphthalene : $C_{10}H_8$



(i) White solid, shining plates, insoluble in water, soluble in alcohol, benzene and ether, characteristic odour like moth balls, sublimes readily, aromatic.

(ii) Gives magenta colour on shaking with conc. H_2SO_4 and benzal chloride.

(iii) Dissolve 2.5 g. of compound in chloroform and add anhydrous $AlCl_3 \rightarrow$ green colour.

Derivative : Picrate M.P. 149° .

TYPE II

1. IDENTIFICATION OF CHLORO-COMPOUNDS

B.P.

61°. Chloroform : $CHCl_3$

(i) Characteristic sweet smell and sweet taste. Colourless and heavier than water, aliphatic, R.D. 1.504 ($21^\circ C$).

(ii) On heating with alc. $AgNO_3$ gives white ppt. of $AgCl$.

(iii) Gives very unpleasant smell on heating with aniline and alc. $NaOH$.

(iv) With resorcinol and aq. $NaOH$ gives red colour on warming.

(v) Gives colour with pyridine.

78°. Carbon tetrachloride : CCl_4

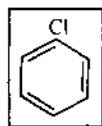
(i) Colourless liquid, non-miscible and heavier than water, aliphatic, R.D. 1.608 ($10^\circ C$).

(ii) On heating with alc. $AgNO_3$ gives white ppt. of $AgCl$.

(iii) Gives blue colour on heating with Cu powder and alk. β -naphthol.

(iv) Gives disagreeable smell of phenyl isocyanide on prolonged heating with aniline and alc. $NaOH$.

132°. Chlorobenzene : C_6H_5Cl



(i) Colourless liquid, characteristic pleasant smell, insoluble in water, aromatic, R.D. 1.107 ($20^\circ C$).

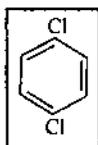
(ii) Take 0.5 c.c. of compound and 2 c.c. mixture containing equal volumes of conc. H_2SO_4 and conc. HNO_3 . Heat and pour into 10 c.c. water taken in a beaker \rightarrow a solid 2 : 4 dinitrochlorobenzene M.P. 52° is formed.

Derivative : 2 : 4-Dinitro chlorobenzene M.P. 52° .

SOLID

M.P.

53°. p-Dichlorobenzene : $C_6H_4Cl_2$ (1 : 4)



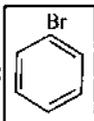
(i) White crystalline solid, characteristic sweet odour, insoluble in water, aromatic, B.P. $172^\circ C$.

(ii) No ppt. with alc. $AgNO_3$.

(iii) Take 1 c.c. of compound add 2 c.c. mixture containing equal volumes of conc. H_2SO_4 and conc. HNO_3 a solid 2 : 5 dichloronitro benzene (M.P. 54°) is obtained.

Derivative : 2 : 5-Dichloronitro benzene M.P. 54° .

157° Bromobenzene :



(i) Light yellow coloured liquid, pleasant odour, insoluble in water, heavier than water, aromatic, R.D. 1.49 ($20^\circ C$).

(ii) No reaction with alc. $AgCl_3$.

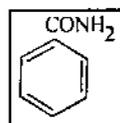
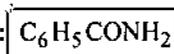
(iii) Take 1 c.c. of compound and a mixture of 2 c.c. each of conc. H_2SO_4 and conc. HNO_3 , shake for few minutes and pour into 20 c.c. cold water. A white ppt. is obtained.

Derivative : 2 : 4-Dinitro bromo benzene M.P. 75° .

TYPE III

1. IDENTIFICATION OF AMIDE SOLID

128° Benzamide :



(i) White crystalline, solid, odourless, soluble in boiling water, aromatic, B.P. 290° .

(ii) Gives smell of ammonia on heating with $NaOH$.

(iii) On heating with soda lime, smell of bitter almonds due to the formation of benzonitrile is produced.

(iv) Take 0.5 gm. of compound add 1 c.c. conc. H_2SO_4 heat strongly, cool and add 2 c.c. cold water → a white solid benzoic acid (M.P. 121°) is obtained.

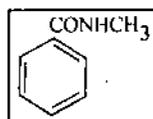
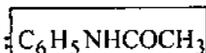
(v) On heating with aniline yields benzanilide M.P. 160° .

Derivative : On heating with aniline forms benzanilide M.P. 160° and on heating with 75% H_2SO_4 gives benzoic acid M.P. 121° .

2. IDENTIFICATION OF ANILIDE SOLID

M.P.

114° Acetanilide :



(i) Colourless shining rhombic plates, odourless, soluble in hot water, aromatic, M.P. 304° .

(ii) On boiling with dil. H_2SO_4 forms acetic acid and aniline salt of H_2SO_4 which on diazotisation and coupling with alk. β -naphthol gives an orange dye.

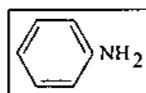
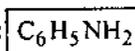
(iii) On sprinkling a little $K_2Cr_2O_7$ on the surface of its solution in conc. H_2SO_4 red to violet colour changing over to green is produced.

Derivative : *p*-Bromo acetanilide, M.P. 167° .

3. IDENTIFICATION OF AMINES LIQUID

B.P.

183° Aniline :

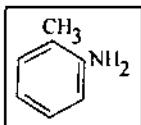


(i) Straw coloured liquid when freshly distilled, but darkness on keeping, aromatic. Slightly soluble in water but soluble in most of the organic solvents. R.D. 1.027 ($17^\circ C$).

- (ii) On boiling with alc. NaOH and CHCl_3 gives very unpleasant smell of phenyl isocyanide.
- (iii) On diazotising and coupling with alk: β -naphthol gives orange red dye.
- (iv) With sod. hypochlorite solution violet coloration changing to brown.
- (v) Its very dilute solution gives light purple colour with bleaching powder solution.
- (vi) Forms Tribromo derivative with Br_2 water (M.P. 118°C):

Derivative : 2 : 4-Dinitrophenyl derivt. M.P. 156° , Acetanilide M.P. 114° , Tribromoaniline 118° .

197°. o-Toluidine : $\text{C}_6\text{H}_4\text{CH}_3\text{NH}_2$ (1 : 2)



(i) Characteristic odour, colourless liquid which changes to red on exposure to light, oily liquid, phenolic smell, insoluble in water, aromatic. R.D. 1.003 (20°C), insoluble in 70 vols water.

(ii) Aq. solution in 50% H_2SO_4 with $\text{K}_2\text{Cr}_2\text{O}_7$ gives blue colour which becomes red on dilution.

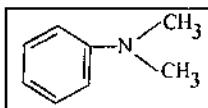
(iii) On heating with alc. NaOH and CHCl_3 forms a very unpleasant smelling o-tolyl isocyanide.

(iv) On diazotisation and coupling with alk. β -naphthol gives orange red dye.

(v) Gives brown colour on shaking with ether its solution in bleaching powder.

Derivative : Picrate yellow prism. M.P. 200° , Dibromo-derivative. M.P. 50° , Benzoyl derivative M.P. 143° , 2 : 4-Dinitro phenyl derivative M.P. 120° .

193°. Dimethyl aniline : $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$



(i) Colourless liquid, ammoniacal fishy odour, insoluble in water, aromatic, R.D. 0.958 (20°C), M.P. 1°C .

(ii) Forms. with HNO_2 in cold, brown nitroso derivative which gives with conc. aq. NaOH green ppt. and smell of NH_3 .

(iii) Take 1 c.c. of the compound, add 5 c.c. saturated solution of picric acid in benzene and cool. Filter crystal, dry and note the melting point 142°C .

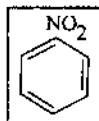
(iv) Forms p-bromo derivative (M.P. 55°) with bromine in acetic acid solution.

Derivative : Picrate, yellow prisms M.P. 163° ; yields additive product with CH_3I M.P. 220° .

4. IDENTIFICATION OF NITRO COMPOUNDS LIQUID

B.P.

201°. Nitrobenzene : $\text{C}_6\text{H}_5\text{NO}_2$



(i) Light pale yellow liquid heavier than water, odour like bitter almonds. Insoluble in water but miscible with organic solvents, aromatic, R.D. 1.197 (25°C), M.P. 5°C .

(ii) Reduces Tollen's reagent after boiling with Zn and CaCl_2 in alcohol.

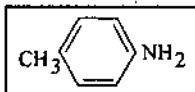
(iii) The compound after reduction with Sn and dil. HCl on diazotisation and coupling with alk. β -naphthol, gives an orange dye.

(iv) Take 2 drops of the compound, add 2 c.c. of glacial acetic acid and a pinch of Zn dust, heat and dilute the solution with 5 c.c. water. Make the solution alkaline by adding sufficient amount of NaOH and add to it a drop of sodium hypochlorite solution a violet colour.

Derivative : On nitration yields m-dinitro benzene, M.P. 90° .

SOLID

54°. p-Nitrotoluene : $\text{CH}_3\text{C}_6\text{H}_4\text{NO}_2$ (1 : 4)

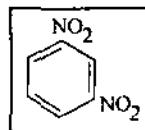


- (i) Pale yellow crystals smelling like that of bitter almonds, insoluble in water, aromatic, B.P. 238°.
- (ii) Reduces Tollen's reagent after boiling with Zn and CaCl₂ in alcohol.
- (iii) On reduction with Sn and HCl forms *p*-toluidine which on diazotisation and coupling with alk. β-naphthol gives orange dye.

