BSCCH- 104

B. Sc. I YEAR
LABORATORY COURSE-I

SCHOOL OF SCIENCES
DEPARTMENT OF CHEMISTRY
UTTARAKHAND OPEN UNIVERSITY

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Title : Laboratory Course-I
ISBN No. : 978-93-85740-56-5

Edition : 2017
Published by : Uttarakhand Open University, Haldwani, Nainital- 263139

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UNIT 1: INTRODUCTION LAB TECHNIQUES: INORGANIC CHEMISTRY

CONTENTS:

1.1.OBJECTIVES

This course is designed to ensure that all the students regardless of their educational backgrounds are competent in necessary laboratory skills. These skills include but are not limited to the use of an analytical balance, volumetric glassware, various pipettes, performing titrimetric and spectrophotometric determinations and learning the proper use and calibration of microscopes and centrifuges. Students should also become familiar with using laboratory apparatus.

Use the proper laboratory techniques to do the following;

- Pour liquids from a glass-stopper bottle.
- Transfer solids from a bottle.
- Heat liquids in a beaker.
- Heat liquids in a test tube.
- Light and adjust a Bunsen burner.
- Measure to 0.1 cm with a metric ruler.
- Use a graduated cylinder to measure volume.
- Use an analytical balance to measure mass.

1.2 INTRODUCTION

Introduction to basic laboratory techniques and procedures necessary for competent performance. Topics will include laboratory Reagents, apparatus, Glassware laboratory safety, volumetric and gravimetric measurements, titrations, critical evaluation of data, laboratory mathematics, preparing solutions and dilutions, and basic spectro photometric measurements. The purpose of this experiment is to introduce several of the tools and techniques necessary for success in this course.

Chemistry is an experimental science, and the laboratory is where you learn about "how we know what we know about it." The laboratory deals with the processes of scientific inquiry that organic chemists use. It demonstrates the experimental basis of what your textbook presents as fact. The primary goal of the laboratory is to help you understand how Chemistry is done by actually doing it. Learning how to obtain and interpret experimental results and draw reasonable conclusions from them is at the heart of doing science. Your laboratory work will give you the opportunity to exercise your critical thinking abilities, to join in the process of science.

1.3 LOCATION OF LABORATORY EQUIPMENT

(a) Chemicals and Solvents Organic and Inorganic:

Acids and Bases - under hood

Solvents - on shelves at end of benches

(b) Ovens and Refrigerators:

Each oven is designated for a specific purpose. Do not place any plastic items in the ovens. All samples must be clearly labeled with the identity of compound, your name and date. Ovens will be cleared weekly and improperly labeled samples will be removed. Refrigerators. Samples must be clearly labeled.

(c) Balances:

Abuse of balances and littering of the area will not be tolerated.

1.4 LABORATORY NOTE BOOK

1.4.1. General Guideline:

1. Use a ballpoint pen (press hard if duplicate pages).Write on one side only.
2. Do not erase or use whiteout. If you make a mistake, draw a single line through the error and write the correct entry on the top or side of it.
3. Do not remove an original page. If the entire page is incorrect, draw a single diagonal line through the page and state the reason for this line.
4. Record all data and results (with units) directly into your notebook.
5. Do not record data on scrap paper, your hand, etc., to be transferred later.
6. Start a new page for each new experiment.
7. Write the title of the experiment, date, and your name at the top of each page.
8. Indicate if a page is continued from the previous page.
9. Never skip a space for later additions.

1.4.2. Components

A. Pre-Lab – a detailed plan of the work that you will be doing:

1. Brief statement of purpose.
2. Paragraph discussion of the safety and environmental issues (ex. waste generation).
3. Step-by-step procedure in your own words. Be concise and complete, but do not cop the lab manual. Use diagrams and sketches when necessary. Reference all sources of Information.

   Note: The lab manual may not be brought into the laboratory or consulted during the laboratory session. However, the appendices are allowed.

B. Factual Record – what to record:

Keep a running account of all procedures carried out and observations made during experimental work.

1. Record observations such as physical appearance, color, odor, and physical properties.
2. Sketch apparatuses and label parts.
3. Use a table to record all information about reactants (see below).
4. Record all data and results, including the crude yield of products and mixtures. Use tables when possible.
5. All of the reactants must be accounted for in the factual record. For example, if you started with 1.0 mol of Reactant 1, you must account for the fate of all 1.0 mols at the end of the reaction. Simply describing the isolated 0.25 mol of product at the end (for example) will not be acceptable.
6. For calculations, show the formula and a sample calculation. If the calculation is repeated; use a table to report your results.
7. All graphs should be constructed with a graphing program. Label all axes and providea title for each graph.
8. Attach all spectra to your notebook, label the axes, and reference the spectra in the procedure section.

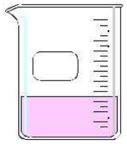
Data Analysis/Conclusions:

Examine and discuss the accuracy and precision of your data. Is the precision reasonable? Discuss possible systematic and random errors. Summarize the key results and provide a conclusion. Describe any difficulties that you had. Discuss which results are poor and provide explanations. Provide suggestions for improvement.

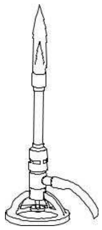
1.5 LABORATORY APPARATUS AND OPERATION

A. Common Laboratory Apparatus:

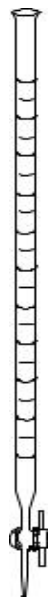
Beakers are useful as a reaction container or to hold liquid or solid samples. They are also used to catch liquids from titrations and filtrates from filtering operations.



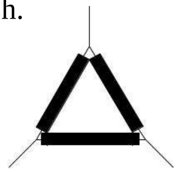
Bunsen Burners are sources of heat.



Burettes are for addition of a precise volume of liquid. The volume of liquid added can be determined to the nearest 0.01 ml. with practice.

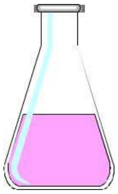


Clay Triangles are placed on a ring attached to a ring stand as a support for a funnel, crucible, or evaporating dish.

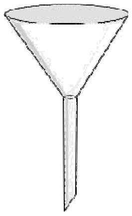


Droppers are for addition of liquids drop by drop

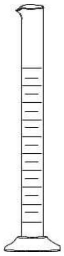
Erlenmeyer Flasks are useful to contain reactions or to hold liquid samples. They are also useful to catch filtrates.



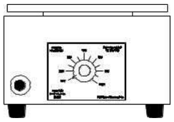
Glass Funnels are for funneling liquids from one container to another or for filtering when equipped with filter paper.



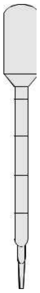
Graduated Cylinders are for measurement of an amount of liquid. The volume of liquid can be estimated to the nearest 0.1 m with practice.



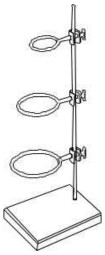
Hot Plates can also be used as sources of heat when an open flame is not desirable.



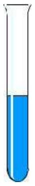
Pipets are used to dispense small quantities of liquids.



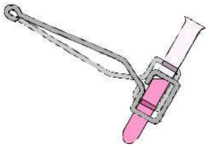
Ring stand with Rings are for holding pieces of glassware in place.



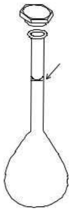
Test Tubes are for holding small samples



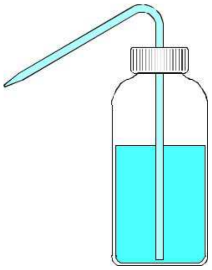
Test tube holders are for holding test tubes when tubes should not be touched



Volumetric Flasks are used to measure precise volumes of liquid or to make precise dilutions.

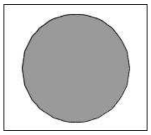


Wash bottles are used for dispensing small quantities of distilled water.



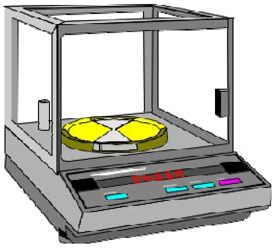
Watch glasses are for holding small samples or for covering beakers or evaporating dishes.

Wire Gauze on a ring supports beakers to be heated by Bunsen burners



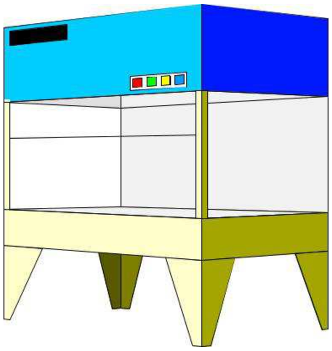
B. Laboratory equipment:

Balances are used to determine the mass of a reagent or object.



Spectrophotometers are used to measure the absorbance or transmittance of a liquid sample.

Fume Hoods are used to ventilate noxious or harmful gases



1.6 COMMON LABORATORY REAGENTS

Name	General Description
Acetic acid	An organic acid; is one of the simplest carboxylic acids.
Acetone	An organic compound: simplest example of the ketones
Acetylene	A hydrocarbon and the simplest alkyne; widely used as a fuel and chemical building block
Ammonia	Inorganic; the precursor to most nitrogen-containing compunds; used to make fertilizer.
Ammonium hydorixde	Aqueous ammonia; used in traditional qualitative inorganic analysis
Ammonium hydoride	Aqueous ammonia; used in traditional qualitative inorganic analysis
Azobisisobutyron trile	Organic compund; often used as a foamer in plastics and rubber and as a radical initiator
Baeyer's reagent	An alkaline solution of potassium permanganate; used in organic chemistry as a qualitive test for the presence of unsaturation, such as double bonds;
N-Bromosuccinimide	Used in radical substitution and electrophilic addition reactions in organic chemistry
Butanone(methyl ethyl ketone)	Organic compoud; similar solvent properties to acetone but has a significantly slower evaporation rate.
Butylated hydroxytoluene	A fat soulbe organic compound that is primarily used as an antioxidant food additive
n-Butyllithium	An organolithium reagent; used as a polymerization initiator in the production of elastomes such as ploybutadience or styrene-butadiene-styrene(SBS)
Carbon disfulifde	A non-polar slovent; used frequently as a building block in organic chemsitry
Carbon	Toxic, and its dissolving power is low; consequently, it has been largely
Tetrachloride	Supersede by deuterated solvents
Carbonylidiimidazole	Often used for the coupling of amino acids for peptide synthesis and as a reagent in organic

	synthesis
Ric ammonium nitrate	An organic compund; used as an oxidising agent in organic synthesis and as a standard oxidant in quantitative analysis
Chloroform	Organic compound; often used as CDC13 (deuterated chloroform) as a solvent for NMR spectroscopy and as a general solvent.
Chromic acid	A strong and corrosive oxidisig agent; an intermediate in chromium plating
Chromium trioxide	The acidic anhydride of chromic acid; mainly used in chrome-plating .
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Colloins reagent	Used to selectivley oxidize primary alchols to an aldehyde
Copper(I) iodide	Useful in a variey of applications ranging from organic sysnthesis to cloud seeding
Dess-martin periodinane	Chemical reagent used to oxidize primary alcohols to aldehydes and secondary alcohos to ketones
Diborance	The central organic synthesis reagent for hydroboration
Diethyl azodicarboxylate	A valuable reagent but alos quite dangerous and explodes upon heating
Diethyl ether	Organic compound; a common laboraory solvent
Dihydropyran	A heterocyclic compound; used as a protecting group for alcools in organic synthesis.
Disobutlyaluminum hydride	An organoaluminium compound; a redcing agent; converts esters and nitriles to aldehydes
Diisopropyl azodicarboxylate	The diisorpropyl ester of azodicarboxylic acid; a reagent in the production of many organic compounds
Dimethyl ether	The simplest ether, a useful precursor to other organic compounds and an aerosol propellant
Dimethylformamde	Organic compound; a common solvent for chemical reactions
Dimethylsulfide	Organosulfur compund; used in petroleum refinint and in petrochemcal production processes; a reducing agent in ozonolysis reactions.
Dimethyl sulfoxide	An organosulfur compound; an important polar

	aprotic solvent that dissovles both polar and nonpolar compounds
Dioxane	A heterocyclic organic compound; classified as an ether
Ethanol	A powerful psychoactive drug; used in alcoholic beverages, in thermometers, as a solvent, and as a fuel.
Fehling’s reagent	Used to differentiate between water-soluble aldehyde and ketone functional groups
Fentons’ reagent	A solution of hydrogen peroxide and an iron catalyst that is used to oxidize contaminants or waste waters.
Formaldehyde	The simplest aldehyde; an important precursor to many other chemical compounds; such as ploymers and polyfunctional alcohols
Formic acid	The simplest caroxylic acid; often used as a source of the hydride ion
Grignard reagents	The most common application is for alkylation of aldehydes and ketones;
Hydrazine	It’s a good reducing agent and is used in the wolff-kishner reaction for reducing carbonyls to its corresponding alkanes. Used as a foaming agent in preparing polymer foams; also a precursor to polymerization catalysts and pharamceuticals; also as an oxygen scavenger in power plants.
Hydrazoic acid	Used primarily for preservation of stock solutions, and as a reagent
Hydrochloric acid	A highly corrosive, strong mineral acid with many industrail uses
Hydrofluoric acid	Valued source of fluorine, precursor to numerous pharamceuticals; highly corrosive
Hydorgen peroxide	Commonly used as a bleach
Imidazole	An organic compound; this aromatic heterocyclic is a diazole and is classified as an alkaloid
Isopropyl alcohol	Simplest example of a secondary alcoho; dissolves a wide range of non-polar compounds
Lime	Used in flue gas desulphurisation in power plants.
Limestone	Used in Flue Gas Desulphurisation in power plants
Manganese dioxide	Used as a pigment and as a precursor to other

	manganese compounds; used as a reagent in organic synthesis for the oxidiation of allylic alcohols
Methyl tert-butyl ether	A gasoline additive; also used in organic chemistry as a relatively inexpensive solvnet.
Millon's reagent	An analytical reagent used to detect the presence of soluble proteins
Nitric acid	Highly corrosive and toxic strong acid; used for the production of fertilizers, production of explosives, and as acomponent of aqua regia
Osmium tetroxide	In organic synthesis, is widely used to oxidise alkenes to the vicinal diols
Oxalyl chloride	Used in organic synthesis for the preparation of acid chlorides from the corresponding carboxylic acids
Palladium(II) acetate	A catalyst for many organic reactions by combining with many common classes of organic compounds to form reactive adduct.
Perchloric acid	A powerful oxidizing agent; readily forms explosive mixtures; mainly used in the production of rocket fuel
Phosphoric aicd	A mineral acid with many industrial uses; commonly used in the laboratory preparation of hydrogen halides
Phosphorus	One of the most important phosphorus chlorides; a chlorinating reagnet.
Pentachloride	Also used as a dehydrating agent for oximes which turn them into nitriles.
Pposphorus trichloride	Most important of the three phosphorus chlorides; used to manufacture organophosphorus compounds; used to convert primary and secondary alcools into alkyl chlorides, or carboxylic acids into acyl chlorides.
Phosphoryl chloride	Used to make phosphate esters such as tricresyl phosphte.
Potassium dichromate	A common inorganic chemical reagent, most commonly used as an oxidizing agent in various laboratory and industrial applications
Potassium hydroxide	A strong oxidizing agent; can be used to quantitatively determine the total oxidisalbe

	organic material in an aqueous sample. A reagent for the synthesis of organic compounds
Raney nickel	An alternative catalyst for the hydrogenation of vegetable oils; in organic synthesis, used for desulfurization
Silver oxide	Used to prepare other silver compounds; in organic chemsitry, used as a mild oxidizing agent.
Silver nitrate	Precursor to man othe silver compounds; commonly used in organic chemsitry to abstract halides
Sodium amide	Used in the industrial production of indigo, hydrzine, and sodium cyanide; used for the drying of ammonia; used as a strong base in organic chemstiry
Sodium azide	Gas-forming component in airbag systems; used in organic synthesis to introduce the azide functional group by displacement of halides
Sodium	A versatile reducing agent; converts ketones and aldehydes to alcohols
Sodium chlorite	In organic synthesis, used for the oxidation of aldehydes to caroxylic acids.
Sodium hydride	A strong base used in organic synthesis.
Sodium hydroxide	Strong base with man industrial uses; in the laboratory, used with acids to produce the corresponging salt, also used as an electrolyte
Sodium nitrite	Used to convet amines into diazo compounds
Sulfuric acid	Strong mineral acid; major industrial use it the production of phosphoric acid
Tert-Butyl hydroperoxide	Used in variety of oxidation processes, industrially, is used as a starer of radical polymerization
Tetrahydrofuran	One of the most polar ethers; a useful solvent; its main use is as a precursor to polymers
Tetramethylsilane	The simplest tetraorganosilane; a building block in organometallic chemistry
Thionyl chloride	An inorganic compound; used in chlorination reactions; converts carboxylic acids to acyl chlorides
Thiophenol	An organosulfur compound; the simplest aromatic thiol

Titanium tetrachloride	An intermediate in the production of tiatnium metal and titanium dioxide
Tollens' reagent	A chemical test most commonly used to determine whether a known carbonyl-containing compound is an aldehyde or a ketone
Triphenylphosphine	Used in the synthesis of organic and organometallic compounds.

1.6. LABORATORY SAFETY

GENERAL SAFETY RULES:

1. The safe way is the right way to do your job. Plan your work. Follow instructions. If you do not know how to do the experiment safely, ask your teaching assistant.
2. Be able to use all safety devices and protective equipment provided for your use and *know their location* (eyewash fountain, shower, fire blanket, fire extinguisher).
3. Safety goggles must be worn at all times.
4. *Do not* eat or drink in the laboratory (and do not store food in the refrigerators). Smoking in the laboratory is absolutely forbidden.
5. Horseplay in any form is dangerous and prohibited. Do not run in laboratory areas.
6. Report to your TA all unsafe conditions, unsafe acts, and "near misses" that might cause future accidents. Report any accident or fire, no matter how trivial, to the TA.

Hazardous Chemicals:

(a) Be especially mindful of fire hazards when you or your lab neighbors are working with flammable liquids.

(b) Hazardous Substances: Know common explosive, toxic, and carcinogen materials and use them only with adequate safeguards.

(c) Never leave a reaction or experiment running unattended, unless you have told your lab partners enough about it to deal with potential hazards while you are away.

(d) Keep hood and bench top areas clean and workable space maximized.

Disposal of solvents, chemicals and other materials:

Never pour solvents or reactive chemicals down a drain. Such careless handling of flammable or toxic liquids presents a serious hazard in the laboratory. Also, never keep an open beaker of such solvents outside a hood. Chlorinated solvents are poured into solvent waste containers kept inside the hoods. When in doubt about how to dispose of something, ask a TA. If drain disposal is necessary and acceptable, always flush the drain before, during, and afterwards with a lot of water, always using the drains in the hoods. All glass must be discarded in the specially designed containers. A dustpan and brush for broken glass can be checked out of Lab Supplies. Spilled mercury is a special safety hazard and should be reported to your TA for cleanup.

1.7. SUMMARY

This course introduces the nntroduction about lab techniques to students. The whole cours material contains the following information.

- Location of laboratory equipment in the laboratory.
- General Guideline of the laboratory.
- A detailed plan of the work that students will be doing.
- Laboratory apparatus and operation.
- Common Laboratory Apparatus used in the Experiments.
- Common Laboratory Reagents used in the Experiments.
- General safety rules.

1.8. TERMINAL QUESTIONS

1. Define various precautions of Chemistry lab.
2. What is the difference between burette & graduated pipette?
3. Name of all apparatuses used.

UNIT 2: IDENTIFICATION OF ANIONS

CONTENTS:

2.1. OBJECTIVES

- To identify common anions in solution using simple qualitative chemical tests.
- Plan a procedure for the analysis of an unknown solution of an anion and describe that procedure with a flow chart.
- Identify different anions using a qualitative analysis technique.
- The purpose of this experiment is to determine what anions are present in an unknown sample. We will be looking for the common anions sulfide (S_2-), sulfate (SO_4^{2-}), sulfite (SO_3^{2-}), phosphate (PO_4^{3-}), carbonate (CO_3^{2-}), chloride (Cl^-), bromide (Br^-), iodide (I^-), acetate ($C_2H_3O_2^-$) and nitrate (NO_3^-).

2.2 INTRODUCTION

In this chapter, you will identify anions in unknown substances. Instead, in this lab, you first will perform some preliminary tests using $AgNO_3$, $BaCl_2$, and H_2SO_4. In these tests, certain groups of anions will react while other groups of anions will not react. By analyzing the results of the first part of the experiment, you should be able to eliminate half - if not more- of the anions as possibilities in your unknown. You will then perform confirmatory tests for the remaining anions in question to determine whether the anions are present or absent.

The goal of this experiment is to develop techniques for identifying unknown substances. You will identify unknown solutions as containing one of the following: Cl^-, Br^-, I-, HPO_4^{2-}, or SO_4^{2-}

The inorganic qualitative analysis involves the identification of ions present in a sample. The salt consists of anion and cation. The basis of identification is the observed chemical behaviour of the components. The salt analysis may be systematically carried out in the following three steps:

i) Preliminary examination
ii) Detection of anions and
iii) Detection of cations

2.3 CLASSIFICATION OF ANIONS (ACIDIC RADICALS)

The anions are provided by the acids in the process of salt formation; hence these are generally referred to as acidic radicals. These radicals cannot be divided in the systematic groups as has been done in the case of the cations. However, for the sake of simplicity, these have roughly been divided into three groups depending upon their reactions with certain regents.

Classification of acidic radicals or anions:

Group	Name and formula of the Radical	Group Reagent	Inference of the group
Class I anions (First group)	Carbonate (CO_3^{2-}) Sulphite (SO_3^{2-}) Sulphide (S^{2-}) Acetate (CH_3COO^-) Nitrite (NO_2^-) Thiosulphate ($S_2O_3^{2-}$)	Dil. HCl or H_2SO_4 (Cold or hot.)	Gases of different colours and smells are evolved.
Class II anions (Second group)	Chloride (Cl^-) Bromide (Br^-) Iodide (I^-) Nitrate (NO_3^-) * Oxalate ($C_2O_4^{2-}$) * Borate (BO_3^{3-}) * Fluoride (F^-)	Conc.H_2SO_4 (hot.)	Gases of different colours and smells are evolved.
Class III anions (Third group)	Sulphate (SO_4^{2-}) * Phosphate (PO_4^{3-})	Barium chloride ($BaCl_2$) in presence of dill. HCl. Ammonium molybdate $(NH_4)_2MoO_4$ in presence of conc.	A white precipitate appears. A yellow precipitate appears.

		HNO_3.	

* Interfering radicals (or anions)

2.4 PRELIMINARY TEST FOR THE ANIONS

A preliminary test for the anions is done on the basis of their class or group.

Preliminary Tests for the Anions of Class I (Group I)

The salts of these anions are decomposed by dil. H_2SO_4 or dil. HCl which serves as their group reagent. These anions with their preliminary tests are summarized below.

Take a small amount of salt or mixture in a dry test tube and add 5-6 ml of dil. H_2SO_4 or dil. HCl. Observe the reaction taking place in the test tube. If there is no reaction, heat the contents of the test tube gently and observe the sound, colour and odour of the gas evolved. From the observation, guess the presence of the anion according to the following table:

S. No.	Anion	Experiment	Observation	Inference
1.	Carbonate anion (CO_3^{2-})	On conducting the above experiment with dil. acids in cold or on heating.	*Brisk effervescence with evolution of colourless, odourless gases (CO_2).	CO_3^{2-} may be present.
2.	Sulphite anion (SO_3^{2-})	In the above experiment.	If the colorless gas with suffocating odour of burning sulphur is evolved (SO_2)	(SO_3^{2-}) may be present.
3.	Sulphide anion (S^{2-})	On conducting the above experiment.	** Evolution of colourless gas with smell of rotten eggs occurs (H_2S)	(S^{2-}) may be present.
4.	Nitrite anion (NO_2^-)	In the above experiment.	***Brown fumes with pungent odour (NO_2) are evolved.	NO_2^- may be present.
5.	Thiosulphate anion ($S_2O_3^{2-}$)	On conducting the above experiment.	If the colorless gas with suffocating odour	($S_2O_3^{2-}$) is expected to be

			is evolved and solution in test tube becomes yellowish white with turbidity.	present.
6.	Acetate anion (CH_3COO^-)	The same experiment as has been given above is conducted and thus	Small of vinegar is noticed without evolution of any gas (CH_3COOH)	(CH_3COO^-) is expected to be present.

Note:

* Basic carbonates of Pb and Bi do not evolve CO_2 with effervescence, but do so gradually.

**Many sulphides, e.g. those of Ag, Hg, As, Co and Ni do not decompose on heating with dil. HCl or dil. H_2SO_4. Therefore, the salt or mixture is heated with conc. HCl alone or with little zinc to observe the evolution of H_2S. If no H_2S smell is noticed, the above sulphides are taken as absent.

***All nitrites are soluble in water. The liberated NO_2 gas turns $FeSO_4$ solution black.

Preliminary Tests for the Anions of class II (group II).

The group reagent for the anions of this class is conc. H_2SO_4, i.e., the salts of these anions are readily decomposed by conc. $H_2SO_4^-$ After performing the preliminary tests of the anions of group I or class I, take a small amount of the salt or mixture in a separate dry test tube and add conc. H_2SO_4(2-3ml). then heat gently for some time. Observe the reactions occurring in the test tube as well as the gases evolved according to the following table.

S. No.	Anion	Experiment	Observation	Inference
1.	Chloride anion (Cl^-)	In the above experiment,	Colorless pungent gas (HCl) is evolved	(Cl^-) may be present.
2.	Bromide anion (Br^-)	In the above experiment,	Red brown gas (Br_2) is evolved and solution becomes orange.	Br^- is expected.
3.	Iodide anion (I^-)	On conducting the above reaction.	Dark violet fumes (I_2) are observed	(I^-) May be present.
4.	Nitrate anion	In the above	* Pungent light	(NO_3^-)

	(NO_3^-)	reaction.	brown gas (NO_2) is evolved.	may be present.
5.	Oxalate anion ($C_2O_4^{2-}$)	On conducting the above experiment (strong heating),	**colorless, odourless gas is evolved which burns with blue flame at the mouth of the test tube on bringing a burning stick near the mouth	($C_2O_4^{2-}$) is expected
6.	Fluoride anion (F^-)	On strong heating the contents of the test tube.	White pungent smelling gas is evolved and test tube becomes greasy	(F^-) is expected
7.	Borate anion (BO_3^{3-})	The borates are not decomposed by only conc. H_2SO_4 but in presence of ethyl alcohol or $CaCl_2$, they give compounds which can easily be detected. It will be discussed latter.		

Note: * All nitrates are soluble in water.

**Oxalates of K^+ and NH_4^+ are soluble in water. Ferrous oxalate is sparingly soluble. All other oxalates are insoluble.

2.5 PREPARATION OF SOLUTION FOR IDENTIFICATION OF THE ANIONS

For the identification of the anion(s) in the salt or the mixture, the anion (s) must be brought in solution, i.e., in free state so that the anion (s) may give suitable tests with the suitable regent (s). Many salts are soluble in water to give free anions and cations in solution, e.g. most of the ammonium salts and those of alkali metals are soluble. All nitrites, nitrates, acetates and many halides are also soluble in water. In the aqueous solution many anions can be detected. It is usually better to bring the anion (s) into the solution as soluble sodium salts by preparing soda or sodium carbonate extract which is obtained after boiling the salt or mixture with an excess of sodium carbonate solution.

Preparation of Soda Extract:

Mix one part of the solid salt or mixture with 3 parts by weight of sodium carbonate and 10-12 ml. distilled water (mineral free) and boil for about 8-10 minutes in a beaker or comical flask. Filter the contents while hot. The filtrate, known as soda extract, is used for detecting (or testing) most of the anions. The residue left on the filter paper may be dissolved in water or dil. HCl and tested for basic radicals whose salts are insoluble both in dil. and conc. HCl.

The excess sodium carbonate taken reacts with salts or mixture of the salts whereby the anions or acidic radicals are converted to their corresponding sodium salts which are water soluble and can be filtered off. Thus the anions come down in the filtrate along with the excess of sodium carbonate. The cations or the basic radicals are converted into their corresponding carbonates almost all of which are insoluble in water and therefore remain as residue on the filter paper along with unchanged salts (amm. carbonate is soluble).

Let X represents the basic radical (cation) and Y the acidic radical (anion) of any salt. When such a salt (XY) is heated with excess of sodium carbonate, the following reactions take place:

$XY+Na_2CO_3 \longrightarrow XCO_3+Na_2Y$ (X and Y are bivalent radicals) **e.g.**

$SnCl_2+Na_2CO_3 \longrightarrow SnCO_3+2NaCl$ (Soda extract)

$CaC_2O_4+ Na_2CO_3 \longrightarrow CaCO_3+Na_2C_2O_4$ (Soda extract)

The filtrate so obtained after neutralization with suitable acid, can be used to detect certain anions. The acid is to be added in excess till bubbles cease to evolve. This indicates the complete neutralization of the solution (soda extract). The common anions which can be identified easily using soda extract along with the acid used for its neutralization and the reagent added for the identification are given in the following table:

Anion	Experiment	observation	Inference
Cl^-, Br^-, I^-	dil. HNO_3	$AgNO_3$ soln.	AgCl: white ppt, AgBr: light yellow ppt., AgI-yellow ppt.
NO_3^-	dil. H_2SO_4	Freshly prepared $FeSO_4$ solution	Brown ring of $FeSO_4$. NO compd. results.
SO_4^{2-}	dil. HCl	$BaCl_2$ soln.	$BaSO_4$: White ppt.
$C_2O_4^{2-}$	dil. CH_3COOH	$CaCl_2$ soln.	CaC_2O_4: White ppt.
CH_3COO^-	dil. HCl	Neutral $FeCl_3$ solution.	Basic ferric acetate: brownish red ppt.
PO_4^{3-}	dil. HNO_3	Conc.HNO_3+$(NH_4)_2MoO_4$, heated and cooled.	Canary yellow ppt.

