

Class XII

LABORATORY MANUAL

CHEMISTRY



Laboratory Manual

Chemistry

Class XII



राष्ट्रीय शैक्षिक अनुसंधान और प्रशिक्षण परिषद्
NATIONAL COUNCIL OF EDUCATIONAL RESEARCH AND TRAINING

FOREWORD

The National Council of Educational Research and Training (NCERT) is the apex body concerning all aspects of refinement of School Education. It has recently developed textual material in Chemistry for Higher Secondary stage which is based on the National Curriculum Framework (NCF)–2005. NCF recommends that children's experience in school education must be linked to the life outside school so that learning experience is joyful and fills the gap between the experience at home and in community. It recommends to diffuse the sharp boundaries between different subjects and discourages rote learning. The recent development of syllabi and textual material is an attempt to implement this basic idea. The present Laboratory Manual will be complementary to the textbook of Chemistry for Class XII. It is in continuation to the NCERT's efforts to improve upon comprehension of concepts and practical skills among students. The purpose of this manual is not only to convey the approach and philosophy of the practical course to students and teachers but to provide them appropriate guidance for carrying out experiments in the laboratory. The manual is supposed to encourage children to reflect on their own learning and to pursue further activities and questions. Of course the success of this effort also depends on the initiatives to be taken by the principals and teachers to encourage children to carry out experiments in the laboratory and develop their thinking and nurture creativity.

The methods adopted for performing the practicals and their evaluation will determine how effective this practical book will prove to make the children's life at school a happy experience, rather than a source of stress and boredom. The practical book attempts to provide space to opportunities for contemplation and wondering, discussion in small groups, and activities requiring hands-on experience. It is hoped that the material provided in this manual will help students in carrying out laboratory work effectively and will encourage teachers to introduce some open-ended experiments at the school level.



21.5.08

PROFESSOR YASH PAL

Chairperson

National Steering Committee
National Council of Educational
Research and Training

New Delhi
21 May 2008

PREFACE

The development of the present laboratory manual is in continuation to the NCERT's efforts to improve upon comprehension of concepts and practical skills among the students. The present laboratory manual will be complementary to the textbook of Chemistry for Class XII.

The expansion of scientific knowledge and consequently the change in the system of education has led to the development of new methods of instructions. Today the stress is laid on the enquiry approach and discussion method instead of lecture method of teaching. Unfortunately, it is believed that study of chemistry means abstract thinking, writing long formulas and complex structures and handling complicated equipments. The reason behind such endeavour is that even well-endowed schools tend to give only the cosmetic importance to the laboratory work. Children's natural spirit of inquiry is often not nurtured.

The new syllabus of practical work in chemistry has been designed to cater to the needs of pupil who are desirous of pursuing science further. The fundamental objective of this course is to develop scientific attitude and desired laboratory skills required at this level. The practical syllabus includes content based experiments, which help in comprehension of the concepts.

The project work is expected to provide thrill in learning chemistry. It is expected to serve the real purpose of practical work, which means inculcating the ability to design an experiment, to make observations methodically and to draw conclusions out of experimental data. The real purpose of practical work should be to enable the students to represent the outcome of experiments logically to conclusion, with genuine appreciation of its limitation.

For each practical work, brief theory, material required, procedure, precautions and the questions for discussion are given in the book. The questions are aimed at testing learner's understanding of the related problems. However, teacher may provide help in case the problem is found to be beyond the capability of the learner. Precautions must be well understood by the learners before proceeding with the experiments and projects.

In order to provide some basic idea about the investigatory projects, a brief description of some investigatory projects is given in the book. However, this list is only suggested and not exhaustive. The students may select projects from subject area of chemistry, interdisciplinary areas or from the environment. While selecting a project, care should be taken to see that the facilities for carrying it out are available.

Appendices related to the chemical data and logarithmic tables are attached at the end of the book. International symbols for hazards and hazard warnings are given at several places in the book. It is expected that this will make the learners more careful about the environment and make them careful while dealing with the chemicals. Some non-evaluative learning material has been given in the boxes to provide interesting information related to the practical work.

It is a pleasure to express my thanks to all those who have been associated at various stages of development of this laboratory manual. It is hoped that this practical book will improve teaching learning process in chemistry to a great extent. The learners will be able to understand the subject well and will be able to apply the acquired knowledge in new situations. I acknowledge with thanks the dedicated efforts and valuable contribution of Dr Alka Mehrotra, **Coordinator** of this programme and other team members who contributed and finalised the manuscript. I especially thank Professor Krishna Kumar, **Director**, and Professor G. Ravindra, **Joint Director**, NCERT for their administrative support and keen interest in the development of this laboratory manual. I am also grateful to the participating teachers and subject experts who participated in the review workshop and provided their comments and suggestions which helped in the refinement of this manual and make it learner friendly. We warmly welcome comments and suggestions from our readers for further improvement of this manual.

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Do You Know

According to the 86th Constitutional Amendment Act, 2002, free and compulsory education for all children in 6-14 year age group is now a Fundamental Right under Article 21-A of the Constitution.

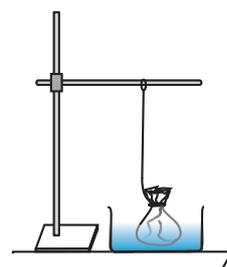
EDUCATION IS NEITHER A PRIVILEGE NOR FAVOUR BUT A BASIC HUMAN RIGHT TO WHICH ALL GIRLS AND WOMEN ARE ENTITLED

***Give Girls
Their Chance !***



UNIT-1

COLLOIDS



In a true solution, solute particles mix homogeneously with the molecules of the solvent and thus form a single phase. However, a colloidal solution is a heterogeneous system in which very fine particles of one substance disperse (**dispersed phase**) in another substance called **dispersion medium**. Particles of the dispersed phase do not form a single phase with the particles of the dispersion medium because of the fact that they are either very large molecules or essentially aggregates of small molecules. Colloidal particles are larger in size than simple molecules but small enough to remain suspended in the dispersion medium (10^{-9} – 10^{-6} m). Some examples of very large molecules which form colloidal dispersion are starch, gum and proteins, whereas colloidal sulphur is an example of aggregates of small molecules. Further, a heterogeneous system of a solid as dispersed phase and a liquid as dispersion medium is called a sol. Depending upon the nature of interaction between the dispersed phase and the dispersion medium, colloidal sols are divided into two categories, namely, **lyophilic** (solvent attracting) and **lyophobic** (solvent repelling). If water is the dispersion medium, the terms used are hydrophilic and hydrophobic. Egg albumin, starch and gum are lyophilic sols. Freshly prepared ferric hydroxide, aluminium hydroxide and arsenic sulphide sols are examples of lyophobic sols. A few methods of preparation of colloids are – chemical methods, electrical disintegration and peptization. In this unit you will learn to prepare both the types of sols. Also, you will learn a method of purification of sols.

EXPERIMENT 1.1

Aim

To prepare (a) lyophilic sol; and (b) lyophobic sol.

Theory

Since particles of dispersed phase in lyophilic sols have an affinity for the particles of dispersion medium, these sols are more stable as compared to lyophobic sols. Two factors responsible for the stability of sols are – charge and the solvation of the colloidal particles by the solvent. Stability of lyophilic sols is primarily due to the solvation of colloidal particles by the solvent whereas lyophobic sols are stabilised by the charge on the colloidal particles. Due to their charges, colloidal

particles remain suspended in solution and coagulation does not take place. These charges may be positive or negative. Some examples of negatively charged sols are starch and arsenious sulphide. Positively charged sol of hydrated ferric oxide is formed when FeCl_3 is added to excess of hot water and a negatively charged sol of hydrated ferric oxide is formed when ferric chloride is added to NaOH solution. The lyophilic sols are directly formed by mixing and shaking the substance with a suitable liquid. Lyophobic sols cannot be prepared by direct mixing and shaking. Special methods are employed to prepare these.