(iv) On boiling with acidic KMnO₄ gives *p*-nitro benzoic acid M.P. 241°.

Derivative : 2 : 4-Dinitrotoluene M.P. 70°.

90°. *m*-Dinitrobenzene : $C_6H_4(NO_2)_2$ (1 : 3)



(i) Light pale yellow solid, crystals, characteristic smell, insoluble in water, aromatic, partially soluble in hot water B.P. 302°.

(ii) Gives brown red colour on boiling with aq. NaOH.

(iii) Gives blue colour with acetone and aq. NaOH which changes to violet by acetic acid.

(iv) 0.2 gm. of the compound, add 2 c.c. aq. NaOH, boil and then add a little of SnCl₂ or glucose, it gives violet colour.

Derivative : Gives molecular compound with naphthalene in benzene M.P. 52°; *m*-Phenylene diamine M.P. 60°.

□

CHAPTER

5

PREPARATION OF DERIVATIVES

The preparation of a solid crystalline derivative is the final stage in the identification of the organic compound.

The properties for a good derivative are as follows :

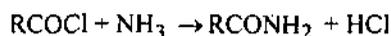
- (i) It should be a solid preferably crystalline melting between 80° to 250°C.
- (ii) It should be quickly and conveniently prepared.
- (iii) It should be readily purified by crystallisation.
- (iv) It should be obtainable by the reagents available in laboratory and through a simple technique.
- (v) It should be obtainable in good yield and within half an hour time.
- (vi) It should not have high melting point but the melting point should always differ with that of original compound at least by five degree.
- (vii) It should differ with original compound in chemical behaviour.
- (viii) The process employed should be generally applicable to whole class of compound rather than an individual compound.

(ix) Before determining the melting point of derivative it should be completely dried. For it, the derivative is placed in thin layer on a filter paper, the filter paper is held by both the hands and moved horizontally 2" to 3" above a small $\frac{1}{2}$ " flame. It is then splitted into many pieces with the help of pen knife and dried again in open air.

The methods for the preparation of different derivatives of different classes of compounds are discussed in the subsequent pages.

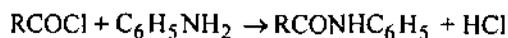
(1) ACIDS (—COOH)

(1) **Amide formation** : Heat 1 gm. of the acid with 3 c.c. of thionyl chloride or PCl_5 in a hard glass test tube for about 15 minutes. Pour this content into 20 c.c. of ice cooled concentrated NH_4OH solution and stir. Filter and wash the precipitate (*i.e.*, amide) and purify by recrystallisation in alcohol.



Amide

(2) **Anilide formation** : Heat 1 gm. of the acid with 3 c.c. of thionyl chloride or PCl_5 in a hard glass test tube for about 15 minutes and cool. Add a solution of 2 c.c. aniline in 10 c.c. benzene and warm the mixture for 4 minutes. Shake well and separate the benzene layer by means of a separating funnel. Evaporate off benzene by heating on water bath. The solid left behind is anilide. Recrystallise it from alcohol.

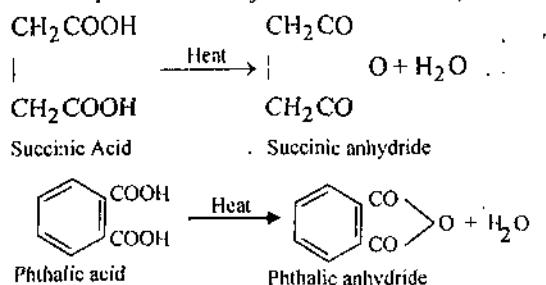


Aniline

Anilide

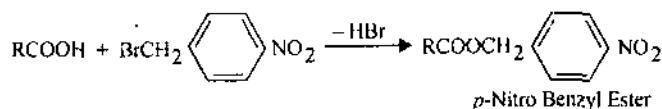
(3) **Anhydride formation** : Heat about 1 gm. of the acid in a porcelain basin covered with an inverted funnel, the stem of which is plugged with cotton wool, above its melting point on a sand bath. Scrap the solid deposited on the funnel. It is the anhydride.

(Only succinic and phthalic acids form this derivative).



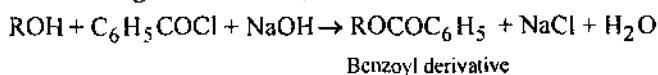
(4) **Ammonium salt formation** : Add NH_4OH gradually to 1 c.c. of the acid and then evaporate the solution to dryness. The residual mass is the ammonium salt of the acid.

(5) ***p*-Nitro benzyl ester formation** : In a 100 ml. conical flask dissolve about 0.5 gm. of the compound in minimum quantity of water or alcohol. Add a drop of phenolphthalein followed by 20% aq. KOH solution till a permanent red colour is just obtained. Now again add a little amount of the compound to remove the red colour of phenolphthalein. Evaporate the contents to dryness on a water bath. Dissolve the residue in 2-3 ml. water. Prepare a solution of 0.5 gm. of *p*-nitrobenzoyl bromide in 7 ml. alcohol. Mix the two solutions and boil under reflux for about half an hour, cool and add 5 ml. water. Filter the product, wash with cold water, crystallise from alcohol and dry.

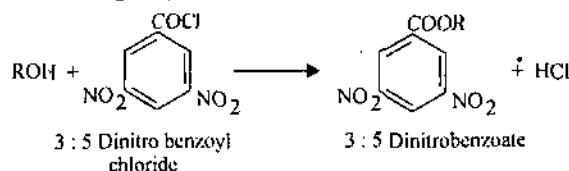


(2) ALCOHOLS (—OH)

(1) **Benzoate** : Add 1 c.c. of alcohol, 10 c.c. of acetone and 5 c.c. of benzoyl chloride contained in a 100 c.c. flask. Add now 50 c.c. of aq. NaOH gradually with constant stirring, till a precipitate is obtained. Pour all the contents in a beaker containing ice cold water, filter and wash with water.



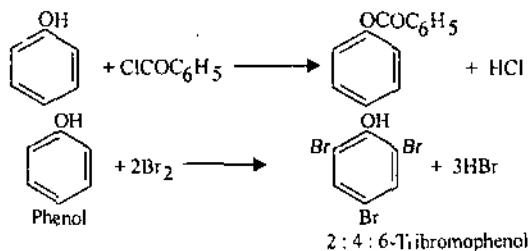
(2) **3 : 5 Dinitrobenzoate** : Take about 0.5 gm 3 : 5-dinitro benzoyl chloride and 2 c.c. of given alcohol in a test tube, boil at least for 5 minutes. Pour this mixture in 10 c.c. of water and cool in ice till solid is formed. Filter, wash with dilute Na_2CO_3 solution and recrystallise it from benzene.



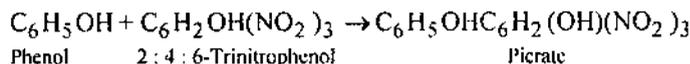
(3) PHENOLS (—OH)

(1) **Benzoyl Derivative** : Prepare as given in 'Benzoate formation' under alcohols.

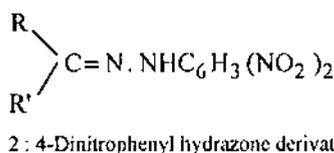
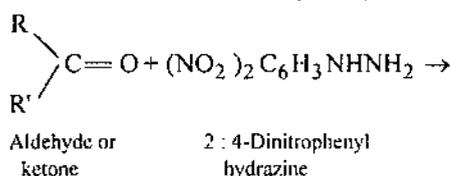
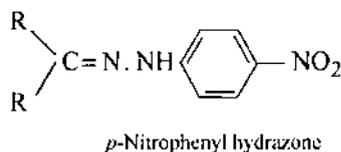
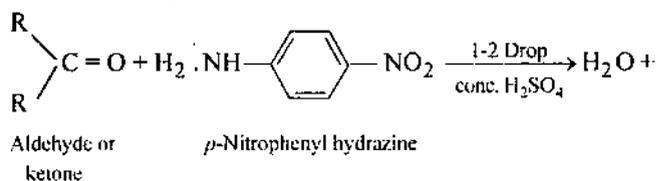
(2) **Bromo derivative** : Dissolve phenol in water, alcohol, acetone or acetic acid and take content in 100 c.c. conical flask. Add strong bromine solution until, after shaking, the liquid is pale yellow. Add 50 c.c. water, cool and shake vigorously. Filter and wash the bromo-derivative with water. Recrystallise the product with alcohol.



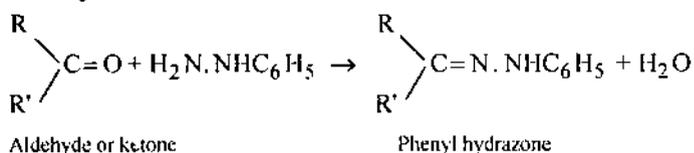
(3) **Picrate** : Mix the saturated solution of phenol in alcohol or benzene with a saturated solution of picric acid in the same solvent. Heat gently, cool and filter out of picrate. Crystallise it with the least amount of hot water or dilute alcohol.