Here,

Column 1 represents the acidic radicals whose sodium salts are found in the extract.

Column 2 gives the acid to be added for neutralizing the excess of sodium carbonate.

Column 3 contains the names of the reagents added for the identification.

Column4 represents the characteristic changes which are observed during identification of the said anions.

Following are the advantages of preparing soda extract:

(i) It removes the basic radicals which may interfere in the systematic identification of the anions, by converting them into insoluble metal carbonates.

(ii) The identification of anions becomes easier in the case of compounds insoluble in water and dil. acids.

(iii) It helps in the identification of certain basic radicals (cations) of compounds insoluble in water, conc. HCl, HNO_3, etc. For example: $BaSO_4$, $SrSO_4$, etc.

Precaution: Na_2CO_3 used in the preparation of soda extract should be pure, free from chloride and sulphate which are generally present as impurities.

Note: Carbonate ion (CO_3^{2-}) is not detected by this method because it already comes from sodium carbonate. Hence it should be detected in the solid salt or mixture.

2.6 CONFIRMATORY TESTS FOR THE ANIONS

The presence of the anions in the salt or mixture is confirmed after the preliminary tests have been done. The confirmatory test for various anions is carried out as follows:

1. CO_3^{2-} anion:

It the colourless gas evolved during the preliminary test is passed into lime water*, it turns milky due to the formation of calcium carbonate, $CaCO_3$. If passing CO_2 is continued for a long time (excess), milky colour disappears, i.e., becomes soluble due to the formation of calcium bicarbonate, Ca $(HCO_3)_2$. This confirms the presence of CO_3^{2} ion.

Note. SO_3^{2-} ion also gives the same test Hence the presence CO_3^{2-} ion is confirmed after testing for SO_3^{2-} ion. It is better to test both CO_3^{2-} and SO_3^{2-} ions simultaneously.

2. SO_3^{2-} anion:

(i)If the colorless gas evolved during the preliminary test is brought in contract with the filter paper moistened with acidified potassium dichromate, solution**, the paper turns green.

(ii)Take 1ml. soda extract, add to it acetic acid in excess to make it neutral. Then add to it $BaCl_2$ solution and filter. To the filtrate, add bromine water and heat, white precipitate of $BaSO_4$ is obtained. These tests confirm the presence of SO_3^{2-} ion.

3. S^{2-} anion:

(i) If the colorless gas evolved during the preliminary test turns filter paper dipped in lead acetate solution black on bringing it at the mouth of test tube, it confirms the presence of S^{2-} ion.

(ii)Take 1 ml. soda extract and add to it few drops of sodium nitroprusside, the solution becomes violet, again confirming the presence of $S^{2—}$ion.

4. NO_2^- anion:

(i) If the brown gas evolved during the preliminary test turns paper dipped in starch + KI solution blue, presence of NO_2^- ion is confirmed.

(ii) Add 2-3 drops of KI and starch solution in the test tube during the preliminary test, deep blue or violet color if appears, it again confirms the presence of NO_2^- ion.

5. $S_2O_3^{2-}$ anion:

(i)If SO_3^{2-}, S^{2-} or SO_4^{2-} is present, shake a portion of the soda extract with $CdCO_3$ or $PbCO_3$ and then with Sr $(NO_3)_2$ solution. Filter and discard the precipitate if formed. Use filtrate for the detection of thio sulphate ion. If S^{2-},SO_3^{2-}, or SO_4^{2-} is absent, use the water extract for testing $S_2O_3^{2-}$. The mixture solution+$AgNO_3$→white precipitate. This ppt. is unstable and decomposes on warming or on addition of HCl into black Ag_2S through colour change from yellow to brown and finally black.

(ii)Soda extract of the substance + iodine solution → decolorization of iodine solution confirms the presence of $S_2O_3^{2-}$ anion.

6. CH_3COO^- anion:

(i) A water extract of the substance gives blood-red colour in cold with neutral ferric chloride, solution, confirming the presence of acetate ion.

(ii) On rubbing the substance + oxalic acid (few crystals) + water (few drops) between the fingers, smell of vinegar is noticed again confirming the presence of acetate ion.

(iii)Solution of the substance + a little ethyl alcohol + a little conc. H_2SO_4 + heat gently → fruity smell is noticed (of ethyl acetate).

Note. *Method of passing CO_2 gas into water: If the delivery tube is available, insert its two ends with corks in the sample tube and line water tube (Delivery tube must be dipped in lime water) and heat the contents of sample (mix.+acid) tuble. Otherwise collect the evolved CO_2 in a test tube which just fits in the mouth of sample tube. After heating the sample tube, close the mouth of the second test tube with the thumb and add line water to it to check the presence or thumb and add line water to it to check the presence or absence of CO_2 gas.

**Preparation of acidified $K_2Cr_2O_7$ solution: Take approx. 1gm. of $K_2Cr_2O_7$ crystals and dissolve in 5ml. water, then add 2-3ml. dil. H_2SO_4. This is acidified dichromate solution.

***The shelf $FeCl_3$ contains free HCl in small amount due to hydrolysis of $FeCl_3$. Add a very dilute solution of NH_4OH drop wise to a little $FeCl_3$ solution taken in a test tube and shaking after each addition till a permanent precipitate is formed. Now boil the contents of the test tube and filter. The filtrate is known as neutral ferric chloride.

7. Cl^- anion:

(i) On bringing a glass rod dipped in NH_4OH near the mouth of the test-tube during the preliminary test, white dense fumes of NH_4Cl are formed.

(ii) On heating the given mixture with conc. H_2SO_4 and MnO_2, greenish yellow, pungent smelling gas (Cl_2) is evolved.

(iii) Soda extract+dil. HNO_3+$AgNO_3$ solution→ a white precipitate (AgCl) is formed which is soluble in NH_4OH solution.

(iv) Chromyl chloride test: Heat a small amount of the mixture, add to it soild $K_2Cr_2O_7$ (3 times of mixture) and conc. H_2SO_4. Orange-yellow vapors of chromyl chloride (CrO_2Cl_2) are evolved and are collected in a test-tube containing NaOH. This is acidified with CH_3COOH and treated with lead acetate solution. A yellow precipitate of lead chromate ($PbCrO_4$) is formed.

All these tests confirm the presence of Cl^- ion.

Note. The chromyl chloride test does not respond in case of chlorides of Ag, Hg, Pb and Sn. In such cases, it can be performed by the residue obtained on evaporating 5 ml. of soda extract.

8. Br^- anion:

(i) On heating the given salt or mixture with a little MnO_2 and conc. H_2SO_4, red-brown vapours of Br_2 are evolved.

(ii) Soda extract+dil. HNO_3+$AgNO_3$ solution→ a pale yellow precipitate is formed (Ag Br) which is partially soluble in NH_4OH.

(iii) Soda extrac+ a little dil. HNO_3 (to neutralise)+ few drops of chloroform or CCl_4+ Cl_2 water or conc. HNO_3 + Shake →chloroform or CCl_4 layer (lower) becomes yellow or orange These tests confirm the presence of Br^- ion.

9. I^- anion:

(i) Given salt or mixture+ MnO_2+conc. H_2SO_4+heat→violet vapours (I_2) in excess are evolved which turn the paper dipped in starch solution blue.

(ii) Soda extract+dil. HNO_3+$AgNO_3$ solution→yellow precipitate of AgI is formed which is insoluble in NH_4OH solution.

(iii) Soda extract+ a little HNO_3(dil.) (to neutralize)+ few drops of $CHCl_3$or CCl_4+conc. HNO_3 or Cl_2 water+ shake well→layer of organic liquid becomes pink or violet These tests confirm the presence of I^- ion.

10. NO_3^- anion:

(i)On heating the salt or mixture with copper turnings and conc. H_2SO_4, deep brown fumes (NO_2) are evolved in excess but the solution does not become yellow or pink.

(ii)Aqueous extract or solution of the salt or mixture in dil. HCl + freshly prepared solution of $FeSO_4$+shake well+add gradually conc. H_2SO_4 by the side of the test tube→a brown ring of $FeSO_4$. NO is formed at the junction of two liquids (This is called ring test)

The above tests confirm the presence of NO_3^- ion.

11. $C_2O_4^{2-}$ anion:

(i)Take soda extract of the salt or mixture in a test tube, acidify it with excess of CH_3COOH and then add $CaCl_2$ solution. A white precipitate of CaC_2O_4 is formed. Dissolve the precipitate in dil. H_2SO_4 and warm it. To the warm solution, add few drops of $KMnO_4$ solution and shake, pink colour of $KMnO_4$ solution disappears.

(ii)Take a little salt or mixture in a test-tube, add dil. H_2SO_4 and heat till effervescence ceases to appear. Add a pinch of MnO_2 and heat again. Effervescence due to evolving CO_2 reappears.

The above tests confirm the presence of $C_2O_4^{2-}$ ion.

12. F^- anion:

(i) Take a little salt or mixture with some sand in a test tube, add conc. H_2SO_4 to it and heat, bring a glass rod moistened with water at the mouth of the test tube. A waxy white deposit on the glass rod is obtained (NH_4Cl and $HgCl_2$ also leave a white deposit on the rod but this deposit is crystalline and not waxy).

After performing this test the contents of the test tube should not be thrown in the sink without cooling and diluting.

(ii)Soda extract+CH_3COOH (to neutralise) + $CaCl_2$ solution + shake → white precipitate appears after sometime. To the precipitate add dil. H_2SO_4+heat+$KMnO_4$ solution → pink color of KMnO4 is not discharged.

These tests confirm the presence of F^- ion.

13. BO_3^{3-} anion:

(i)Take a little salt or mixture in a porcelain dish, add a little conc. H_2SO_4 just to make the paste of the substance, 1/2ml. of ethyl alcohol or methylated spirit well by a glass rod and ignite →a green edged flame is developed (copper and barium salts also give the same test and interfere in the detection of BO_3^{3-} ion by this test. Hence test should be performed in a test tube instead of porcelain dish and the vapours evolved after heating should be burnt at the mouth of the test-tube).

(ii) Make a paste of little mixture + calcium fluoride (CaF_2) with a little conc. H_2SO_4. Take a portion of this paste with a thin glass rod or Pt-wire and bring it near the edge of the flame (do not introduce the paste into the flame)→green flame is obtained (Cu & Ba-salts do not interfere).

These tests confirm the presence of BO_3^{3-} ion.

14. SO_4^{2-} anion:

Take the solution of the substance in dil. HNO_3 or soda extract + dil. HCl. Add $BaCl_2$ solution. A curdy white precipitate is formed ($BaSO_4$) which is insoluble in all the conc. acids. This confirms the presence of SO_4^{2-} ion.

15. PO_4^{3-} anion:

(i)Boil a little substance with conc. HNO_3 and add ammonium molybdate solution to it, boil again and cool. A canary yellow precipitate is formed which is soluble in ammonium and alkali hydroxides.

(ii)This ion can also be tested in the soda extract as has already been given above These are the confirmatory tests for PO_4^{3-} ion.

(iii)

Reactions Involved:

Carbonate : $Na_2CO_3 + 2\,HCl \rightarrow 2NaCl + H_2O + CO_2\uparrow$
anion (CO_3^{2-}) $Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O$
White (milky)

$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$ (Soluble)
excess

Salphite $Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2\uparrow$
anion (SO_3^{2-}) $Ca(OH)_2 + SO_2 \rightarrow CaSO_3$ (Milky) + H_2O
$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)$ (Green) + H_2O

Sulphide $FeS + H_2SO_4 \rightarrow H_2S\uparrow + FeSO_4$
anion (S^{2-}) $(CH_3COO)_2Pb + H_2S \rightarrow PbS$ (black) $\downarrow + 2CH_3COOH$
$Na_2S + Na_2[Fe(NO)(CN)_5] \rightarrow Na_4[Fe(NOS)(CN)_5]$
Sod. Nitroprusside
(Violet Complex)

Nitrite $2NaNO_2 + H_2SO_4 \rightarrow Na_2SO_4 + 2HNO_2$
anion (NO_2^-) $3HNO_2 \rightarrow HNO_3 + 2NO\uparrow + H_2O$
$2NO + O_2 \rightarrow 2NO_2\uparrow$ (Brown)
$2KI + 2NO_2 \rightarrow 2KNO_2 + I_2$
I_2 + starch → Starch-Iodide (Blue)
Ring test:
$FeSO_4 + NO \rightarrow FeSO_4.\,NO$ (Brown ring)
Thiosulphate: $Na_2S_2O_3 + 2AgNO_3 \rightarrow Ag_2S_2O_3\downarrow$ (white) $+ 2NaNO_3$
anion ($S_2O_3^{2-}$) $Ag_2S_2O_3 + H_2O \rightarrow Ag_2S\downarrow$ (Black) $+ H_2SO_4$
$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$ (tetrathionate)
Acetate:
$2CH_3COONa + H_2SO_4 \rightarrow 2CH_3COOH$ (vinegar smell) $+ Na_2SO_4$
Anion (CH_3COO^-)
$3CH_3COOH + FeCl_3 \rightarrow (CH_3COO)_3Fe$ (Blood red color) + 3NaCl

Chloride anion (Cl-)

$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$ (pungent gas)

$HCl + NH_4OH \rightarrow NH_4Cl\uparrow$ (white fumes) $+ H_2O$

$2NaCl + MnO_2 + 3H_2SO_4 \rightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2\uparrow$

(greenish yellow gas)
$NaCl + Ag NO_3 \rightarrow AgCl \downarrow$ (ppt) $+ NaNO_3$
$AgCl \downarrow + 2NH_4OH \rightarrow Ag (NH_3)_2 Cl$ (soluble) $+ 2H_2O$

Bromide: $K Br + H_2SO_4 \rightarrow KHSO_4 + HBr$
anion (Br^-) $2HBr + H_2SO_4 \rightarrow Br_2\uparrow$(reddish brown vapours)$+ SO_2\uparrow + 2H_2O$
$2KBr + MnO_2 + 3H_2 SO_4 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + Br_2 \uparrow$
$Na Br + AgNO_3 \rightarrow Ag Br \downarrow$ (Light yellow ppt.)$+Na NO_3$
$2 NaBr + 4 HNO_3 \rightarrow Br_2\uparrow + 2NaNO_3 + 2NO_2 \uparrow + 2H_2O$
$2HBr + Cl_2 \rightarrow Br_2 \uparrow + 2HCl$
$Br_2 + CHCl_3$ or $CCl_4 \rightarrow$ Orange yellow colour (Br_2 dissolves)

Iodide $NaI + H_2 SO_4 \rightarrow NaHSO_4 + HI$
anion (I^-) $2HI + H_2SO_4 \rightarrow I_2 \uparrow$ (Violet vapours) $+ SO_2 \uparrow + 2H_2O$
$2 NaI + MnO_2 + 3H_2SO_4 \rightarrow I_2 \uparrow + 2NaHSO_4 + MnSO_4 + 2H_2O$
I_2 + starch → starch – iodide (Blue)
$NaI + AgNO_3 \rightarrow AgI \downarrow$ (yellow ppt.) $+ NaNO_3$
$2NaI + Cl_2 \rightarrow 2 NaCl + I_2$
$2NaI + 4HNO_3 \rightarrow I_2 \uparrow + 2NaNO_3 + 2NO_2 \uparrow + 2H_2O$
$I_2 + CHCl_3$ or $CCl_4 \rightarrow$ Pink or purple color (I_2 dissolves)

Nitrate: $NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$
Anion (NO^-_3) $4 HNO_3 \rightarrow 4 NO_2 \uparrow$ (Brown fumes)$+ O_2 \uparrow + 2H_2O$
$3Cu + 8HNO_3 \rightarrow 3 Cu (NO_3)_2 + 2NO \uparrow + 4 H_2O$
$2 NO + O_2 \rightarrow 2 NO_2 \uparrow$ (Brown)
Ring Test: $6 FeSO_4+2 HNO_3 + 2 H_2SO_4 \rightarrow 3 Fe_2 (SO_4)_3 + 4 H_2O + 2NO\uparrow$
$FeSO_4 + NO \rightarrow FeSO_4. NO$ (Brown ring)
Oxalate : $Na_2C_2O_4 + 2H_2SO_4 \rightarrow 2NaHSO_4 + H_2O +CO_2 \uparrow + CO \uparrow$
anion ($C_2O_4^{2-}$): $2CO + O_2 \rightarrow 2CO_2$
$Na_2C_2O_4 + CaCl_2 \rightarrow CaC_2O_4 \downarrow$ (white ppt.) $+ 2NaCl$
$Ca C_2 O_4 + H_2 SO_4 \rightarrow Ca SO_4 + H_2 C_2O_4$ (oxalic acid)
$2 KMnO_4 + 3 H_2SO_4 + 5 H_2C_2O_4 \rightarrow K_2SO_4+ 2 MnSO_4 + 10 CO_2 \uparrow + 8 H_2O$
$Na_2C_2O_4 + MnO_2 + 2 H_2SO_4 \rightarrow Na_2 SO_4 + MnSO_4 + 2 H_2O + 2 CO_2 \uparrow$

Fluoride: $2 NaF + H_2 SO_4 \rightarrow Na_2 SO_4 + 2 HF \uparrow \rightarrow$
Anion (F-) $Si O_2 + 4 HF \rightarrow Si F_4 + 2 H_2O \rightarrow$
$3 Si F_4 + 3 H_2O \rightarrow 2 H_2 Si F_6 + H_2Si O_3$ (white deposit)

Borate: $Na_3BO_3 + 3\ H_2SO_4 \rightarrow 3\ NaHSO_4 + H_3\ BO_3$ (Boric acid)

Anion (BO_3^{3-}) $H_3\ BO_3 + C_2H_5OH \rightarrow (C_2H_5)_3\ BO_3 \uparrow$ (ethyl borate) + $3\ H_2O$

$CaF_2 + H_2SO_4 \rightarrow Ca\ SO_4 + 2HF$

$Na_3\ BO_3 + 3\ H_2\ SO_4 \rightarrow 3\ Na\ HSO_4 + H_3\ BO_3$

$2\ H_3\ BO_3 \rightarrow B_2\ O_3 + 3\ H_2O$

$B_2\ O_3 + 6\ HF \rightarrow 2\ BF_3$ (burns with green flame)+ $3\ H_2O$

Sulphate $Na_2\ SO_4 + BaCl_2 \rightarrow Ba\ SO_4$ (white ppt) +2 NaCl
anion (SO_4^{2-})

Phosphate $Na_3\ PO_4 + 3\ HNO_3 \rightarrow H_3\ PO_4 + 3\ NaNO_3$
anion (PO_4^{3-}) $H_3PO_4 + 12\ (NH_4)_2\ Mo\ O_4 + 21\ HNO_3 \rightarrow$
$(NH_4)_3\ PO_4\ 12\ Mo\ O_3 \downarrow + 12\ H_2O + 21\ NH_4\ NO_3$.
(amm, phospho molybdate - canary yellow ppt.)

Special Tests for the Mixtures of Anions (Combinations).

1.Carbonate and Oxalate.

If given as a combination in a mixture, decompose carbonate anion completely by dil. H_2SO_4 (oxalate remains unaffected and then add MnO_2. If effervescence appears again, it indicates the presence of oxalate which can be confirmed by decolorization of $KMnO_4$ solution.

2.Carbonate and Sulphite.

Carbonates and sulphites both are decomposed by dil. H_2SO_4 to give CO_2, and SO_2 gases which give white ppt. with lime water. But sulphite only (SO_2) reacts with pot. dichromate in presence of dil. H_2SO_4 to change the colour from light yellow to green [$Cr_2\ (SO_4)_3$].

3.Sulphide, Sulphite and Sulphate.

Sulphide can be tested with sod. nitroprusside solution. Where, sulphite and sulphate do not interfere. If all the three anions are given together, remove sulpide by $Pb\ CO_3$ or $Cd\ CO_3$ as Pb S (black) or CdS (yellow). Filter and add dil. HCl and $BaCl_2$ solution to the filtrate to give white ppt. of $BaSO_4$, filter again and boil the filtrate with conc. HNO_3 or bromine water to oxidize sulphite to sulphate [Na_2SO_3 + O (from HNO_3 or Br_2 water] which can be tested with $BaCl_2$ solution (white ppt. $BaSO_4$ appears again).

4.Chloride, Bromide and Iodide.

Chloride is tested by chromyl chloride test where bromide and iodide do not interfere. Bromide and iodide given together are tested by organic layer test. Acidify one ml. soda extract with dil. HCl or dil. H_2SO_4, add few drops of $CHCl_3$ or CCl_4 followed by freshly prepared chlorine water drop by drop while shaking. If organic layer is pink or violet, iodide is confirmed. Continue adding excess of chlorine water with vigorous shaking. If organic layer becomes orange brown or yellow, bromide is also confirmed.

5.Nitrite and Nitrate.

If nitrite gives positive test as given above, decompose it by urea or NH_4Cl as below:

$NaNO_2 + H_2SO_4 \rightarrow NaHSO_4 + HNO_2$

$(NH_2)_2\ CO + 2\ HNO_2 \rightarrow 2\ N_2 \uparrow + 3\ H_2O + CO_2 \uparrow$

$NaNO_2 + NH_4Cl \rightarrow NaCl + N_2 \uparrow + 2\ H_2O$

Now reduce nitrate using zinc and dil. H_2SO_4 to nitrite and test it by KI and starch solution as given below:

$Zn + H_2SO_4 \rightarrow ZnSO_4 + 2H$

$NaNO_3 + 2H \rightarrow NaNO_2 + H_2O$ (rest as given above)

6.Nitrite and Iodide.

If both are preset in the mixture, add conc. H_2SO_4 to it heat and then add starch solution. Blue color of starch iodide confirms the presence of both anions.

7.Nitrate and Bromide.

Reduce nitrate to nitrite by zinc and dil. H_2SO_4 and test as usual.

Confirm bromide by organic layer as usual.

8.Nitrate and Iodide.

Reduce nitrate to nitrite and then nitrite and iodide can be tested by starch solution (blue). Iodide can also be detected by organic layer test.

The reactions of the tests for combination of acidic readicals or mixtures of anions are the same as given above. Therefore the reactions involved in the tests can be referred to the above.

2.7 SUMMARY

This unit gives the classification of anions (Acidic Radicals). Preliminary test are given for the identification of class I, class II and class III anions. Basic carbonates of Pb and Bi do not evolve CO_2 with effervescence, but do so gradually. Many sulphides, e.g. those of Ag, Hg, As, Co and Ni do not decompose on heating with dil. HCl or dil. H_2SO_4 . Oxalates of K^+ and NH_4^+ are soluble in water. Soda extract preparation should be used to prepare to prepare solution of anions. It is is obtained after boiling the salt or mixture with an excess of sodium carbonate solution. Na_2CO_3 used in the preparation of soda extract should be pure, free from chloride and sulphate which are generally present as impurities. Carbonate ion (CO_3^{2-}) is not detected by this method because it already comes from sodium carbonate. Hence it should be detected in the solid salt or mixture.

UNIT 3: IDENTIFICATION OF CATION (KNOWN)

CONTENTS:

3.1. OBJECTIVES

- To separate different cations in aqueous mixtures using selective precipitation and to confirm their identities using chemical tests.
- To classification of the cation into Analytical groups.
- Preliminary Investigation of the Sample.
- To preparation of solution for the analysis of Cations.
- Separation of cation into Analytical Groups.
- Analysis of the cations of Analytical Group I,II, III, IV, V VI and zero group.

3.2. INTRODUCTION

Qualitative analysis involves the identification of the substances in a mixture. When chemical methods are used in the identification of mixtures of metal cations, these ions are usually separated before identification can occur. After they have been separated, identification of each cation depends on the observation of a characteristic chemical reaction. Solubility equilibria and complex-ion equilibria play crucial roles in the separations and subsequent identifications.

3.3 CLASSIFICATION OF CATIONS INTO ANALYTICAL GROUPS

The cations (or the basic radicals) have been classified into seven groups, *viz.* from zero, I to VI group according to their nature to form the precipitate with various reagents. Because no single reagent is available which could form precipitate with all the cations, hence they have been classified into groups and the cations of each group give precipitate with a particular reagent called group regent.

3.4 SOLUBILITY AND SOLUBILITY PRODUCT

In the simple terms if a substance dissolves in a solvent, it is said to be soluble (more accurately solute) and the resulting mixture is known as solution (may be unsaturated or saturated). This tendency of a solute to get dissolved in a solvent is called, in a general sense, its solubility. The solubility depends on the nature of both the solute (substance) and the solvent. It is more accurately defined as "**the number of grams of the substance which is dissolved in 100 grams 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 very slightly on the pressure. For most solid substances, it increases with increasing temperature, e.g., solubility of $AgNO_3$ increases rapidly but that of NaCl increases slowly. The change in solubility with changing temperature is usually expressed by means of solubility curves(plots of the number of grams of solute dissolved in 100 grams of solvent along ordinate against the temperature along abscissa) There are also some substances whose solubility decreases with rising temperature, e.g. Li_2CO_3, NaOH, etc.

Solubility Product and Precipitation.

When a sparingly soluble substance, say AB, is kept in contact with water for sometime at a definite temperature, the following equilibrium is established:

$$\underset{\text{Solid}}{AB} \rightleftharpoons \underset{\text{Dissolves}}{AB} \rightleftharpoons \underset{\text{Ions}}{\underline{A^+ + B^-}} \text{ and } \frac{[A^+]\,[B^-]}{[AB]} = K \text{ (from law of mass action)}$$

The concentration of the unionised [AB] is constant at a given temperature if excess of AB is present. Hence, $[A^+] [B^-]$ = K [AB] = constant. Therefore, "**In equilibrium, the product of the ionic concentration is constant at a given temperature. This constant product, $[A^+] [B^-]$, is called the solubility product (Ks)**". When the ionic product exceeds the solubility product, the solution is super saturated and precipitation occurs but if the ionic product is less than the solubility product, the solution is unsaturated and precipitation does not occur. This is called theory of precipitation. This can also be represented as
Ionic product < solubility product, Ks, the salt dissolves.

Ionic product > solubility product, Ks precipitation takes place.

Relation between Solubility and Solubility Product.

The solubility of a sparingly soluble substance (electrolyte) of 1:1 can be calculated using the principle of the solubility product. Let it be AB.

$Ks\ (AB) = [A^+]\ [B^-]$

If $[A^+] = [B^-] = s$ moles per liter

$Ks\ (AB) = s.s = s^2$

Or $s = \sqrt{Ks}$

Where s = solubility of AB in moles per liter and Ks (AB) is the solubility product of AB.

But for the substances (electrolytes) or 1:2 or 2:1 type, i.e., AB_2 or A_2B type

$Ks = s \times (2s)^2$ or $(2s)^2 \times s = 4s^2$

$\therefore s = \sqrt[3]{\frac{Ks}{4}}$ moles per liter

3.5 THE COMMON ION EFFECT

The phenomenon of lowering the degree of ionisation of a weak electrolyte substance by adding to its solution a solution of strong electrolyte having a common ion and thus decreasing the concentration of the ion other than the common ion of the weak electrolyte is known as **Common ion effect.** For example, NH_4OH, a weak base (electrolyte) dissociates in solution as $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

On applying the law of mass action $[NH_4^+]\ [OH^-] = K\ [NH_4OH]$ = constant, on adding strong electrolyte, NH_4 Cl, $NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$, NH_4^+ ions are added to the solution. Thus the concentration of NH_4^+ ions coming both from NH_4Cl and NH_4OH (common ion) increases but K remains constant at any given temperature. As a result, the value of $[NH_4OH]$ must increase thereby decreasing the value of $[OH^-]$. This indicates that the degree of ionisation of NH_4OH is decreased by the addition of NH_4Cl which furnishes the common ion, NH_4^+. Similarly the ionisation of H_2S, a weak electrolyte, is diminished in the presence of HCl, a strong electrolyte, giving common H^+ ions.

The principle of common ion effect is of immense importance in qualitative analysis because this provides a valuable method for controlling the concentration of the ions furnished by a weak electrolyte. The common examples are: precipitation of second group radicals as sulphides using H_2S in presence of HCl and that of fourth group cations as sulphides in presence of NH_4OH. Similarly precipitation of third group cations as hydroxides using NH_4OH in presence of NH_4Cl. The detailed account will be given in the respective groups.

Complex Formation.

Complex ion formation is of great importance in qualitative analysis (i) to dissolve a precipitate alone or from a mixture of two or more (ii) to check the precipitation of a particular cation by complex ion formation. For example,

(a) AgCl is soluble in ammonia solution due to the formation of the complex ion, $[Ag(NH_3)_2]^+$.

$$Ag^+ + 2\,NH_3 \rightarrow [Ag(NH_3)_2]^+.$$

This capacity of Ag^+ ion is utilized in its separation from Pb^{2+} and Hg_2^{2+} ion.

(b) Separation of Cu^{2+} and Cd^{2+} ions is also based on the complex formation tendency with CN^- ions from KCN solution: $K_3[Cu(CN)_4]$ and $K_2[Cd(CN)_4]$. Of the two complex ions $[Cu(CN)_4]^{3-}$ and $[Cd(CH)_4]^{2-}$, the value of instability constant for copper complex ion is less than cadmium comlex ion and hence more Cd^{2+} ions are available in the solution than Cu^{2+} ions. In presence of H_2S gas, CdS (yellow ppt) is formed but copper ion remains unaffected.

$$[Cd(CN)_4]^{2-} \rightleftharpoons Cd^{2+} + 4CN^- \text{ and } H_2S \rightleftharpoons 2H^+ + S^{2-}$$

$$Cd^{2+} + S^{2-} \rightleftharpoons CdS \text{ (yellow ppt.).}$$

3.6 SEPARATION OF CATIONS INTO GROUPS

(i) Precipitation of group I cations. The cations of group I are precipitated as insoluble chlorides in the presence of dil. HCl.