Material Required

	• Beaker (250 mL) : One		• Egg : One
	• Watch glass : One		• Sodium chloride : 5g
	• Porcelain dish : One		• Ferric chloride : 2g
	• Measuring cylinder : One (100 mL)		• Aluminium chloride : 2g
	• Pipette (10 mL) : One		• Starch/gum : 500 mg
	• Graduated pipette : One (20 mL)		• Arsenious oxide : 0.2 g

Procedure

A. Preparation of Lyophilic Sol

I. Egg Albumin Sol

- (i) Prepare 100 mL of 5% (w/v) solution of NaCl in water in a 250 mL beaker.
- (ii) Break one egg in a porcelain dish and pipette out the albumin and pour it in sodium chloride solution. Stir well to ensure that the sol is well prepared.

II. Starch/gum Sol

- (i) Measure 100 mL of distilled water with the help of a measuring cylinder and transfer it to a 250 mL beaker and boil it.
- (ii) Make a paste of 500 mg starch or gum in hot water and transfer this paste to 100 mL of boiling water with constant stirring. Keep water boiling and stirring for 10 minutes after addition of paste. To judge the efficacy of the prepared sol, you may compare it with the original paste prepared.

B. Preparation of Lyophobic Sol

I. Ferric hydroxide/Aluminium hydroxide

- (i) Take 100 mL of distilled water in a 250 mL beaker and boil it.

Aluminium
chloride



Arsenic
compounds



Hazard Warning

- While doing experiment do not eat, drink or smoke.

- (ii) Add 2g of ferric chloride/aluminium chloride powder to boiling water and stir it well.
- (iii) Take 100 mL of distilled water in another 250 mL beaker and boil it.
- (iv) Pour 10 mL of ferric chloride/aluminium chloride solution prepared in step (ii) drop by drop into the boiling water with constant stirring. Keep the water boiling till brown/white sol is obtained.

II. Arsenious Sulphide Sol

- (i) Transfer 100 mL of distilled water to a beaker of 250 mL capacity.
- (ii) Add 0.2 g of arsenious oxide to it and boil the content of the beaker.
- (iii) Cool and filter the solution.
- (iv) Pass hydrogen sulphide (H_2S) gas through the filtered solution till it smells of H_2S . (Use Kipp's apparatus to pass hydrogen sulphide gas).
- (v) Expel H_2S gas from the sol by slow heating and filter it.
- (vi) Label the filtrate as arsenious sulphide sol.

Precautions

- (a) While preparing colloidal solutions of starch, gum, ferric chloride, aluminium chloride etc., pour the paste or solution gradually into the boiling water with constant stirring. Addition of these substances in excess may cause precipitation.
- (b) Arsenious oxide is poisonous in nature; so wash your hands immediately every time after handling this chemical.



Discussion Questions

- (i) How will you differentiate between a true solution and a colloidal dispersion?
- (ii) Identify some sols (colloids) that you use in your daily life and mention their importance.
- (iii) How do colloids acquire a charge? Why is ferric hydroxide/aluminium hydroxide sol prepared in the experiment, positively charged while arsenious sulphide sol is negatively charged?
- (iv) What is coagulation? How is coagulation different from peptization?
- (v) How can you convert a colloidal dispersion of sulphur into a true solution?
- (vi) Out of lyophilic and lyophobic sols, which one can be easily converted into a gel and why?
- (vii) Differentiate between a gel and a sol.
- (viii) What are the applications of colloids in the field of Medicine, Defense and in Rocket Technology?

EXPERIMENT 1.2

Aim

To purify prepared sol by dialysis.

Material Required

	• Parchment/ cellophane paper	: One sheet (30 cm 30 cm)		• Colloidal dispersion of egg albumin	: Prepared in experiment 1.1
	• Trough	: One		• Distilled water	: As per requirement
	• Thread	: As per need		• Uranyl zinc acetate	: As per requirement
	• Test tubes	: Two		• Silver nitrate	: As per requirement

Procedure

- (i) Take a square sheet (30 cm 30 cm) of parchment/ cellophane paper.
- (ii) Soak the sheet in water and give it a conical shape.
- (iii) Pour the colloidal dispersion of egg albumin in the cone of parchment/ cellophane paper.
- (iv) Tie the cone with a thread and suspend it in a trough containing distilled water as shown in Fig. 1.1.

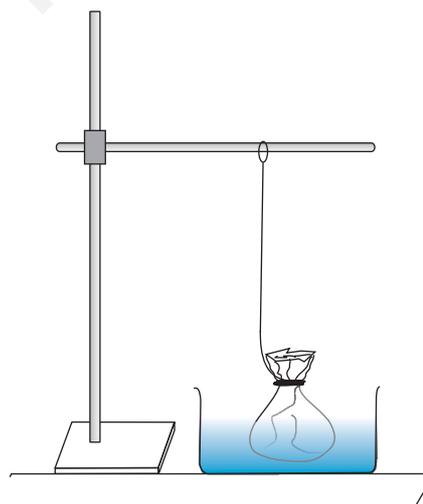


Fig. 1.1 : Purification of a colloid

- (v) After about half an hour, test for the presence of ions in the trough water.

- (vi) Change the water present in the trough after every half an hour till it is free of the impurities of Na^+ and Cl^- ions. To check the presence of Na^+ and Cl^- ions take water from the trough in two test tubes. To one test tube add uranyl zinc acetate and to the other add silver nitrate solution. A yellow precipitate with uranyl zinc acetate indicates the presence of Na^+ ions, while a white precipitate of silver nitrate indicates the presence of chloride ions.
- (vii) Note the time required for the purification of colloidal dispersion.

Note : In some cases, dialysis may be a very slow process. Therefore, in such cases, it is advisable to change the water of the trough twice or thrice till the colloidal dispersion is free of ions.

Precautions

- (a) For dialysis make the parchment bag air tight to prevent the entry of water into the bag. Keep the neck of the parchment bag above the surface of water.
- (b) Change the water in the trough from time to time during dialysis.



Discussion Question

- (i) How can you make the process of dialysis quick? What are the limitations of this technique?

EXPERIMENT 1.3

Aim

To study the role of emulsifying agents in stabilising the emulsions of different oils.

Theory

Emulsion is a type of colloid in which, both the dispersed phase and the dispersion medium are liquids. Here the dispersed phase and the dispersion medium are distinguished by their relative amounts. The one, which is present in smaller proportion, is called **dispersed phase**, while the other, which is present in relatively large quantity, is known as the **dispersion medium**.

When oil is shaken with water, a faint milky solution is often observed, which is unstable and is called an **emulsion of oil in water**. On standing, it gets separated into two layers, i.e. oil and

water. The mixing capacity of different oils with water is different. This mixing capacity of the oil in addition to its nature depends upon the method of shaking also (i.e. vigorous shaking or swirling).

The stability of an oil and water emulsion is increased by the addition of a suitable emulsifying agent such as soap solution. Soap contains sodium salt of long chain aliphatic carboxylic acids with the carboxyl group as the polar group, which decreases the interfacial surface tension between oil and water. Hence oil mixes with water and emulsification takes place. The concentration of soap required for complete emulsification is called **optimum concentration**. Any amount less or more than this optimum amount does not cause an effective stabilisation. In the presence of optimum amount of soap solution, oil in water emulsion is more stable and the separation of oil and water layers takes more time.

Material Required

	• Test tubes	: Six		• Soap/detergent	: 5g
	• Droppers	: Five		• Mustard oil,	
	• Test tube stand	: One		linseed oil,	
	• Glass rod	: One		castor oil and	: 10 mL each
	• Stop watch	: One		machine oil	brand

Procedure

- (i) Dissolve 1 g of soap/detergent in 10 mL of distilled water in a test tube with vigorous shaking and heat the content of the test tube if needed. Label it as 'A'.
- (ii) Take four test tubes. Mark these as B, C, D and E and to each of the test tubes, add 5 mL distilled water followed by 10 drops of mustard oil in test tube B, linseed oil in test tube C, castor oil in test tube D and machine oil in test tube E, respectively.
- (iii) Shake test tube B vigorously for five minutes, keep it in a test tube stand and simultaneously start the stopwatch. Record the time taken for the separation of the two layers.
- (iv) Repeat the same procedure with test tubes C, D and E and record the time for the separation of the layers in each case.
- (v) Now add two drops of soap/detergent solution from test tube 'A' into each test tube (B, C, D and E). Shake each test tube for five minutes and record the time of separation of the layers in each case again.
- (vi) Record your observations in a manner detailed in Table 1.1.