**(4) ALDEHYDES (—CHO) AND (5) KETONES (>C = O)**

(1) 2 : 4-Dinitrophenyl hydrazone : Take about 5 c.c. of 2 : 4 dinitrophenyl hydrazine reagent solution in a test tube. Add 5 drops of the given liquid, shake vigorously and warm it for few minutes. Cool and filter the precipitate thus formed. Recrystallise it from alcohol.

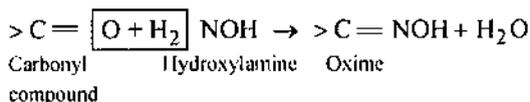


(2) Phenyl hydrazone : Heat the equal volumes of the given compound and phenyl hydrazine hydrochloride solution for few minutes. Now cool the solution under tap water, filter and wash the yellow crystalline product. Recrystallise it from alcohol.



(3) Benzal derivative : Boil a mixture of equal quantities of an aromatic aldehyde and aniline for about 15 minutes. Cool, add dil. HCl, filter and wash the product with water. Crystallise it again from alcohol.

(4) Oxime derivative : Heat the equal volume of the given compound and hydroxylamine for few minutes. Now cool the solution under tap water, filter and wash the crystalline product. Recrystallise it from alcohol.

**(5) ESTER (RCOOR')**

(1) Acid Derivative : Reflux 1 gm. of an ester with 10 percent aq. NaOH solution till a transparent solution is obtained. Cool and dilute with water. Filter and acidify with dilute H_2SO_4 . Filter out the acid and crystallise from hot water or dilute alcohol.

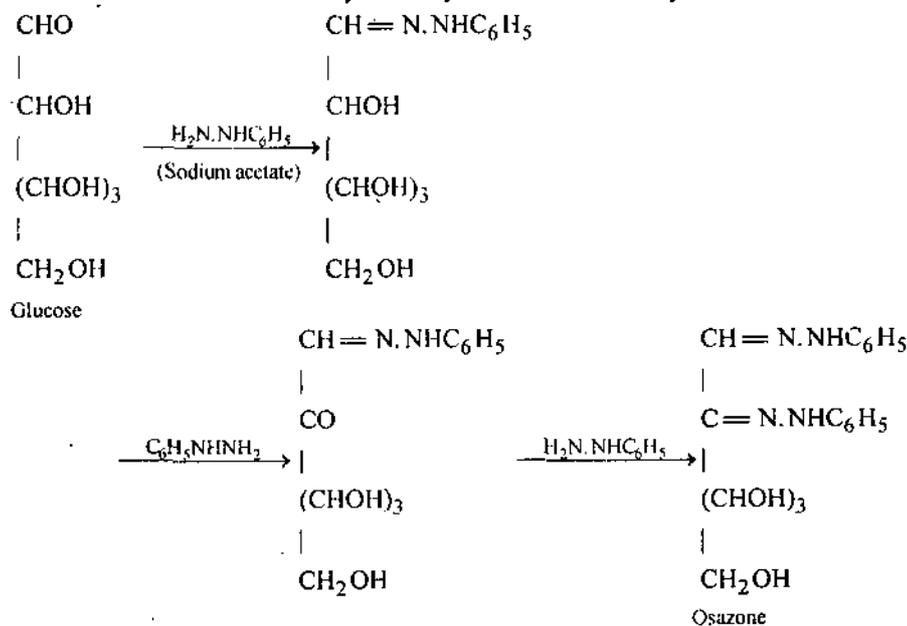
(2) 3 : 5-Dinitrobenzoate : 0.5 gm. of the ester refluxed with 0.7 gm of 3 : 5-dinitro benzoic acid in presence of a drop of conc. H_2SO_4 till a clear solution is obtained. Heat for 5 minutes, cool and add excess of Na_2CO_3 solution. Filter, wash the solid with water and crystallise the product from benzene.

(3) Amide derivative : Add 0.5 gm. of the compound in 10 c.c. of conc. NH_4OH and shake well till a solid is formed. Filter, wash with water and crystallise from alcohol.

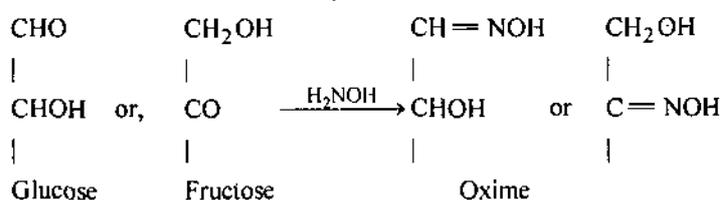
(4) **Anilide derivative** : Heat 0.5 gm. of the compound with 2 c.c. of aniline for about 30 minutes. Cool and add dilute HCl to remove unreacted aniline. Filter and wash the product with water. Recrystallise it from alcohol.

(7) CARBOHYDRATES

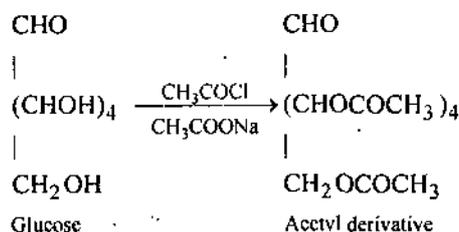
(1) **Osazone formation** : Dissolve 0.5 gm of sodium acetate in 15 c.c. water and add 0.5 gm. of phenyl hydrazine hydrochloride. Shake, filter the solution and add 0.3 gm. of the compound to the filtrate. Heat for about 10 minutes. Cool and filter out yellow crystallised mass. Recrystallise it from alcohol.



(2) **Oxime Formation** : See under Aldehyde and Ketone :



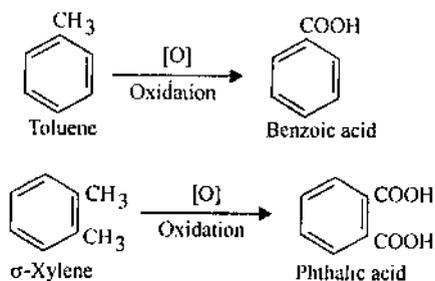
(3) **Acetyl derivative** : Heat the mixture of about 0.5 gm. compound with 3 c.c. of acetic anhydride (or acetyl chloride) and a small piece of anhydrous ZnCl_2 in boiling water bath for an hour at least. Cool and dilute the mixture with ice cold water and shake. Filter and crystallise the product again from alcohol.



(8) AROMATIC HYDROCARBONS

(1) **Nitro derivative** : Add 2 c.c. of conc. HNO_3 drop by drop and with shaking to a suspension of 0.5 gm. of the substance in 2 c.c. of conc. H_2SO_4 . Heat the mixture for about 5 minutes on a water bath. Pour all the contents into a beaker containing ice cold water. Filter and wash the product with water. Recrystallise it from alcohol.

(2) **Oxidation products** : If the aromatic hydrocarbon contains some side chain then the later can be easily oxidized by alkaline KMnO_4 to give the carboxylic group. The acid thus obtained serves as a very good derivative for the hydrocarbon e.g.



(9) ARYL HALIDES (—Cl, —Br, —I)

(1) **Nitro derivatives** : Add 2 c.c. of fuming HNO_3 , drop by drop and with shaking, to a suspension of 0.5 gm. of the substance in 2 c.c. of conc. H_2SO_4 . Heat the mixture for about 10 minutes on a boiling water bath. Pour the contents with ice cold water, filter and wash the product with water. Recrystallise it from alcohol.

(2) **Picrate formation** : Prepare as given under 'phenols'.

(10) AMIDES (—CONH₂)

(1) **Acid derivative** : Heat 1 gm. of the compound with 2 percent aq. NaOH solution till a clear solution is obtained. Cool and acidify with dilute H_2SO_4 , filter the solid and crystallise it with hot water or dilute alcohol.

(2) **Picrate formation** : Prepare as given under 'Phenols'.

(11) AMINES (—NH₂, >NH, >N)

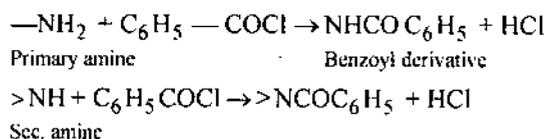
(1) **2 : 4-Dinitrophenyl derivative** : Dissolve the equivalent proportion of 2 : 4-Dinitro-benzene and the amine in alcohol and then add some anhydrous sodium acetate. Cool and add dil. HCl to remove the unreacted amine. Filter and wash the product with water. Recrystallise it from alcohol.

(2) **Acetyl derivative** : Take about 1 c.c. or 1 gm. of the amino compound in a test tube, add 2 c.c. each of acetic anhydride (or acetyl chloride) and glacial acetic acid. Heat the mixture for about 3-4 minutes, pour it into a beaker containing ice cooled water. Filter and crystallise the product from boiling water.

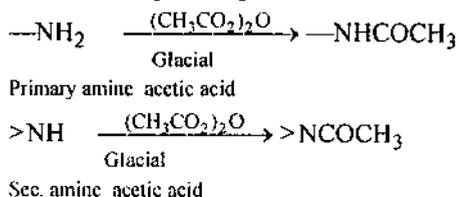
(3) **Benzal derivative** : Boil the equivalent amounts of the compound and benzaldehyde for about 5 minutes. Cool, filter and crystallise the product with alcohol.