(ii) Separation of group II cations from group IV cations. The cations of both these groups are precipitated as sulphides but in different media, group II cations are precipitated in acidic medium (HCl) and those of group IV in basic medium (NH_4OH). As has already been stated, the precipitation of sulphides can occur only when $[M^{2+}]$ $[S^{2-}]$ exceeds the solubility product of the sulphide, MS at given temperature,

i.e. $[M^{2+}]$ $[S^{2-}] > KS$

In presence of HCl, due to common H^+ ions, the ionisation of H_2S is suppressed thereby giving less concentration of S^{2-} ions in solution. Under this condition, the ionic product of metal and sulphide ions only exceeds the solubility product of sulphides of group II cations (such metal sulphides have low values of solublility products) and as a result these sulphides are precipitated. The solubility product values for sulphides of group IV cations being high are not surpassed by ionic product and these cations remain in the filtrate. These cations are then precipitated as sulphides in presence of excess S^{2-} ions in basic medium, i.e., NH_4OH.

(iii) Precipitation of group III cations. The group III cations are precipitated as hydroxides with the help of NH_4OH in the presence of NH_4Cl. NH_4Cl suppresses the ionisation of NH_4OH thereby giving less OH^- ions in solution, just sufficient to precipitate the group III cations and keeping higher group, i.e. IV, V & VI, cations in solution. This happens because of the low values of solubility products of the hydroxides of group III cations which are surpassed by ionic products of $[OH^-]$ and $[M^{3+}]$.

(iv) Precipitation of group V cations. These cations are precipitated as carbonates using $(NH_4)_2CO_3$ in presence of NH_4OH when Mg remains in solution.

3.7 PRELIMINARY INVESTIGATION OF THE SAMPLE

Basic radicals or cations in a sample can be tested by two types of tests:

(1)Dry tests, (2) Wet tests.
(1)Dry tests: These are the preliminary tests and include the following:
(a)Dry heating test
(b)Flame test
(c)Borax bead test
(d)Cobalt nitrate test
(e)Charcoal cavity test
(f)Microcosmic bead test

Of these, flame test, borax bead test, cobalt nitrate test and charcoal cavity test are more important and impart more valuable information about the cations in the sample under investigation.

(b) Flame test. Chlorides of certain metals when heated strongly using a loop of Pt-wire cleaned by conc. HCl, are volatilized easily in non-lumious flames of bunsen burner and their vapours become incandescent in the flame. The salt or group ppt. is picked by Pt-wire loop and kept into the edge of non-luminous flame. The imparted colour by the metals can be observed by naked eye:

Na – golden yellow, K-violet, Cu-bluish green,

Ca – brick or dull red, Sr – crimson red, Ba- apple green.

(C) Borax bead test. This test is performed mainly for the coloured substances and sometimes for white substances leaving coloured residue on dry heating.

The loop at the tip of the Pt-wire is heated in the flame, then dipped into borax powder, heated again strongly till borax swells up and finally converted into a transparent glassy bead. This bead is touched with the substance or group ppt. heated strongly in non-luminous flame and then in luminous flame, and color is observed.

Cation	Non-luminous flame (Oxidising)	Luminous flame (reducing)
Copper	green or light blue	red or colorless
Iron	Yellow	bottle green
Chromium	Green	Green
Cobalt	deep blue	deep blue
Nickel	light brown	Black
Manganese	Violet	Colorless

Chemistry of borax bead test: On strongly heating borax transforms into glassy bead:

$$Na_2B_4O_7\ 10H_2O \xrightarrow{-10H2O} Na_2\ B_4O_7 \rightarrow B_2O_3 + 2NaBO_2 \text{ (glassy bead)}$$

B_2O_3 combines with basic oxides to form meta borates which have characteristic colours.

(d) Cobalt nitrate test. Cobalt nitrate on heating is decomposed to CoO which combines with certain metallic and non-metalic oxides to give colored compounds. The powdered substance or mixture is mixed with an equal amount of solid Na_2CO_3 placed in a charcoal cavity, moistened with water and heated with the help of blow pipe. It is then moistened with few drops of cobalt nitrate and heated again. The color of the residue indicates the radical.

Blue- Al^{3+}, PO_4^{3-}, BO_3^{3-}

Green- Zn^{2+}

Dirty blue-green- Sn^{2+}

Pink- Mg^{2+}

Example. $ZnSO_4\ Na_2CO_3 \rightarrow ZnCO_3 + Na_2SO_4$

$ZnCO_3 \rightarrow ZnO + CO_2\uparrow$

$2CO(NO_3)_2 \rightarrow 2CoO + 4NO_2\uparrow + O_2\uparrow$

$ZnO + CoO \rightarrow ZnO.CoO \rightleftharpoons CoZnO_2$

(e) Charcoal cavity test. In this test, the powdered sample is mixed with an equal amount of solid Na_2CO_3, placed in a charcoal cavity, moistened with water and strongly heated in a reducing flame by means of blow pipe. From the color of the bead or deposit round the cavity (incrustation), cation/metal is identified.

Hot residue	**Cold residue**	**Inference**
Yellow	White	Zn
Reddish brown	reddish brown	Cd
Brown	yellow	Pb
Orange	yellow	Bi
Yellow	white	Sn
White	white	As, Al, Mg, Ca, Ba
Red	Red	Cu
Black	white	Fe, Co, Ni, Mn

(2) Wet tests. These are most important tests and are performed to confirm the presence of almost all the cations. The first step for the wet tests is the preparation of the original solution.

3.8 METHODS FOR THE PREPARATION OF ORIGINAL SOLUTION

The solution that contains all the cations is known as original solution. It can be prepared as follows:

(i) A little of the mixture sample is boiled with water with shaking. If does not dissolve then,

(ii) Mixture is boiled with dil. HCl. Still if does not dissolve then,

(iii) About 1gm mixture is boiled with 5ml. conc. HCl in 100ml beaker for a while, diluted with water and boiled again. Mostly the mixture is dissolved and solution becomes transparent.

(iv) If the mixture is insoluble in conc. HCl, then solubility should be observed in least quantity of dil. HNO_3, then conc. HNO_3 and finally in aqua regia.

(v) If the solution is made in HNO_3 or aqua regia, it has to be evaporated to dryness and dry residue is dissolved in dil. HCl or water after boiling. Sulphuric acid is never used as a solvent as it precipitates Ba, Sr, Ca & Pb as sulphates which are insoluble even in aqua regia.

3.9 SEPARATION OF CATIONS INTO ANALYTICAL GROUPS

On the basis of solubility product and reagents, the cations are divided into the following six groups:

1. First group: Pb^{2+}, Ag^{+}, Hg_2^{2+} (ous)
2. Second group A : Pb^{2+}, Cu^{2+}, Bi^{3+}, Cd^{2+}, Hg^{2+} (ic)
   B : As^{3+}, Sb^{3+}, Sn^{2+} + (ous), Sn^{4+} (ic)
3. Third group: Al^{3+}, Cr^{3+}, Fe^{3+}
4. Fourth group: Ni^{2+}, Co^{2+}, Zn^{2+} Mn^{2+}
5. Fifth group: Ba^{2+}, Sr^{2+}, Ca^{2+}
6. Sixth group: Mg^{2+}

Zero group is also there containing NH_4^{+} ion.

The cations, group reagents and salts precipitated along with their colors are summarized below:

5. Fifth group: $Ba^{2+}, Sr^{2+}, Ca^{2+}$

6. Sixth group: Mg^{2+}

Zero groups are also there containing $NII_4 +$ ion.

The cations, group reagents and salts precipitated along with their colors are summarized below:

S.No.	Group	Group Radiclas	Group Reagent	Salt Reprecipitated	Colour of the precipitate
1.	First Group	Ag^{+}, Pb^{++}, Hg_2 (ous)	Dil. HCl	(Chlorides) AgCl,	White ppt.

				AgCl, $PbCl_2$, $HgCl_2$	
2.	Second group	Pb^{++}, Hg^{++} (ic.) Bi^{+++}, Cu^{+++}, Cd^{++}, Sb^{+++}, Sn^{++}, Sn^{+++}, Sn^{++++}(ic), As^{+++}	Dil. HCL+H_2s	(Sulphides)	Black ppt. (Sometimes red ppt.)
3.	Third group	$Al^{+++}, Cr^{+++}, Fe^{+++}$,	After removing H_2S boil the solution with V_2	(Hydroxides) Al(OH_3) Fe(OH_3) $Cr(OH_3)$	White ppt. Brown ppt. Green ppt.
4.	Fourth group	Ni^{++}, $Co^{++}, Zn^{++}, Mn^{++}$	Iiird Group	(sulphides) Zns	White or state ppt. Chocoloate-pink ppt. Black ppt. White ppt.
5.	Fifth group	$Ba^{++}, Sr^{++}, Ca^{++}$	Boil off $H_2S$and then add $NH_4CL + NH_4Oh$	(Carbonates) $BaCO_3$, $CaCO_3$, $SrCO_3$	Black ppt. White ppt.
6.	Sixth Group	Mg^{++}	& (NH^4) $_2CO_3$ and shake well. Fifth Group (Phosphate) Filtrate+ Na_2HPO_4 Solution	(Phosphate) $MgNH_4PO_4$	White crystalline ppt.

Important Hints for proceeding with the tests of Basic Radicals

(i) Group reagents should be added in systematic order.

(ii) A little excess of the group reagent must be added to ensure the complete precipitation fot he group radicals.

(iii) Solution in every group, if after adding group reagent is heated, granular precipitate is obtained.

(iv) The volume of the solution should not be unnecessarily increased at any step. If the volume of solution at any stage has become too large (in spite of great precautions) do not throw any a portion. Put it in a dish, and evaporate it to a small volume.

(v) There are Na^+, K^+ and $NH_4{}^+$ radicals also, among them Na^+ and K^+ are examined by flame test and for $NH_4{}^+$ radical, special test is performed.

(vi) Group reagent is added to original solution one after another, till the ppt. in any group is obtained. The ppt. shows the presence of any radical in that group. The complete precipitation of the radical in that group should be judged by adding sufficient amount of the group reagent otherwise it will create a great disturbance in the usual analysis of the subsequent group radicals.

(vii) Hydrogen sulphide is a very important gas reagent for the precipitation of IInd and IV th group radicals. It is prepared in the Kipp's apparatus by the action of dil. H_2So_4 on ferrous sulphide. Through the kipps apparatus continuous supply of the gas is available. See fig ahead.

3.10 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP I

Analysis of first group (silver group)

A white ppt. is obtained after the addition of dil. HCL to the original solution. It is filtered and washed with water and then boiled with 5-10 ml water. Filter and keep the filtrate for II group.

Note: If solution is prepared in dil. HCL, 1 st group is considered to be absent.It is not necessary that there should be complete precipitation of metallic ions of a particular group by means of that group reagent before proceeding of the next group. Mercuous salts are partially oxidized to mercuric salts and so are precipitate as mercuric sulphide also.

Analysis of second group

This group is divided in two groups:

(i)II nd A group(copper Group)
(ii)IInd B group (arsenic group)

II A copper Group:

Copper Group consists of
$Pb^{++}, Hg^{++}(ic), Bi^{+++}, Cu^{++}$ and Cd^{++} while Arsenic group contain

$Sb^{+++}, As^{+++}, Sn^{++}(ous) and\ Sn^{++++}(ic.)$

In this group H_2S is passed in a little portion of the 1st group filtrate. If precipitate does not come, then it should be diluted with water, warmed and then H_2S is passed in the rest of the solution. It is faltered and washed well with H_2S water. The filtrate is kept for III group. Different radicals give the following coloured precipitates.

Hgs	Black(sometimes red)	Cds	Yellow
Pbs	Black(or Brown)	As_2S_2	Yellow
Bi_2S_2	Brown	SnS_2	Yellow
CuS	Black(or Brown)	Sb_2S_3	Orange

Yellow ammonium sulphide contains excess of sulphur dissolved in colourles ammonium sulphide solution and is expressed as (NH_4) $_2Su$.

The washed precipitate is warmed with a little yellow ammonium sulphide solution and filtered.

Residue	Filtrate
(II A Group)	(II B Group)
Hg(ic), Pb, Bi, Cu, Cd	As, Sb, Sn (ous), Sn(ic)

3.11 ANALYSIS OF THE CATIONS OF GROUP II

II A copper group- Residue is washed with water and then treated with 50% HNO_3 boiled cooled and filtered.

<table>
<tr><td rowspan="3">Black residue
It may be HgS. Dissolve it in aqua regia and evaporate it to almost dryness. Add water and divide it in two parts (i) To first part add $SnCl_2$ Soln white or</td><td colspan="3">Filtrate: It may contain the nitrates of Pb, Bi, Cu. Take a little part of it add dil. H2SO$_4$. If a white ppt. appears then add alcohol and dil. H_2SO_4 to the whole filtrate and filter.</td></tr>
<tr><td rowspan="2">White residue
It may contain Dissolve this residue in conc. Solution of CH_3COONH_4 and</td><td colspan="2">Filtrate: It may contain Bi, Cu and Cd as nitrate. Add to it excess of NH_4OH and filter:</td></tr>
<tr><td>White residue: It may be</td><td>Filtrate: It may contain Cu and Cd. If it is bule Cu is there if it is colourless Cu is absent. First</td></tr>
</table>

<table>
<tr>
<td rowspan="2">grey ppt (II) To second part add Cu turnings whitish deposti on Cu Hg^{++} confirmed.</td>
<td rowspan="2">add K_2CrO_4 yellow ppt pb (Lead) confirmed.</td>
<td rowspan="2">$Bi(OH)_3$. Dissolve the residue in the least quantity of conc. HCl divide it in two parts: (I) To first part add excess of water white ppt. (II) To second part add. Sod stannite soln. black ppt. (Bismuth confirmed)</td>
<td colspan="2">**Method:**
(i)To first part add ch3cooh in excess K4 Fe(CN)6 brown coloured ppt. Cu++ (copper)confirmed.
(ii) To second part add KCN soin. Till the filtrate becomes colourless. Now pass H_2S yellow ppt. Cd++ (cadrnium) confirmed. Second method: Add. conc. HCl and pass H_2S and filter.</td>
</tr>
<tr>
<td>**Black residue:** Cu^{++} (Copper) confirmed.</td>
<td>**Filtrate:** Dilute it and pass H_2S again yellow ppt. (cadmium)confirmed.</td>
</tr>
<tr>
<td colspan="3" rowspan="2"></td>
<td colspan="2">(iii) To third part add 1 c.c. of conc. HCl
and $FeSO_4$ soln. and filter.</td>
</tr>
<tr>
<td>**Residue** Cu^{++} (copper) confirmed.</td>
<td>**Filtrate:** Dilute it with water and pas H_2S gas yellow ppt. Cd^{++} (Cadmium) confirmed.</td>
</tr>
</table>

3.12 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP III

IIB Arsenic Group

Dilute the filtrate with water obtained after treating the second group ppt. with yellow ammonium sulphide and dil. HCl (in excess). A coloured ppt. indicates the presence of arsenic group but if a white ppt. is obtained it shows the absence of arsenic group radicals and reject it. Fiter the ppt. and boil it with conc. HCI and filter.

Yellow residue:	**Filtrate :**
It may be As_2S_3. Dissolve it in conc. $HNO_3$and add	It may contain chlorides of Sb and Sr which may be confirmed by two different methods.

<table>
<tr><td rowspan="3">ammonium molybdate solution and heat Yellow ppt. As^{+++}(Arsenic) Confirmed.</td><td colspan="2">First Method:
Make the filtrate just alkaline by adding NH_4OH soln.
Add 1-2 gms. solid oxalic acid boil and pass H_2S gas. Filter if a ppt. is obtained.</td></tr>
<tr><td>Orange residue:
It may be Sb_2S_3:
Dissolve it in least quantity of conc. HCl Dilute it with water white ppt. or turbidity.
Sb^{+++} (Antimony) confirmed.</td><td>Filtrate:
It may contain Sn. To it add NH_4OH to make it alkaline and pass H_2S gas
Dirty yellow ppt.
Sn^{+++} (Stannic) confirmed</td></tr>
<tr><td colspan="2">Second Method:
To the filtrate add iron filling and heat for five minutes and filter.</td></tr>
<tr><td></td><td>Black residue:
Sb^{+++} (Antimony confirmed.)</td><td>Filtrate
It may contain $SnCl_2$. To it add $HgCl_2$ Soln.
White or gray ppt. Sn^{++} (Stannous) confirmed.</td></tr>
</table>

ANALYSIS OF THIRD GROUP

Boil off H_2S completely (test with lead acetate paper for this) from filtrate of the second group and concentrate it. Boil it again with 1 c.c. of conc. HNO_3 as to convert all ferrous salt (if present) to ferric salt; otherwise ferrous hydroxide will not be completely precipitated in this group and thus will interfere in IVth group giving a black precipitate of Fes. Then after cooling add NH_4CL and NH_4OH (in excess) till the solution distinctly smells of ammonia.

Filter and wash the precipitate with water and keep the filtrate for IVth group. Dissolve the ppt. in 2 c.c. of H_2O_2 or in excess of Br_2water + $NaOH_2$, boil* it and filter. Boiling at this stage is essential since this ensures the complete oxidation of Fe^{++} to Fe^{+++}

$Fe(OH)_3$ – Brown ppt.
$Al(OH)_3$ – White ppt.
$Cr(OH)_3$ - Green or light bluish green ppt.

Residue :	**Filtrate :**
Brown ppt . it may contain $Fe(OH)_3$ or $MnO(OH)$.	It may contain $NaAlO_2$ and $NaCr_4$. if it is yellow Na_2CrO_4 will be there otherwise $NaAIO_2$ may be there. Divide it in two parts.

Divide the precipitate in two parts: (i) ppt. +conc. HNO_3 + PbO_2 Boil and cool By adding a little water Light, pink, violet colour Mn^{++} (Manganese) confirmed. (ii) Dissolve the precipitate in dil. HNO_3 or dill. HCI and divide it in two parts: To first part add $K_4[Fe(CN)_6]$ deep blue colour or ppt. (b) To second part add ammonium Sulphocyanide Blood red colour Fe^{+++}(Ferric) Confirmed.	(a) First part CH_3COOH + ($CH_3COOH)_2$ Pb $\downarrow$ Yellow ppt. (b)Second part + $AgNO_3$ Brick red ppt. Cr^{+++} (Chromium) confirmed.	To the part add NH_4CI and boil White gelatinous ppt. Al^{+++} (Alumunium) confirmed.

Notes:

(i)H_2S should be completely removed before adding conc. HNO_3; otherwise it will be oxidized into H_2SO_4; and thus will precipitate the Vth group radicals as sulphates.

(ii)Sometimes Mn also precipitates as MnO.OH(Brown ppt.) in this group so its test becomes necessary.

(iii) After boiling off H_2S addition of conc. HNO_3 is essential so as to convert all ferrous salts into ferric salts.

(iv) Addition of NH_4Cl before NH_4OH is absolutely essential otherwise the basic radicals of IV^{th} and V^{th} groups will precipitate out as hydroxide in this group.

(v)Interfering radicals should be removed before proceeding in this group.

(vi) H_2S should be passed in hot solution. At higher temperatures sulphides precipitated are granular and easy to filter.

3.13 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP IV

ANALYSIS OF FOURTH GROUP

Some of the characteristics of the basic radicals of this fourth group are tabulated as follows:

Form of the salt	**Nickel (NI^{++})**	**Cobalt (Co^{++})**	**Zinc (Zn^{++})**	**Manganese (Mn^{++})**
Sulphide	Black (NIS) Green- Green	Black (CoS) Pink Pink	White or Grey (ZnS) White Colourless	Light Pink(MnS) White Colouriess Light pink, pink

				violet.

Pass H_2S continuously in the hot ammonical filtrate of II group. Formation of the precipitate shows the presence of fourth group. Filter and wash the ppt. and keep the filtrate for fifth group.

Different radicals give the following coloured precipitates:

NIS	Black	ZnS	White or grey
CoS	Black	MnS	Light pink

Notes:

(i)H_2S must be passed in hot solution otherwise ZnS and MnS will from colloidal solution.

(ii)H_2S should not be passed for a very long time otherwise NiS and MnS will turn into colloidal solution.

Ppt. is treated with dill. HCI and filtered:

<table>
<tr><td colspan="2">Residue:
It may contain NiS and CoS. Dissolve it in aqua-regia(3HCI+ HNO_3) and evaporate to dryness+ water and divide it in number of parts.</td><td colspan="2">Filtrate:
it may contain $MnCl_2$ and $ZnCl_2$. Boil off H_2S, and add excess of NaOH and filter.</td></tr>
<tr><td>To one part and NH_4OH (in excess) + dimethyl glyoxime Scarlet red ppt.
Ni^{++} (Nickel) Confirmed</td><td>(i)To one part add NH_4OH (in excess) + CH_3COOH (in excess) + KNO_2 solution. Yellow crystalline ppt. Co^{++} (Cobalt) Confirmed.
(ii) To other part in a porcelain dish + $NaHCO_3$ solid (in excess) + Br_2 water. Shake for some time Apple green colour (in cold) Co^{++} (Cobalt) confirmed.
Apple green colour in cold changing to black on heating Co^{++}(Cobalt) and Ni^{++} (Nickel) both confirmed.</td><td>Residue
White turning brown due to oxidation.
(i) Dissolve the residue in conc. HNO_3 and add PbO_2. Boil for 2-3 minutes and dilute with water Pink or violet colour.
Mn^{++}(manganese) confirmed.
(ii) Residue + oxidizing fusion mixture (KNO_3+ Na_2CO_3).
Heat strongly on a porceian piece green mass is obtained which dissolves to give pink solution Mn^{++} (Manganese) confirmed.</td><td>Filtrate:
It may contain zinc. Pass H_2S in the filtrate. A white grey ppt. Zn^{++} (Zinc) confirmed.</td></tr>
</table>

3.14 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP V

After boiling off H_2S, concentrate the fourth group titlrate to one-third (1/3) of its original volume. Then add $NH_4OH$and $(NH_4)_2CO_3$ (never boil at this state.) Formation of white precipitate shows the presence of fifth group. Filter and was the ppt. keep the filtrate for the radicals of sixth group. Dissolve the precipitate in least quantity of acetic acid and boil for a few minutes. Take a small part of this soln. and add. K_2CrO_4 soln. If a yellow ppt appears, heat the whole solution with excess of K_2CrO_2 so as to precipitate barium completely. If no ppt. appears on adding K_2CrO_4 soln, then do not add K2CrO$_4$ solution to the whole soln. Now proceed as follows:

Residue: Yellow ppt. $BaCrO_{4.}$ Ba^{++} (Barium) confirmed.	It may contain $(CH_3COO)_2$ and $CH_3COO)$ Ca. To it add $(NH_4)_2$SO4 solution in excess and boil it filter it.	
	Filtrate: it may contain ca. to it add $(NH_4)_2C_2O_4$ soln. white ppt. Ca^{++} (calcium) confirmed.	Residue: White ppt. $(SrSO_4)$ Sr^{++} (strontium) confirmed.

Notes:

(1) It is better to use saturated solution of (NH4) $_2SO_4$ to detect Sr^{++} radical. After addition of the reagent, wait for few minutes to see if a precipitate of $SrSO_4$ is obtained.

(2) Sometimes calcium does not get precipitated in its group due to the formation of $Ca(HCO_3)_2$ on addition of $(NH_4)_2$ CO_3 to the concentrated filtrate of IVth group. As $Ca(HCO_3)_2$ is soluble and it passess into the filtrate of Vth group. Hence filtrate of Vth group must be tested for calcium before proceeding to VIth group.

(3) They are tested in the order BSC(Barium, strontium, Calcium).

3.15 ANALYSIS OF THE CATIONS OF ANALYTICAL GROUP VI

Heat the fifth groups filtrate with ammonium oxalate and discard the precipitate, if comes. Add 2-3 c.c. of NH4OH and excess of sodium phosphate (Na_2HPO_4) to the filtrate. Shake the solution with a glass rod. After a few minutes a white crystalline precipitate results. Mg^{++}(Magnesium) confirmed.

Analysis of ammonium (NH4+) Radical (zero group)

(1) Heat a little mixture with 2-3 c.c NaOH in a test tube. A characteristic smell of (NH_3) is obtained. On bringing a glass rod dippedin conc. HCl at the mouth of the test tube , enormous white fumes are produced.

(2) On adding Nessler's regent to the solution of the mixture →brown color of ppt. is obtained. This test is extremely sensitive and characteristic.

Note. Nesster's reagent is prepared by adding KI to Hg Cl_2 solution until the red ppt (HgI_2) formed, is dissolved. It is mixed with NaOH solution.

CHEMICAL REACTIONS INVOLVED IN THE TEST OF BASIC RADICALS

First Group: Lead (Pb^{++}), Silver(Ag^{+}) Mercurous (Hg_2^{++}) and lead (Pb^{++}).

$$Pb(NO_3)_2 + 2\,HCl \longrightarrow \underset{\text{White ppt}}{PbCl2\downarrow} + 2\,HNO3$$

$$PbCl_2 + 2\,KI \longrightarrow \underset{\text{Yellow ppt.}}{PbI_2\downarrow} + 2HCl$$

$$PbCl_2 + K_2CrO_4 \longrightarrow \underset{\text{Yellow ppt}}{PbCrO_2\downarrow} + 2KCl$$

$$PbCl_2 + H_2SO_4 \longrightarrow \underset{\text{White ppt}}{PbSO_4} + 2KCl$$

SILVER (Ag+) :

$$AgNO_3 + HCl \longrightarrow \underset{\text{White ppt}}{AgCl\downarrow} + HNO_3$$

$$AgCl + 2\,NH_4OH \longrightarrow \underset{\text{Silver ammonichloride}}{Ag(NH_3)_2Cl} + 2H_2O$$

$$Ag(NH_3)_2Cl + 2\,HNO_3 \longrightarrow \underset{\text{White ppt}}{AgCl\downarrow} + 2NH_4NO_3$$

Mercurous (Hg^{++}):

$$Hg_2(NO_3)_2 + 2HCl \rightarrow \underset{\text{White ppt}}{Hg_2Cl_2\downarrow} + 2HNO_3$$

$$Hg_2Cl_2 + 2NH_4OH \rightarrow \underbrace{HgNH_2Cl}_{\substack{\text{Ammino mercuric chloride}\\ \text{Black}}} + Hg + NH_4Cl + 2Cl$$

$$HNO_3 + 3HCl \rightarrow 2H_2O + NOCl + 2Cl$$

$$Hg + 2Cl \rightarrow HgCl_2$$

$$2HgCl_2 + SnCl_2 \rightarrow \underset{\text{White ppt}}{Hg_2Cl_2\downarrow} + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 \rightarrow \underset{\text{Grey ppt}}{2Hg\downarrow} + SnCl_4$$

Second Group : Mercuric (Hg^{++}), Lead(Pb^{++}), Bismuth(Bi^{++}), Copper(Cu^{++}), Cadmium(Cd^{++}), Arsenic(As^{+++}), Antimony(Sb^{+++}), Tin (Sn^{++}, Sn^{+++})

Sometimes, in second group, white or a light yellow ppt. is observed which is due to sulphur precipitated from H_2S by excess of HNO_3 or osther oxidizing agents e.g. (NO_2^-, SO_3^{--}, Fe^{+++}). The ppt. should be rejected.

$$2HNO_3 + 3H_2S \rightarrow 4H2O + 2NO\uparrow + 3S\downarrow$$

$$2NaNO_2 + 2HCl + H_2S \rightarrow 2NaCl + 2NO\uparrow + 2H_2O + S\downarrow$$

$$Na_2SO_3 + 2HCl + 2H_2S \rightarrow 2NaCl + 3H_2O + 3S\downarrow$$

$$2FeCl_3 + H_2S \rightarrow 2FeCl_2 + 2HCl + S\downarrow$$

Mercuric (Hg^{++}) :

$$HgCl_2 + H_2S \rightarrow \underset{\text{Black ppt}}{HgS\downarrow} + 2HCl$$

$$3HgS + 2HNO_3 + 6HCl \rightarrow 3HgCl_2 + 2NO\uparrow + 3S + 4H_2O$$

$$\underset{\text{Mercuric Chloride}}{2HgCl_2} + SnCl_2 \rightarrow \underset{\text{White ppt.}}{Hg_2Cl_2\downarrow} + SnCl_4$$

$$\underset{\text{Mercurous chloride}}{Hg_2Cl_2} + SnCl_2 \rightarrow \underset{\text{Grey ppt.}}{2Hg\downarrow} + SnCl_4$$

Lead (Pb^{++}) :

$PbCl_2 + H_2S \longrightarrow PbS \downarrow + 2HCl$

Black ppt.

$3PbS + 8HNO_3 \longrightarrow 3Pb(NO_3)_2 + 2NO \uparrow + 3S + 4H_2O$

$Pb(NO3)2 + H2SO4 \longrightarrow PbSO_4 \downarrow + HNO_3$

White ppt

$PbSO_4 + 2CH_3COONH_4 \longrightarrow (NH_4)_2Pb(SO_4)_2 + (CH_3COO)_2Pb$

$(CH_3COO)_2Pb + K_2CrO_4 \longrightarrow PbCrO_4 \downarrow + 2CH_3COOK$

Bismuth (Bi^{+++})

$2BiCl_3 + 3H_2S \longrightarrow Bi_2S_3 \downarrow + 6HCl$

Brown ppt.