Table 1.1 : Emulsification of different oils by soap/detergent

Test tube specification	Name of oil used for emulsification	Time taken for the separation of layers	
		Without Soap/detergent	With Soap/detergent
B			
C			
D			
E			

Precautions

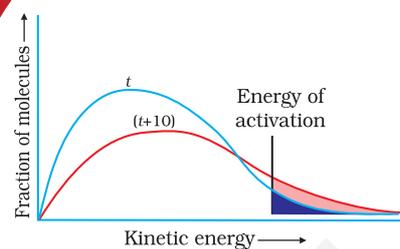
- Add equal number of drops of a soap/detergent solution to all the test tubes.
- To minimise the error in recording the time required for the separation of layers in different systems, shake all the test tubes for identical time span.
- Start the stopwatch immediately after shaking is stopped and stop it immediately when the two layers separate.

**Discussion Questions**

- Name a reagent other than soap, which can be used as an emulsifying agent in the **oil in water type emulsion**.
- Milk is said to be a stable emulsion. What provides stability to milk?
- Can two miscible liquids form an emulsion?
- Why do separation of layers of different oils forming an emulsion with water take different time?
- What are the points of similarity and dissimilarity among sol, gel and emulsion?
- Suggest a test to distinguish between **Oil in Water** and **Water in Oil** type of emulsions.
- Give some examples of emulsions that you come across in daily life.
- Dettol forms an emulsion in water. How does this emulsion get stabilised?

UNIT-2

CHEMICAL KINETICS



RATE of reaction can be measured either in terms of decrease in concentration of any one of the reactants or increase in concentration of any one of the products with time. For a hypothetical reaction,



$$\text{Rate of reaction} = \frac{[A]}{T} = \frac{[B]}{T}$$

Factors such as concentration, temperature and catalyst affect the rate of a reaction. In this unit you will learn the technique of determining the rate of a reaction and technique of studying the effect of concentration and temperature on the reaction rate.

EXPERIMENT 2.1

Aim

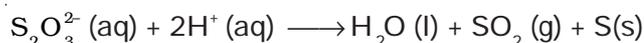
To study the effect of concentration and temperature variation respectively on the rate of reaction between sodium thiosulphate and hydrochloric acid.

Theory

Sodium thiosulphate reacts with hydrochloric acid and produces a colloidal solution of sulphur, which makes the solution translucent. The reaction occurs as follows:



Ionic form of the above reaction is written as:



The property of the colloidal solution of sulphur to make the system translucent is used to study the rate of precipitation of sulphur. The rate of precipitation of sulphur increases with an increase in the concentration of the reacting species or with an increase in the temperature of the system. With an increase in the concentration, the number of molecular collisions per unit time between the reacting species increase and consequently chances of product formation increase. This results in an increase in the rate of precipitation of sulphur. Similarly, on increasing the temperature, the kinetic energy of the reacting species increases, so the number of collisions that result in the formation of products increase leading to a faster rate of reaction.

Material Required



- Beaker (100 mL) : One
- Burette (50 mL) : One
- Pipette (25 mL) : One
- Pipette (5 mL) : One
- Burette stand : One
- Stop watch : One
- Thermometer (110°C) : One



- 0.1M Sodium thiosulphate : As per need
- 1.0 M Hydrochloric acid : As per need

Procedure

A. The effect of concentration on the rate of reaction

- (i) Take a trough and fill half of it with water. This will serve as constant temperature bath, maintained at room temperature.
- (ii) Rinse and fill the burette with 1.0 M HCl solution.
- (iii) Take a 100 mL beaker and make a mark 'X' in the centre of the outer surface of the bottom with the help of a glass marker pencil. Fill 50 mL of 0.1M sodium thiosulphate solution in it. Place the beaker in the trough. The mark 'X' will be visible to the naked eye on account of the transparent nature of the system. Allow the beaker to stand in the trough for a few minutes so that it attains the temperature of the bath.
- (iv) Add 1.0 mL of 1.0 M HCl solution with the help of a burette. Start the stopwatch when half the HCl solution i.e. (0.5 mL) has been transferred. Swirl the beaker while adding HCl.
- (v) Record the time required for the mark 'X' on the bottom of the beaker to become invisible (This is considered as a stage of completion of the reaction).
- (vi) Repeat the experiment by adding 2 mL, 4 mL, 8 mL and 16 mL of 1.0 M hydrochloric acid solution to fresh sodium thiosulphate solution every time and record the time required for the disappearance of the mark 'X' in each case separately.

Hydrochloric acid



B. The effect of temperature on the rate of reaction

- (i) Take 50 mL of 0.1M sodium thiosulphate solution in a 100 mL beaker, on the outer surface of the bottom of which a mark 'X' has been made. Keep the beaker in a thermostat maintained at 30°C. Add 5 mL of 1.0 M hydrochloric acid solution with swirling. Start the stopwatch immediately when half the amount (i.e. 2.5 mL) of hydrochloric acid has been transferred.
- (ii) Record the time at which the mark 'X' becomes invisible.
- (iii) Repeat the experiment at temperatures 40°C, 50°C, 60°C and 70°C using fresh sodium thiosulphate solution each

time and record the time required for the disappearance of the mark 'X'.

- (iv) Record your observations in Tables 2.1 and 2.2.
- (v) Plot two graphs, one for the volume of HCl added (which determines concentration of HCl) and the time taken for the mark to become invisible and the other between temperature and the time taken for the mark to become invisible. For plotting the graph, the variation in time is plotted on **x**-axis and the variation in volume or temperature is plotted on **y**-axis.

Note : *If thermostat (i.e. constant temperature bath) is not available for studying the rate of the reaction. Ordinary water bath may also be used for maintaining constant temperature but in this case heating of the bath from outside might be required for the adjustment of temperature. Water in the bath should also be stirred continuously.*

Table 2.1 : Effect of concentration of HCl on the rate of reaction between sodium thiosulphate and hydrochloric acid

Amount of $\text{Na}_2\text{S}_2\text{O}_3$ solution used each time = 50 mL
 Concentration of $\text{Na}_2\text{S}_2\text{O}_3$ solution = 0.1M, Room temperature = $^{\circ}\text{C}$
 Concentration of the HCl solution used in the reaction mixture = 1.0 M

Sl. No.	Volume of HCl added in mL	Time 't' in seconds for the mark 'X' to become invisible
1.	1.0	
2.	2.0	
3.	4.0	
4.	8.0	
5.	16.0	

Table 2.2 : The effect of temperature on the rate of reaction between sodium thiosulphate and hydrochloric acid

Volume of sodium thiosulphate solution used each time = 50 mL
 Volume of HCl used each time = 5 mL

Sl. No.	Temperature of the reaction mixture/ $^{\circ}\text{C}$	Time 't' in seconds for the mark 'X' to become invisible
1.	30	
2.	40	
3.	50	
4.	60	
5.	70	

Result

Write your conclusions on the basis of data in Tables 2.1 and 2.2.

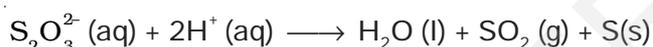
Precautions

- Start the stopwatch when half of the hydrochloric acid solution has been transferred to the reaction flask and stop the watch when the mark 'X' becomes invisible.
- If a constant temperature bath is not available to maintain the constant temperature, heat the water of the bath in which the beaker is kept from time to time with constant stirring, and remove the burner when the required temperature is attained.
- Select suitable scale for plotting the graph.



Discussion Questions

- (i) The reaction under examination is as follows:

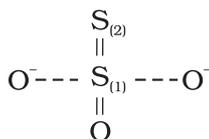


Write the conditions under which the rate law expression for this reaction can be written in the following manner.

$$\text{Rate of precipitation of sulphur} = k [\text{S}_2\text{O}_3^{2-}][\text{H}^+]^2$$

- Suppose the above rate law expression for the precipitation of sulphur holds good, then on doubling the concentration of $\text{S}_2\text{O}_3^{2-}$ ion and H^+ ion, by how many times will the rate of the reaction increase?
- Comment on the statement that for a given reaction, rate of the reaction varies but the rate constant remains constant at a particular temperature.
- How does the rate constant of a reaction vary with temperature?
- Devise an experiment to study the dependence of rate of precipitation of sulphur upon the nature of monobasic acid for the reaction given below :

$$\text{S}_2\text{O}_3^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l}) + \text{SO}_2(\text{g}) + \text{S}(\text{s})$$
- Why is the stop watch/stop clock started when half of the reactant is delivered into the beaker?
- The structure of $\text{S}_2\text{O}_3^{2-}$ ion is described as follows:



The two sulphur atoms are marked here as (1) and (2). Which of the sulphur atoms, according to you, is precipitated as colloidal sulphur? How can you verify your answer experimentally?