(4) **Phenyl thiourea derivative** : Boil the equal amounts of the amino-compound and phenyl isothiocyanate for about 5 minutes. Cool the whole mixture in ice. Recrystallise this solid from alcohol.

(5) **Benzoyl derivative** : Prepare as given under 'Alcohols'.



(6) **Acetyl derivative** : Prepare as given under 'Carbohydrates'.

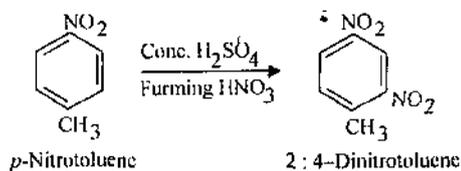


(7) **Picrate** : Prepare as given under 'Phenols'.

(12) NITRO (—NO₂)

(1) **Nitro derivative** : Take 1 gm. of the compound in a test tube and add 4 ml. of conc. H_2SO_4 . Now add 4 ml. of conc. HNO_3 dropwise with continuous shaking and cooling the tube in cold water. Heat the

contents on a boiling water bath at 50°-60°C for 15-20 minutes. Cool and pour the contents in ice water. Filter off the solid, wash with cold water, crystallise with dil. alcohol and dry.



(2) Amine formation : In a conical flask fitted with an air condenser take 1 gm. of the compound and 2 gms. of granulated zinc or Sn. Through the condenser add 6 ml. of conc. HCl in portion (1 ml. each time) with occasional shaking. Cool the flask in ice containing water if it becomes too hot. Heat on a boiling water bath for about 10 minutes. Decant the hot solution in a beaker and add 3-4 ml. water and 4 gm. solid NaOH. Shake well and cool in an ice bath. Filter off the solid, wash with water and crystallise from alcohol.

(13) ANILIDE

(1) Nitro derivative : Take 1 gm. of the compound and 1 ml. of the glacial acetic acid in a test tube. Warm the contents to get a clear solution. Now add 2 ml. of conc. H₂SO₄ gradually with stirring. Cool the tube in ice containing water and add dropwise 1 ml. conc. HNO₃. Allow to stand for 15 minutes and then pour, wash with cold water and crystallise from methyl alcohol.

(2) Bromo derivative : Take 1 gm. of the compound and 5 ml. glacial acetic acid in a test tube. Add 15 ml. of bromine solution in acetic acid (0.5 ml bromine in 1 ml. glacial acetic acid) dropwise with continuous shaking. Allow to stand for 10 minutes and then pour the contents in 50 ml. ice containing water. Filter the product, wash with cold water and crystallise from alcohol.

METHOD OF RECORDING THE RESULT

Date :

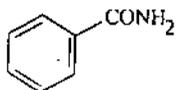
S.No. :

Object : Identify the given organic compound.

Sl. No.	Experiment	Observation	Inference
1.	Preliminary examination	(a) Physical state—Crystalline Solid. (b) Colour-White (c) Odour-Odourless (d) Saturated.	
2.	Heating effect	Burns with a smoky flame.	Aromatic compound
3.	Detection of elements (N, S or Halogen)	Gives blue coloration on adding FeSO ₄ in sodium extract, boiling and then adding FeCl ₃	Nitrogen only
4.	Melting point	128°C	
5.	Solubility	Soluble in water	I Group
6.	Tests for functional group		
(a)	On adding aq. NaNO ₂ soln. in cold solution of compound in dil. HCl	Brisk efferevescence	Aliphatic primary amine amide
(b)	On heating the compound with CHCl ₃ and alc. NaOH	No-pungent smell	Aliphatic primary amine or amide present
(c)	On heating the compound with conc. NaOH	Smell of ammonia	Acid amide present

7.	Possibility of compound.		Benzamide
8.	Specific tests On heating with sodalime	Smell of bitter almonds is produced due to benzonitrile	Benzamide confirmed
9.	Derivative prepared	Benzanilide, M.P. 160°C	Benzamide
10.	Conclusion		Benzamide

Result : The given compound is



□

PAPER CHROMATOGRAPHY

Chromatography is an analytical technique employed for the purification and separation of organic and inorganic substances. It is also very useful for the fractionation of complex mixtures, separation of closely related compounds such as isomers, homologues etc. and in the isolation of unstable substances.

Chromatography consists in separating substance by filtering their solution through a column of a finely powdered adsorbent, filled with glass-wool and then washing (developing) the column with a solvent.

Chromatography can be classified into following types :

(1) Paper chromatography :

Liquid-liquid (Paper partition chromatography)

(2) Column chromatography

Liquid-liquid (Partition chromatography) and liquid-solid (Adsorption chromatography).

(3) Gas chromatography

Gas-liquid (Gas partition chromatography) and gas-solid (Gas-adsorption chromatography).

(4) Ion exchange chromatography

Liquid-liquid (Ion exchange adsorption chromatography).

(1) PAPER CHROMATOGRAPHY

The principle of paper chromatography is based on the fact that solutes have the capacity to migrate through filter paper at different rates as a solution is drawn into strips of paper by capillary action.

Paper chromatography may be regarded as a type of partition chromatography in which the stationary phase is water adsorbed on the hydrophilic surface of the paper. The organic solvent then acts as a mobile phase. Water can be replaced by a non-polar stationary liquid phase by suitable treatment of paper. Aqueous solution can then be used as developer. In paper chromatography the silica gel as the solid support for the polar phase is replaced by a filter paper and an organic solvent partially miscible with water e.g., butanol or pyridine is most suitable in paper chromatography. A drop of the solution containing the sample is introduced at some point on the paper which acts in lieu of a packed column, migration then occurs as a result of flow by a mobile phase called the developer. Movement of the developer is caused by capillary forces. When the movement of the mobile phase is in upward direction, the development is called ascending development, if the flow is in downward direction, it is called descending development. When it is outward from a central spot, it is called radial development. It should be noted that the process of allowing the solvent to move along the filter paper is called development. The ratio of the distance the substances moves is compared with the distance reached by the solvent front, both measured from the point of application of the sample, is termed the R_F . The R_F value is characteristic of a particular species, in any given type of separation and is sometimes used for the quantitative identification of the unknown species.

In paper partition chromatography, a filter is used as an adsorbent.

A strip of filter paper about 1" by 6" in size is taken and a small drop of the solution to be analysed is placed in the centre about an inch from one end. The point should be marked with a pencil. At the bottom a paper clamp is affixed as to give weight at the base. The bottom of the paper is dipped into the pool of a suitable solvent. The drop of the vessel is closed in which the paper is suspended so that the upper portion of the glass cylinder be saturated with vapour of the solvent. The liquid rises up by the capillary, carrying the

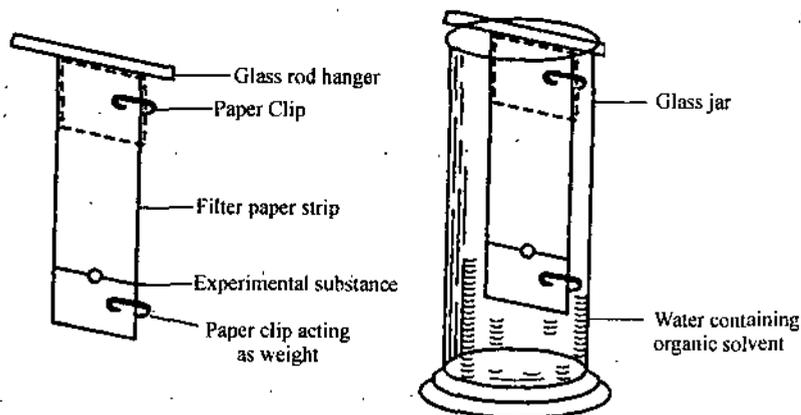


Fig. 1. Identification by paper chromatography.

constituents along with it with various speeds according to their partition coefficient. When the solvent reaches at the top this point is marked. The strip is dried in air and sprayed with a solution of suitable developer. A number of spots appear and they should be encircled with a pencil for permanent record. The individual components are characterised from their respective rates of flow *i.e.*, R_F .

$$R_F = \frac{\text{Distance moved by the component}}{\text{Distance moved by the solvent front}}$$

Experiment 1. To separate and identify the sugars present in the given mixture by the technique of paper chromatography and report the R_F values.

Apparatus : Chromatographic chamber, air oven, chromatographic filter paper.

Test tubes	—	4 (ordinary)
Droppers	—	4
Reagent Bottles	—	500 ml (Two)

Measuring cylinder 100 ml (one) and 25 ml (one)

Solutions :

Glucose	10 ml	(10 mg. in 10 ml)
Fructose	10 ml	(10 mg. in 10 ml)
Sucrose	10 ml	(10 mg. in 10 ml)

Unknown mixture of sugars.

Developer : A mixture of *n*-butanol, pyridine and water in the proportion of 6 : 4 : 3 by volume is used.

Spraying reagent : 1.66 g of phthalic acid and 0.91 ml of aniline are dissolved in 48 ml of *n*-butanol and mixture with 48 ml of ether and 4 ml of water.