$Bi2S_3 + 8HNO_3 \longrightarrow 2Bi(NO_3)_3 + 2NO \uparrow 3S \downarrow 4H_2O$

$Bi(OH)_3 + 3HCl \longrightarrow BiCl_3 + 3H_2O$

$BiCl_3 + H_2O \longrightarrow BiOCl + 2HCl$

Milky

$2BiCl_3 + 3Na_2SnO_2 + NaOH \longrightarrow 2Bi + 3Na_2SnO_3 + 6NaCl + 3H_2O$

Copper (Cu++) :

$CuCl_2 + H_2S \longrightarrow CuS \downarrow + 2HCl$

Black ppt.

$3CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO \uparrow + 3S \downarrow + 4H2O$

$Cu(NO3)2 + 4NH4OH \longrightarrow Cu(NH_3)_4(NO_3)_2 + 4H_2O$

Tetraaminecoppernitrate

Blue colour

$Cu(NH_3)_4(NO_3)_2 + 4CH_3COOH \longrightarrow Cu(NO_3)_2 + 4CH_3COONH_4$

$2\ Cu(NO_3)_2 + K_4[Fe(CN)_4] \longrightarrow Cu_2[Fe(CN)_6] \downarrow + 4KNO_3$

Pott. Ferocyanide — Copper ferrocyanide

Chocolate red ppt

Cadmium (Cd++):

$CdCl_2 + H_2S \longrightarrow CdS \downarrow + HCl$

Yellow ppt

$CdS + 2HCl \longrightarrow CdCl_2 + H_2S \downarrow$

$CdCl_2 + 2NH_4OH \longrightarrow Cd(OH)_2 \downarrow + 2NH_4Cl$

$Cd(OH)_2 + 2NH_4Cl + 2NH_4OH \longrightarrow [Cd(NH_3)_4]Cl_2 + 4H_2O$

Tetramine cadmium chloride

Colourless

Copper- Cadmium Separation :

$$CuSO_4 + 2KCN \longrightarrow K_2SO_4 + Cu(CN)_2 \downarrow$$

$$2Cu(CN)_2 \longrightarrow \underset{\text{White ppt.}}{Cu_2(CN)_2 \downarrow} + (CN)_2 \uparrow$$

$$\underset{\text{Cuprous cyanide}}{Cu_2(CN)_2} + 6CN \longrightarrow \underset{\text{Pot. Cuprocyanide}}{2K_3[Cu(CN)_4]}$$

$$CdSO_4 + 2KCN \longrightarrow Cd(CN)_2 + K_2SO_4$$

$$\underset{\text{Cadmium cyanide}}{Cd(CN)_2} + 2KCN \longrightarrow \underset{\text{Pot. Cadmicyanide}}{K_2[Cd(CN)_4]}$$

The complex of Cu and Cd dissociate as follows:

Primary : $\underset{\text{Pot. Cuprocyanide}}{K_3[Cu(CN)_4} \rightleftharpoons 3K^+ + [Cu(CN)]^{3-}$

Secondry : $[Cu(CN)] \rightleftharpoons Cu^+ + 4\,CN^-$

(Very small dissociation due to to greater stability of the complex ion)

Primary : $\underset{\text{Pot. Cadmicyanide}}{K_2[Cd(CN)_4]} \rightleftharpoons 2K^+ + [Cd(CN)]^{2-}$

Secondary : $[Cd(CN)_4]^{2-} \rightleftharpoons Cd^{++} + 4CN^-$

(Considerable dissociation due to lesser stability of the complex ion)

Thus when H_2S is passed through a solution containing these complexes, solubility product of CdS only is exceed and therefore it gets precipitated.

Arsenic (As^{+++}):

$AsCl_3 + 3H_2S \longrightarrow As_2S_3\downarrow + 6HCl$

Yello ppt.

$As_2S_3 + 3(NH_4)2S_2 \longrightarrow 3(NH_4)3AsS_3$

Ammonium thio arsenite

$3(NH_4)3AsS_3 + 6HCl \longrightarrow As_2S_3\downarrow + 6NH_4Cl + 3H_2S\uparrow$

Ammonium thio arsenite — Yello ppt

As_2S_3 dissolves in nitric acid forming arenic acid(H_3AsO_4)

$H_3AsO_4 + 12(NH_4)2MoO_4 + 21HNO_3 \longrightarrow (NH_4)_3AsO_4.12MoO_3\downarrow + 21NH_4NO_3 + 12H_2O$

Yello ppt

Ammonium arsenomolybdate

Antimony (Sb^{+++}):

$3SbCl_3 + 3H_2S \longrightarrow SbS_3\downarrow + 6HCl$

Orange ppt.

$SbS_3 + 3(NH_4)2S_2 \longrightarrow 2(NH_4)3SbS_3$

$SbS_3 + 3(NH_4)2S_2 \longrightarrow 2(NH4)_3SbS_4 + S\downarrow$

Ammonium thio-antimonate

$2(NH_4)_3SbS_4 + 6HCl \longrightarrow Sb2S_3\downarrow + 6NH_4Cl + 3H_2S\uparrow$

$2(NH_4)_3SbS_4 + 6HCl \longrightarrow Sb2S_5\downarrow + 6NH_4Cl + 3H_2S\uparrow$

$SbS_3 + 6HCl \longrightarrow 2SbCl_3 + 3H_2S\uparrow$

$SbS_5 + 6HCl \longrightarrow 2SbCl_3 + 3H_2S\uparrow + 2S\downarrow$

$SbCl_3 + H_2O \longrightarrow SbOCl + 2HCl$

Milky(Antomony oxychloride)

Tin (Sn^{++},Sn^{++++}):

$SnCl_2 + H_2S \longrightarrow SnS\downarrow + 2HCl$

Brown ppt.

$SnCl_4 + 2H_2S \longrightarrow SnS_2\downarrow + 4HCl$

SnS- Insoluble in ordinary amm. sulphide but soluble in yello amm. sulphide.

SnS_2- Soluble in ordinary amm. sulphide

$SnS + (NH_4)_2S_2 \longrightarrow (NH_4)_2SnS_2$

$SnS_2 + (NH_4)_2S \longrightarrow (NH_4)_2SnS_2$

Amm. thio-stannate

$(NH_4)_2\,SnS_3 + 2HCl \longrightarrow SnS_2\downarrow + 2NH_4Cl + H_2S\uparrow$

$SnS_2 + 4HCl \longrightarrow SnCl_4 + 2H_2S\downarrow$

$SnCl_4 + Fe \longrightarrow SnCl_2 + FeCl_2$

$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2\downarrow + SnCl_4$

White ppt.

$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg\downarrow + SnCl_2$$

Third Group

IRON, ALLMINIUM, CHROMIUM

Fe^{+++}, Al^{+++}, Cr^{+++}

In the third group ferrous salts(Fe^{++}) areoxidized to ferric salts (Fe^{+++}) by boiling it with few drops of con. HNO_3.

$$2FeCl_2 + 8HNO_3 \longrightarrow 2Fe(NO_3)_3 + 4HCl + 2NO_2\uparrow + 2H_2O$$

Iron (Fe^{+++}):

$$FeCl_3 + 3NH_4OH \longrightarrow Fe(OH)_3\downarrow + 3NH_4Cl$$

Brown ppt.

$$Fe(OH)_3 + 3HCl \longrightarrow FeCl_3 + 3H_2O$$

$$2FeCl_3 + 6NH_4CNS \longrightarrow Fe[Fe(CNS)_6]_3\downarrow + 12KCl$$

Ammo. thiocyanate

Ferric sulphocyanide
Blood red colour

$$4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow Fe[Fe(CNS)_6]_3 + 12KCl$$

Pot. ferrocyanide

Ferric ferrocyanide
Deep blue colour

Aluminium (Al^{+++}):

$$AlCl_3 + 3NH_4OH \longrightarrow Al(OH)_3\downarrow + NH_4Cl$$

White ppt.

$$Al(OH)_3 + NaOH \longrightarrow NaAlO_3 + 2H_2O$$

$$NaAlO_3 + NH_4Cl + H_2O \longrightarrow Al(OH)_3\downarrow + NH_3 + NaCl$$

Chromium (Cr+++):

$$2CrCl_3 + 3NH_4OH \longrightarrow Cr(OH)_3\downarrow + 3NH_4Cl$$

Green ppt.

$$Cr(OH)_3 + 4NaOH + 3H_2O_2 \longrightarrow 2Na_2CrO_4 + 8H_2O$$

$$2NaOH + Br_2 \longrightarrow NaBr + NaOBr + H_2O$$

$$Cr(OH)_3 + 4NaOH \quad 3H_2O_2 \longrightarrow Na_2CrO_4 \quad 5H_2O \quad 3NaBr$$

$$Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow PbCrO_4\downarrow + 2CH_3COONa$$

Yello ppt.

Fourth group

ZINC, MAGNASIUM, COBALT

Zinc (Zn^{++})

$$ZnCl2 + H2S \longrightarrow ZnS\downarrow + 2HCl$$

White grey ppt.

$$ZnS + 2HCl \longrightarrow ZnCl_2 \quad 2H_2S\uparrow$$

$$ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2 + 2NaCl$$

White ppt.

$$Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2HCl$$

MANGANESE (Mn^{++}) :

$$MnCl_2 + H_2S \rightarrow MnS\downarrow + 2HCl\uparrow$$

Buff coloured ppt.

$$MnS + 2HCl \rightarrow MnCl_2 + H_2S\uparrow$$

$$MnCl_2 + 2NaOH \rightarrow Mn(OH)_2\downarrow + 2NaCl$$

$$2Mn(OH)_2 + O \rightarrow 2MnO(OH)\downarrow + H_2O$$

Brown ppt.

$$MnO(OH) + 2PbO_2 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + 2H_2O + HMnO_4$$

Pink colour
(Permanganic acid)

COBALT (Co^{++}) :

$$CoCl_2 + H_2S \rightarrow CoS\downarrow + 2HCl$$

$$3CoS + \underbrace{2HNO_3 + 6HCl}_{\text{Aqua-regia}} \rightarrow 3CoCl_2 + 2NO\uparrow + 3S\downarrow + 4H_2O$$

$$CoCl_2 + 2HNO_2 \rightarrow Co(NO_2)_2 + 2KCl$$

$$CO(NO_2)_3 + 4KNO_3 \rightarrow K_4[Co(NO_2)_6]$$

Pot. cobaltonitrite

$$2K_4[Co(NO_2)_6] + 2CH_3COOH + O\ (air) \rightarrow 2K_3[Co(NO_2)_6]\downarrow + 2CH_3COOK + H_2O$$

Pot. cobaltonitrite

Yellow ppt.
Pot. cobaltinitrite

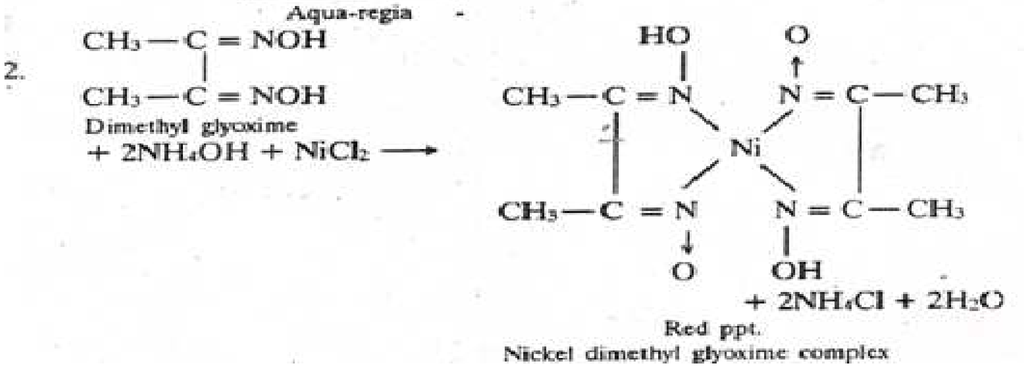
NICKEL (Ni^{++}) :

$$NiCl_2 + H_2S \rightarrow NiS\downarrow + 2HCl$$

Black ppt.

$$3NiS + \underbrace{2HNO_3 + 6HCl}_{\text{Aqua-regia}} \rightarrow 3NiCl_2 + 2NO\uparrow + H_2O + 3S\downarrow$$

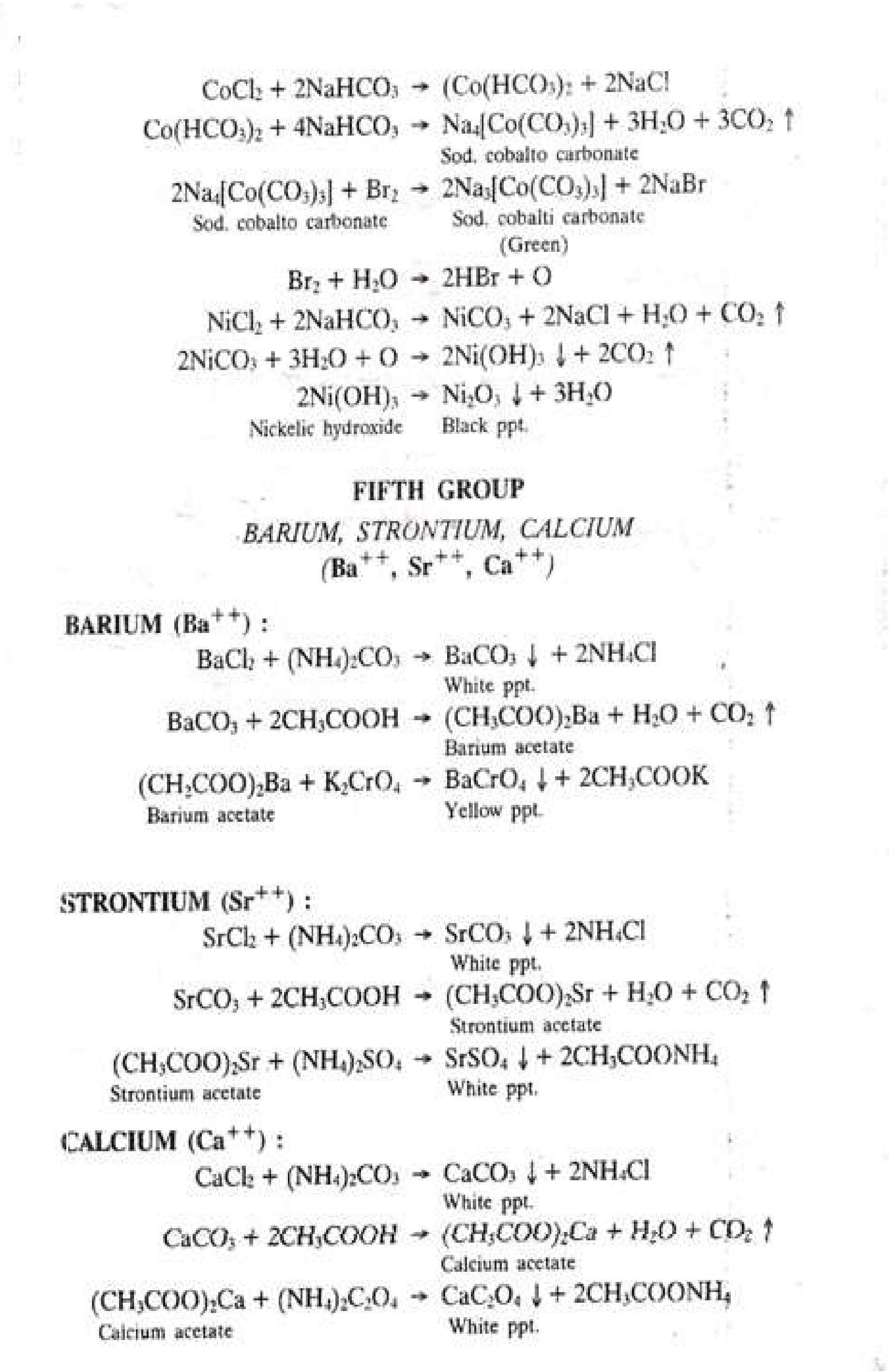
2.



Red ppt.
Nickel dimethyl glyoxime complex

Test of Co and Ni with $NaHCO_3$-Br_2 water (Palit's test):

When the solution of cobalt and nickel salt is treated with excess of sodium bicarbonate, cobalt forms a pink coloured complex sodium cobalto-carbonate. Which on treated with bromine wateris oxidised to green coloured sodium cobalti--carbonate. Nickel does not form a complex with NaHCO3 but on heating with bromine water, it is oxidised to black nickelic oxide.



$$CoCl_2 + 2NaHCO_3 \rightarrow (Co(HCO_3)_2 + 2NaCl$$

$$Co(HCO_3)_2 + 4NaHCO_3 \rightarrow \underset{\text{Sod. cobalto carbonate}}{Na_4[Co(CO_3)_3]} + 3H_2O + 3CO_2\uparrow$$

$$\underset{\text{Sod. cobalto carbonate}}{2Na_4[Co(CO_3)_3]} + Br_2 \rightarrow \underset{\text{Sod. cobalti carbonate (Green)}}{2Na_3[Co(CO_3)_3]} + 2NaBr$$

$$Br_2 + H_2O \rightarrow 2HBr + O$$

$$NiCl_2 + 2NaHCO_3 \rightarrow NiCO_3 + 2NaCl + H_2O + CO_2\uparrow$$

$$2NiCO_3 + 3H_2O + O \rightarrow 2Ni(OH)_3\downarrow + 2CO_2\uparrow$$

$$\underset{\text{Nickelic hydroxide}}{2Ni(OH)_3} \rightarrow \underset{\text{Black ppt.}}{Ni_2O_3\downarrow} + 3H_2O$$

FIFTH GROUP

BARIUM, STRONTIUM, CALCIUM

$(Ba^{++}, Sr^{++}, Ca^{++})$

BARIUM (Ba^{++}) :

$$BaCl_2 + (NH_4)_2CO_3 \rightarrow \underset{\text{White ppt.}}{BaCO_3\downarrow} + 2NH_4Cl$$

$$BaCO_3 + 2CH_3COOH \rightarrow \underset{\text{Barium acetate}}{(CH_3COO)_2Ba} + H_2O + CO_2\uparrow$$

$$\underset{\text{Barium acetate}}{(CH_2COO)_2Ba} + K_2CrO_4 \rightarrow \underset{\text{Yellow ppt.}}{BaCrO_4\downarrow} + 2CH_3COOK$$

STRONTIUM (Sr^{++}) :

$$SrCl_2 + (NH_4)_2CO_3 \rightarrow \underset{\text{White ppt.}}{SrCO_3\downarrow} + 2NH_4Cl$$

$$SrCO_3 + 2CH_3COOH \rightarrow \underset{\text{Strontium acetate}}{(CH_3COO)_2Sr} + H_2O + CO_2\uparrow$$

$$\underset{\text{Strontium acetate}}{(CH_3COO)_2Sr} + (NH_4)_2SO_4 \rightarrow \underset{\text{White ppt.}}{SrSO_4\downarrow} + 2CH_3COONH_4$$

CALCIUM (Ca^{++}) :

$$CaCl_2 + (NH_4)_2CO_3 \rightarrow \underset{\text{White ppt.}}{CaCO_3\downarrow} + 2NH_4Cl$$

$$CaCO_3 + 2CH_3COOH \rightarrow \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + H_2O + CO_2\uparrow$$

$$\underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + (NH_4)_2C_2O_4 \rightarrow \underset{\text{White ppt.}}{CaC_2O_4\downarrow} + 2CH_3COONH_4$$

Sixth group

Magnesium (Mg^{2+}):

$Mg(NO_3)_2 + Na_2HPO_4 + NH_4OH \rightarrow Mg(NH_4)PO_4\downarrow + 2NaNO_3$ (white ppt.) $+ H_2O$

zero group:

Ammonium (NH_4^+)

$NH_4Cl + NaOH \rightarrow NaCl + H_2O + NH_3\uparrow$

$NH_3 + HCl \rightarrow NH_4Cl$ (white fumes)

SUMMARY

The purpose of this lab is to identify the cations present in an unknown solution. Qualitative analysis was used to identify the substances present in the unknown solution. Qualitative analysis is used by reacting the unknown solution with a number of different reagents.

UNIT 4: INTRODUCTION LAB TECHNIQUES: ORGANIC CHEMISTRY

CONTENTS:

4.1 OBJECTIVES

In this chapter students learn the following objectives.

- To determine the melting point procedure.
- Determination of boiling point and Distillation.
- To determine the process of Crystallisation.
- To determine the sublimation of camphor, phthalic acid and succinic acid.

4.2 INTRODUCTION

The purpose of the first part of the laboratory course is to introduce you to many of the techniques used to purify and separate compounds. Melting point and to a much lesser extent, boiling point is one important way of establishing whether the desired purification. Melting point is the temperature at which a solid and liquid exist in equilibrium with each other at a given pressure, or it is the temperature at which a solid begins to change to a liquid under a pressure of one atmosphere. The boiling point of a liquid is that temperature at which the vapour pressure of the liquid equals the atmospheric pressure. Crystallization is a separation technique that is used to separate. a solid that has dissolved in a liquid and made a solution. Sublimation is the transition of a substance directly from the solid to the gas phase without passing through the intermediate liquid phase

4.3 DETERMINATION OF MELTING POINT

This is the most important and significant step in the identification of a solid organic compound or to test the purity of a given solid organic compound. The experiment is usually carried out by capillary tube method using Thiele's tube (fig. 4.3.1) or most conveniently using the flask and test tube (fig. 4.3.2) available in every chemistry lab. In actual practice, a small quantity of the organic substance whose melting point is to be determined is finely powdered between the pieces of filter paper or on a porous plate with the help of a spatula and introduced in a glass capillary tube closed at one end by heating in a Bunsen flame. The material is picked by gentle tapping the capillary on the table, the capillary is then attached to the lower end of the thermometer with its sealed end down. The thermometer is then placed in a thiele's tube or test tube containing conc. H_2SO_4 or paraffin oil in such a way that the liquid covers the filled length of the capillary and the open end of the capillary remains above the surface of the liquid (to avoid the entry of the liquid into the capillary). The test tube (in the flask and test tube method) in turn, is placed in a flask containing the same bath liquid as in the test tube as shown in fig. 4.1.2 The flask is gently heated and the burner is removed from time to time so that the slow steady rise in temperature is maintained and this rise in the temperature is observed carefully. The temperature at which the solid substance melts completely and becomes almost transparent is recorded. This is the melting point of the organic solid substance used. Traces of impurities or moisture considerably lower the melting point. Hence the solid organic compound taken for the determination of melting point should be pure and dry.

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 se pure compound from the laboratory and 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 its melting point is lower than that of the pure compound, the compound taken is impure. Thus this technique not only helps in the identification of an organic compound but also in establishing the purity of known organic compound.

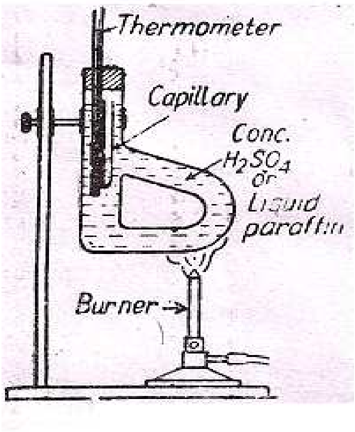


Fig. 4.3.1 D. of Melting point by Thiele’s method

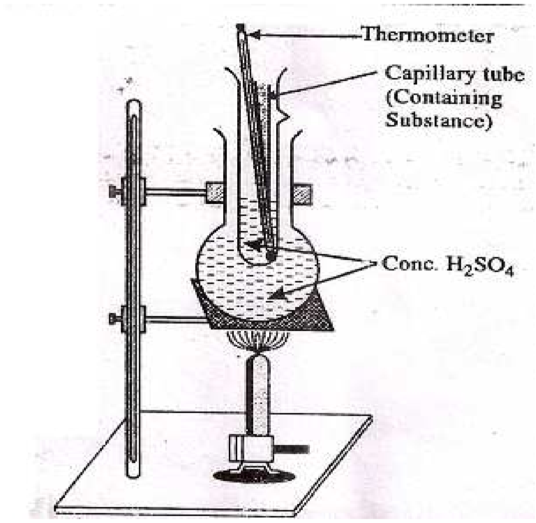


Fig. 4.3.2 Determination of melting point by flask and test tube method

4.4 DETERMINATION OF MELTING POINT OF NAPHTHALENE, UREA, BENZOIC ACID, SUCCINIC ACID ETC

Melting point of compounds given below is measured by using any of above procedure given in point 4.3.

(i)Naphthalene. It sublimes on heating, m.p. 80^0C.
(ii)Urea, m.p. 132^0C.
(iii)Benzoic acid, m.p. 121^0C.
(iv)Succinic acid. It also sublimes on heating, m.p. 185^0C

4.5 DETERMINATION OF BOILING POINT

The boiling point of a liquid may be recorded in either of the two ways depending on the availability of the appliances.

(a)First Method.

A few drops or a little liquid whose boiling point has to be determined is taken in a ignition tube. A capillary tube sealed at the upper and is put inside the ignition tube and the latter is attached to the lower part of the thermometer with the help of a rubber thread. The thermometer along with the ignition tube is placed inside a pyrex test tube in such a way that the liquid inside the ignition tube is covered by conc. H_2SO_4 taken in the test tube as shown in fig. 4.5.1 below. The test tube is heated slowly and the rise of bubbles inside the capillary is carefully observed. The temperature at which a regular and speedy stream of bubbles begins to escape is recorded and is taken as the boiling point of the given liquid.

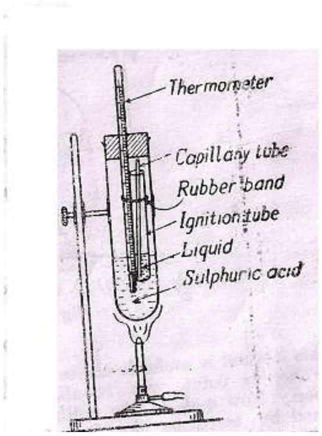
(b)Second Method.

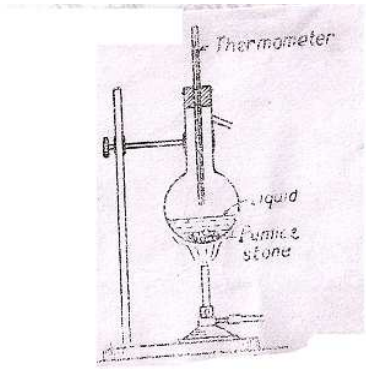
The simple apparatus for the determination of boiling point by this method is shown below in fig. 4.5.2 (a) & (b). The liquid whose boiling point is to be determined is taken in a distillation flask or sometimes in a hard glass tube having two holes in the cork. Some pumice stone or porcelain pieces are added to avoid bumping. A thermometer is fitted in the flask or glass tube through a cork. The delivery tube of the flask or a bent glass tube corked with the glass tube is connected to a water condenser if available (or the vapours of the liquid can also be collected in a long test tube).

The thermometer is adjusted about one cm. above the surface the liquid. The flask or glass tube is heated very gently using a burner. Heating should be very carefully regulated so that the temperature rises slowly and boiling takes place gently. The liquid begins to distil over after sometimes and the bulk of the liquid distils over within a certain temperature range which remains almost constant throughout the distillation. At this moment a rapid stream of bubbles starts issuing from the liquid. This constant temperature is the boiling point of the liquid.

Distillation: It is a mixed process of vaporization (heating) and condensation (Cooling) of a liquid substance. The boiling point determination by the second method involves this process.

The distillation method is useful in purifying the given liquid in addition to determining the boiling point. Now a days, the boiling point is usually determined by using the hard glass tube method (Fig. 4.5.2) (b).





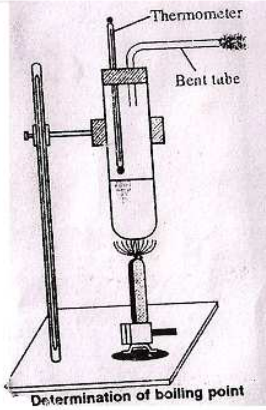


Fig. 4.5.1 Fig. 4.5.2 (a) Fig. 4.5.2 (b)

4.5 DETERMINATION OF BOILING POINT

Boiling point of compounds given below is measured by using any of above procedure given in point 4.4.

(1) Toluene, b. p. 110^{0}C.
(2) Ethanol, b. p. 78^{0}C.
(3) Propanol (iso), b. p. 83^{0}C
(4) Ethyl acetate, b.p. 77^{0}C

4.6 CRYSTALLIZATION

The formation of crystals from the solution of a compound as a result of reduction in the solvent volume or temperature is called crystallization. The separation and purification of the crystalline compounds are usually carried out by using crystallization methods which are based on the difference in the solubilities of the substances in a solvent. There are two main crystallization methods available for the separation and purification of solid organic compounds: (i) simple crystallization and (2) fractional crystallization.

(1)Simple crystallization.

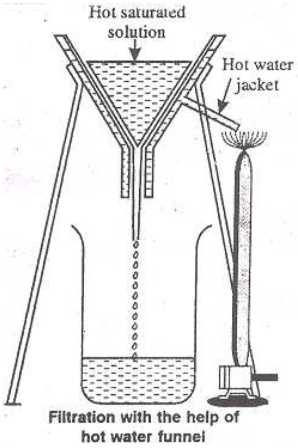
The purification and separation of an organic compound is carried out by this method if an impurity of small amount of insoluble substance or the small amount (less than 5%) of a soluble substance is present.