- (viii) What is the difference between the order and the molecularity of a reaction?
- (ix) The molecularity of a reaction can't be zero but the order can be zero? Explain.
- (x) Can the order of a reaction be a fractional quantity?
- (xi) Suppose the above reaction follows third order kinetics, then in what units, will the rate of the reaction and the rate constant be expressed?

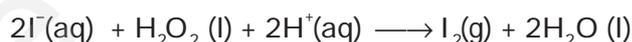
EXPERIMENT 2.2

Aim

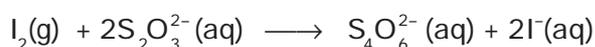
To study the effect of variation in concentration of iodide ions on the rate of reaction of iodide ions with hydrogen peroxide at room temperature.

Theory

The reaction between iodide ions and hydrogen peroxide occurs in the acidic medium and can be represented in the following manner:



In this reaction, hydrogen peroxide oxidises iodide ions (I^{-}) to molecular iodine. If calculated amount of sodium thiosulphate is added in the presence of starch solution as an indicator to the above reaction mixture, the liberated iodine reacts with thiosulphate ions as fast as it is formed and is reduced back to iodide ions till all the thiosulphate ions are oxidised to tetrathionate ions.



After the complete consumption of thiosulphate ions, the concentration of iodine liberated in the reaction of hydrogen peroxide with iodide ions increases rapidly to a point where iodine forms intense blue complex with starch. The time required to consume a fixed amount of the thiosulphate ions is reproducible. Since the time for the appearance of colour is noted, the reaction is some times called a **clock reaction**.

Material Required

 <ul style="list-style-type: none"> • Conical flasks (250 mL) : Five • Conical flask (500 mL) : One • Stop watch : One • Measuring cylinder (100 mL) : One • Trough : One 		• Starch solution : As per need
		• 2.5 M Sulphuric acid solution : As per need
		• 0.1 M Potassium iodide solution : As per need
		• 0.04M Sodium thiosulphate solution : As per need
		• 3% Hydrogen peroxide solution : As per need

Procedure

- (i) Take 25 mL of 3% hydrogen peroxide, 25 mL of 2.5 M H_2SO_4 solution, 5 mL of freshly prepared starch solution and 195 mL distilled water into a 500 mL conical flask marked as A. Stir this solution well and place it in a water bath maintained at room temperature.
- (ii) Take four 250 mL conical flasks and mark them as B, C, D and E.
- (iii) Take the sodium thiosulphate solution, potassium iodide solution, and distilled water in the flasks B, C and D in a proportion given in the following steps and keep the flask E for carrying out the reaction.
- (iv) Take 10 mL of 0.04 M sodium thiosulphate solution, 10 mL of 0.1 M potassium iodide solution and 80 mL of distilled water in the conical flask marked B. Shake the contents of the flask well and keep it in a water bath.
- (v) Take 10 mL of 0.04 M sodium thiosulphate solution, 20 mL of 0.1M potassium iodide solution and 70 mL of distilled water in the conical flask marked C. Shake the resulting solution well and place it in the same water bath in which reaction mixture of step (iv) is kept.
- (vi) Take 10 mL of 0.04 M sodium thiosulphate solution, 30 mL of 0.1 M potassium iodide solution and 60 mL of distilled water in the conical flask marked D. Shake the solution well and keep this flask also in the above water bath.
- (vii) Take conical flask E. Pour 25 mL solution from flask A into it after measuring it with the help of a measuring cylinder. Now add 25 mL of solution from flask B into this flask with constant stirring. Start the stop watch when half of the solution from flask B has been transferred. Keep the flask E in a water bath to maintain the constant temperature and record the time required for the appearance of blue colour.
- (viii) In exactly the same manner, repeat the experiment with the solutions of flasks C and D separately by using once again 25 mL of the solution of these flasks and 25 mL of solution

Sulphuric acid



Hydrogen peroxide



Hazard Warning

- **Contact of hydrogen-peroxide with combustible material may cause fire.**

- from flask A. Note the time required for the appearance of blue colour in each case.
- (ix) Repeat the experiment with solutions of flasks B, C and D twice and calculate the average time for the appearance of blue colour.
 - (x) Record your observations as given in Table 2.3.
 - (xi) Compare the time required for the appearance of blue colour for all the three systems and make a generalisation about the variation in the rate of the reaction with concentration of iodide ions.

Table 2.3 : Study of reaction rate between iodide ions and hydrogen peroxide in acidic medium

Sl. No.	Composition of the system	Time taken for appearance of the blue colour		Average Time
		First reading	Second reading	
1.	25 mL solution from flask A + 25 mL solution from flask B			
2.	25 mL solution from flask A + 25 mL solution from flask C			
3.	25 mL solution from flask A + 25 mL solution from flask D			

Result

Write your conclusions on the basis of the data recorded in Table 2.3.

Precautions

- (a) Always keep the concentration of sodium thiosulphate solution less than that of potassium iodide solution.
- (b) Always use freshly prepared starch solution.
- (c) Use fresh samples of hydrogen peroxide and potassium iodide.
- (d) Always use the same measuring cylinders for measuring solutions in two different sets of observations. If after measuring one solution, the cylinder is used for measuring another solution, clean it before using.
- (e) Record the time immediately after the appearance of blue colour.



Discussion Questions

- (i) Distinguish between the role of iodine and iodide ions in this experiment.
- (ii) Calculate the oxidation number of sulphur in tetrathionate ion ($S_4O_6^{2-}$). Can the oxidation number be a fractional number?

- (iii) Why does iodine impart blue colour to starch?
- (iv) Explore the possibility of using an oxidant other than H_2O_2 in this experiment.
- (v) Why is the reaction given the name clock reaction?
- (vi) Why should the concentration of sodium thiosulphate solution taken be always less than that of potassium iodide solution?

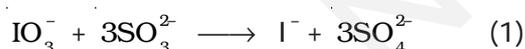
EXPERIMENT 2.3

Aim

To study the rate of reaction between potassium iodate (KIO_3) and sodium sulphite (Na_2SO_3).

Theory

The reaction between KIO_3 and Na_2SO_3 indirectly involves the formation of iodide ions, which are oxidised in acidic medium by IO_3^- ions to iodine. The overall reaction proceeds in the following two steps.



The evolved iodine produces blue colour with the starch solution in a manner described in the previous experiment. This reaction like the earlier reaction is also known as 'clock reaction'.

Material Required



- Conical flasks (250 mL) : Six
- Measuring cylinder (100 mL) : One
- Stopwatch : One
- Trough : One



- 2 M Sulphuric acid : As per requirement
- 5% Starch solution : As per requirement
- 6% Potassium iodate solution : As per requirement
- 6% Sodium sulphite solution : As per requirement

Procedure

- (i) Take a 250 mL conical flask and mark it as 'A'. Transfer 25 mL of 6% potassium iodate solution, 25 mL of 2.0 M H_2SO_4 and 50 mL of distilled water into it and shake the content of the flask well. Keep the flask in a trough half filled with water. This serves as constant temperature bath.
- (ii) Take five 250 mL conical flasks and mark these as B, C, D, E and F respectively. Take 6% sodium sulphite solution, starch solution and distilled water in flasks B, C, D and E in the proportion given in the following steps and keep flask F for carrying out the reaction.
- (iii) In the conical flask marked 'B' take 20 mL of sodium sulphite solution, 5 mL of starch solution and 75 mL of distilled water. Shake the contents of the flask well and keep it in the water bath.
- (iv) In the conical flask marked 'C', take 15 mL of sodium sulphite solution, 5 mL of starch solution and 80 mL of distilled water. Shake the resulting solution well and keep it in the water bath.
- (v) In conical flask 'D', take 10 mL of sodium sulphite solution, 5 mL of starch solution and 85 mL of distilled water. Shake the solution well and place the flask in the water bath.
- (vi) In conical flask 'E', take 5 mL of sodium sulphite solution, 5 mL of starch solution and 90 mL of distilled water. Shake the content of the flask well and keep it in the water bath.
- (vii) Take conical flask 'F'. In this flask pour 25 mL of the solution from the conical flask marked 'A' and add 25 mL of the solution from the conical flask marked 'B'. Start the stop watch when half of the solution from flask B has been added. Mix these two solutions thoroughly by constant stirring and keep it in the water bath. Record the time required for the appearance of blue colour (you may use stop watch/wrist watch for noting the time).
- (viii) In a similar manner, repeat the experiment with the solutions in flasks C, D and E respectively by using 25 mL of the solution as in the experiment with solution from flask B and record the time required for the appearance of blue colour in each case.