Method : A strip of Whatmann No. 1 chromatographic paper (30-40 cm. × 5 cm.) is cut from a sheet. It should be such that it does not touch the sides and the bottom of the chromatographic chamber. A line is drawn about 2" from the top of the paper with pencil. Now four small circles are drawn on the line with pencil and these are marked out as *G* for glucose *F* for fructose, *S* for sucrose and *M* for unknown mixture. *G*, *F*, *S* and *M* are spotted carefully with a drop or two of the respective solutions. These spots are now dried in air for about 20-25 minutes. Meanwhile place the rack filled with developer in the chromatographic chamber and close the chamber by means of cover. This chamber is kept undisturbed for half an hour for proper equilibrium. Spotted paper is placed in the chromatographic chamber in such a way that the spotted marks do not dip into the rack. Paper is allowed to develop till the wet surface just reaches the other end of the paper. Now it is taken out from the chamber and allowed to dry.

Developed surface is marked with pencil and spraying agent is sprayed. Paper is heated to 110°C in an air oven so that the brownish spots are clearly visible. Identify the constituent sugar of the mixture by

comparing the R_F values of the spots with those for the known sugars. Distance of each of the spot and of the liquid front is measured from the spotted place. Hence R_F values of the constituents are found out.

Observations :

S. No.	Sugars	Distance travelled by pure sugar from the origin	Distance travelled by the solvent
1.	Glucose	—	—
2.	Fructose	—	—
3.	Sucrose	—	—

R_F values are calculated. Similarly the R_F values for each spot present in the mixture are evaluated.

Result : Identification of the sugars in the mixture is done by comparing the R_F values of pure sugar with that of the spot in the mixture.

The following sugars are present in the mixture.

S. No.	Sugars	R_F value in the mixture	R_F value of pure sugar
1.	Glucose	—	—
2.	Fructose	—	—
3.	Sucrose	—	—

Experiment 2. To separate and identify amino acids (glycine, aspartic acid, glutamic acid and tyrosine) in a mixture of amino acids with the help of paper chromatography.

Apparatus :

- (i) Chromatographic chamber
- (ii) Whatmann filter paper No. 1 or 3
- (iii) Capillary tubes or syringes.

Reagents : Glycine, aspartic acid, glutamic acid, tyrosine and a concentrated solution of their mixture.

Spraying agent : 0.1 or 0.2% alcoholic solution of ninhydrin.

Developer : A solution prepared by mixing *n*-butanol, glacial acetic acid and distilled water in the ratio of 6 : 1 : 2.

Procedure : Whatmann filter paper is cut in rectangular shape (30-35 cm × 3.5 cm). A line is drawn with the help of pencil at a distance of 2-3 cm from one of the end. On this line five small circles are drawn which are marked as :

G_1	—	Glycine
A	—	Aspartic acid
G_2	—	Glutamic acid
T	—	Tyrosine
M	—	Mixture

Prepare separately concentrated solutions of above amino acids and their mixture. With the help of capillary or dropper put one drop each of these solutions in the marked circle on the paper. Dry these drops in the hot air. For this purpose hair drier may be used. The jar containing developer is placed inside the chromatographic chamber and the chamber is closed for some time. Then the filter paper is hung, like in ascending chromatography, in the chamber in such a way that the lined end of the filter paper remains downwards; but it does not dip in the developer solution. When developer reaches at the top end, the filter paper is taken out of the chamber and dried. The finish line of the developed is marked on the filter paper.

Now, 0.1% or 0.2% alcoholic solution of ninhydrin is sprayed on the filter paper and the paper is dried in the oven at 100°C. The spots of different amino acids become visible. The distance travelled by the mixture, solvent and individual amino acid is measured.

Observations :

Temperature of chamber = ... °C

Time spent in development = second

S. No.	Amino acid	Distance travelled by pure amino acid from the marked place	Distance travelled by the amino acid in the mixture from the marked place	Distance travelled by the solvent
1.	Glycine	—	—	—
2.	Aspartic acid	—	—	—
3.	Glutamic acid	—	—	—
4.	Tyrosine	—	—	—

Calculations : R_F value of individual pure amino acid and the acids present in the mixture is calculated. From the values the amino acids present in the mixture are identified.

$$R_F = \frac{\text{Distance travelled by amino acid}}{\text{Distance travelled by solvent}}$$

□

CHAPTER

7

VIVA VOCE FOR PRACTICE

ORGANIC ANALYSIS

1. What is Lessaigne's test ?
2. What is this filtrate known as ?
3. Is it essential for sodium extract to be colourless ?
4. Why do you fuse sodium with organic compound ?
5. Why is metallic sodium kept under kerosene oil ?
6. Then you may use metallic calcium or magnesium ?
7. Can potassium be used in place of sodium ?
8. Why is the use of the distilled water necessary in the preparation of sodium extract ?
9. Why is it necessary to break down red hot ignition tube in distilled water ?
10. Ignition tube and sodium piece both should be completely dry. Why ?
11. How will you test the presence of nitrogen in an organic compound ?
12. Why should ferrous sulphate sodium be fresh and saturated ?
13. How will you detect halogens ?
14. Why is the carbon tetrachloride layer coloured with liberated Br_2 or I_2 and not the aqueous layer ?
15. NaCl and CHCl_3 both contain chloride but AgNO_3 gives the precipitate with NaCl and not with CHCl_3 . Explain.
16. Why is it essential to boil sodium extract with conc. nitric acid before detecting halogens ?
17. Is there any other test for the detection of halogens ?
18. What is Beilstein's test ?
19. How is sulphur tested by sodium nitroprusside and lead acetate solution ?
20. Some times a blood red colour is produced on addition of FeCl_3 to sodium extract. Why ?
21. How is it confirmed, whether the given compound is aromatic or aliphatic ?
22. Why do aromatic compounds burn with smoky flame ?
23. What is Fehling's solution and where it is used in organic analysis ?
24. What is Schiff's reagent and where it is employed in organic analysis ?
25. What is Tollen's reagent and where it is employed in organic analysis ?
26. What is Milisch's test ?
27. What is phthalein test ?
28. What is Liebermann's nitroso test ?
29. What biuret test ?
30. What is iodoform test ?
31. Where is 2 : 4 dinitro phenyl hydrazine reagent employed in organic analysis ?

32. Where is ceric ammonium nitrate reagent employed ?
33. How will you proceed to detect whether halogen is present in side chain or in nucleus ?
34. What is the importance of preparation of a derivative in the identification of organic compound ?
35. What are characteristics of a good derivative ?

CHROMATOGRAPHY

36. What is Chromatography ?
37. What is the principle of paper chromatography ?
38. What is R_F value in paper chromatography ?
39. Give the detailed classification of chromatography ?



CHAPTER

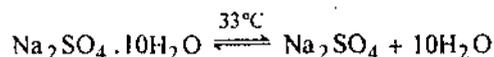
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TRANSITION TEMPERATURE

INTRODUCTION

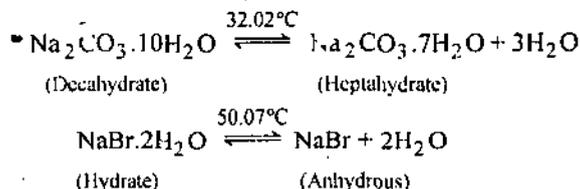
There are many substances which are capable of existing in more than one crystalline form e.g., sulphur, phosphorus, mercuric iodide etc. In general these different polymorphous forms are not equally stable at a given temperature. Thus at ordinary temperatures, rhombic sulphur is the more stable form, and monoclinic sulphur; if kept sufficiently long, will change spontaneously into rhombic sulphur. If the temperature is raised to 96°C, rhombic sulphur changes into monoclinic sulphur, and this form of sulphur is stable at all temperatures above 96°C, upto the melting point. At 96°C both rhombic and monoclinic sulphur may exist together in stable equilibrium. This temperature is known as the **Transition temperature** or **Transition point**. Similar is the case with mercuric iodide. Its vermilion coloured variety which crystallises in tetragonal crystals, is the stable form at all temperatures upto 127°C while above 127°C the stable form is coloured yellow and crystallises in rhombic crystal. Both the forms may coexist in stable equilibrium at the transition point 127°C.

Transition points are not only in the case of polymorphous substances, but they are also found in the case of all hydrated and double salts. When a salt combines with water to form one or more different hydrates it is found that under given conditions of temperature etc. only one of the hydrates, or it may be the anhydrous salt, is stable. Thus Glauber's salt, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is stable at ordinary temperatures but on raising the temperature it passes into the anhydrous salt at 33°C. At this temperature both the anhydrous salt and the decahydrate are stable in the presence of one another and of water. Below 33°C the decahydrate is stable in the presence of water. Below 33°C the decahydrate is stable in the presence of water and the anhydrous salt is unstable—that is, it is converted into the decahydrate. Hence at 33°C the equilibrium is represented by the equation



is set up. At temperature above 33°C the reaction proceeds from left to right and the temperature below 33°C the reaction proceeds from right to left.

Similarly the equilibrium of other salts hydrate at transition point may be represented as follows :



Various methods have been employed for the determination of the transition point of a polymorphous solid of a salt hydrate. The more important of these are :

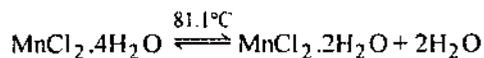
- (i) The thermometric method
- (ii) The dilatometric method
- (iii) The solubility method
- (iv) The conductance method
- (v) The optical method.