Procedure:

The given impure organic compound is powdered and dissolved in suitable hot solvent just sufficient to dissolve the whole solute in a beaker. The hot saturated solution (mixture) is then quickly filtered through a filter paper placed in a glass funnel enclosed with a hot water jacket (fig. 4.6.1). The hot water keeps the solution hot and prevents crystallization during filtration. The insoluble and suspended impurities remain on the filter paper and a clear filtrate is collected in the beaker placed below the funnel.

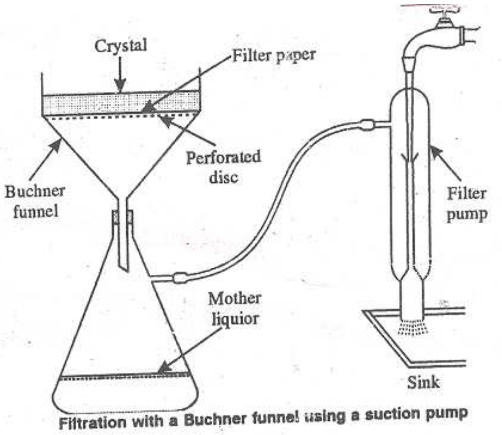
The hot filtrate is allowed to cool undisturbed at room temperature. After sometime, the substance is obtained as crystals leaving behind the impurities in the mother liquor. Now the crystals are separated from the mother liquor by filtration using filter paper with the help of a Buchner funnel and suction pump **(fig. 4.6.2).** The crystals are again dissolved in the minimum amount hot solvent and are allowed to crystallize on cooling. This process if repeated two or more times, crystals of the compound are obtained in pure form.

Fig. 4.6.1

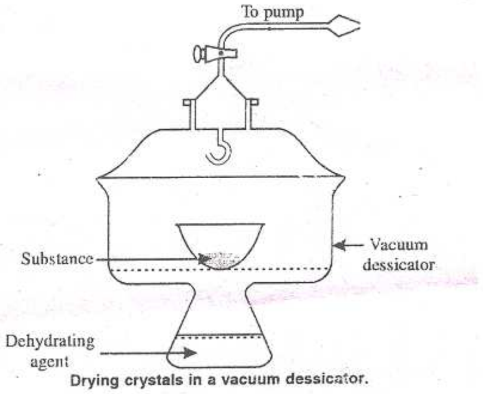


Filtration with the help of hot water funnel

Fig. 4.6.2



Filtration with a Buchner funnel using a suction pump



Drying crystals in a vacuum dessicator.

`Fig. 4.6.3

The crystals are now dried by pressing between folds of filter paper and finally over anhydrous calcium chloride in a vacuum desiccators (fig. 4.6.3).

(2)Fractional crystallization.

When the organic compound and the impurities present in it are both soluble in the solvent and their relative amounts are larger, their separation and purification are carried out by fractional crystallization method. Fractional crystallization is the process in which the crystallization procedures are repeated several times to separate the substances from their mixture solution.

The principle of the fractional crystallization is based on the fact that if the two substances are dissolved in minimum amount of a hot solvent and the solution is allowed to cool, then that substance is crystallized first whose amount is more than that required to saturate the solvent at room temperature. The procedure adopted at various steps is the same as that discussed in simple crystallization method.

4.7 SUBLIMATION

This method is used in the purification of those solids which on heating sublime or distil over directly as vapours or in gaseous form without getting converted into the liquid state. The vapours or gases, in turn, are converted directly to the solid form on cooling without changing into liquid state (fig. 4.7). This solid obtained as a result of cooling of the vapours or gases is called sublimate.

Naphthalene, camphor, Phthalic acid and succinic acid are purified by this method.

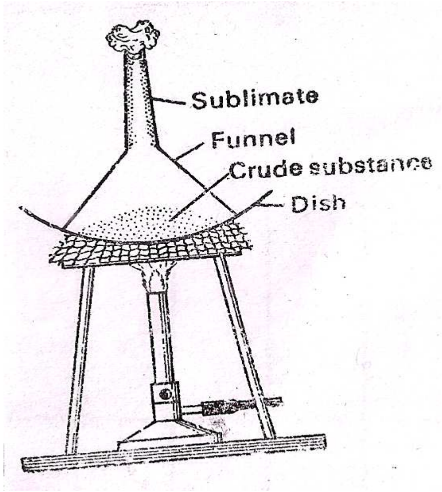


Fig. 4.7 Sublimation

4.8 SUMMARY

The melting point of a solid is the temperature at which it changes state from solid to liquid at atmospheric pressure. At the melting point the solid and liquid phase exists in equilibrium. The melting point of a substance depends on pressure and is usually specified at standard pressure. The boiling point of a substance is the temperature at which the vapor pressure of the liquid equals the pressure surrounding the liquid and the liquid changes into a vapor. The boiling point of a liquid varies depending upon the surrounding environmental pressure. Crystallization is also a chemical solid–liquid separation technique, in which mass transfer of a solute from the liquid solution to a pure solid crystalline phase occurs. When anything solid turns into a gas without first becoming liquid is called sublimation.

UNIT 5: SEPARATION TECHNIQUES

CONTENTS:

5.1 OBJECTIVES

In this chapter students learn the following objectives.

- To know that mixtures are composed of constituents which are not combined?
- To apply methods of distillation, to separate mixtures.
- To understand the terms filtrate, residue, filtration, distil, distillate.
- To know that distillation can be used to separate a liquid from the solids which are dissolved in it and that it is a process of evaporation and condensation.
- To know the process of solvent Extraction method.

5.2 INTRODUCTION

A separation process is a method to achieve any phenomenon that converts a mixture of chemical substance into two or more distinct product mixtures, which may be referred to as mixture. at least one of which is enriched in one or more of the mixture's constituents. In some cases, a separation may fully divide the mixture into its pure constituents. Separations differ in chemical properties or physical properties such as size, shape, mass, density, or chemical affinity, between the constituents of a mixture. They are often classified according to the particular differences they use to achieve separation.. There are many methods that one can use to separate one substance from another. The method that one would choose will be dependent on the physical properties of the substances involved. Solvent extraction is a very useful process for the separation and isolation of compounds from mixtures. Simple distillation is a procedure by which two liquids with different boiling points can be separated. Simple distillation (the procedure outlined below) can be used effectively to separate liquids that have at least fifty degrees difference in their boiling points.

5.3 SIMPLE DISTILLATION METHODS

Organic liquids are generally purified by employing distillation methods. As has already been stated that the process of conversion of liquid into vapours by heating followed by the cooling of the vapours to convert back to the liquid is called distillation. Thus, this process involves both the evaporation and the condensation procedures. There are many methods available for distillation of liquids which depend on the nature of the liquids and the impurities present in them.

1. Simple Distillation When the liquid contains soluble impurities of non-volatile substances, it is purified by the simple distillation method. The liquid must have volatile nature. The impure liquid is heated in a distillation flask. The liquid is vapourised and the vapours are allowed to pass through a water condenser when they condense and the distillate is collected in a receiver. Thus gradually the whole liquid is vapouriesd and condensed and non-volatile impuries are left behind in the distillation flask (fig. 5.3.1).

At the same time, when there is large difference between the boiling points of two miscible liquids such as a mixture of benzene, b. p. 80^0C and nitro benzene, b.p. 211^0C, they are also separated by simple distillation method because in such cases distillation of fractions again and again for few repetitions, pure fractions can be obtained.

2. Fractional Distillation

This method is employed for the purification of a liquid containing the impurities of other volatile liquids or for the separation of two or more liquids having different boiling points from a mixture. Thus fractional distillation is based on the difference of boiling points of the liquids contained in the sample.

In the fractional distillation process, the mixtures of volatile liquids are heated slowly in the special distillation apparatus (fig 5.3.2) and the liquid fractions obtained as distillates in the suitable temperature ranges are collected in separate receiver flasks. This affects the partial separation of constituents of the mixture. The fractions obtained first contain higher amount of low boiling point liquid and the last fractions contain the excess of high boiling point liquid. The fractions obtained are again distilled to get purer fractions than obtained earlier. This process is repeated again and again to obtain the pure liquids.

In the apparatus used for factional distillation, the flask is attached with a fractionating column the upper end of which is connected with a water condenser which in turn is attached with the receiver flask. In the fractionating column, the process of vapourisation and condensation of the fractions occurs automatically thereby separating the constituents and the fractions need not to be distilled again and again.

The fractionating column is a long glass tube which has many obstructions. These obstructions increase the surface area for cooling of vapours. When the liquid mixture is heated slowly, the liquids are vapourised and the vapours enter the fractionating column. As these vapours move upwards in the column, less volatile or high boiling point liquid component is condensed (liquefied) and comes down the column. This liquid comes in contract with up moving vapours and further condenses the less volatile liquid component thus bringing it down to the distillation flack. The vapours of more volatile or low boiling point liquid component move upwards and escape through the condenser pipe where they are condensed (liquefied). The process is repeated several times with the liquid remaining in the distillation flack and that collected in the receiver. This makes effective separation of the components of a liquid mixture.

This method is employed to separate the components of a liquid mixture having closer boiling points such as that of benzene, b.p. 80^0C and toluene, b.p. 110^0C and also to purify the liquids.

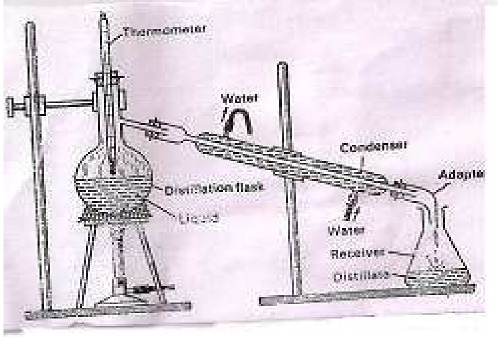


Fig. 5.3.1 Apparatus for simple distillation

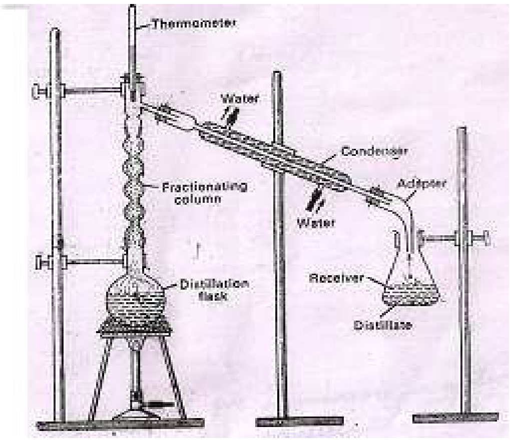


Fig. 5.3.2 Fractional distillation apparatus

3. Steam Distillation

The organic liquids or solids which are immiscible in water and steam volatile, are purified by steam distillation method, for example: aniline, nitrobenzene, chlorobenzene, benzaldehyde, *o*-nitrophenol, etc. The essential oils are also extracted from flowers and plants by this method.

In this method impure organic liquid is mixed with some water and is heated in the distillation flask. To this hot mixture is passed the steam from steam generator. At the boiling point of the mixture, both water and organic liquid are vapourised together and the vapours are condensed after passing through the water condenser. The distillate is collected in the receiver as the two layers. Water and the organic liquid are separated by the separating funnel

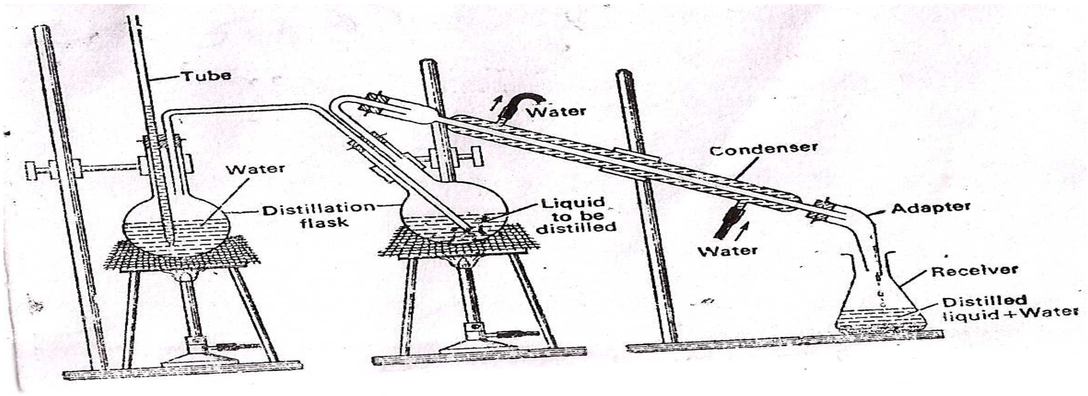


Fig. 5.3.3 steam distillation apparatus.

(1) Distillation Under Reduced Pressure

This method is employed for the purification of the liquids which are decomposed at or before their boiling points. By reducing the atmospheric pressure the liquid boils at lower temperature then its normal boiling point and distils without decomposing. The apparatus used in the method is shown in fig. 5.3.4 below. The distillation is carried out using Claisen flask. For example, glycerine is purified by this method. Glycerine decomposes at its normal boiling point (290^{0}C). At 10-12 mm pressure, glycerine boils at 180^{0}C and does not decompose.

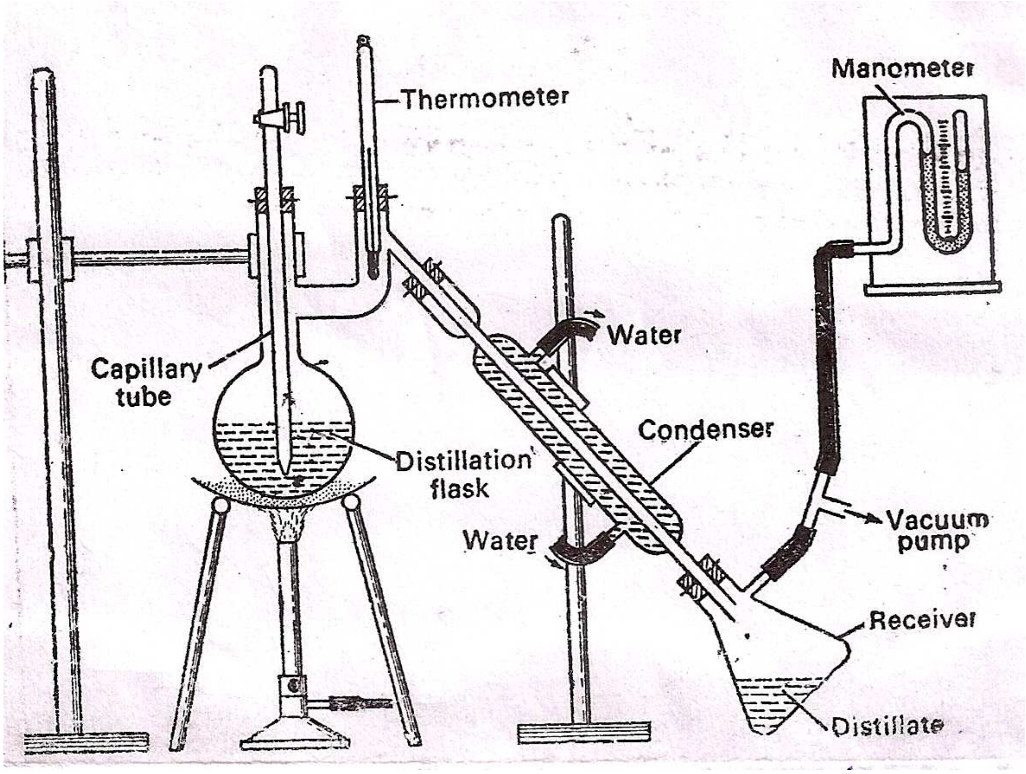


Fig. 5.3.4 Distillation under reduced pressure (apparatus)

5.4 SOLVENT EXTRACTION METHOD

This is a recent or modern method of separation and has much in common with fractional distillation. This technique involves the partition or distribution of a solute between two immiscible liquids in contact with each other. It furnishes clean separation in a short span of time and uses simple apparatus.

The process of solvent extraction is generally employed either for the isolation of dissolved substances from solutions or from solid mixtures or for the removal of undesired soluble impurities from the mixtures. The principle of solvent extraction is based on the distribution law. According to this law if a solute is soluble in both of two immiscible liquids in contact with each other, the solute will distribute itself between the two liquids so that the ratio of concentrations in them is a constant, expressed as $K_d = C_o/C_w$ where K_d is distribution (or partition) coefficient, C_o and C_w are concentrations of extractable species in organic and water layers. Sometimes the equation $D = M_o/M_w$ is also used where D = distribution, M_o and M_w are molar concentrations of the species in organic and water layers.

The efficiency of extraction is of interest in the extraction processes under a given set of conditions. Thus the use of the percent of extraction (%E) is more meaningful than either K_d or D which is expreseed as $\% E = 100D/D+\frac{V_w}{V_o}$, where V_w and V_o are volumes of water and organic phases.

Extraction Techniques

There are various methods employed for the extraction:

(1) Batch Extraction.

This is the most common type of extraction technique in which the organic liquid is added to the solution to be extracted in a separating funnel. After agitation for sufficient length of time, the layers are allowed to separate. Now the top is opened and the lower heavier layer is drained out of the stop-cock. If more extractions are required and the lower layer is the organic layer, a second portion of the organic liquid is added and process is repeated. If the organic liquid is present in the upper layer, the aqueous layer is transferred to a second separation funnel and a second portion of the organic liquid is added. The process is repeated as many times as required to ensure satisfactory separation. The efficiency of batch separation can be obtained as given earlier. This method has been modified for more effective separation which involves multiple batch extractions called continuous extraction method. This method employs separate equipments for extraction using organic liquids lighter or heavier than water.

(2) Back extraction or stripping.

The extracted material, after it is extracted into organic layer, is usually returned to water for the analytical procedure to be used in the determination. This is known as back extraction or stripping. For the systems sensitive to pH, usually the practice is to agitate the organic solution with an aqueous solution which has been adjusted to a pH value which is below the pH range in which the material (generally metal) is extracted into the organic phase. In some cases, the organic liquid having the solute is agitated with an aqueous solution having a complexing agent which reacts with metals to form metal complexes that are more soluble in water than in the organic liquid used in the extraction.

(3) Counter-Current extraction.

In a true counter-current extraction, the two immiscible liquids contact each other as they flow through one another in opposite directions. Such extraction procedures have been found to be very efficient because fresh extractant is brought into contact with the solute depleted phase and the solute enriched extractant is brought into contact with fresh aqueous solution. The amount of solute in either phase after any number of contact steps can be calculated. Various devices have been proposed for carrying out the counter-current extractions.

(4) Extraction of Solids.

Although the extraction or leaching of solids is not a true liquid-partitioning process, it is an important example of an extraction phenomenon. In the simplest procedure, the solid is covered with the liquid and after agitation for a suitable time period, the liquid and solid are separated by decantation, centrifugation or filtration. Most continuous extraction procedures for solids utilize the soxhlet extractor which allows the extraction in less time and can work unobserved for a long time.

The solvent extraction method is widely used nowadays for the separations and determination of metals. For example, ferric ion can be extracted from aqueous solution with a 1% solution of 8-hydroxyquinoline in chloroform by double extraction. The optical density of chloroform layer is determined by using a spectrophotometer. The process is repeated with further portion of the reagent and optical density is measured again. Similarly, it is also possible to determine uranium as 8-hydroxy quinolate in the presence of some EDTA at pH 8.8. The EDTA masks the interfering ions such as Fe^{3+}, Al^{3+}, etc. Now the optical density is determined as usual.

Likewise, by using suitable organic reagents, various metal ions can be estimated, e.g., (i) D. of nickel as nickel dimethylglyoximate complex, (ii) D. of molybdenum as Mo-thiocyanate complex, (iii) D. of lead by dithizone method, etc.

5.5 SUMMARY

Solvent extraction is a method to separate compounds based on their relative solubilities in two different immiscible liquids, usually water and an organic solvent. It is an extraction of a substance from one liquid into another liquid phase. Simple distillation is a procedure by which two liquids with different boiling points can be separated. Simple distillation can be used effectively to separate liquids that have at least fifty degrees difference in their boiling points. Separation of a liquid mixture into fractions differing in boiling point by means of distillation, typically using a fractionating column is called fractional . Distillation of a liquid in a current of steam, used especially to purify liquids that are not very volatile and are immiscible with water called steam distillation.

UNIT 6: QUALITATIVE ANALYSIS

CONTENTS:

6.1 OBJECTIVES

In this chapter students learn the following objectives.

- To detect nitrogen, sulphur and halogen in given mixture.
- To identify functional groups with known samples.

6.2 INTRODUCTION

Qualitative analysis of an organic compound refers to the detection of the elements present in a compound. The most common elements present in an organic compound are carbon, hydrogen, oxygen, nitrogen, halogen and sulphur. Sometimes, elements such as phosphorus and some metals may also be present. Therefore, qualitative analysis is limited to the detection of only a small number of elements usually present in organic compounds.

6.3 DETECTION OF N, S AND HALOGENS

In organic compounds the most commonly occurring elements are nitrogen (N), sulphur (S) and halogens along with carbon (C), hydrogen (H) and oxygen (O). In the identification of an organic compound N, S and halogens are detected before the functional groups are to be looked for. This is done by **Lassaigne's Test** in which these elements are converted into ionisable inorganic substances. This is because these elements along with the others are covalently linked in the organic compounds and do not respond to ionic reactions. This may be accomplished by fusing the substance with metallic sodium in an ignition tube. Thus N, S and halogens are converted to sodium cyanide, suphide and halides respectively. If N and S both are present in the same compound these are converted into NaCNS (thiocyanate).

In the Lassaigne's test, sodium extract is first prepared as follows: A sodium metal piece is dried by pressing between the folds of a filter paper. It is then introduced into a clean ignition tube and covered by pouring the given substance into the tube. The ignition tube is first heated very gently in the flame holding it by means of a pair of tongs, taken it away from the flame and heated again. This process is repeated three to four times till the bottom of tube becomes red hot and reaction begins. The red hot ignition tube is plunged into a beaker or porcelain dish containing about 10 to 15 ml. distilled water. The contents are stirred and allowed the remaining sodium to react with water. The mixture is boiled for five minutes and filtered. This filtrate is known as Lassaigne's solution or sodium extract which should be colourless and transparent. Otherwise the fusion is repeated with larger piece of sodium and sodium extract is prepared as above. The conversion of the elements into ionic form occurs as follows:

$$Na+C+N \rightarrow NaCN \rightleftharpoons Na^+ + CN^-$$

$$2Na + S \rightarrow Na_2S \rightleftharpoons 2Na^+ + S^{2-}$$

$$2Na + X_2 \rightarrow 2NaX \rightleftharpoons 2Na^+ + 2X^- \text{ (X =Cl, Br, I)}$$

(1) Detection of Nitrogen.

About 2 ml. of sodium extract is treated with 3-4 drops of fresh and saturated solution of $FeSO_4$ followed by 2-3 drops of NaOH. The contents are boiled for two minutes. Then the solution is cooled and 2 ml. of dil. H_2SO_4 are added to it to dissolve the precipitate of ferrous hydroxide if formed and make the solution acidic. Then added 2-3 drops of $FeCl_3$ solution. Formation of Prussian blue or greenish blue precipitate or colouration indicates the presence of nitrogen. The reactions involved are given below:

$$Fe\,SO_4 + 2NaOH \rightarrow Fe\,(OH)_2 \downarrow + Na_2SO_4$$

$$Fe\,SO_4 + 6NaCN \rightarrow Na_4\,[Fe(CN)_6] + 2NaOH$$

$$3Na_4\,[Fe(CN)_6] + 4FeCl_3 \rightarrow Fe_4\,[Fe(CN)_6]_3 \text{(Prussian blue)} + 12NaCl$$

In the presence of N and S both in the compound, the above test gives blood red colour as follows:

$Na + C + N + S \rightarrow Na\,CNS$

$3Na\,CNS + Fe\,Cl_3 \rightarrow Fe\,(CNS)_3$ (blood red) $+ 3NaCl$

Ferric sulphocyanide

(2) Detection of Sulphur.

(1) 2ml. of freshly prepared sodium nitropursside solution (colourless) are added to 1ml. of sodium extract. A violet or purple colour is developed confirming the presence of sulphur, $Na_2S + Na_2\,[Fe(CN)_5\,NO] \rightarrow Na_4\,[Fe(CN)_5\,NOS]$ (violet colour).

(2) Alternately, to 2ml. of sodium extract acidified with acetic acid is added 2ml. of lead acetate solution, a black precipitate of PbS if formed, it also indicates the presence of sulphur.

$$Na_2S + (CH_3COO)_2\,Pb \xrightarrow{a.c.} PbS(\text{Black ppt.}) + 2CH_3COO\,Na$$

Acid

(3) Detection of Halogens.

The halogens (Cl, Br, I) present in an organic compound are detected in two ways:

(i) By silver nitrate test. - This is done as follows: 2ml. of sodium extract is boiled with 1ml. conc. HNO_3 and then $AgNO_3$ is added to it:

(a)White curdy precipitate is formed; soluble in NH_4OH-Cl is present.
(b)Pale (light) yellow precipitate appears; partially soluble in NH_4OH-Br is present.
(c)Yellow precipitate is formed, insoluble in NH_4OH-I is present.

$$Na\,Cl + Ag\,NO_3 \rightarrow Ag\,Cl \downarrow (\text{White ppt.}) + NaNO_3$$

$$Ag\,Cl + 2NH_4OH \rightarrow [Ag\,(NH_3)_2]Cl\ (\text{soluble}) + 2H_2O$$

$$Na\,Br + Ag\,NO_3 \rightarrow Ag\,Br \downarrow (\text{light yellow ppt.}) + NaNO_3$$

$$Ag\,Br + 2NH_4\,OH \rightarrow [Ag\,(NH_3)_2\,Br]\ (\text{partially soluble}) + 2H_2O$$

$$NaI + Ag\,NO_3 \rightarrow Ag\,I \downarrow (\text{Yellow ppt}) + NaNO_3$$

$$AgI + NH_4\,OH \rightarrow \text{insoluble}$$

(ii) By chloroform test. - 2ml. of sodium extract are acidified with dil. HNO_3, then added 2-3 drops of chloroform or CCl_4, followed by chlorine water shaking first gently and then vigorously, if chloroform layer turns pale-brown-bromine is present but if it turns purple or violet iodine is present.

$$2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$$
$$Br_2 + CHCl_3 \rightarrow \text{Pale- brown colour.}$$
$$2\,Nai + Cl_2 \rightarrow 2NaCl + I_2$$
$$I_2 + CHCl_3 \rightarrow \text{purple or violet colour.}$$

6.4 IDENTIFICATION OF FUNCTIONAL GROUPS

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

For the sake of convenience all the organic compounds are divided into four types depending upon the presence or absence of N, S and halogens. After detecting the elements by Lassaigne's test, it is advised to perform further tests as per the types I, II, III or IV whichever be suitable according to the presence of the special elements in the compounds.

Type I : Compounds containing C and H with or without oxygen.

S.N.	Experiment	Observation	Inference
1.(a) (b)	On treatment of the compound with $NaHCO_3$ solution On treating of the compound with blue litmus,	Brisk effervescence appears Blue litmus turns red	Acids Acids
2.	On adding ceric ammonium nitrate solution to the compound,	Red colouration is observed	Alcohols
3.(a) (b)	Two drops of $FeCl_3$ are added to an aqueous of alcoholic solution of the compound, Phthalein test is performed,	Typical colour changes are observed Positive result is observed	Phenols Phenols
4.	The compound is heated with Fehling's solution or Benedict's solution,	Red priapitate is formed	Aldehydes or reducing sugars
5.	The compound is treated with Schiff's solution.	Pink colouration is observed.	Aldehydes
6.	On Shaking the compound with sodium bisulphite solution,	White precipitate is formed.	Aldehydes or Ketones
7.	The compound is treated with alkaline sodium nitroprusside solution,	Red colouration appears	Methyl Ketones
8.	Molisch's test is performed,	Result is positive	Sugars
9.	On heating the compound with dil. NaOH solution containing a drop of phenolphthalein	Pink colour is slowly discharged	Esters
10.	On heating the compound with fuming H_2SO_4,	(i) Soluble (ii) Insoluble	Aromatic or unsaturated hydrocarbons Saturated aliphatic hydrocarbons or ethers

Type II: Compounds containing C, H and halogens with or without oxygen.

S.N.	Experiment	Observation	Inference
1.	On boiling the compound with alcoholic $AgNO_3$,	(i) White ppt. soluble in NH_4OH (ii) Ligth yellow ppt. Partially soluble in NH_4OH (iii) Deep yellow ppt. insoluble in NH_4OH	Chloro compounds Bromo compounds Iodo compounds
2.	If the compound is heated with fuming H_2SO_4,	(i) Soluble (ii) Insoluble	Aromatic or unsaturated alkyl halides Saturated aliphatic alkyl halides

Type III. : Compounds containing C, H and N with or without oxygen.

S.N.	Experiment	Observation	Inference
1.	The compound is boiled with aq. NaOH,	Smell of ammonia is noticed	Amides
2.	The compound is treated with dil. HCl followed by $NaNO_2$ drowse in cold,	(i) Brisk effervescence occurs (ii) Brown or green ppt. is formed (iii) Blue colouration appears	Amides, amino acids, primary amines or urea
3.	On treating the above contents with alkaline β - naphthol solution ,	Bright orange-red dye in formed	Aromatic primary amines

4.	The compound is boiled with water,	Yellow colouration	Nitro phenols or nitro compounds
5.	The compound is boiled with zinc dust and aq. NH_4Cl, filtered and filtrate is treated with Tollen's regent,	Grey precipitate is formed	Nitro compounds

Type IV (A) : Compounds containing C, H and S with or without oxygen.