(Once again care should be taken to repeat the experiment for each case twice so as to take the average time required for the appearance of blue colour in each set).

Note :

- Total amount of solution in each flask is 100 mL
- Same amount of indicator has been used.

Sulphuric acid



- (ix) Record your observations as given in Table 2.4.
- (x) From the tabulated results, find out the relationship between the time of appearance of blue colour and the variation in concentration of sodium sulphite.

Table 2.4 : Study of the reaction rate between potassium iodate (KIO_3) and sodium sulphite (Na_2SO_3) in acidic medium

Sl. No.	Composition of the system	Time taken for appearance of the blue colour in seconds		Average Times/sec.
		First reading	Second reading	
1.	25 mL solution from flask A + 25 mL solution from flask B			
2.	25 mL solution from flask A + 25 mL solution from flask C			
3.	25 mL solution from flask A + 25 mL solution from flask D			
4.	25 mL solution from flask A + 25 mL solution from flask E			

Result

Write your conclusions on the basis of data recorded in Table 2.4.

Precautions

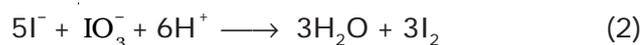
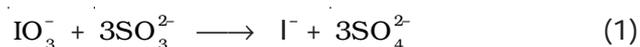
- As sodium sulphite is likely to be easily oxidised in air, therefore, always use its fresh solution.
- Keep the concentration of potassium iodate solution higher than the concentration of sodium sulphite solution.
- Use a freshly prepared starch solution.
- Start the stop watch when half of the solution from conical flask B, C, D or E is added to the conical flask F containing 25 mL solution from flask A.



Discussion Questions

- How would the time for the appearance of blue colour vary if the temperature of the experiment in the above case is enhanced by 10°C ?
- Mention the factors that affect the rate of reaction in the present study.

- (iii) Which of the acids, hydrochloric or nitric, would be suitable to make the medium acidic in this experiment? Explain your answer with reasons.
- (iv) Out of the reactions (1) and (2) given below:

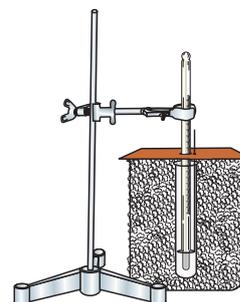


which could be the rate determining reaction? What is the molecularity of the rate determining reaction?

- (v) Can AsO_3^{3-} be used in place of SO_3^{2-} in the above reaction? Support your answer with proper reasoning.
- (vi) Why is the concentration of potassium iodate solution kept higher than the concentration of sodium sulphite solution?

UNIT-3

THERMOCHEMICAL MEASUREMENT



MOST of the reactions are carried out at atmospheric pressure, hence heat changes noted for these reactions are enthalpy changes. Enthalpy changes are directly related to the temperature changes by the relation:

$$\begin{aligned}\Delta H &= q_p \\ &= m C_p \Delta T \\ &= \mathbf{VdC_p \Delta T} \quad \dots (1)\end{aligned}$$

where **V** = Volume of the solution.

d = Density of the solution

C_p = Heat capacity

ΔT = Change in temperature

Measurement of heat changes are carried out in vessels called **calorimeters**. Reactions may also be carried out in beakers placed in thermos flask or in thermally insulated box or in styrofoam cup. Metallic calorimeters are not used for measuring thermochemical changes because metals may react with substances. Stainless steel or gold plated copper calorimeters may be used. During measurement of heat changes, calorimeter, thermometer and stirrer also absorb some heat; this amount of heat should also be known. It is called **calorimeter constant**. In the case of a glass vessel, (e.g. beaker) calorimeter constant for that part is found, which is actually in contact with the reaction mixture. This is so because when thermal conductivity of the material of calorimeter is low, only the area of the calorimeter in contact with the liquid absorbs maximum heat. Method of mixtures is used to determine the calorimeter constant. To determine calorimeter constant, known volume of hot water at a specified temperature is added to known volume of water contained in the calorimeter at room temperature. Since energy is conserved, the heat taken by calorimeter and cold water should be equal to heat given by hot water. Thus, we can write the following equation :

$$\begin{array}{rcccl} \Delta H_1 & + & \Delta H_2 & = & -\Delta H_3 & \dots (2) \\ \text{Enthalpy change} & & \text{Enthalpy} & & \text{Enthalpy} & \\ \text{of calorimeter,} & & \text{change of} & & \text{change of} & \\ \text{stirrer and} & & \text{cold water} & & \text{hot water} & \\ \text{thermometer} & & & & & \end{array}$$

Let t_c , t_h and t_m be temperatures of cold water, hot water and mixture respectively. Then, in view of the definition of enthalpy change given in equation

(1) we can rewrite equation (2) as

$$m_1 C_{p_1} (t_m - t_c) + m_2 C_p (t_m - t_c) + m_3 C_p (t_m - t_h) = 0 \quad \dots (3)$$

where m_1 , m_2 and m_3 are masses of calorimeter, cold water and hot water respectively and C_{p_1} and C_p are heat capacities of calorimeter and water respectively. Since, thermal conductivity of glass is low, only that part of the beaker gains maximum heat which comes in contact with water therefore, we can calculate only effective $m_1 C_{p_1}$ (i.e. calorimeter constant, W). On rewriting equation (3) we get

$$W (t_m - t_c) + m_2 C_p (t_m - t_c) + m_3 C_p (t_m - t_h) = 0$$

$$W = \frac{m_2 C_p (t_m - t_c) + m_3 C_p (t_m - t_h)}{(t_m - t_c)} \quad \dots (4)$$

but $mC_p = VdC_p$, where V , d and C_p are volume, density and heat capacity of water respectively. By definition, heat capacity of a substance is the amount of energy required to raise the temperature of 1 g of substance by 1 K (or 1°C). The amount of energy required to raise the temperature of 1 g of water by 1 K (or 1°C) is 4.184 Joules. This means that for 1 g water for rise of 1 Kelvin temperature $VdC_p = 4.184 \text{ JK}^{-1}$. Therefore, product of density and heat capacity can be taken as $4.184 \text{ J.mL}^{-1}.\text{K}^{-1}$. Thus, equation (4) can be written as :

$$W = \frac{(4.184) [V_c (t_m - t_c) + V_h (t_m - t_h)]}{(t_m - t_c)} \text{ J K}^{-1} \quad \dots (5)$$

where V_c = volume of cold water

V_h = volume of hot water

Technique for measuring the enthalpy changes are given in the following experiments.

EXPERIMENT 3.1

Aim

To determine the enthalpy of dissolution of copper sulphate/potassium nitrate.

Theory

In thermochemical measurements generally aqueous solutions are mixed therefore, water in the reaction medium and the temperature changes result due to the chemical reactions taking place in solution.

According to law of conservation of energy, the sum of enthalpy changes taking place in the calorimeter (loss and gain of energy) must be zero. Thus, we can write the following equation-

$$\begin{array}{ccccccc}
 (\Delta H_1) & & (\Delta H_2) & & (\Delta H_3) & & (\Delta H_4) \\
 \text{Heat gained by} & + & \text{Enthalpy} & + & \text{Enthalpy change} & + & \text{Enthalpy} \\
 \text{calorimeter,} & & \text{change of} & & \text{of added solution/} & & \text{change of} \\
 \text{thermometer} & & \text{solution/water} & & \text{water in} & & \text{reaction} \\
 \text{and stirrer} & & \text{in calorimeter} & & \text{calorimeter} & & \\
 & & & & & & = 0 \quad \dots (6)
 \end{array}$$

In these reactions we take the product of density and heat capacity of solutions, dC_p , to be $4.184 \text{ J}\cdot\text{mL}^{-1}\cdot\text{K}^{-1}$, nearly the same as that of pure water.*

Solution formation often accompanies heat changes. Enthalpy of solution is the amount of heat liberated or absorbed when one mole of a solute (solid/liquid) is dissolved in such a large quantity of solvent (usually water) that further dilution does not make any heat changes.