The thermometric method is employed here.

Experiment 1. To determine the transition point of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ by the thermometric method.

Apparatus & Chemicals : $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, thermometer, test tube, beaker, stirrer, burner, water etc.

Principle : Thermometric method is based on the principle that when one form changes into another with the rise of temperature, absorption of heat takes place and an equivalent amount of heat is liberated on lowering the temperature. Thus, when $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ begins to change into its $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ form at a certain point the temperature remains stationary until the conversion is completed. This certain point determines, of course, the transition temperature.



Method : Place about 50 g of finely powdered $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in a thin walled test tube so as to surround entirely the bulb of a 'thermometer' graduated in tenth of degree. Insert a thermometer and stirrer made of silver wire also. Support this tube in a large beaker of water, provided with a glass stirrer and a thermometer.

Raise the temperature of bath to 70°C and keep it for thirty minutes. Raise the temperature of the bath very gradually and regularly to 90°C at the rate of about 1°C in 10 minutes. Note the temperature of the salt in every two minutes and record both the time and temperatures. Now allow the bath to cool slowly and read the temperature of the salt in every two minutes, as before both time and temperature until it reaches 70°C . It will be noticed that at $84\text{--}86^\circ\text{C}$, the salt becomes partially liquid (It is the transition temperature) and at this temperature the rate of heating and cooling of the salt will be slower than at other temperatures.

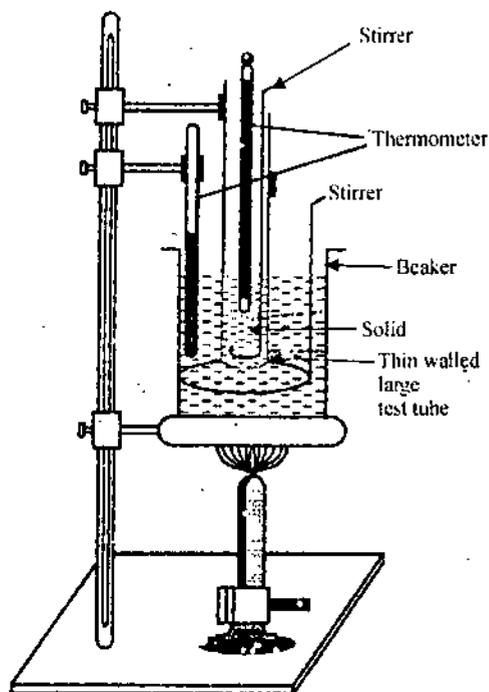


Fig. 1. Thermometric method for determining the transition temperature.

S.No.	Time in minutes	Temperature $^\circ\text{C}$
1.	2
2.	4
3.	6
4.	8
5.	10
6.	12

A similar table should be made for the observations when the temperature is lowered gradually.

Calculations : Plot a graph between temperature as abscissa (x-axis) and the number of minutes counted from the time at which heating or cooling commenced as ordinates (y-axis) and draw a heating curve AFT_1CD and a cooling curve DCT_2EFA . The mean of the points T_2, T_1 will give the transition temperature.

Result : The transition temperature is the 85.1°C .

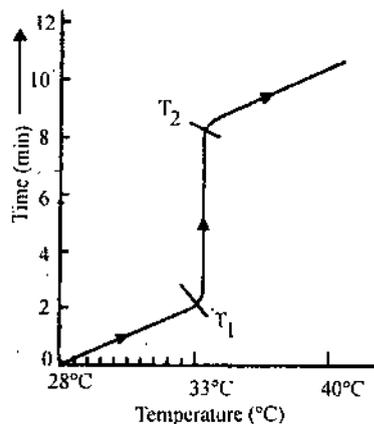


Fig. 2. Heating curve obtained in the thermometric method of determination of transition temperature of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$

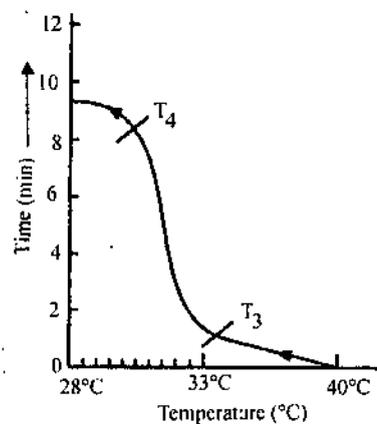


Fig. 3. Cooling curve obtained in the thermometric method of determination of transition temperature of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$

Precautions : (1) $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ should be carefully stirred for rise of temperature.

(2) The rate of increase and decrease of temperature near transition temperature should not be very fast.

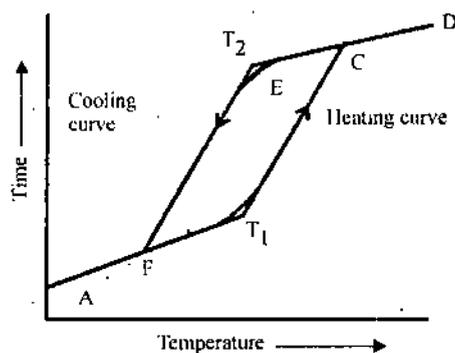


Fig. 4. Transition temperature curve

CHAPTER 9 SOLUBILITY

INTRODUCTION

Before the experimental methods are considered, the exact meaning of the term **Solubility** must be made clear and this can be best done by considering a definite example.

When a small quantity of powdered alum is placed in a beaker of water at constant temperature and stirred or left as such, it will slowly disappear, more rapidly if it is stirred than when left alone. Further small quantities added successively will also disappear. The alum is said to have dissolved in water and to have formed a **Solution**. An indefinite quantity of alum will not, however, dissolve in given amount of water, after a certain amount has dissolved in the water will not dissolve any more at that temperature. When this stage has been reached the water is **Saturated** and the solution is then termed a **Saturated solution**. But if the temperature is increased still more alum will dissolve until the solution becomes saturated at the higher temperature at which it is saturated with the undissolved substance. When dealing with solutions at least two substances have to be considered :

(i) The substance which is dissolved, in the above example alum, which is known as the dissolved, substance or **Solute**, and

(ii) The substance in which the solute is dissolved, in the above example water, which is known as the **Solvent**.

The **solubility** is dependent on the nature of both the substances and is defined as :

"The number of grams of the substance which is dissolved in 100 gram of the solvent in a saturated solution at a given temperature."

The solubility of a solid substance in a given solvent depends mainly on the temperature and but slightly on the pressure. The solubility of most solid substance increases with increase in temperature. In case of some substances, e.g. AgNO_3 the solubility increases rapidly with increase of temperature, while with others e.g., NaCl , increases but slowly. The change in solubility with changing temperature is usually expressed by means of **Solubility Curves**, which are constructed by plotting the number of grams of solute dissolved in 100 g of solvent as ordinates against the temperature as abscissae and drawing a curve through the points. A few solid substance like Li_2CO_3 decrease in solubility as the temperature increases. Some solids e.g.,

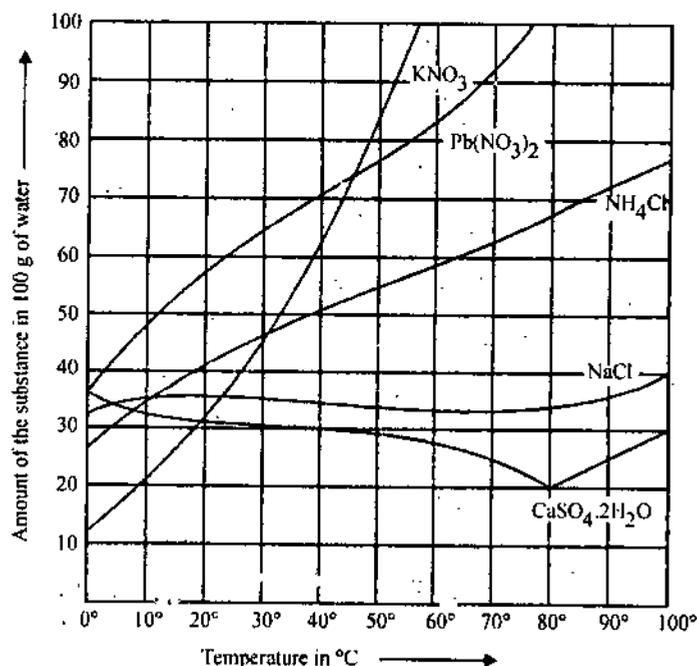


Fig. 5. Solubility curve

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ increase in solubility as the temperature increases upto a certain point, after which the solubility decreases with further rise in temperature. The solubility of a substance in a liquid is often affected by the presence of second solute thus the presence of hydrochloric acid reduces the solubility of sodium chloride, barium chloride etc. in water, nitric acid reduces the solubility of many nitrates in water and the presence of alcohol reduces the solubility of most salts in water.

Experiment-1. To determine the solubility of potassium nitrate in water at 30°, 40°, 50°, 60°, and 70° C and thus to plot a solubility curve also.

Apparatus and Chemicals : Two thermometers, small beaker, water bath, porcelain dish, potassium nitrate, water, balance etc.