S.N.	Experiment	Observation	Inference
1.	To the aq. solution of the substance is added few drops of $FeCl_3$ solution,	Violet or red colour is observed	Sulphonic acids of phenols or hydrdro carbons
2.	Equal quantities of substance and animal charcoal are mixed and filled one third of the ignition tube with it and heated,	Disagreeable garlic like odour is noticed	Sulphones

(B): Compounds containing C, H, S and N with or without oxygen.

S.N.	Experiment	Observation	Inference
1.	2ml. of NaOH solution are added to a trace of the substance in a test tube, heated to boiling, cooled and added 2 drops of aq. lead acetate,	Brown or black colour or precipitate appears	Thioureas
2.	A trace of the substance is dissolved in 2ml. of water by boiling in a test tube and a piece of blue litmus paper is	(i) If colour changes to red. (ii) If no change in colour	Test (a) given below is performed Test (b) is performed as given below

	introduced in it,		
(a)	A trace of the substance is dissolved in 3ml. of dil. HCl, cooled in ice cold water and added 3ml. of 2% sodium nitrite solution and then 4ml. of alkaline β naphthol solution	Red colouration appears	Amino sulphonic acids
(b)	5 drops of conc. H_2SO_4 are added to a trace of substance and heated gently for few minutes, cooled and diluted with 2ml. water. Then added flakes of NaOH and a piece of moistened red litmus paper is brought near the mouth of the test tube,	Colour changes to blue and smell of NH_3 is noticed	Sulphonamide or saccharin

Confirmation of Functional Groups.

The functional groups are then confirmed by normal and sometimes by performing some special test.

1.Carboxylic acid group (-COOH).

(i) ***Litmus paper test.*** If the blue litmus paper or solution is added to the aq. solution or suspension of the compound, it turns red.

(ii) ***Sodium bicarbonate test.*** If a small amount of the compound is added to about 3ml. of saturated sodium bicarbonate solution, brisk effervescence is noticed.

(iii) ***Fluorescence test.*** 0.2gm. of organic compound is heated gently with 0.5gm. of resorcinol and few drops of conc. H_2SO_4 in a hard test tube for two minutes, cooled and poured the contents into a beaker containing NaOH diluted largly with water. Intense green fluorescence is formed indicating the presence of 1,2 or ortho dicarboxylic group (i.e. phthalic acid)

(iv) ***Ester formation.*** A small quantity of the substance is heated with ethyl alcohol and a little conc. H_2SO_4, cooled and poured in a tube containing water. A fruity smell due to the formation of an ester indicates the presence of carboxylic group.

(v) ***Ferric chloride test.*** 0.5gm. of the acid is neutralised with excess of ammonia in a boiling test tube, the solution is boiled to remove excess of ammonia, cooled and added few drops of neutral $FeCl_3$ solution:

If reddish brown precipitate is formed: aliphatic carboxylic acids; Buff ppt. is formed: Aromatic acids and certain dibasic acids; If violet colour appears: Aromatic hydroxy acids

Note. Phenols and α-naphthylamine also produce colour with $FeCl_3$.

2. Alcoholic –OH group.

(i) ***Ceric ammonium nitrate test.*** 2drops of the organic substance are treated with 0.5ml. of ceric ammonium nitrate solution, then diluted with 2ml. water. A red colouration is observed.

(ii) ***Sodium test.*** About 2ml. of the compound are taken in a test tube, added to it a piece of anhyd. $CaCl_2$ to absorb any water if present. The clear liquid is transferred to another dry test tube and added to it a dry piece of sodium. The effervescence appears due to liberation of hydrogen.

Distinction among primary, secondary and tertiary alcohols.

If 2ml. of the compound is treated with about 5ml. of Lucas reagent (8 gm of anhyd, $ZnCl_2$ in 5ml. conc. HCl) and shaken, an insoluble layer at once is formed by a tertiary alcohol, cloudiness within 4-5 minutes appears in case of a secondary alcohol and the solution remains clear for a primary alcohol.

2. Phenolic –OH group.

(i) ***Ferric chloride test.*** On adding 2-3 drops of ferric chloride to 2ml. of aqueous or alcoholic solution of the compound, a green, blue or violet colour shows the presence of phenolic –OH group but nitro phenols do not show this test.

Exceptions. α-naphthylamine and benzoic acid also respond to this test as follows:

α - naphthylamine -blue colour

Benzoic acid-buff coloured ppt.

(ii) ***Liebermann's test.*** A little amount of the compound is fused with a crystal of sodium nitrite in a tube, the mixture is cooled and to it added 1ml. conc. H_2SO_4, a deep green to blue solution is formed which turns red when poured in large excess of water. The red aqueous solution again becomes deep green or blue if made alkaline with NaOH.

(iii) ***Azo-dye formation.*** 2drops of aniline are treated with 0.5ml. conc. HCl in a test tube, diluted with water and cooled in a freezing bath, then added dil. $NaNO_2$ solution while shaking. This diazotized solution is poured to that of phenol in excess of 2N-NaOH solution. Formation of a dye or orange or red colour indicates the phenolic group.

(iv) ***Phthalein test.*** 0.5gm. of compound is heated with 1gm. phthalic anhydride and 2drops of conc. H_2SO_4 for 1minute, cooled and made alkaline with dil. NaOH solution. If few drops of this alkaline liquid are poured in 20ml. water, characteristic colour appears due to phenolic group:

Phenol, O-Cresol-red colour
Catechol, m-Cresol-blue colour
Resorcinol-fluorescent green
p-Cresol-no colouration
Hydroquinone-deep blue
α – Naphthol-green
β – Naphthol-light green

3. Aldehyde group (-CHO)

(i) ***Test with Schiff's reagent.*** 5-6 drops of liquid or (0.1gm) of compound are added to 2ml. of the reagent, contents are shaken vigorously, a deep red or violet colour after waiting for 2-3 minutes. (no heating)

(ii) ***Test with Tollen's regent.*** 0.1gm. of solid or 0.1ml. of liquid compound is added to 2ml. of Tollen's reagent, warmed and allowed to stand for 2-3 minutes when a silver mirror or a grey precipitate is formed.

(iii) ***Test with Fehling's solution.*** 0.1gm. of soid or 0.2ml. of liquid compound is added to 5ml. of fehling's solution and the mixture is boiled when red precipitate is formed.

(iv) ***Test with Benedict's solution.*** 0.1gm. of the compound is boiled with 2-3ml. of Benedict's solution for few minutes while a red yellow precipitate appears.

The compounds can be quickly guessed by the following points:

(a)Smell of bitter almonds – benzaldehyde
(b)If bad pungent odour is there, NaOH is added to the liquid compound and shaken
(i)Brown resin formed – acetaldehyde
(ii)No such change – formaldehyde

4. Ketone group (>C = O).

(i) ***2,4- Dinitrophenyl hydrazine test.*** 2drops of the substance are added to about 2ml. of the reagent solution, shaken vigorously and heated if necessary, when a yellow or orange red precipitate separates out.

(ii) ***Sodium bisulphite test***. 0.2gm. or 0.3ml of the compound is added to 1ml. of saturated sodium bisulphite solution and shaken vigorously, a white precipitate is formed.

(iii) ***Sodium nitroprusside test.*** 0.1gm. of solid or 0.2ml. of liquid compound is added to 2ml. of aq. sodium nitroprusside solution and contents are made alkaline with 2-3 drops of sodium hydroxide, a red or purple colour appears (benzophenone does not respond to this test).

Note: The first two tests, i.e. with 2,4 dinitrophenyl hydrazine and sodium bisulphite, are also given by aldehydes but the difference is that ketones do not respond to the tests with Tollen's reagent, Fehling's solution, Schiff's solution, etc.

5. **Ester group (RCOOR').**

All the esters possess fruity smell.

(i) ***Phenolphthalein test.*** To 3ml. of the compound are added 2-3 drops of very dilute NaOH solution followed by a drop of phenolphthalein and heated gently, the pink colour is gradually discharged (due to hydrolysis of ester).

6. **Carbohydrate.**

(i)*Molisch's test.* To 1ml. aqueous suspension of compound are added 2drops of 10% alcoholic solution of α – naphthol and shaken well. Now added carefully 2ml. of conc. H_2SO_4 along the side of the test tube, a reddish-violet ring is formed at the junction of two layers in case of carbohydrate.

In the Molisch's test 8ml. conc. HCl is added in place of conc. H_2SO_4 and the solution is boiled, a violet colour is produced immediately for sucrose or fructose but glucose gives this colour after 1-2 minutes of continuous boiling.

(ii)*Sulphuric acid test.* A small amount of the powdered compound is treated with 1ml. cold conc. H_2SO_4, colour varying from yellow, brown and black appears.

(iii)*Test with Tollen's reagent.* 0.1gm. of the compound is added to 2ml. of Tollen's reagent and heated gently, a silver mirror is obtained inside the wall of the vessel.

(iv)*Test with Fehling's solution or Benedict's solution.* 1ml. of the aq. solution of the compound is boiled with 2ml. of Fehling's solution or Benedict's solution for two minutes, red precipitate is formed in case of reducing sugars. If the mixture with Benedict's solution remains blue or only slight turbidity appears then sucrose is present.

7. **Hydrocarbon and Ether.**

If the compound does not respond to any above test, it may be suspected to be either a hydrocarbon or ether. Ethers are soluble in phosphoric acid while hydrocarbons are rendered insoluble. All ethers are sweet smelling. Liquid benzene and toluene have characteristic sweet petrol like odour.

i. ***Feigl's test for ethers.*** 1-2ml. of ether are taken in a boiling tube and its mouth is covered with a filter paper moistened with a mixture of cupric acetate and benzidine hydrochloride solution. On heating to boiling, a deep blue colour appears on filter paper due to the formation of benzidine blue due to the ether group.

ii. To 0.5 ml. of the compound is added 1ml. of iodine solution in CS_2 and shaken well the purple colour of CS_2 layer changes due to ether group.

iii. 1ml. of compound is mixed with 4ml. of glacial acetic acid and 1ml. conc. H_2SO_4, heated under reflux condenser for about 5 minutes, cooled well and extracted with benzene purple colour appears due to ether group (This test can be applied only when ester group is absent, otherwise not). If the above tests are negative, then the compound is a hydrocarbon.

8. Halogen containing compound.

(i) ***Alcoholic silver nitrate test.*** A little amount of the compound is heated with 2ml. of alcoholic silver nitrate solution for a few minutes and the observed the following:

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

(b)No precipitate indicates the presence of halogen atom attached to benzene nucleus (but 1-chloro-2, 4-dinitro benzene does not respond to this test).

Quick guess.

(a)If the Cl-containing compound is solid, aliphatic and crystalline containing –CHO group, it is chloral-hydrate.

(b)Cl-containing compound is aromatic solid, colourless and crystalline with characteristic smell, it is p-dichlorobenzene.

9.Amide group (-CONH$_2$)

(i) ***Sodium hydroxide test.*** 0.2gm. of the compound is heated with 4ml. of aq. NaOH, ammonia gas is evolved due to amide group.

(ii) ***Nitrous acid group.*** To 0.2gm. of substance is added 2ml. dil. HCl followed by 2ml. of 2% aq. $NaNO_2$ and shaken, brisk effervescence due to the evolution of nitrogen indicates amide group.

(iii) ***Hydroxylamine hydrochloride test.*** In a test tube 0.2gm of the compound, 0.2gm of hydroxylamine hydrochloride and 2ml. ethyl alcohol are taken, boiled for five minutes, cooled and added few drops of $FeCl_3$. Blue-red colour appears indicating an aliphatic amide.

(iv) To the aq. solution of the compound are added 7-8 drops of 6% H_2O_2 and heated nearly to boiling, cooled and added 1-2 drops of 5% $FeCl_3$ solution, Bluish red colour appears in cold within 2mintues or a brown colour on warming shows the presence of an aromatic amide.

(**Quick test**: Compound is dissolved in water by heating cooled and added 1ml. conc. HNO_3

(a)Crystalline ppt formed -urea

(b)No ppt. and aliphatic-acetamide

(c)No ppt. and aromatic -benzamide)

10.Amine groups (-NH$_2$, > NH and≡ N).

(a)Primary amine.

(i)***Nitrous acid test.*** 0.2gm. of the compound is dissolved in 10ml. dil. HCl and cooled. Now added 10% aq. $NaNO_2$ solution, brisk effervescence appears-aliphatic primary amine.

(ii)***Carbylamine test.*** A mixture of 2 drops of the compound, 2drops of chloroform and 2ml. of alcoholic caustic potash (KOH) is boiled. An intolerable offensive odour of carbylamine indicates a primary amine.

(iii)***Diazotisation test.*** About 0.2gm. of the compound is dissolved in dil. HCl, cooled and added to it 10% aq. $NaNO_2$ This is poured into a beaker containing 10% alkaline β – naphthol, a bright orange-red dye appears-aromatic primary amine

(iv)***Rimini test.*** To about 0.3gm. of the compound taken in a test tube are added 5ml. water, 1ml. acetone and a few drops of sodium nitroprusside, allowed to stand for 2minutes: a violet red colour appears for aliphatic primary amines.

(b)Secondary amine.

(i)*Nitrous acid test.* Ice cold dil. HCl is added to a solution of 1% aq. $NaNO_2$. This solution is added gradually to the solution of compound in HCl (0.5gm. in l0ml. HCl). An oily dark coloured liquid or low melting solid is formed due to aliphatic or aromatic secondary amine.

(ii)*Libermann's nitroso test.* In the above test, if 1ml. conc. H_2SO_4 is added cautiously to the reaction mixture, a blue colouration which changes to red on dilution with water and blue or green with aq. alkali confirms the secondary amine.

(c)Tertiary amine.

(i)*Nitrous acid test*. Ice cold dil. HCl is added to 1% aq. $NaNO_2$. To this solution is added gradually 0.2gm. of the compound in 10ml. dil. HCl:

(a)If there is no reaction-tertiary aliphatic amine.

(b)If green or brown coloured salt is produced-aromatic tertiary amine.

11.Nitro group (-NO_2).

Almost all nitro compounds are light yellow or yellow in colour.

(i)*Sodium hydroxide test.* A small amount of the compound is shaken with 2ml. of NaOH solution, yellow, intense yellow or orange colour is produced due to nitro group.

(ii)*Zinc-ammonium chloride test.* A small amount of the substance is boiled with 5ml. of 5% alcohol, 0.2gm. each of NH_4Cl and zinc dust, cooled, filtered and added to the filtrate 2 ml. of Tollen's reagent. On heating, a black grey precipitate is formed due to nitro compounds.

(iii)*Azo-dye test.* 0.1gm. of the substance is heated with 0.5ml. conc. HCl and 2-3 small pieces of metallic tin for 3-4 minutes, filtered, cooled and added 3ml. of aq. $NaNO_2$ solution. This is poured into a beaker containing alkaline β naphthol solution. An orange red dye is formed.

12.Sulphonic acid group (-SO_3H).

The compound having sulphonic acid group gives positive test for S element.

(i)*Sodium bicarbonate test.* A little amount of the compound is added to a few ml. of aq. $NaHCO_3$ and the contents are stirred. Brisk effervescence of CO_2 and positive test of element S confirms the sulphonic acid group.

(ii)*Fusion test.* Equal amounts of the compound and solid NaOH/KOH are fused and treated with dilute mineral acid. A penetrating smell of SO_2 is noticed. The gas if passed into acidic $K_2Cr_2O_7$ solution, green colour is developed.

6.7 SUMMARY

Detection of nitrogen (N), sulphur (S), and halogens (X) is done by Lassaigne's Test in which these elements are converted into ionisable inorganic substances. This can be done by fusing the substance with metallic sodium in an ignition tube. On fusion with sodium N, S, and halogens are converted to sodium cyanide, sulphide and halides respectively. If N and S both are present in the same compound these are converted into NaCNS (thiocyanate). Functional groups are specific atoms, ions, or groups of atoms having consistent properties. For the sake of convenience all the organic compounds are divided into four types depending upon the presence or absence of N, S and halogens. After detecting the elements by Lassaigne's test, it is advised to perform further tests as per the types I, II, III or IV whichever be suitable according to the presence of the special elements in the compounds. The functional groups are then confirmed by normal and sometimes by performing some special test.

UNIT 7: INTRODUCTION LAB TECHNIQUES: PHYSICAL CHEMISTRY

CONTENTS:

7.1 OBJECTIVES

In this chapter students learn the following objectives.

- Students will learn how to carry out independent experimental work in a laboratory setting while investigating a research problem, utilize appropriate instrumentation and techniques.
- Become familiar with different volumetric measurements and use laboratory apparatus correctly.
- Interpret experimental results and draw reasonable conclusions and write them properly.
- Apply safety rules in the practice of laboratory investigations.

7.2 INTRODUCTION

Behavior of matter: Chemistry is concerned with the composition, structure and properties of matter. Anything which occupies space and has mass is known as matter. Matter can exists in three states solid, liquid and gas.

Solutions: Solvent, solute and solution

Solvent: The liquid which allows the solute to dissolve in it to form a solution is called solvent.

Solute: The substance which dissolves in a solvent is called a solute.

Solution: A homogenous mixture of a solute in solvent is called solution.

If the amount of solute is relatively small compared to the amount of solvent is called a dilute solution.

A solution in which the amount of solute is relatively large compared to the amount of solvent is considered concentrated solution.

7.3 USE OF APPARATUS: PIPETTE, BURETTE, VOLUMETRIC FLASK, BALANCE, USE OF BURNER

In chemistry experiments the glassware used is pipette, burette, test tube, boiling tube, beaker, measuring flask, conical flask, graduated cylinder, funnel steam bath etc. For measuring fixed amount of a liquid either pipette or burette (sometimes graduated cylinders) are used. For titration purposes conical flask is used it may be 100 ml or 250 ml balance is used for weighing purposes. Now a day's electrical balance is used.

Bunsen burner:

Bunsen burner is shown in fig 7.1. To get steady blue flame proceed as follows

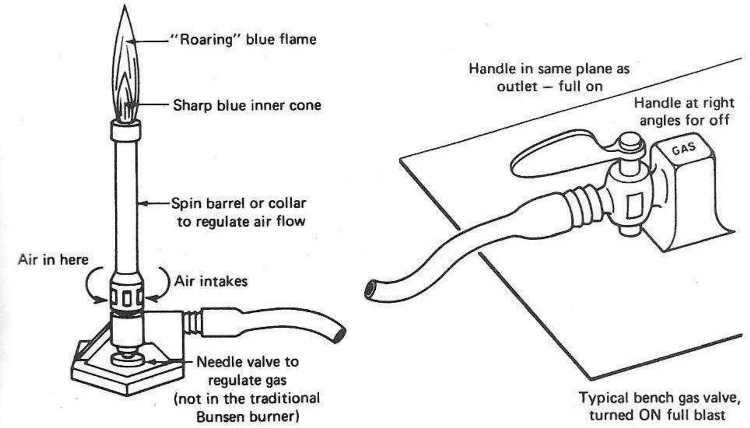


Fig 7.1 Bunsen burner

(i)Find the round knob controlling the needle valve which is at the base of the burner. Turn it clockwise to stop the flow of gas completely. If your burner does not have a needle valve the gas flow has to be regulated at the bench stopcock (fig 7.1).

(ii)There is a movable collar at the base of the burner which controls air flow. Now see that all the holes are closed (i.e. no air gets in).

(iii)Connect the burner to the bench stopcock by some tubing and turn the bench valve fallen. The bench valve handle should be parallel to the outlet (fig 7.1).

(iv)Now, slowly open the needle valve. You may be just able to hear some gas escaping. Light the burner. Mind your face. Don't look down at the burner as you open the valve.

(v)You will get a wavy yellow flame, something you don't really want. But at least it will light. Now open the air collar a little, the yellow disappears a blue flame forms. This is what you want.

(vi)Now adjust the needle valve and collar for a steady blue flame.

7.4.TYPES OF FLAMES

7.4.1 Oxidising and reducing flame

Oxidizing flame is produced by placing nozzle of the blowpipe about one third within the flame and blowing vigorously in a manner so as to cause the extreme tip of the flame to act on the substance under examination.

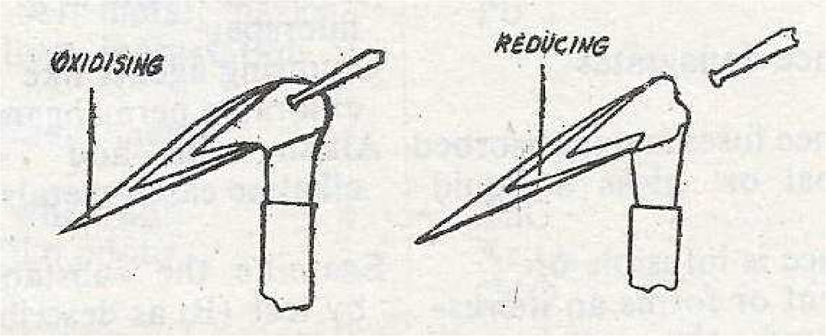


Fig 7.2 oxidizing and reducing flame

Reducing flame is produced by blowing gently the flame with a mouth blowpipe, the nozzle of which of which kept just outside the flame in a manner so that the inner cone of the flame acts upon the substance under examination.

7.4.2 Luminous and Non luminous flames

A luminous flame is burning flame which is brightly visible. Much of its output is in the form of visible light, as well as heat or light in the non-visible wavelengths. A luminous flame is a bright, light emitting, usually yellow flame. For example, if you light a match and watch it burn, this is luminous flame. One of the most familiar instances of a luminous flame is produced by a Bunsen burner. This burner has a controllable air supply and a constant gas jet: when the air supply is reduced, a highly luminous, and thus visible, orange 'safety flame' is produced. For heating work, the air inlet is open and the burner produces a much hotter blue flame.

A non-luminous flame is a flame in which the fuel is undergoing complete, or near complete combustion. A non-luminous flame (as the name implies) is much darker than a luminous flame and does not emit as much light. The colour is generally blue and the flame temperature is much higher than a non-luminous flame. One can easily adjust a Bunsen burner or propane torch to make a non-luminous flame.

7.5 INTRODUCTION TO INSTRUMENTS

7.5.1Calorimeter

For the measurement of heat of various reactions, a thermos flask or a calorimeter is used. A calorimeter suitable for general experiments with solutions may be constructed by loosely packing the space between two large boiling tubes or two beakers with cotton wool. The modern vacuum flask has the merit of very good insulation, but the narrowed neck of the ordinary of thermos type prevents the use of an efficient stirrer, and if mixing is done by shaking, the water equivalent has absurd values. An unsilvered, straight sided Dewar flask (fig 7.3). Avoids this serious disadvantages without serious loss of heat insulation.

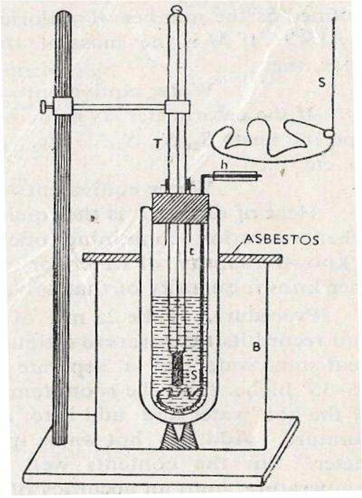


Fig 7.3 calorimeter

7.5.2Conductivity bridge

An electric current flowing through an electrolyte is governed by Ohm’s law. According to Ohm’s law the current strength (I) is directly proportional to the difference of potential (E) between the two ends of the conductor through which the current is flowing, thus mathematically.

$I \propto E$

or $I= KE$ or $IR=E$

where R and K are constants. The ratio E/I is the resistance of the circuit to the passage of electric current and so the constant R is known as resistance. The K is known as conductance.

The conductance of a substance i.e., its power of conducting an electric current, is thus reciprocal of resistance.

Measurement of conductivity of a solution

The resistance of a conductor is measured by means of Wheatstone bridge. When a direct current is passed through solution, the following difficulties arise.

1. The electrodes are polarized i.e., the products of the electrolysis accumulate on them.
2. The passage of current involves the decomposition of a portion of the solute, so the concentration of this substance changes during the passage of electric current.

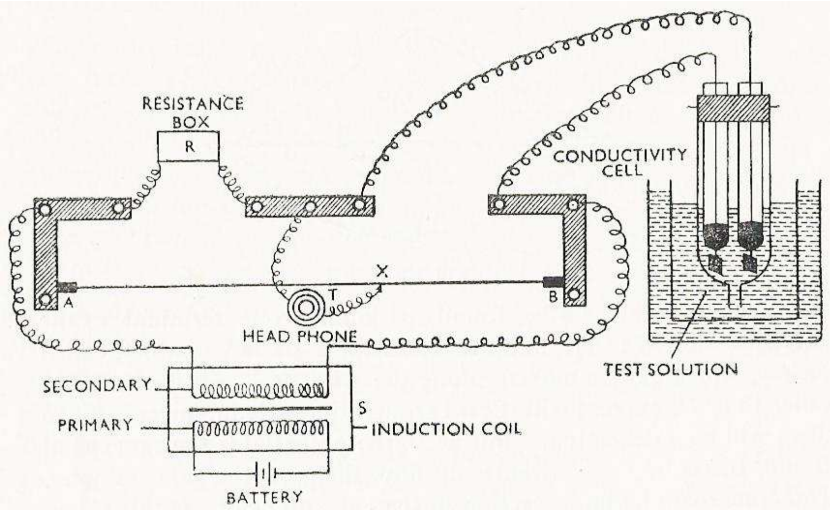


Fig 7.4 Conductivity Bridge (Wheatstone bridge)

To remove these difficulties we use alternating current in place of direct current. It is obtained in the laboratory from the secondary coil of small induction coil. In this case galvanometer is replaced by a head phone the arrangement is shown in fig 7.4

7.6 SOLUBILITY

Different solution dissolve to different extent in the same mass of solvent, i.e., they have different solubilities. Solubilities is thus the ability of a salute to dissolve in a particular solvent. To obtain a uniform result, the amount of solvent is fixed, it is 100 gm and the solution should be saturated at a particular temperature.

Hence solubility of a solute at t^{0}C

$$\frac{weight\ of\ solute(g)}{weight\ of\ solvent(g)} x100 = \frac{weight\ of\ solute(g)}{weight\ of\ solution - weight\ of\ solute(g)}\ x100$$

Thus if we say solubility of cane sugar is x at t^{0}C, means x gm of solute are dissolved in 100 g of solvent at t^{0}C.

Standard solution:

The solution of accurately known concentration is known as standard solution. It contains accurately known amount of substance in unit volume of solution. It may be in terms of molarity, molality, normality, mole fraction or percentage compostion.

Preparation of standard solution

Standard solution may be prepared by any of the following two methods.

(1)By direct weighing.
(2)By titration.

(1)By direct weighing:

The standard solution of certain substances can be prepared, provided they are available in pure state, by weighing a definite amount of the substance, dissolving in a suitable solvent, usually water and making up the solution to known volume.

The amount of substance to be weighed is calculated keeping in view the ultimate volume of desired normality of the solution. Such substance whose standard solution can be prepared by direct weighing are called primary standard substances. In practice, it is often more convenient to prepare a little more concentration solution than it is actually required. This is then diluted with distilled water until the solution of desired normality is obtained. The extent to which the solution is to be diluted is calculated from the normality equation.

$N_1V_1 = N_2V_2$
Where N_1= Original normality
V_1= Original volume taken
N_2= Required normality
V_2= Volume after dilution

Then $V_2= N_1V_1/N_2$ and the volume of water to be added to the volume $V_1=(V_2-V_1)$ ml. standard solution of oxalic acid can be prepared by this method.

2. By titration:

This is an indirect method employed for the preparation of standard solution of those substances which are not available in a state of purity, sodium hydroxide, mineral acids and many other substances. In such case a little more concentrated solution then is ultimately required, is first prepared. This solution is then standardised by titration against a solution of pure substance and of known concentration. Thus the normality of the solution to be prepared is known, from which solution of desired normality is prepared by dilution with distilled water.

Primary standards:

There are certain substances whose standard solution can be prepared by directly weighing the known amount of substance available in a state of purity, in a suitable solvent usually water and making up the solution to a definite volume. Such substances are called primary standards. Therefore, a primary standard is a solid substance which is used for the direct standardsation of a given solution. The volume of the given solution required to react with the dissolved standard gives a measure of normality of the solution. Only a few substances are available as primary standards because a primary standard is required to fulfill certain requirements.

Requirement of primary standard:

A primary standard must fulfill the following conditions:

(i) It should be easily available in a state of purity.
(ii) It must be easy to obtain, to purify, to dry and to preserve it in pure state.
(iii) It must be of definite known composition and capable of reacting quantitatively and in a known way with a solution to be standardized.
(iv) Its composition should remain unchanged during storage and in air during weighing i.e., it should not be hygroscopic or efflorescent nor oxidized by air affected by carbon- dioxide.
(v) It should have high equivalent weight, to minimize weighing errors.

For example if you have to prepare N/10 oxalic acid solution in 250 ml you weigh 1.5750 gm and transfer the weighed oxalic acid into a 250 ml measuring flask, dissolve it in water and make the volume 250 ml. Its normality will be N/10. It is primary standard.

In contrast suppose you have to prepare N/5 sodium hydroxide solution in 250 ml. if you weigh 2 gm and dissolve it in 250 ml, the normality will be not be N/5 it will be much less than that, because if you are weighing 2 gm and dissolving it in 250 ml flask, by the time you pour the weighed amount into measuring flask it hydrolyses and the dissolved amount becomes much less than 2 gm.

If you have to prepare exactly N/5 NaOH solution in 250 ml, weigh excess of sodium hydroxide say approximately 3 gm and dissolve in 250 ml. To know its exact strength titrate it against standard oxalic acid solution.