Material Required

	• Beakers (250 mL)	: Three		• Copper sulphate/ potassium nitrate : 2g
	• Beaker (500 mL)	: One		
	• Thermometer (110°C)	: One		
	• Glass rod	: One		
	• Cotton wool	: As per need		
	• Small wooden block	: One		
	• Small piece of cardboard	: One		
	• Stirrer	: One		

Procedure

A. Determination of Calorimeter constant of calorimeter (Beaker)

- (i) Take 100 mL of water in a 250 mL beaker marked 'A'.
- (ii) Place this beaker on a wooden block kept in a larger beaker of capacity 500 mL (Fig. 3.1).
- (iii) Pack the empty space between the large and the small beaker with cotton wool. Cover the beaker with a cardboard. Insert thermometer and stirrer in the beaker through it.

* *Density of the solutions is 4 to 6% higher than that of pure water and heat capacity is about 4 to 8% less than pure water so the product of density and heat capacity (dC_p) is nearly the same as the product of pure water.*

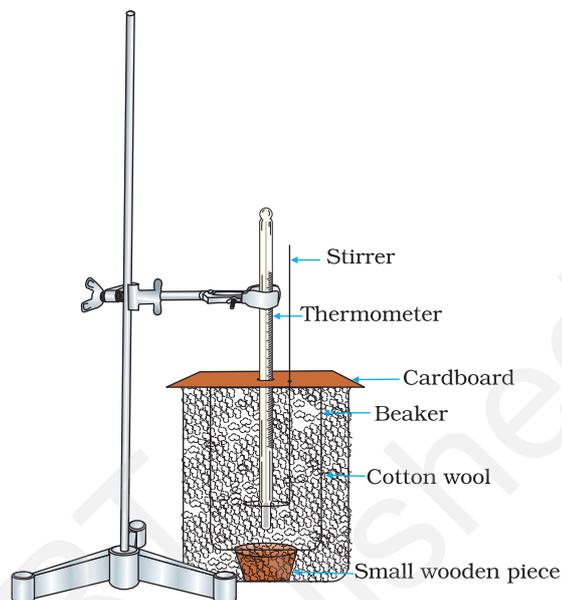


Fig. 3.1 : Determination of calorimeter constant

- (iv) Record the temperature of water. Let this temperature be t_c °C.
 - (v) In another beaker of 250 mL capacity marked 'B' take 100 mL of hot water (50-60°C).
 - (vi) Note the exact temperature of hot water. Let this temperature be t_h °C.
 - (vii) Lift the card board and pour the hot water contained in beaker B into beaker A. Stir the mixed water and note the temperature. Let this temperature be t_m °C.
 - (viii) Calculate the calorimeter constant of the beaker by using the expression (5) given above.
- (Remember the three temperatures are in the order $t_h > t_m > t_c$).

B. Determination of Enthalpy of Dissolution

- (i) Take 100 mL of distilled water in the beaker of which calorimeter constant has been determined and place it on a wooden block kept in a larger beaker of capacity 500 mL (Fig. 3.1).
- (ii) Pack the empty space between the larger and the smaller beaker with cotton wool and cover with a cardboard.
- (iii) Record the temperature of water already taken in the small beaker. Let this be t'_1 °C.
- (iv) Add weighed amount, say W_1 g of well powdered copper sulphate in water and stir the solution with a stirrer till the entire amount of copper sulphate dissolves.

- (v) Note down the temperature attained by the solution after the addition of copper sulphate. Let this be t'_2 °C. Calculate the enthalpy of dissolution of copper sulphate as follows:

$$\begin{aligned} \text{Total mass of the solution} &= \text{Mass of Solvent} + \text{Mass of Solute} \\ &= (100 + W_1) \text{ g} \end{aligned}$$

(Assuming density of water to be equal to 1 gL^{-1} at the experimental temperature)

$$\text{Change in temperature} = (t'_2 - t'_1) \text{ }^\circ\text{C}$$

$$\text{Enthalpy change of the calorimeter (beaker)} = W (t'_2 - t'_1)$$

where, W = Calorimeter constant

$$\text{Enthalpy change of solution} = [(100 + W_1) (t'_2 - t'_1)] 4.184 \text{ J}$$

for $(t'_2 - t'_1)$ °C rise in temperature

Total enthalpy change

$$\text{of the Calorimeter} = [W (t'_2 - t'_1) + (100 + W_1) (t'_2 - t'_1)] 4.184 \text{ J}$$

(beaker) and solution

Heat liberated
on dissolution
of 1 g copper
sulphate

$$\frac{[W (t'_2 - t'_1) + (100 + W_1) (t'_2 - t'_1)] \times 4.184 \text{ J}}{W_1}$$

Since 1 mol of copper sulphate weighs 249.5 g. Therefore,

$$\Delta_{\text{sol}} H \text{ of } \text{CuSO}_4 \cdot 5\text{H}_2\text{O} = 249.5 \times \frac{[W(t'_2 - t'_1) + (100 + W_1)(t'_2 - t'_1)] 4.184}{W_1} \text{ J mol}^{-1}$$

Result

Enthalpy change in the dissolution of copper sulphate/potassium nitrate is _____ Jmol^{-1} .

Precautions

- To record the temperature of water, use a thermometer with 0.1 °C graduation.
- In the determination of calorimeter constant record the temperature of hot water just before mixing.
- Avoid using very large amounts of copper sulphate/potassium nitrate.
- Stir the solution well to dissolve the solid and record the temperature. Avoid too much stirring, it may produce heat due to friction.
- Weigh copper sulphate carefully as it is hygroscopic in nature.
- Use cotton wool to create insulation between the two beakers.

Note : To find out enthalpy change for the dissolution of potassium nitrate, use potassium nitrate in place of copper sulphate in this experiment.



Discussion Questions

- (i) What is meant by the term, calorimeter constant?
- (ii) Why is $\Delta_{\text{sol}}H$ for some substances negative while for others it is positive?
- (iii) How does $\Delta_{\text{sol}}H$ vary with temperature?
- (iv) Will the enthalpy change for dissolution of same amount of anhydrous copper sulphate and hydrated copper sulphate in the same amount of water be the same or different? Explain.
- (v) How will the solubility of copper sulphate and potassium nitrate be affected on increasing the temperature? Explain.

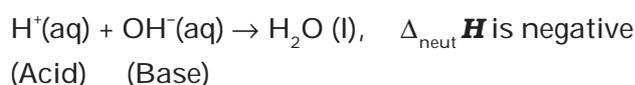
EXPERIMENT 3.2

Aim

To determine the enthalpy of neutralisation of a strong acid (HCl) with a strong base (NaOH).

Theory

A neutralisation reaction involves the combination of $\text{H}^+(\text{aq})$ ions furnished by an acid and $\text{OH}^-(\text{aq})$ ions furnished by a base, evidently leading to the formation of $\text{H}_2\text{O}(\text{l})$. Since the reaction envisages bond formation, therefore, this reaction is always exothermic. Enthalpy of neutralisation is defined as the amount of heat liberated when 1 mol of H^+ ions furnished by acid combine with 1 mole of OH^- ions furnished by base to form water. Thus:



where $\Delta_{\text{neut}}H$ is known as enthalpy of neutralisation.

If both the acid and the base are strong then for the formation of 1 mol $\text{H}_2\text{O}(\text{l})$, always a fixed amount of heat, viz, 57 kJ mol^{-1} is liberated. If any one of the acid or the base is weak or if both of these are weak, then some of the heat liberated is used for the ionisation of the acid or base or both of them (as the case may be) and the amount of heat liberated is less than 57 kJ mol^{-1} .