Method : Support a 100 ml. beaker in water bath, (or a large beaker) with the help of string or with a piece of metal sheet which has the hole cut in the centre large enough to admit the beaker, but not large enough to allow it to slip through. A thermometer reading upto 100°C is placed in the beaker and glass stirrer is placed in the beaker. Place about 30 g of finely powdered potassium nitrate and 75 ml. of water in the beaker. Raise the temperature of the bath to 70°C and keep it there. Stir the water in large beaker and the solution in small beaker, continuously for five minutes, keeping the temperature constant at 70°C, then with a dry 20 ml. pipette withdraw a quantity of a saturated solution. Allow this liquid to run into a previously weighed porcelain dish and now weigh it.

Evaporate the solution to dryness on a water bath. Cool the dish in a desiccator and weigh it. Stir the solution on small beaker for further ten minutes at 70°C, extract a further quantity of solution and determine the weight again as before. If the two analysis gives the same result, the solubility may be calculated as given below.

Now allow the temperature to fall to 60°C and determine the solubility at this temperature exactly in the same way. When the determination has been made at 60°C, allow the temperature to fall further to 50°C and make a determination so on at 40°C and 30°C also. Plot the solubility values as ordinates against the temperature as abscissae.

Observations :

S.No.	Temp.	Weight of Porcelain dish	Weight of dish and solution	Weight of dish and residue	Weight of residue	Weight of water
1.	70°C	x g	y g	z g	(z - x) g	(y - z) g
2.	60°C	x ₁ g	y ₁ g	z ₁ g	(z ₁ - x ₁) g	(y ₁ - z ₁) g
3.	50°C	x ₂ g	y ₂ g	z ₂ g	(z ₂ - x ₂) g	(y ₂ - z ₂) g
4.	40°C	x ₃ g	y ₃ g	z ₃ g	(z ₃ - x ₃) g	(y ₃ - z ₃) g
5.	30°C	x ₄ g	y ₄ g	z ₄ g	(z ₄ - x ₄) g	(y ₄ - z ₄) g

Calculations :

Solubility of KNO_3 in 100 g at

$$70^\circ\text{C} = \frac{(z - x)}{(y - z)} \times 100$$

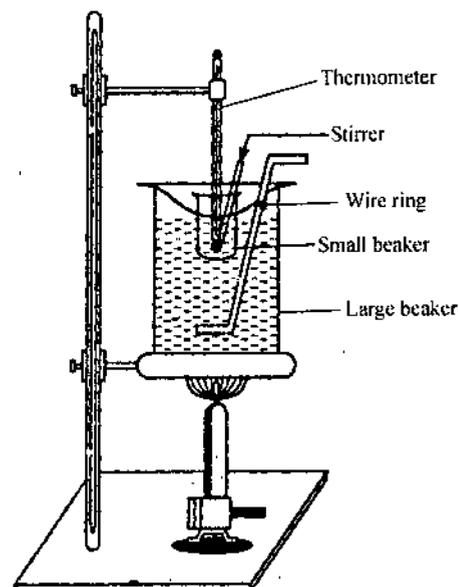


Fig. 6. Determination of the solubility.

$$60^{\circ}\text{C} = \frac{(z_1 - x_1)}{(y_1 - z_1)} \times 100$$

$$50^{\circ}\text{C} = \frac{(z_2 - x_2)}{(y_2 - z_2)} \times 100$$

$$40^{\circ}\text{C} = \frac{(z_3 - x_3)}{(y_3 - z_3)} \times 100$$

$$30^{\circ}\text{C} = \frac{(z_4 - x_4)}{(y_4 - z_4)} \times 100$$

Result :

The Solubility of KNO_3 at ... $^{\circ}\text{C}$ = ... gram per 100 g

Some standard values at 20°C . (Room temperature).

NaCl 35.7; Na_2CO_3 7.1; NaNO_3 73; NH_4Cl 30; BaCl_2 31; FeSC_4 16.0; $\text{Pb}(\text{NO}_3)_2$ 38.

Precautions :

1. Only the supernatant liquid should be pipetted out at the desired temperature.
2. During evaporation, the liquid should be dried completely.
3. Weighing should be made accurately.
4. At least three such experiments should be performed with the same solution at the same temperature.

Experiment 2. To determine the solubility of benzoic acid at 40°C and at a temperature lower than the room temperature by titration method.

Theory : A saturated solution of the acid is first prepared slightly above 40°C i.e., at $55-60^{\circ}\text{C}$. The solution is then cooled to 40°C and a definite volume of it is titrated against a standard solution of an alkali, say sodium hydroxide.

A saturated solution is also prepared at room temperature and its temperature is lowered by surrounding the beaker containing the solution with ice. When the temperature has fallen to the desired value, a known volume of the solution is pipetted out and titrated against a standard solution of alkali.

Procedure : Take about 25 ml distilled water in a beaker and heat it to about $55-60^{\circ}\text{C}$. Prepare a saturated solution of benzoic acid at this temperature. Allow the solution to cool gradually, stirring from time to time. As soon as the temperature falls to 40°C , pipette out 10 ml of the solution in a conical flask. Now titrate this solution against $\text{N}/50$ NaOH , using phenolphthalein as an indicator.

For measuring the solubility at a temperature lower than the room temperature, prepare a saturated solution of benzoic acid at room temperature in about 50 ml of distilled water. To lower the temperature, the beaker containing the solution is surrounded with ice pieces contained in a bigger beaker. When the required temperature is reached, say 10°C , pipette out about 25 ml of the supernatant liquid in a clean beaker (the tip of the pipette should be tied with a filter paper). Then take 10 ml of this solution in a conical flask and titrate it against $\text{N}/50$ NaOH , using phenolphthalein as an indicator.

Observations :

S.No.	Temperature ($^{\circ}\text{C}$)	10 ml of the solution required ... ml of $\frac{\text{N}}{50}$ NaOH	Normality of the solution
1.	40°	v_1	$\frac{Nv_1}{50 \times 10}$
2.	10°	v_2	$\frac{Nv_2}{50 \times 10}$

Calculations : (i) Solubility at 40°C .

From normality equation, we have

$$N_1 V_2 = N_2 V_1$$

Acid Alkali

or

$$N_1 \times 10 = \frac{N}{50} \times v_1$$

or

$$N_1 = \frac{N \times v_1}{50 \times 10}$$

Amount of benzoic acid per 100 gram of water, *i.e.*, solubility of 40°C

$$= \frac{v_1 \times 122 \times 100}{50 \times 10 \times 1000}$$

(Eq. wt. of benzoic acid = 122)

(i) Solubility at 10°C

Similarly, we can calculate the amount of benzoic acid per 100 g of water, *i.e.*, solubility at 10°C

$$= \frac{v_2 \times 100 \times 122}{50 \times 10 \times 1000} \text{ g}$$

Result : The solubility of benzoic acid at 40°C is g and at 10°C is g.

□

CHAPTER 10 ADSORPTION

INTRODUCTION

The molecules (or atoms or ions) on the surface of a liquid or solid are relatively fixed and the moving molecules in the surrounding gas or liquid phase interact with the relatively fixed molecules of the surface and as a result they are held by the surface by rather weak forces. Adsorption may be defined as accumulation or superficial adhesion of molecules on an interface. Generally the accumulation is only one molecule thick and is referred to as monomolecular adsorption. The solid which takes up gas, vapour or solute from a solution is known as **adsorbent**, while the gas or the solid which is held to the surface of the solid is called **adsorbate**.

The amount of the substance adsorbed is proportional to the concentration of the solution and is given by the relationship (**Freundlich adsorption isotherm**).

$$\frac{x}{m} = kc^{1/n} \quad \dots(i)$$

where x = Amount of solute adsorbed.

m = Quantity of adsorbent

k = A constant depending upon the nature of adsorbent and adsorbate.

c = Equilibrium concentration of adsorbate in the solution.

n = A constant depending upon the nature of the adsorbate.

The value of $\frac{1}{n}$ is generally less than unity. Taking logarithms of equation (i), we get

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log c$$

If the values of $\log \frac{x}{m}$ are plotted as ordinate against $\log c$ as an abscissa, we get a straight line, with a slope $\frac{1}{n}$ and intercept on the ordinate $\log k$.

Experiment 1. To study the adsorption of acetic acid on charcoal and prove the validity of Freundlich's adsorption isotherm.

Apparatus : Burette, pipette, reagent bottles etc.

Method : Prepare $\frac{N}{2}$ CH_3COOH and $\frac{N}{10}$ NaOH by dilution method.

Take six stoppered bottles, clean and dry them. Now prepare the following solutions in each bottle.

Now add 1 g of activated charcoal in each of the five flasks, stopper them. Shake all the flasks thoroughly well and then place in a thermostat for about 70-80 minutes. Now filter each solution and titrate 10 ml of the solution against standard NaOH solution using phenolphthalein as indicator.

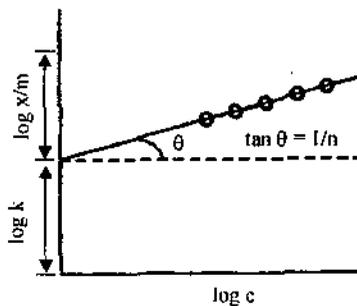


Fig. 7

*In absorption, the substance is not only retained on the surface but passes through the surface to become uniformly distributed throughout the body of a solid or liquid. In adsorption the substance is only retained on the surface, but does not pass through the surface of a solid or liquid.