At this stage you will get the exact strength of NaOH solution (from N_1V_1 (oxalic acid)= N_2V_2 (NaOH).

Suppose you get the strength of NaOH solution equal to N/3. Now for preparing N/5 NaOH solution in 250 ml the following formula is used

$N_1V_1 = N_2V_2$

N/5.x250 = N/3. x_1

X_1= 250x3/5 = 150 ml

That means 150 ml of N/3 sodium hydroxide is poured into 250 ml measuring flask and make up to the volume to 250 ml by adding 100 ml of water. This solution is now standard solution of sodium hydroxide of strength N/5.

Density:

The density or specific gravity of a liquid is defined as its mass per unit volume. We use the term density at a given temperature; it means the relative density at that temperature with respect to density of water. It is measured with the help of density bottle (fig 7.5).

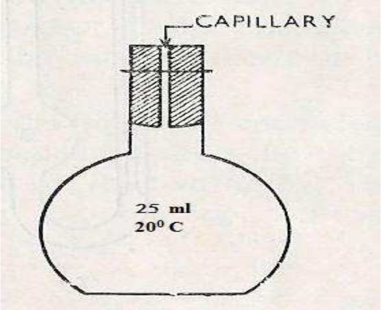


Fig 7.5 Density bottle

Equivalent weight:

Equivalent weight of a substance is most commonly defined as the number of parts by weight of which combines or displaces 1.0078 parts by weight of hydrogen or 8 parts by weight of oxygen.

This definition of equivalent weight though very simple and covers most of the reactions, but is very difficult to give such a definition of equivalent weight which covers all the reactions. Equivalent weight varies with the type of reaction. Therefore, a compound may possess different equivalent weights in different chemical reactions and under different experimental conditions.

The gram equivalent weight of a substance is the equivalent weight expressed in grams.

From the above discussion it is clear that the equivalent weight of a compound can be decided only after considering the reaction which it undergoes.

Equivalent weight of an acid is that weight of an acid which contains one replaceable hydrogen i.e., 1.0078 gm of hydrogen.

Eq wt. of an acid $= \frac{mol\ wt\ of\ acid}{no\ of\ replaceable\ hydrogen\ atoms}$

Thus oxalic acid $(COOH)_2 2H_2O$ is dibasic acid its equivalent weight will be

= Mol. Wt. of oxalic acid/basicity of oxalic acid

= 166/2

= 63

7.7DATA ANALYSIS AND ERROR CALCULATON

If you have performed the experiment and obtained the results calculate the error. Compare it with the exact one. Suppose in a particular experiment the surface tension of the supplied liquid say benzene is obtained 27.90 dynes/cm at 20^0C. from standard table you know the value of surface tension at 20^0C for benzene is 28.88 dynes/cm. in this case the percentage error will be $\frac{28.88-27.90}{28.88}$ x100. =3.40 %

Types of errors:

Two main types of errors can affect the accuracy of a measured quantity, these are

(a)Determinate and
(b)Indeterminate errors

Determinate errors – determinate errors are those that are determinable and can be either avoided or corrected. They may be constant, as in the case of uncelebrated weight that is used in all weighings or may be variable but of such a nature that they can be accounted for any correction. The determinate errors can be generally classified as

(i) Instrumental errors
(ii) Operative errors
(iii) Errors of the method

(i) Instrumental errors:

These errors are common to all instruments as each one has a limited accuracy. The manufacturer of the instrument generally provides the table quoting the reliability of the results in the respective ranges. It should be kept in mind that the calibration of the instrument in one range may not be valid of the entire range. In the case of volumetric analysis, the glass apparatus like burette, pipette and measuring flask are calibrated. If the working temperature is different, the volume measured may be incorrect. The chemist has to consider all these errors which may be introduced during experiments.

(ii) Operative errors:

These include personal errors and can be reduced by experience and in case of the analyst in the physical manipulations involved operations in which these errors may occur include transfer of solutions, effervescence and bumping during sample dissolution, incomplete drying of samples etc. These are difficult to correct for personal errors which may also be introduced due to physical disability, like colour blindness which may make in correct judgment of colour. Other personal errors include mathematical errors in calculations.

(iii) Errors of methods:

These are most serious errors of an analyst. Most of the errors discussed above can be minimized or corrected for, but the errors that are inherent in the method can not be changed unless the conditions of the determination are changed

(b) Indeterminate errors:

The second type of errors includes the determinate errors, generally accidental or random errors. They are revealed by small difference in successive measurements made by the same analyst under virtually identical conditions. These errors cannot be predicted or determined. These accidental errors will follow a random distribution, thus mathematical law of probability can be applied to arrive at some conclusion regarding the most probable results of a series of some conclusion regarding the most probable results of a series of measurements. To give a simple example, an analyst reads incorrectly, the instrument panel reading in pH meter or spectrophotometer. He notes down this reading which is used in calculations based on this reading. The error is random and each observation is isolated and unique.

7.8 GRAPH PLOTTING

While plotting a graph, scale should be chosen so that entire picture is easily obtained from the graph sheet. Both the axes should be clearly indicated which is which. The scale on both the axes should be mentioned in the graph sheet. If you have been asked to determine some property by means of graph, then plot that property along x-axis as shown in fig 7.6. suppose you have to determine the composition of the given mixture of two liquids A and B by viscosity measurements than plot the time of flow along y- axis and concentration of A or B along x-axis as shown in **fig 7.6.** A perpendicular is drawn from that point on the x-axis, from which the composition of unknown solution can be read directly.

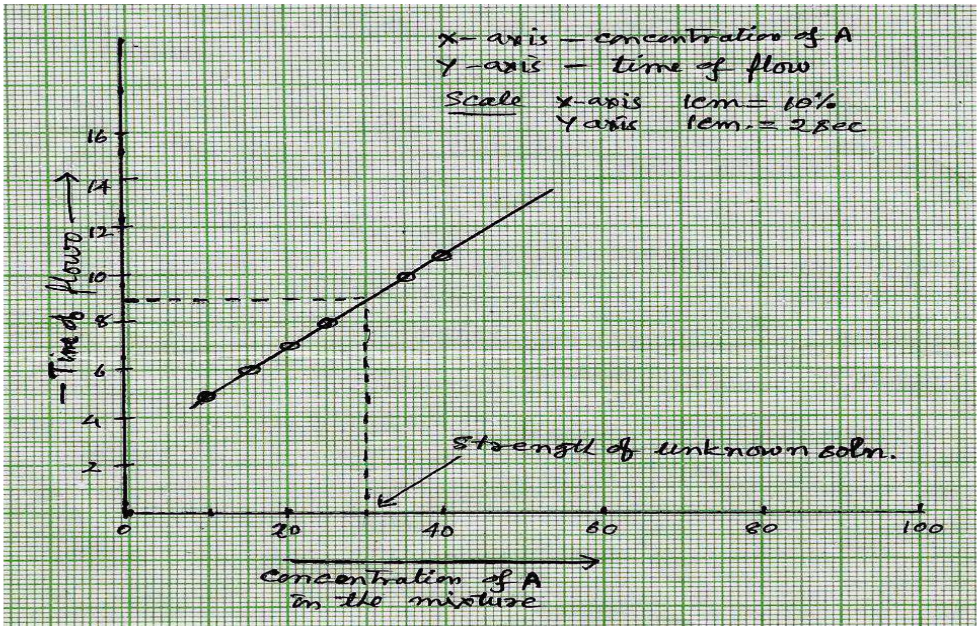


Fig 7.6 Graph plotting

7.9 SAFETY PRACTICES

General: Never work in the laboratory alone. Avoid unnecessary flames. Check the area near you for volatile substances before lighting a burner.

Chemicals:

Handle every chemical with care. Avoid contact with skin and clothing. Wipe up spills immediately, especially near the balances and reagent shelf. Replace caps on bottles as soon as possible. Do not use an organic solvent to wash a chemical from the skin as this may actually increase the rate of absorption of the chemical through the skin. Avoid the inhalation of organic vapours, particularly aromatic solvents and chlorinated solvents. Take care in smelling chemicals and do not taste them unless instructed to do so.

Disposal of chemicals:

Small quantities of non hazardous water soluble substances can be flushed down and drain with the large quantity of water. Hazardous waste, non hazardous solid waste, organic solvents and halogenated organic waste should be placed in the four containers provided.

Fire:

Burning clothing: Prevent the person from running and fanning the flames. Rolling the person on the floor will help extinguing the flames and prevent inhalation of the flames. If a safety shower is nearby hold the person under the shower until the flames are extinguished and chemical washed away. Do not use a fire blanket if the shower is nearby. Remove contaminated clothing. Wrap the person in a blanket to avoid shock. Get prompt medical attention. Be very careful using carbon dioxide extinguisher (the person may smother).

Burning reagents:

Extinguish all nearby burners and remove compitable material and solvents.use a dry chemical or carbondioxide fire extinguisher directed at the base of the flame. Do not use water.

Burns, either thermal or chemical:

Flush the burned area with water for at least 15 minutes. Resume if pain returns. Wash off chemicals with a mild detergent and water. No neutralizing chemicals. Creams, lotions or salves be applied. If chemicals are spilled on a person on a large area quickly remove the contaminated clothing while condor the safety shower. Get prompt medical attention.

Chemicals in the eye:

Flush the eye with copious amount of water for 15 minutes by placing the injured person face up on the floor and pouring water in the open eye. Hold the eye open to wash behind the eyelids. After fifteen minutes of washing obtain prompt medical attention.

Cuts: Minor cuts.

This type of cut is common in the laboratory and usually arises from broken glass. Wash the cut, remove any pieces of glass, and apply pressure to stop the bleedings. Get medical attention.

Major cuts:

If blood is spurting, place a pad directly on the wound. Apply firm pressure, wrap the injured to avoid shock, get immediate medical attention. Never use a tourniquet.

Poisons:

Call the immediate emergency number, which is normally 108.

7.10 SUMMARY

Laboratory glassware refers to a variety of equipment, traditionally made of glass, used for scientific experiments and other work in science, especially in chemistry. pipette, burette, test tube, boiling tube, beaker, measuring flask, conical flask, graduated cylinder, funnel steam bath etc. are used in chemistry lab experiments. For measuring fixed amount of a liquid either pipette or burette (sometimes graduated cylinders) are used. For titration purposes conical flask is used it may be 100 ml or 250 ml balance is used for weighing purposes. For the measurement of heat of various reactions, a thermos flask or a calorimeter is used. The resistance of a conductor is measured by means of Wheatstone bridge. Density can be measured with the help of density bottle.

UNIT 8: DETERMINATION OF SURFACE TENSION

CONTENTS:

8.1 OBJECTIVES

In this chapter students learn the following objectives.

- Objective of this chapter is to provide students with a concise and succinct detail on the basic fundamentals of the surface tension.
- Explain the use of stalagmometer and density bottle.
- Describe how to determine the surface tension of given liquid.
- Explain the determination of composition of solvent mixture.
- Explain the precaution taken during experiment.

8.2 INTRODUCTION

"The force in dynes action on the surface of at right angles to any line of unit length" As we all know the surface of the liquid remains in a state of tension because the molecules which are present in it are being constantly subjected to inward pull because of the unbalanced forces.

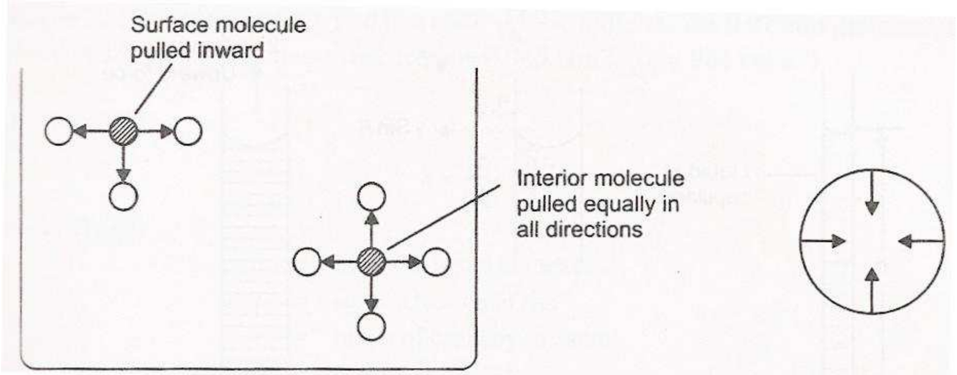


Fig 8.1 Surface tension is caused by the net inward pull on the surface molecules.

A molecular on the bulk is attracted from all sides hence net force on the molecule is new but this is not the case for a molecule which is situated at the surface. The surface molecules are pulled sideways by the surrounding molecules. Since the sideway forces are equal and opposite, fig 8.1 in magnitude so they cancel each other. But the inward pull is there. Thus the tension at the surface is known as surface tension.

The surface tension is represented by the symbol γ, since it is a force; its unit is dynes per centimeter.

Apparatus: Stalagmometer, thermometer, density bottle, balance, beaker etc.

When liquid is allowed to how through the stalgmemeter then $\gamma \alpha w$. That is weight (w) of liquid falling.

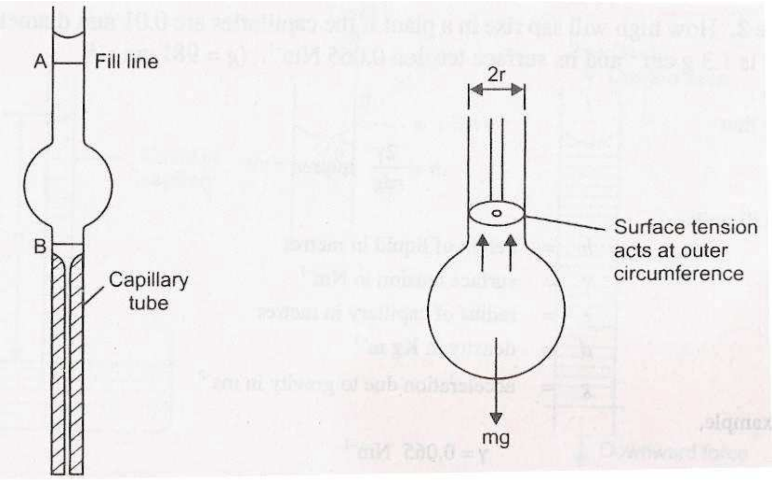


Fig 8.2 Stalagmometer

From a capillary tube held vertical, is approximately proportional to surface tension of the liquid. Hence if surface tensions of two liquids be γ_1 and γ_2 and w_1 and w_2 be the mean weights of their drops falling from the same capillary tube,

Then

$\gamma_1/\gamma_2 = w_1/w_2$

the drop falls out from the capillary when its weight becomes equal to $2\pi r\gamma$, where r is radius of the capillary tube

Stalagmometer:

The instrument used for determining surface tension in the laboratory is known as stalagmometer. It consists of a pipette with a capillary outflow tube, the end of which is flattened out. This is done to give a larger droping surface. The surface is carefully ground flat and polished. There are two marks, one just above the bulb and the other is just below (x and y) fig 8.2 precautions while using stalagmometer:

The stalagmometer should be carefully washed with a solution of chromic acid and with distilled water to remove grease like things. Finally it is washed with alcohol and dried. The tip of the lower end should not come in contact with hand, desk or some other thing, otherwise it will be contaminated with a trace of grease. Even slight traces of grease may alter the size of the drops, hence their number. Also the stalagmometer should be held vertical and not shaken, otherwise the drop will fall out even before attaining maximum size.

You must also keep in mind that the rate of flow of the liquid through the tip of stalagmometer should not be fast. It should be about 12-18 drops per minute. If the rate of flow is greater, then it can be decreased by attaching a piece of rubber tubing with a screw pinch cock to the open end and adjusting the pressure, so that only 12-18 drops fall out per minute.

Once this adjustment of pressure is done, it should be kept unchanged during the whole experiment.

The stalagmometer is washed with solution of chronic acid, then with water and finally with alcohol and dried. The rubber tubing with a screw pinch cock on it is used to regulate the flow of liquid by limiting the influx of flow of air.

Fill the stalagmometer with water dipping it in a beaker containing water and sucking till the water rises above the mark x (fig 8.2). Now bring the level of water to mark x. open the pinch cock and adjust it so that the rate of flow of drops is about 12-18 drops per minute. When this is adjusted, refill the stalagmometer with distilled water as above and without changing the pressure i.e. does not disturb the pinch cock throughout the experiment. Then start counting number of drops when meniscus passes the upper mark x and stop when it just crosses the lower mark y. repeat the procedure 3-4 times.

Now remove the rubber tubing from the stalagmometer and rinse it with the experimental liquid. Now fill the stalagmometer with the liquid. Adjust the pinch cock again so that 12-18 drops fallout per minute and count the number of drops for the flow of liquid from x to y. Repeat the process 3-4 times.

8.3 EXERCISE (ORGANIC LIQUID, ALCOHOL)

Object: To determine the surface tension of the given liquid (alcohol) by drop weight method

Method: The liquid whose surface tension is to be determined is sucked from the rubber tubing above the mark x and number of drops are counted when the liquid level moves from x to y. suppose the volume of the liquid from x to y is V and number of drops formed in this volume V are n then volume of one drop will be V/n_1 and weight of one drop $W_1 = \frac{V}{n1}$ x d_1 where d_1 is density of the liquid.

The same procedure is adopted for water. In case of water if in the volume V i.e. when water level moves from x to y if n_2 number of drops are formed and density of water if d_2 then weight of one drop of water will be $W_2 = \frac{V}{n2} d_2$

Hence $W_1/W_2 = \gamma_1/\gamma_2 = V/n_1.d_1/V/n_2.d_2$

$= n_2d_1/n_1d_2$

So $\gamma_1 = \frac{n2d1}{n1d2}\gamma_2$

This is the formula used for calculating surface tension of a liquid. The density of the liquid and water are measured by density bottle and γ_2 surface tension of water is taken from standard table.

Determination of density:

Density of a liquid is mass per unit volume. It is measured by using density bottle (fig 8.3). For measuring density of a liquid the density bottle is washed with chromic acid solution and then with distilled water and finally with alcohol. It is then dried. The density bottle is then weighed. It is then filled with distilled water and again weighed. It is then emptied of water, washed with alcohol and dried. The density bottle is then filled with experimental liquid and weighed again.

Observations:

Room temperature= t^0C

Weight of empty density bottle= w_1 gm

Weight of density bottle and water = w_2 gm

Weight of density bottle and liquid= w_3 gm

S. No.	**liquid**	**no of drops**	**Mean value**	
1	water	1	n_1=	
		2		
		3		
2	Liquid	1	n_2=	
		2		
		3		

Calculations:

$$\frac{Density\ of\ liquid(d_2)}{density\ of\ water\ (d_1)} = \frac{Weitht\ of\ liquid}{Weight\ of\ water}$$

$$= \frac{(w_3 - w_1)}{(w_2 - w_1)}$$

Hence surface tension of liquid

$\gamma_2 = \frac{n_1d_2}{n_2d_1}\gamma_1$

Surface tension of water can be had from standard table.

Result: The surface tension of the given liquid is dynes/cm at t^0C.

Precautions:

1. The stalagmometer should be washed properly with chromic acid
   water and finally with alcohol
2. The stalagmometer should be held vertically.
3. The tip of the stalagmometer should not come in contact with hands or working table.
4. The drops should be allowed to fall off from stalagmometer tip under their own weight and should not be pushed away by kinetic flow.
5. The rate of flow of liquid be 12-18 drops per minute.

8.4 EXERCISE (DETERMINATION OF COMPOSITION OF SOLVENT MIXTURE)

Object: To determine the composition of the given mixture of two components A and B.

Apparatus: Stalagmometer, thermometer, balance density bottle, beakers etc.

Theory:

A number of solutions of A and B are prepared. Suppose we have to determine the composition of sucrose solution. Then prepare sucrose solution of different concentration say 10 gm of sucrose and 90 gm water i.e. 10% of sucrose solution, 20 gm of sucrose and 80 gm of water i.e. 20% of sucrose solution and so on. Now number of drops in each is determined as usual. A graph is then plotted between no of drops (or surface tension) and concentration of one liquid say water (A). the number of drops of the unknown mixture is also determined. It's composition can be determined from the graph.

Procedure: Prepare 5%, 10%, 15%, 20%, 25%, 30% mixture of sucrose in water in beakers. Wash the stalagmometer with chronic acid solution. Then with water and finally with alcohol and dried. Attach a small piece of clean rubber tube to the upper end of the stalagmometer. The rubber tubing with a screw pinch cock on it is used to regulate the flow of liquid, by limiting the flux of air.

Now fill the stalagmomete with say first with 5% solution of sucrose by dipping it in a beaker containing the 5% solution and sucking till the solution rises above the mark x. now bring the level of solution to the x. open the pinch cock and adjust it so that the rate of flow of drops is about 12-18 drops per minute. When it is adjusted, refill the stagmometer with 5% solution without changing the pressure. Now start counting the drops when meniscus passes from the upper mark x and stop when it just crosses the lower mark y. Repeat this process for 5% solution 3-4 times.

Now the rubber tubing is removed from the stalagmometer and rinse with 10% solution. Now repeat the process you have followed for 5% solution. Apply the same procedure for all the solutions prepared above and count the number of drops for each solution. The number of drops of unknown solution is also counted.

Observation:

Room temperature = t^0C

Sl. No	Composition of Sucrose (A)	Mixture water B	No of drops
1	5%	95%	
2	10%	90%	
3	15%	85%	
4	20%	80%	
5	25%	75%	
6	30%	70%	

Table 8.1

Calculations: Plot of a graph between composition of sucrose A (X-axis) and number of drops Y-axix. The point corresponding to the number of drops of the unknown composition is found. From that point draw a perpendicular on the composition axis, the value will give the required concentration.

Result: The percentage composition of the given mixture is = % of A (in this case sucrose) and % of B (water).

Precautions:1. The stalagmometer should be washed properly with chromic acid water and finally with alcohol
2. The stalagmometer should be held vertically.
3. The tip of the stalagmometer should not come in contact with hands or working table.
4. The drops should be allowed to fall off from stalagmometer tip under their own weight and should not be pushed away by kinetic flow.
5. The rate of flow of liquid be 12-18 drops per minute.

Viva voce

1.Define surface tension?
2.Unit of surface tension?
3.What is the effect of temperature on surface tension?
4.Why stalagmometer should be kept vertical during the experiment?
5.What is the relation between surface tension and intermolecular attractional forces?
6.How density of a liquid is measured?

UNIT 9: DETERMINATION OF VISCOSITY

CONTENTS:

9.1 OBJECTIVES

In this chapter students will learn the following objectives.

- Objective of this chapter is to provide students with a concise and succinct detail on the basic fundamentals of the viscosity.
- Explain the use of Ostwald's viscometer and principal.
- Describe how to determine the viscosity of given liquid like cane sugar solution .
- Determine the composition of the given mixture consisting of two liquids A & B by viscometer.
- Explain the various precautions taken during experiment.

9.2 INTRODUCTION

Some liquids like water, alcohol move very fast, on the other hand liquids like honey, glycerol etc move very slowly. The property of the liquid which determines its flow is termed as viscosity. Thus we can say that viscosity is a property of liquid which retards its flow.

When temperature is applied to the liquid its intermolecular attractions forces are weakened, because kinetic energy of molecules increases. As viscosity depends on intermolecular forces, hence by the application of temperature viscosity decreases.

The unit of viscosity is poise. Scientist Poiseuille, who did pioneer work in the field of viscosity, to honour him unit of viscosity is poise. Smaller unit of viscosity are centipoise and millpoise. Viscosity is represented as η (eita).

Coefficient of viscosity:

If a liquid is allowed to flow on a surface each layer moves parallel to its adjacent layer without intermixing. The unparallel flow of layers is called turbulent flow. In the laminar flow the force F required to maintain a steady difference v between velocities of two adjacent layers is directly proportional to v, and area A of the surface of contact of two layer and inversely proportional to distance x between them. Hence

$F \propto A.v/x$

or $F = \eta\, Av/x$

Here η is called coefficient of viscosity of the liquid if A= 1 sq. cm., v=1 cm/sec and x=1 cm then $F=\eta$. Hence η is defined as the force necessary to maintain a velocity difference of unity between two adjacent parallel layers of liquid, one cm apart and having area of surface of contact unity.

The pressure p at any instant driving the liquid of coefficient of viscosity η through the capillary tube depends upon the difference of the height h, in the levels of liquid in the two limbs, the density d and the gravitational force g.

that is $p \propto hdg$

from equation 9.1

$\eta \propto p.t$

$\therefore\ \eta \propto hdgt$

If η_1 and η_2 be the viscosities of the two liquids under study and d_1 and d_2 be their respective densities and t_1 and t_2 be the respective time of flow the same volume

Then $\eta_1 \propto g_1 d_1 t_1$

And $\eta_2 \propto g d_2\, t_2$

Since same apparatus is used for both the liquids

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \qquad \text{.................9.3}$$

Thus by determining the densities and the time of flow of the two liquids, the coefficient of viscosity of one of them can be easily calculated, provided the coefficient of viscosity of the other liquid is known.

Description of the apparatus:

Ostwald’s viscometer: The apparatus generally used for the determination of coefficient of the viscosity of liquid is known as Ostwald’s viscometer as it was designed by Ostwald. It is shown in fig 9.1.

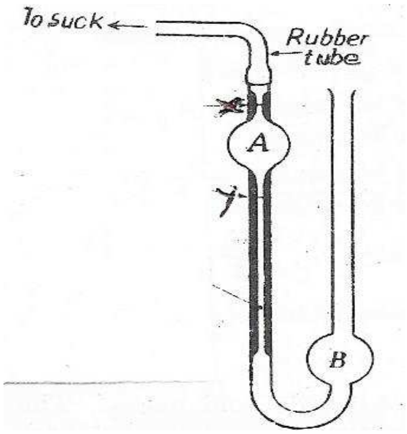


Fig 9.1 Ostwald's viscometer

The viscometer consists of a capillary tube connected at its upper part with a bulb A and at its lower part with a wider U-tube provided with a bulb B. Two marks x and y are etched on the capillary tube above and below the bulb A.

Cleaning of viscometer:

The viscometer should be cleaned thoroughly so that there are no obstructions in the capillary tube. It must be free from any greasy material. The viscometer is cleaned with chromic acid by filling with the acid which is prepared by reaction between potassium chromate and concentrated sulphuric acid.

The acid solution is kept in the viscometer for some hours. It is washed with water then with alcohol. It is then dried.

Density of the liquid is measured with the help of density bottle. Density of the liquid is mass per unit volume. The density at a given temperature means the relative density at that temperature with respect to the density of water. For all practical purposes, the density of water is taken to be unity at all temperatures.

9.3 EXERCISE CANE SUGAR SOLUTION OR GLYCEROL (MORE THAN 5%)

Object: To determine viscosity of the given liquid (say cane sugar solution) at room temperature.

Apparatus: Viscometer, unknown liquid, stop watch, distilled water, density bottle, pipette etc.

Formula used: $\eta_l = (d_l t_l / d_w t_w)\, \eta_w$

Where η_l d_lt_l are coefficient of viscosity, density and time of flow respectively of the experimental liquid and η_w, d_w and t_w are coefficient of viscosity, density and time of flow respectively of water.

Procedure: Clean the viscometer with chromic acid then wash with distilled water. It is finally washed with alcohol and then dried. A sufficient volume of distilled water is introduced by pipette in bulb B so that bend-portion of tube and half or little more than half of bulb B are filled up. Now suck up water until it rises above the mark x above the bulb A. Now bring water to touch the mark x and hold it there by placing your index finger at the top of the narrow limb. Remove your finger and start the stop watch. Stop it as soon as water touches the mark y. Repeat this process 3-4 times and take the mean value. The viscometer is kept in a thermostat for 10-15 minutes before the mean value, so that the contents acquire the room temperature.

Now remove water from the viscometer and dry it. Introduce in bulb B some cane sugar solution and rinse the viscometer. Now fill the viscometer with the experimental liquid and keep it also in the thermostat for 10-15 minutes, so that cane sugar solution attains room temperature. Note the time during the flow of solution between the marks x and y. Repeat the process 3-4 times and take the mean value.

Wash the density bottle and dry it. First weight it empty. Then fill it with water and finally with cane sugar solution and weight it both the times. Note the room temperature, by recording the temperature of water in the thermostat.

Observations:

1.Room temperature = t^0
2.Time of flow between x and y

Sl No.	Water		Cane sugar solution	
	Time of flow	mean	Time of flow	Mean
1		t_w		t_e
2				
3				
4				

9.3 Density of cane sugar solution and water.

Weight of empty density bottle = w_1 gm
Weight of density + water = w_2 gm
Weight of density bottle + cane sugar solution = w_3 gm

Calculation: Weight of water = w_2-w_1 gm

Weight of cane sugar solution= w_3-w_1 gm

Density of glycol = weight of glycol/weight of water x density of water d_w

= weight of glycol/weight of water = $(w_3-w_1)/(w_2-w_1)$

As density of water d_w =1

Coefficient of viscosity of glycol

$\eta_l = (d_l\ t_l) / (d_w\ t_w)\ \eta_w$

Now the viscosity of water η_w at t^0C from standard table, and substitute in the above expression, the value of η_l is calculated.

Result: The coefficient of viscosity of the given liquid at t^0C is poise.

Precautions:

1. Viscosity must be kept in vertical position.
2. Some volume of water and glycol should be taken in the viscometer.
3. Observe accurately when the meniscus of glycol and water just passing the upper and lower marks (x and y).
4. Before performing the experiment viscometer should be properly cleaned as described before.

9.4 EXERCISE

Object: To determine the composition of the given mixture consisting of two liquids A & B by viscometer.

Apparatus: Ostwald viscometer, density bottle, thermostat, thermometer, stop watch, beakers etc.