Material Required

	• Beakers (250 mL) : Three		• 1 M HCl : 100 mL
	• Beaker (500 mL) : One		• 1 M NaOH : 100 mL
	• Thermometer (110°C) : One		
	• Glass rod : One		
	• Cotton wool : As per need		
	• Small wooden block : One		
	• Piece of cardboard : One		
	• Stirrer : One		
	• Calorimeter : One		

Procedure

A. Determination of calorimeter constant

This may be determined by following the procedure, as detailed in experiment 3.1.

B. Determination of Enthalpy of Neutralisation

- Take 100 mL of 1.0 M HCl solution in the calorimeter (beaker) and cover it with cardboard. In another beaker of 250 mL capacity take 100 mL of 1.0 M NaOH solution.
- Note down the temperature of both the solutions, which is likely to be the same. Let it be t_1 °C.
- Pour 100 mL 1 M NaOH solution into the calorimeter containing 100 mL of 1.0 M HCl solution.
- Mix the solutions by stirring and note the final temperature of the mixture. Let it be t_2 °C.

Calculate the enthalpy of neutralisation as follows:

- Note the rise in temperature of the mixture, which in this case is $(t_2 - t_1)$ °C.
- Calculate the total amount of heat produced during the neutralisation process, using the following expression
Heat evolved = $(100 + 100 + W) (t_2 - t_1) 4.18$ J
(where W , is the calorimeter constant)
- Finally calculate the heat evolved when 1000 mL of 1M HCl is allowed to neutralise 1000 mL of 1M NaOH. This quantity would be ten times the quantity obtained in step (ii).
- Express the quantity of heat evolved in kJ mol^{-1} .

Result

Enthalpy change in the neutralisation of hydrochloric acid solution with sodium hydroxide solution _____ kJ mol^{-1} .

Precautions

- Record the temperature carefully with the help of a thermometer graduated up to 0.1°C .
- Measure the volume of hydrochloric acid and sodium hydroxide solution to be taken for the experiment carefully.
- Proper insulation should be made between the two beakers.
- Avoid unnecessary and excessive stirring to prevent heating due to friction.



Discussion Questions

- Why do we calculate the heat evolved for the neutralisation of 1000 mL of a (1 M) acid by 1000 mL of a (1 M) monoacidic base?
- In comparison to heat evolved in neutralisation reaction between a strong acid and a strong base. Why is lesser quantity of heat evolved when any one of the acid or the base is weak and still less when both are weak?
- Why does the reaction: $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$ proceed in the forward direction with rise in temperature of the system?

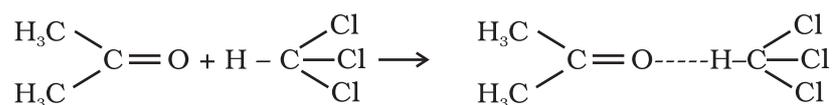
EXPERIMENT 3.3

Aim

To determine the enthalpy change for the interaction between acetone and chloroform (hydrogen bond formation).

Theory

On mixing, liquid pairs show departure from ideal behaviour. Acetone and chloroform form non-ideal liquid pair system, which shows a negative deviation from Raoult's law. This negative deviation from Raoult's law implies that the two components are strongly held together in liquid state on mixing due to hydrogen bonding. On the other hand in the pure state, only weak Van der waal's forces hold molecules of chloroform as well as acetone. The hydrogen bonding between the molecules of acetone and chloroform is depicted as follows:



Hydrogen bonding between chloroform and acetone

In this process enthalpy change takes place due to hydrogen bond formation. The enthalpy change is an extensive thermodynamic property, therefore, the heat evolved from the system depends upon the amount of the liquid components mixed. It is for this reason that the heat change is reported for specified amount. Therefore, enthalpy change during mixing of 1 mol chloroform with 1 mol acetone is reported.

$$\begin{array}{ccccccc}
 (\Delta H_1) & & (\Delta H_2) & & (\Delta H_3) & & (\Delta H_4) \\
 \text{Heat gained by} & + & \text{Enthalpy} & + & \text{Enthalpy} & + & \text{Enthalpy} \\
 \text{calorimeter,} & & \text{change of} & & \text{change for} & & \text{change of} \\
 \text{thermometer} & & \text{chloroform} & & \text{acetone} & & \text{interaction} \\
 \text{and stirrer} & & & & & & = 0
 \end{array}$$

$$\Delta H_4 = -(\Delta H_1 + \Delta H_2 + \Delta H_3)$$

Material Required

	• Beaker (250 mL)	: One			
	• Boiling tube	: One			
	• Thermometer (110°C)	: One			
	• Cotton wool	: As per need			
	• Glass rod	: One		• Chloroform	: 20 mL
	• Measuring cylinder (250 mL)	: One		• Acetone	: 10 mL
	• Piece of cardboard	: As per need			
	• Stirrer	: One			

Procedure

A. Determination of calorimeter constant

This may be determined in a manner detailed in previous experiments; except that here instead of a beaker, boiling tube may be taken and 8 mL of cold and 7.5 mL of hot water can be used instead of 100 mL.

Chloroform 

Acetone 

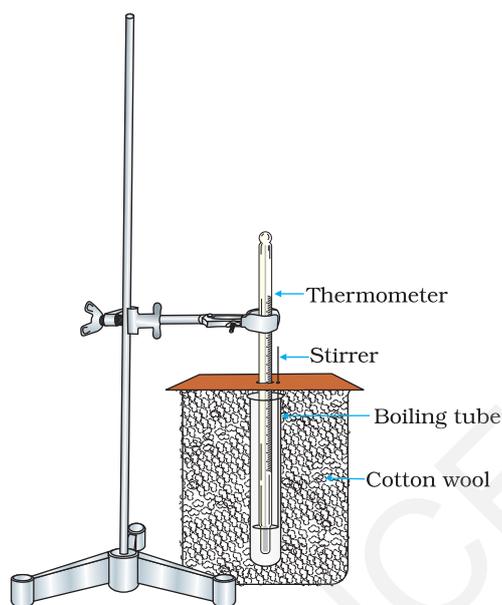


Fig. 3.2 : Determination of enthalpy of interaction of chloroform and acetone

B. Determination of Enthalpy Change on Mixing Chloroform and Acetone*

- (i) Transfer the volume of chloroform equivalent to 0.1 mol (≈ 8.14 mL) after measuring from a measuring cylinder into the insulated boiling tube as shown in Fig. 3.2. Let the mass of chloroform taken be m_1 grams.
- (ii) Record the temperature of chloroform. Let it be t_1 °C.
- (iii) Transfer the volume of acetone equivalent to 0.1 mol of acetone (≈ 7.34 mL) in a clean measuring cylinder. Let its mass be m_2 grams.
- (iv) Record the temperature of acetone. Let it be t_2 °C.
- (v) Pour acetone from the measuring cylinder into the chloroform contained in the insulated boiling tube.
- (vi) Stir gently the mixture of chloroform and acetone carefully with the help of a stirrer.
- (vii) Record the temperature of the mixture of chloroform and acetone. Let it be t_3 °C.

$$\text{*Volume of one mole of } \text{CHCl}_3 = \frac{\text{Molar mass of } \text{CHCl}_3}{\text{Density of } \text{CHCl}_3}$$

$$\text{Volume of 0.1 mole} = \frac{1}{10} \text{ th of the above volume}$$

(Similarly you can calculate the volume of 0.1 mole of acetone).

Density of chloroform = 1.47 g/mL

Molar mass of chloroform = 119.5 g

1.47 g = 1 mL volume

$$119.5 \text{ g} = \frac{119.5}{1.47} \text{ mL}$$

1 mole = 81.4 mL

0.1 mole = 8.14 mL

Density of acetone = 0.79 g/mL

Molar mass of acetone = 58.0

0.79 g = 1 mL

$$58 \text{ g} = \frac{58}{0.79} \text{ mL}$$

1 mole = 73.4 mL

0.1 mole = 7.34 mL

$$\text{Total volume of acetone and chloroform} = 8.14 + 7.34 = 15.48 \text{ mL}$$

Calculate the enthalpy of interaction as follows :

- (i) Let the room temperature be $t^\circ\text{C}$, then heat gained by calorimeter (boiling tube) is $W (t_3 - t)$, where W is the calorimeter constant, i.e. boiling tube in this experiment.
- (ii) Note the value of specific heat of chloroform from literature. Let it be q_1 .
Then heat gained by chloroform = $m_1 q_1 (t_3 - t_1)$.
- (iii) Note the value of the specific heat for acetone from literature. Let it be q_2 . Thus heat gained by acetone = $m_2 q_2 (t_3 - t_2)$.
- (iv) Total heat gained by all the three components, i.e. boiling tube, chloroform and acetone = $-\{W(t_3 - t_1) + m_1 q_1(t_3 - t_1) + m_2 q_2 (t_3 - t_2)\}$. This in fact is the enthalpy change of interaction, on mixing 0.1 mol chloroform with 0.1 mol acetone.