In the last or beginning, titrate the stock solution of acetic acid (10 ml) also by means of $\frac{N}{10}$ NaOH solution.

Bottle no.	$\frac{N}{2}$ - CH ₃ COOH (ml)	Volume of distilled water	Amount of charcoal (gm)
1.	50	0	1.0
2.	40	10	1.0
3.	30	20	1.0
4.	25	25	1.0
5.	20	30	1.0
6.	10	40	1.0

Observations : 10 ml of stock acetic acid sol. $\equiv x$ ml of $\frac{N}{10}$ NaOH.

Bottle No.	Initial conc. of acid before adsorption (C_0) (NaOH in ml)	Equilibrium conc. of acid after adsorption (C_e) (NaOH in ml)	Amount of acid adsorbed ($C_0 - C_e$) (NaOH in ml)
1.	x	—	—
2.	$4/5x$	—	—
3.	$3/5x$	—	—
4.	$1/2x$	—	—
5.	$2/5x$	—	—
6.	$1/5x$	—	—

Calculations : $x = C_0 - C_e$
 $m = 1$ gm in each case.*

Thus, we can calculate x/m for each bottle and find the value of $\log x/m$, the logarithm of C_e term is also noted in each case.

Now a graph is plotted between $\log x/m$ as ordinate and $\log C_e$ as abscissa. We observe that it is straight line. The slope of this line will thus be equal to $1/n$. This proves the validity of Freundlich's adsorption isotherm.

Precautions :

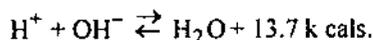
- (i) The flasks should be absolutely dry and clean.
- (ii) NaOH used should be free from CO₂.
- (iii) For filtration small filter papers should be used so that error due to any adsorption of the acid by the filter paper is minimized.

CHAPTER 11

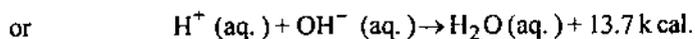
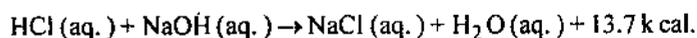
HEAT OF NEUTRALISATION

INTRODUCTION

The neutralization reaction of the strong acid with a base is essentially the combination of 1 equivalent of hydrogen ions with one equivalent of hydroxyl ions.



13700 cal. of heat is liberated at 25°C. This is the heat of neutralization of all strong acids and bases.



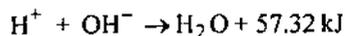
Heat of neutralization is defined as the amount of heat evolved when one gram equivalent of an acid neutralises one equivalent of a base in **dilute solution**.

Experiment 1. To determine the heat of neutralization of hydrochloric acid and sodium hydroxide.

Apparatus : Calorimeter*, pipette, beaker, thermometer; etc.

Chemicals : 1.0 N HCl, 1.0 N NaOH solution etc.

Principle : Strong acid and strong base ionise completely to give H^+ and OH^- ions respectively. These ions combine to form water molecule. In this process 57.32 kJ equiv⁻¹ heat is evolved.



Method : First, determine the water equivalent** of calorimeter as follows :

Take a definite weight (m_2g) of ordinary cold water in the calorimeter and determine the temperature ($t_2^\circ\text{C}$). Add to this definite amount of hot water (m_1g) of known temperature ($t_1^\circ\text{C}$) and note the temperature ($t_3^\circ\text{C}$) of the mixture. Water equivalent of calorimeter is calculated as follows :

$$m_1 (t_1 - t_3) = (m_2 + w)(t_3 - t_2)$$

or
$$w = \frac{m_1 (t_1 - t_3)}{(t_3 - t_2)} - m_2$$

Take the calorimeter. Place 100 ml. of NaOH in it, add 100 ml. of N—HCl. Mix with the help of a stirrer (The thermometer itself may be used as a stirrer) and note the final temperature.

Observations :

Volume of acid	= 100 ml.
Volume of alkali	= 100 ml.
Initial temperature of acid	= $t^\circ\text{C}$
Initial temperature of alkali	= $t^\circ\text{C}$
Final temperature of the mixture	= $t_1^\circ\text{C}$

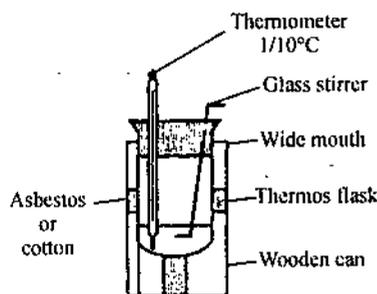


Fig. 8. Determination of heat of neutralisation

*It is an apparatus in which neutralization of an acid by base is carried out. It consists of two beakers, one placed inside the other. The space between the two is filled with cloth or lagging material.

**It is defined as the number of calories required to heat the calorimeter by 1°C.

Rise in temperature = $(t_1 - t)$ °C

Water equivalent of calorimeter = w

Calculations :

The heat produced on mixing acid with alkali

$$= (100 + 100 + w)(t_1 - t) \text{ calories}$$

$$= x \text{ calories}$$

Result : x calories are the heat produced when 100 ml. of N—HCl are completely neutralized. Hence this is the heat of neutralization.

Precautions :

- (i) Final temperature should be recorded after thoroughly mixing the contents.
- (ii) When the experiment is completed, add a drop of phenolphthalein to the mixture of HCl and NaOH. If a pink colour is observed, then the neutralization is not complete and experiment should be repeated.

Experiment 2. To find out the heat of solution of the given substance.

Apparatus : Calorimeter, thermometer, stirrer etc.

Theory : The heat of solution is the quantity of heat absorbed or evolved when one mole of the substance is dissolved in a large excess of solvent or water, so that further dilution does not bring any more heat change.

It is important to note that while expressing the heats of solution the exact condition of the solid substance is to be mentioned, *i.e.*, whether it contains water of crystallisation or not. Because the heat of solution is generally quite different in the two cases.

Procedure : First of all measure the water equivalent of the calorimeter as described in experiment no. 1.

Now take about 200 ml of distilled water in the calorimeter. Record its temperature-time curve. Now add a known quantity of the given substance (say KCl) and dissolve it in water present in the calorimeter, by means of a stirrer. Record the temperature-time curve as usual. Repeat the above procedure by adding more quantities of the substance and note the final temperature of the solution.

Observations :

(1) Volume of water taken = M_1 ml

Temperature of water = t_1 °C

Volume of hot water = M_2 ml

Temperature of hot water = t_2 °C

Final temperature of mixture = t_3 °C

(2) Volume of water taken = M_3 ml

Temperature of water = t_1 °C

Amount of substance dissolved = W_1 g

Final temperature after mixing the substance = t_4 °C

Calculations :

(1) The water equivalent (W) of the calorimeter is calculated as follows :

$$W = \frac{M_2(t_2 - t_3) - M_1(t_3 - t_1)}{(t_3 - t_1)}$$

(2) Heat absorbed by solution after adding the substance

$$= (M_3 + W_1)(t_4 - t_1)$$

Heat absorbed by the substance per litre

$$= \frac{(M_3 + W_1)(t_4 - t_1)(1000)}{M_3} = Q \text{ cal.}$$

Let M be the molecular mass of the substance, the heat of solution

$$= \frac{Q \times M}{W_1} \text{ cal mol}^{-1}$$

Result : The heat of solution of the given substance

$$= \dots \text{ cal mol}^{-1}$$

Precautions :

- (i) The temperatures should be accurately recorded.
- (ii) The hot water must be added to cold water immediately.
- (iii) The calorimeter should be completely insulated.

Apparatus : Calorimeter, thermometer, stirrer etc.

Theory : When an anhydrous salt, which is capable of forming hydrates (e.g. CaCl_2 , CuSO_4 etc.) is dissolved in water heat is evolved. The difference in the behaviour of hydrated and anhydrous salts is due to the heat evolved in the formation of hydrates. This heat is known as the heat of hydration of the salt. Evidently, heat evolved when one mole of solid anhydrous copper sulphate combines with water to form solid pentahydrate is called heat of hydration of CuSO_4 to form $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Its value is $+78.21 \text{ kJ mol}^{-1}$.

Procedure : First of all measure the water equivalent of the calorimeter as described in experiment no. 1.

Now weigh about 15.9 g of anhydrous copper sulphate (obtained by heating $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ at 150°C for 30 minutes) and determine the heat of solution in 360 g of water as described in experiment no. 2. The value obtained will be the heat of solution of one mole of anhydrous copper sulphate in 20 g mole of water. Weigh about 24.9 g of crystalline copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and determine the heat of solution in 360 g of water as described in experiment no. 2 which give the heat of solution of one mole of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 20 g mole of water. Let H_1 and H_2 be the heats of solution of anhydrous copper sulphate (CuSO_4) and pentahydrated copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) respectively.

Then, heat of hydration of $\text{CuSO}_4 = H_1 - H_2$

(The specific heat of copper sulphate solution containing one gram mole of 20 g mole of water is 0.9516 over the temperature range $18^\circ\text{-}50^\circ\text{C}$).

Observation and Calculations : As described in experiment no. 2.

Result : The heat of hydration of $\text{CuSO}_4 = \dots \text{ cal mol}^{-1}$.

Precautions : As described in experiment no. 2.

□