Theory: By plotting the values of time of flow of solution against their concentrations, we get a curve from which the concentrate of unknown solution is determined.

Procedure: The viscometer is thoroughly cleaned so that there are no obstructions in the capillary tube. It must be free from any greasy material. The viscometer is first cleaned by first keeping it filled with a solution of chromic acid, which is prepared by the reaction between potassium dichromate and sulphuric acid, for some hours. It is then washed with distilled water and finally with alcohol. It is then dried.

Now prepare a number of solutions by mixing the two liquids A and B in different proportions. The solutions are made up with 90%, 80%, 70%, 60%, 50%, 40%, 30%, 20%, 10% of A by volume. (90 ml of A and 10 ml of B in first case, 80 ml of A and 20 ml of B in the second case and so on.) The time of flow of each solution noted by means of Ostwald's viscometer, by allowing the solution to flow from x-mark to y- mark. Repeat this process 3 & 4 times and take the mean value. Before noting the time, the viscometer is kept in a thermostat for 10.to15 minutes, so that the contents acquire the room temperature. The time of flow for the unknown solution is also measured, as usual.

If we are to calculate the viscosity of the liquids then the density of each solution and that of unknown solution is also determined.

Observations: **Room temperature = t^0C**

Sl. No.	Percentage of components		Time of flow in secs
	A	B	
1	90	10	
2	80	20	
3	70	30	
4	60	40	
5	50	50	
6	40	60	
7	30	70	
8	20	80	
9	10	90	
10	Unknown solution		

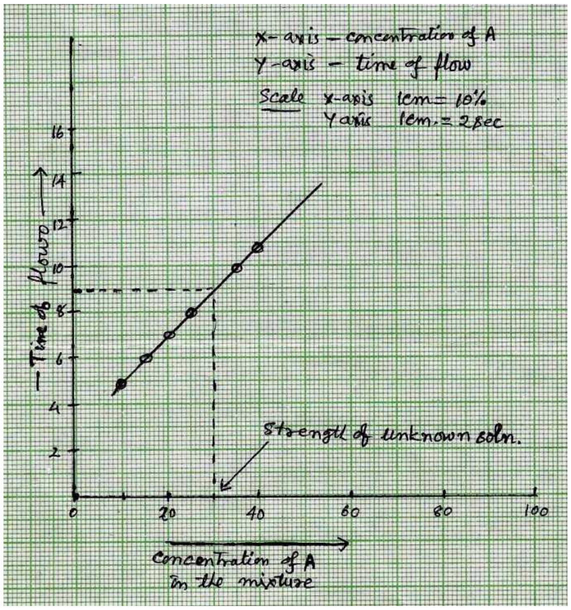


Fig 9.2 strength of unknown solution

Conclusions:

A curve is plotted between the concentration of one component say A and time of flow in seconds. You will see that a straight line is obtained (fig 9.2). The composition of unknown solution is calculated by locating and marking the point on the straight line corresponding to its measured time of flow. A perpendicular is drawn from that point on the concentration axis, from which the composition of unknown solution can be read directly.

Result: The composition of given mixture is ……..% of A and ……..% of B

Precautions:

Viscosity must be kept in vertical position.

5.Same volume of liquids should be taken in the viscometer.

6.Observe accurately when the meniscus just passing the upper and lower marks (x and y).

7.Before performing the experiment viscometer should be properly cleaned as described before.

Viva–Voce

1. Define the term coefficient?
2. What is the unit of coefficient of viscosity?
3. Why relative viscosity has no unit?
4. What is the effect of temperature on coefficient of viscosity? If decreases why?
5. Why unit of viscosity is poise?

UNIT 10: pH MEASUREMENT

CONTENTS:

10.1 OBJECTIVES

In this chapter students learn the following objectives.

- Objective of this chapter is to provide students with a concise and succinct detail on the basic fundamentals of the pH.
- Explain the methods of determination of pH.
- Explain the use of various indicators.
- Describe how to measurement the pH of simple solution (aq. Strong acid/ strong base or weak acid / weak base at different dilution).
- Explain the various precautions taken during experiment.

10.2 INTRODUCTION

pH value

Sorenson (1909) expressed the hydrogen ion concentration in solution in term of a number called pH which can be defined as the logarithm of reciprocal of hydrogen ion concentration.

Mathematically it can be expressed,

$$pH = \log_{10}\frac{1}{H^+} = \log_{10}\frac{1}{C_{H+}}$$

$$= -\log_{10}[H^+] = -\log 10\, C_H^+$$

For pure water

$$H_2O = H^+ + OH^-$$

Ionic product of water $K_w = C_H^+ . C_{OH}^-$

At 25^0 C Kw = 10^{-14}

So $C_H^+ = C_{OH}^- = 10^{-7}$ gm. Ion /litre

And pH = $-\log_{10} 10^{-7} = 7$

H^+	=	10^{-0}	10^{-1}	10^{-2}	10^{-3}	10^{--4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
pH	=	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14

← acidic solution → ↓ neutral ← alkaline solution →

Hence

For neutral solution: $C_H^+ = 10^{-7}$ and pH = 7

For acidic solution: $C_H^+ > 10^{-7}$ and pH > 7

For alkaline solution: $CH^+ < 10^{-7}$ and pH< 7

Methods of determining pH

To determine pH value you can use the following methods:

(1) Conductivity method
(2) Potentiometric method
(3) Catalytic method
(4) Calorimetric method
(5) E.M.F. method

Before determining the pH value of a given solution by any method you should have some knowledge of buffer solutions. The solution which is capable of opposing any change in its pH caused by addition of acid, alkali or water within a certain limit are defined as buffer solutions or in other words buffer possesses reserve acidity or alkalinity.

Buffer solution generally consist of a weak acid and one of its salt or weak base and one of its salts, There are few cases of buffer which are composed of strong acid and one of its salt, such as HCl + KCl . The resistance offered by buffer solution against change in its pH is called buffer action.

Buffer solutions can be obtained by mixing fixed amount of weak acid and one of its salt from pH value one to ten.

The pH of a buffer solution is controlled by the ratio of salt to acid or base. Hence buffer of different pH values can be prepared by varying this ratio. In this regard the following equations are of great importance.

(a)Buffer composed of weak base and its salt:-

$$pH = pK_a + \log_{10} \frac{conc.of\ salt}{conc\ of\ acid}$$

Where K_a is dissociation constant of weak acid.

(b) Buffer composed of weak base and its salt :-

$pH = pK_w - pK_b - \log_{10} \frac{conc.of\ salt}{conc\ of\ base}$

Where K_w is ionic product of water and K_b is dissociation constant of weak base.
For example if 4.7 ml N/5 HCl is added to 25 m N/5 KCl and the mixture is diluted to 100 ml, pH of the solution will be one, Similarly if equal part of M/40 $NaHCO_3$ and M/40 Na_2CO_3 are mixed its pH will be ten.

Universal indicator: It consists of a mixture of indicators which goes through a series of colour change with pH and thus helps in selecting the appropriate indicator for determining pH of a solution by indicator method, it tells approximate value of pH.

Calorimetric method:

The method is based on the fact that indicator changes its colour according to pH of the solution been in which it had been added. Hence from the color variation of indicator in a given solution , the pH can be determined.

This method employs a number of buffer solution of known pH and a suitable indicators.

At first the approximate value of pH of the given solution is determined with the universal indicator which is a mixture of several indicators to select approximate indicator. Then a definite amount pf appropriate indicator is added to a certain volume of the test solution and a colour is developed which is solution then matched against the shades produced by the same amount of the same indicator added in the same volume of a series of suitable chosen buffer solution of known pH. The buffer solution which gives the same shade as the test solution has the same pH.

For more accurate pH determination (within 0.5 to 0.1 unit)indicators of short working pH ranges are prepared so as to produce more distinct colour changes .the pH ranges of indicators which are generally used in pH determination can be known from the following tables :

Indicator	**pH-range**	**Colour – change**
Metacrisol purple	1.2 -2.8	red to yellow
Methyl violet	0.3 – 3.2	yellow to violet
Methyl orange	3.1 – 4.4	red to orange
Bromophenol blue	3.6 - 4.6	yellow to blue
Methyl red	4.2 –6.3	red to yellow
Bromocresol green	4.0 – 5.6	yellow to blue
Phenol red	6.8 – 8.4	yellow to red

Phenolphthlien	8.2 – 10.0	colorless to pink

10.3 EXERCISE (MEASUREMENT OF PH OF SIMPLE SOLUTION (AQ. STRONG ACID/ STRONG BASE OR WEAK ACID / WEAK BASE AT DIFFERENT DILUTION)

Object- To determine the pH of the given solution by indicator method (using buffer solutions of known pH).

Apparatus used: Test tube, indicators, pipette, burette, Test tubes etc.

Procedure:

To a small portion of the test solution, add a few drops (5 drops) of the universal indicator and observe the color change. Then by referring to the colour chart and find the approximate value of pH of the solution.

Let the pH as indicated by the universal indicator lies within 3.2 and 4.5 then to find out the correct pH value, you must select an appropriate indicator having short working pH range including the pH limit ie, 3.1 to 4.5. From the inspection of the table, the suitable indicator will be methyl orange.

Prepare a series of buffer solutions (of known pH value differing by .1 unit covering the pH range 3.1 to 4.5) by mixing a salt and a weak acid (or a weak base) in a definite ratio which can be calculated by the equation described earlier.

Now arrange ten or more test tubes of same dimensions in a rack. Place in each of these in turn 5 ml of buffer solution of definite value of pH value, ie, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, 4.0, 4.1, 4.2, 4.3, 4.4, 4.5. Mark the pH value on the test tubes. To each test tube, add .5 ml of methyl orange solution. Observe the different shades of colour from red to orange.

Now 5 ml of test solution in a test tube of same shape and size and 5 ml of same indicator (methyl orange). The color produced in the test solution is then matched with the colours produced in buffer solutions. When complete match is found, the test solution and the corresponding buffer solution have the same pH. If complete match is not found, but the colour lies between those of two successive standard colours then pH value will lie between those two standards.

Precautions:

1. While preparing buffer solutions of different pH, there should be correct weighing.
2. Measurement of volume should be proper

3. If pH meter is used it should be first standardized by taking a buffer of known pH.

VIVA—VOCE

1. Define pH.
2. What are buffer solutions?
3. How buffer solution maintains their pH value,
4. Why water is said to be neutral?
5. What is the equation relating hydrogen ion concentration and Ph.?

UNIT 11: THERMOCHEMISTRY

CONTENTS:

11.1 OBJECTIVES

In this chapter students learn the following objectives.

- Explain basic principle of thermochemistry.
- Describe the experiment related to heat capacity measurement.
- Explain the experiment related to measurement of enthalpy of solution.
- Explain the enthalpy of neutralization for weak acid with strong base or weak base with strong acid Enthalpy of ionization.
- Explain the various precautions taken during experiment.

11.2 INTRODUCTION

Thermochemistry is the branch of physical chemistry which deals with the heat changed by chemical reaction.

Internal energy:

Every substance has a definite amount of energy is known as internal energy E. its exact value cannot be determined, but the change in internal energy, ΔE, can be accurately measured experimentally.

$\Delta E = E_{products} – E_{reactants} = E_P - E_R$

When ΔE is positive, the reaction is endothermic and when ΔE is negative reaction is exothermic.

The energy changes are usually expressed in calorie (cal) kilo calorie (1 kcal = 1000 cal), Joule (J) and kilojoule.

The change in internal energy (E) is the heat change accompanying a chemical reaction at constant volume.

The enthalpy of a system is defined as the sum of internal energy and the product of its pressure and volume.

Thus H= E+PVIt is also called heat content.

Heat capacity of a system is the heat absorbed by unit mass in raising its temperature by one degree at a specific temperature.

Molar heat capacity of a system is defined as the amount of heat required to raise the temperature of one mole of the substance (system) by one degree.

11.3 EXERCISE: TO DETERMINE WATER EQUIVALENT OF CALORIMETER

A Calorimeter or a thermos flask:

For the measurement of heat of various reactions, we can suitably use a thermos flask or a calorimeter. A calorimeter is suitable for general experiments with solutions. It may be constructed by loosely packing the space between two large boiling tubes or two beakers with cotton wool. Though the modern vacuum flask has merit of very good insulation, but the narrowed neck of the ordinary thermos type prevents the use of an efficient stirrer, and if mixing is done by shaking, the water equivalent becomes large and quite indefinite in value.

The water equivalent or heat capacity of a calorimeter is defined s the number of calories required to heat the calorimeter by 1^0C. If M is the mass of the calorimeter and S be its specific heat then MS will be the water equivalent of the calorimeter.

An unsilvered, straight sided Dewar flask is shown in fig 11.1. It avoids the serious diadvantage without serious loss of heat insulation. Its transparency is quite invaluable in experiments on heat of solution etc. the vessel should be closed with a coak or rubber cock, groved for the stirrer S, and carrying a shortwide tube t, through which passes an accurate thermometer T having accuracy of 0.1^0. The thermometer is supported externally by a retort clamp.

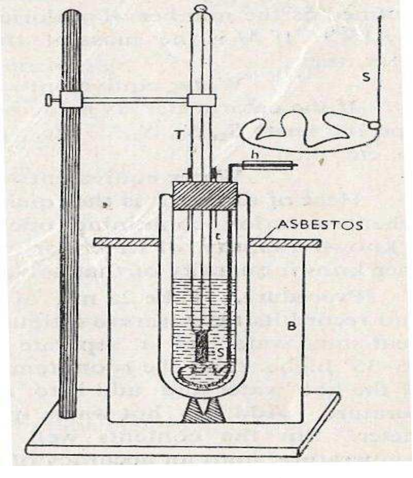


Fig 11.1 Devar flask

The tube t should be stoppered with a plug of cotton wool and serves as inlet for the introduction of liquids or solids into the calorimeter. The stirrer S should be quite efficient and may be formed of bent copper or silver wise a shown in the figure. A sleeve of stout rubber or ebonite tubing n serves as a heat insulating handle. The empty glass beaker B placed as a shield round the calorimeter usually improves the regularity of the temperature observations.

Apparatus: Calorimeter, thermometer, stirrer, water heater, pipette, burette, beaker

Theory: During the heat changes, the calorimeter will also take up some of heat evolved, which should be taken into account by taking into account by determining the water equivalent or heat capacity of the calorimeter.

If M is the mass of calorimeter and S the specific heat then water equivalent of calorimeter will be MS.

Procedure:

Take 25 ml of distilled water in the calorimeter and record its temperature accurately to its nearest 0.1^0. now heat 50-60 ml of water in a separate beaker to a temperature about $25\text{-}35^0$ higher than the room temperature. Now pipette about 25 ml of the hot water and add it to another beaker and read its temperature. Add this hot water quickly to the water in the calorimeter stir the contents well with stirrer. Read the highest temperature, upto an accuracy of 0.1^0 attained immediately after mixing.

Observations:

Volume of cold water taken = M_1 ml.
Volume of hot water mixed= M_2 ml.
Initial temperature of water = t_1^0 C
Temperature of hot water= t_2^0 C
Temperature of the mixed solution= t_3^0 C

Calculations:

Heat taken by calorimeter and water = $(W+M_1)(t_3-t_1)$ cal.

Here W is water equivalent of calorimeter.

Specific gravity of water is taken as unity (S=1)
Heat given by the hot water = $M_2(t_2-t_3)$ cal.
Heat taken up = Heat given out
$(W+M_1)(t_3-t_1) = M_2(t_2-t_3)$
$W(t_3-t_1) + M_1(t_3-t_1) = M_2(t_2-t_3)$
$W(t_3-t_1) = M_2(t_2-t_3) - M_1(t_3-t_1)$
So $W= [M_2(t_2-t_3) – M_1(t_3-t_1)]/(t_3-t_1)$

Since t_1, t_2, t_3, M_1 and M_2 are known; hence water equivalent of calorimeter can be calculated.

Result: Water equivalent of calorimeter =

Precautions:

1. Hot water must be added to cold water and that too immediately.
2. The temperature should be accurately recorded.
3. The calorimeter should be completely insulated.
4. The glass should be of high quality and so transparent that temperature can be easily read.

Exercise – 2

Object: To find out heat of dilution of sulphuric acid

Apparatus: calorimeter, thermometer, stirrer, beaker, pipette 5m and 25 ml water heater etc.

Theory: we know during the heat changes, calorimeter will also take up some heat, known as water equivalent of calorimeter. This heat must also be taken into account. If M is mass of the calorimeter and S be its specific heat, than its water equivalent is MS.

Procedure:

Now take 25 ml of distilled water in the calorimeter and note down its temperature to the nearest 0.1^0C, now pipette out exactly known quantity say 5 ml of sulphuric acid of known strength. Now pour this acid in the calorimeter by holding the tip of the pipette below the water surface and stir the contents of the calorimeter with the pipette itself. Continue stirring and note the temperature. Now record the maximum temperature attained.

11.4 EXERCISE (ENTHALPY OF SOLUTION)

Object: To determine enthalpy of solution of the given substance

Apparatus: Calorimeter thermometer, stirrer, beaker, burette, pipette, water heater etc.

Theory: The quantity of heat absorbed or evolved when one gram molecule of a substance is dissolved in a large excess of water or solvent, so that further dilution does not produce any more heat change, is known as heat of solution.

It is most important in expressing the heat of solution to state the exact condition of the solid substance, i.e., it contains water of crystallisation or not. The heat of solution is often quite different in the two cases.

Procedure: Take 25 ml. of distilled water in the calorimeter and record its temperature estimating it to the nearest 0.1^0C. Now heat some water in a separate beaker to a temperature about $250\text{-}35^0$ higher than the room temperature. Now pipette out 25 ml. of hot water and add it to another beaker and read its temperature. Add this hot water quickly to the water in the calorimeter. Stir the contents well with a stirrer. Read the highest temperature upto an accuracy of 0.1^0, attained immediately after mixing.

Now take 200 ml. of distilled water in the calorimeter. Record its temperature. Now add a known quantity of the given substance, say KCl. and dissolve it in the water present in the calorimeter, by means of a stirrer. Note the final temperature. Now repeat the above procedure by taking more quantity of substance, dissolve it in the water present in the calorimeter. If initially 1 gm of KCl was dissolved in water, now take 1.5 gm of KCl. Note the final temperature this time also.

Observations:

For water equivalent
Volume of water taken =M_1 ml.
Initial temperature of water= $t_1{}^0$C
Volume of hot water taken= M_2 ml
Temperature of hot water= $t_2{}^0$C
Final temperature of mixing= $t_3{}^0$C

For heat of solution:

Volume of water taken =M_3 ml
Initial temperature of water = $t_1{}^0$C
Amount of substance dissolved= W_1 gm.
Final temperature after mixing the substance= $t_4{}^0$C

Calculations:

1. For water equivalent of calorimeter

Heat taken by calorimeter and cold water
= $(W+M_1)(t_3-t_1)$ cal.
W is water equivalent of calorimeter, specific gravity of water is taken as unity (s=1).
Heat given by hot water
= $M_2(t_2-t_1)$
So $(W+M_1)(t_3-t_1) = M_2(t_2-t_3)$
So w = $\frac{[M_2(t_2-t_3)-M_1(t_3-t_1)]}{t_3-t_1}$

2. For heat of solution:

Heat absorbed by the solution after adding the substance

$$(M_3+W_1)(t_4-t_1)$$

Heat absorbed by the substance per litre

$$= \frac{(M_3 + W_1)(t_4 - t_1)x1000}{M_3}$$

= Q cal. (suppose)

If M is molecular weight of the substance, then heat of solution is then given by $\frac{QxM}{W_1}$ cal. per litre.

Result: The enthalpy of solution of the given substance = cal

Precautions:

1. The temperature should be accurately recorded.
2. The hot water must be added to cold water and that too immediately.
3. The calorimeter should be completely insulated.
4. The glass should be of high quantity and so transparent that the temperature can be read easily.

11.5 EXERCISE (ENTHALPY OF NEUTRALIZATION FOR WEAK ACID WITH STRONG BASE OR WEAK BASE WITH STRONG ACID ENTHALPY OF IONIZATION)

Object: To determine enthalpy of neutralisation of a weak acid by strong base. (Suppose weak acid acetic acid is being neutralised by strong base sodium hydroxide).

Apparatus used: Calorimeter, thermometer, beakers, stirrer, pipette, burette,water heater etc.

Theory:

The enthalpy of neutralisation is the quantity of heat evolved when one gram equivalent of an acid is neutralised by one gram equivalent of a base. When any strong acid in dilute solution is neutralised by any strong base in dilute solution of about the same concentration, the heat evolved is practically a constant quantity for strong acids and bases this quantity is 13,700 cal. this can be explained in the following way.

Strong acids and strong bases in dilute solution are almost completely ionized and the salt formed by their union is also completely ionised. So neutralization of strong acid say HCl by strong base say NaOH can be expressed in the following way

$HCl + NaOH = NaCl + H_2O + 13700$ cal

or$H^+ + Cl^- + Na^+ + OH^- = Na^+ + Cl^- + H_2O + 13700$ cal

or$H^+ + OH^- = H_2O + 13700$ cal

So heat of neutralization of strong acid with strong base is nothing but heat of formation of water from H^+ ions and OH^- ions. Here one gram equivalent of hydrogen ions combine with one gram equivalent of hydrogen ions, and hence heat evolved is always 13700 cal.

The enthalpy of neutralization of weak acids by strong bases or strong acids by weak bases is less than 13700 cal. Weak acids or weak bases are not completely ionised. In case of neutralization of weak acid by strong base (say CH_3COOH by NaOH), the incompletely ionised acid (CH_3COOH) has to become ionised before the hydrogen ion can combine with the hydrogen ion. The ionization of the weak acid usually takes place with absorption of heat and the heat change due to ionization occurring during the reaction adds algebraically to 13700 cal.

In the neutralisation of acitic acid by sodium hydroxide we have the following initial condition on mixing the two solutions

$NaOH + CH_3COOH$

$Na^+ + OH^- + (1-\alpha)\ CH_3COOH + \alpha\ H^+ + \alpha\ (CH_3COO^-)$.

Hence α is the degree of ionization of acetic acid.

As sodium acetate is completely ionized in the solution, the reaction yields $Na^+ + CHCOO^- + H_2O$

So enthalpy of neutralization of weak acid and strong base will be less than 13700 cal.

Procedure:

Take 25 ml of distilled water in the calorimeter…….

Now prepare extract 1Msolution of acetic acid and sodium hydroxide. Note down their initial temperature .Now take 100ml of 1Msolution of acetic acid in the calorimeter and add 100ml of 1Msolution of NaOH to it. Still well and record the maximum temperature after mixing .If the mixture of acetic acid and sodium hydroxide are not exact 1Mthen it will be very difficult to calculate heat of neutralization, if the M of acetic acid is more than 1M then after reacting with sodium hydroxide some acid will be there after addition in the calorimeter. Similarly if sodium hydroxide is stronger than 1Msome alkali will be left unreacted and the mixture in the calorimeter will be alkaline even after reaction .So whether it is acetic acid or sodium hydroxide the solution should be exactly1M.

Observations:

1.For water equivalent :
2.Volume of (cold)water taken = M_1ml
Initial temperature of water = t_1C
Volume of hot water = M_2ml
Temperature of hot water = $t_2{}^0$C
Final temperature after mixing = $t_3{}^0$C

3.For heat of neutralization

Volume of 1M CH3COOH = $m_3$ml

Volume of 1M NaOH = $m_4$ml at

Initial temperature of either CH3COOH or NaOH = t_4C

Final temperature after addition of CH_3COOH and NaOH = t_5c

4.Calculation:

For water equivalent calorimeter

(1)Heat taken up by calorimeter and water =$(W+M_1)(t_3-t_1)$ cal.

Here W is water equivalent of calorimeter.

Heat given out by hot water = $M_2(t_2-t_3)$

As heat given out = heat taken up

$(W+M_1)(t_2-t_1) = M_2(t_2-t_3)$

So $W = (M_2(t_2-t_3)-M_1(t_3-t_1))/(t_3-t_1)$

For heat of neutralization:

Rise in temperature after mixing 100m 1MNaOH in100ml 1M NaOH in 100ml 1M CH_3COOH

$= (t_5-t_4)$C

Heat given out by the above solution

$= (M_3+M_4+W)(t_5-t_4)$

= Q cal.(say) (Since every term is known Q can be calculated)

Hence molar heat of neutralization

= Qx1 mole/0.1 cal.

= Qx10 cal.

Result: Molar enthalpy of neutralization of weak acid (CH_3COOH) and strong base (NaOH) is ……..……cal.

Precautions:

1.Hot water must be added to cold water and that too immediately.

2.The temperature should be accurately recorded.

3.The calorimeter should be completely insulated.

4.The glass should be of high quality and so transparent that temperature can be easily read.

For preparing 1M solution of acetic acid and 1M solution of sodium hydroxide you will have to proceed as follows. Prepare a solution of acetic acid of approximately 1.5M in 250ml flask. To determine its strength you will have to titrate it against sodium hydroxide, which is standardized by titrating it against standard solution of oxalic acid. Standard solution of oxalic acid is prepared weighing certain amount and dissolving it in fixed quantity of solvent. Once strength of NaOH has been determined it can be used as titrate against acetic acid

Exercise:

Exercise-4

Object: To determine enthalpy of ionization of weak acid (say acetic acid).

The enthalpy of neutralization of weak acid by strong base or strong acid by weak base is less than 13700 cal.Weakacid or weak base are not completely ionized. In case of neutralization of weak acid by strong base (say CH3COOH by NaOH), the incompletely ionized acid (CH_3COOH)has to become ionized before the hydrogen ion can combine with the hydroxyl ion . The ionization of the weak acid usually takes place an absorption of heat, and the heat change due to ionization occurring during the reaction adds algebraically to 13700 cal.

In the neutralization of acetic acid by sodium hydroxide we have the following initial condition, onmixing two solutions

$NaOH + CH_3COOH$

$Na^+ + OH^- + (1-\alpha) CH_3COOH + \alpha H^+ + \alpha(CH_3COOH).$

Here α is degree of ionisation of acetic acid.

Assodium acetate is completely ionized in the solution, reaction yields

$Na^+ + CH_3COO^- + H_2O$

So in the reaction mixture following process occur:

(1-α) gram molecule of acetic acid ionized and if His the enthalpy of ionization of acetic acid per gram molecule, then (1-α) H is the heat change due to ionisation.

One gram equivalent of hydrogen ion combine with one gram equivalent of hydroxyl ion giving heat of evolution of 13700 cal.

The algebraic sum of the above two quantities is heat of neutralization measured, say H1.

That means $H_1=(1-\alpha)H + 13700$

$H = (H_1 - 13,700)/(1-\alpha)$

Here H is negative quantity that means ionization of acetic acid is accompanied by absorption of heat .Hence the value of H_1 will be less then13, 700 cal.

Procedure:

Measure first the enthalpy of neutralization of a normal solution of acetic acid by normal solution of sodium hydroxide. Take the enthalpy of neutralization of strong acid and strong base as 13,700 cal, or determine it experimentally.

Measure the degree of ionization of normal solution of acetic acid by any known method (say conductivity method), otherwise this can be taken from standard table.

Observations:

For water equivalent of calorimeter,

Volume of water taken = M_1 ml

Initial temperature of water = $t_1{}^0C$

Volume of hot water taken =M_2 ml.

Temperature of hot water = $t_2{}^0C$
Final temperature of the addition = $t_3{}^0C$
For enthalpy of ionization
Volume of 1M CH_3COOH solution =M_3 ml.
Volume of 1M NaOH =M_4ML
Initial temperature of acetic acid or sodium hydroxide = $t_4{}^0C$
Final temperature on mixing of CH_3COOH and NaOH = $t_5{}^0C$

Calculation:

Water equivalent of calorimeter = $(W= M_2(t_2-t_3)-M_1(t_3-t_1)/(t_3-t_1)$
Rise in temperature on mixing acetic acid and sodiumhydroxide= $(t_5-t_4)^0C$
Heat given by the solution=$(W+M_3+M_4)(t_5-t_4) = Q_1$ cal.
Molar heat of neutralization is =H_1-13,700/(1-α) cal.

Result: Enthalpy of ionization of acetic acid =……………………..cal.

Precautions:

1.Hot water must be added to cold water and that too immediately.
2.The temperature should be accurately recorded.
3.The calorimeter should be completely insulated.
4.The glass should be of high quality and so transparent that temperature can be eas

Viva voce

1. What is Thermochemistry?
2. Define enthalpy of a reaction.
3. What is heat capacity?
4. Define heat of solution.
5. Define heat of neutrilisation.
6. Why heat of neutrilisation of strong acid with strong base is always 13700 cal?
7. Why heat of ionization is negative quantity?
8. Why standard solution of sodium hydroxide cannot be prepared by weighing only?
9. What is primary standard?
10. How you will determine whether neutralization is complete or not?

11.6 SUMMARY

Thermochemistry is a branch of chemistry that qualitatively and quantitatively describes the energy changes that occur during chemical reactions. Energy is the capacity to do work. Mechanical work is the amount of energy required to move an object a given distance when opposed by a force. Thermal energy is due to the random motions of atoms, molecules, or ions in a substance. The temperature of an object is a measure of the amount of thermal energy it contains. Heat (***q***) is the transfer of thermal energy from a hotter object to a cooler one. Energy can take many forms; most are different varieties of potential energy **(***PE***)**, energy caused by the relative position or orientation of an object. Kinetic energy **(***KE***)** is the energy an object possesses due to its motion. The most common units of energy are the joule (J)**,** defined as 1 $(kg\cdot m^2)/s^2$, and the calorie**,** defined as the amount of energy needed to raise the temperature of 1 g of water by 1°C (1 cal = 4.184 J).

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