The negative sign simply implies that the mixing of chloroform and acetone is an exothermic process.

Note : Here, care should be taken that the total volume of acetone and chloroform is equal to the volume of water for which water equivalent of the calorimeter has been calculated.

Precautions

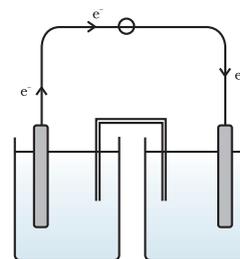
- (a) Measure chloroform and acetone carefully.
- (b) Record the temperature very carefully with a thermometer graduated up to 0.1°C .

**Discussion Questions**

- (i) Chloroform and acetone do not form an ideal liquid pair, whereas acetone and benzene do form. Why?
- (ii) Why does liquid pair of ethanol and water show positive deviation from Raoult's law?
- (iii) Give two examples of each of the liquid pairs for which $\Delta_{\text{Mixing}} H$ is negative and positive respectively.
- (iv) How is the vapour pressure of the liquids related to interaction pattern between the molecules of the components of a liquid mixture?
- (v) How can you correlate the heat evolved from the system with the strength of the hydrogen bond?

UNIT-4

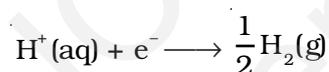
ELECTROCHEMISTRY



THE potential difference between two electrodes of a galvanic cell is called **Cell Potential** and is measured in volts. It is the difference between the reduction potentials (or oxidation potentials) of the cathode and anode. When no current is drawn from the cell it is called electromotive force (emf) of the cell.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

The potential of individual half-cells cannot be measured. We can measure only the difference between the two half-cell potentials that gives the emf of the cell. According to convention, standard hydrogen electrode represented by Pt, H₂ (g, 1 bar)/H⁺ (aq, 1M) is assigned zero potential at all temperatures corresponding to the reaction.



Half cell potentials are measured with respect to standard hydrogen electrode.

A cell is constructed by taking standard hydrogen electrode as anode (reference half cell) and under standard conditions of which cell potential is to be measured, is made cathode the other half cell. Then the cell potential is equal to the standard electrode potential of the other half cell.

$$E_{\text{cell}}^{\ominus} = E_{\text{cathode}}^{\ominus} \quad \text{because } E_{\text{anode}}^{\ominus} = 0$$

Nernst showed that electrode potential of a cell with respect to standard hydrogen electrode can be measured at any concentration. For the electrode reaction of the type:



The electrode potential at any concentration measured with respect to standard hydrogen electrode can be represented by:

$$E_{\text{M}^{n+}/\text{M}} = E_{\text{M}^{n+}/\text{M}}^{\ominus} - \frac{RT}{nF} \ln \frac{[\text{M}]}{[\text{M}^{n+}]}$$

the concentration of solid M is taken as unity and we have

$$E_{\text{M}^{n+}/\text{M}} = E_{\text{M}^{n+}/\text{M}}^{\ominus} - \frac{RT}{nF} \ln \frac{1}{[\text{M}^{n+}]}$$

Here R is the gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$), F is Faraday constant (96487 C mol^{-1}), T is the temperature in Kelvin and $[M^{n+}]$ is the concentration of the species, M^{n+} .

In the following experiment the variation in the cell potential of $\text{Zn}/\text{Zn}^{2+} \parallel \text{Cu}^{2+}/\text{Cu}$ cell with concentration of electrolytes will be studied.

EXPERIMENT 4.1

Aim

To study the variation in cell potential of the cell $\text{Zn}/\text{Zn}^{2+} \parallel \text{Cu}^{2+}/\text{Cu}$ with change in concentration of electrolytes ($\text{CuSO}_4/\text{ZnSO}_4$) at room temperature.

Theory

The cell under investigation in this experiment is represented as follows:



Here $x\text{M}$ denotes varying concentrations of $\text{Cu}^{2+}(\text{aq})$ ions. In other words, to study the variation in cell potential with concentration, the concentration of $\text{Cu}^{2+}(\text{aq.})$ is varied while that of $\text{Zn}^{2+}(\text{aq.})$ is kept constant. The measured cell potential enables us to calculate the electrode potential of Cu^{2+}/Cu electrode for each concentration of copper (II) ions. This variation is theoretically depicted according to the equation:

$$E_{\text{Cu}^{2+}/\text{Cu}} = E_{\text{Cu}^{2+}/\text{Cu}}^{\ominus} - \frac{0.059}{2} \log[\text{Cu}^{2+}] \quad (1)$$

The variation in the electrode potential of Cu^{2+}/Cu electrode consequently brings variation in the cell potential according to the relation:

$$E_{\text{cell}} = E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{Zn}^{2+}/\text{Zn}}^{\ominus} \quad (2)$$

Equation (2) clearly suggests that even if $E_{\text{Zn}^{2+}/\text{Zn}}^{\ominus}$ is kept constant, the variation in $E_{\text{Cu}^{2+}/\text{Cu}}$ would bring corresponding variation in E_{cell} (cell potential). Similarly, keeping the concentration of Cu^{2+} ions constant, one can study the variations in the cell potential with the variation in concentration of Zn^{2+} ions.

Material Required



- Zinc plate : One
- Copper plate : One
- Beaker (50 mL) : Six
- Voltmeter (Potentiometer) : One
- Salt bridge : One



- 1.0M Zinc sulphate solution : 40mL
- 0.25 M, 0.1M, 0.05M, 0.025 M and 0.0125M Copper sulphate solutions : 40 mL each

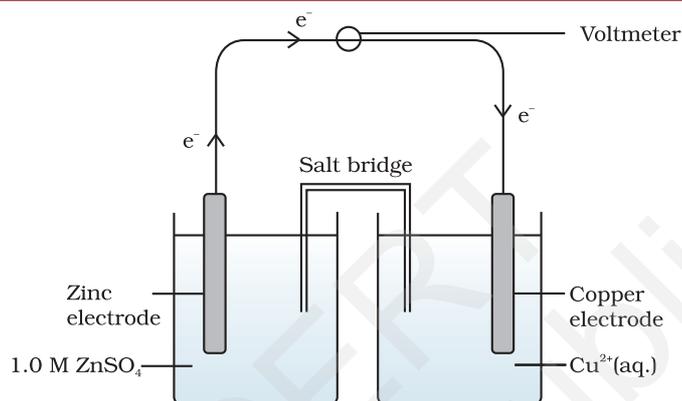


Fig. 4.1 : Set up of $Zn(s)/Zn^{2+}(aq.)$, (1.0M) || $Cu^{2+}(aq., xM)/Cu(s)$ cell

Procedure

- (i) Set up the cell as given in Fig. 4.1, using 1.0 M $ZnSO_4$ and 0.2 M $CuSO_4$ solution.
- (ii) Measure the potential difference of the cell and also keep record of the polarity of the electrodes (this will enable us to give a sign to the cell potential E_{cell}).
- (iii) Remove the salt bridge as soon as the cell potential measurement is over.
- (iv) Replace the beaker of 0.2 M $CuSO_4$ with 0.1 M $CuSO_4$ solution in the beaker. Place the salt bridge in position and note the cell potential.
- (v) Repeat this procedure for other solutions of copper sulphate in decreasing order of concentrations of copper sulphate solution.
- (vi) Calculate $\log [Cu^{2+}(aq)]$ and then $E_{Cu^{2+}/Cu}$ for each variation in the concentration of copper (II) in the solution.
- (vii) Record electrode potential values of $Cu^{2+}(aq)/Cu(s)$ electrode for different concentrations of Cu^{2+} ions as given in Table 4.1.
- (viii) Plot a graph for the variation of cell potential with concentration taking ($E_{Cu^{2+}/Cu}$) on **y**-axis and $\log [Cu^{2+}(aq)]$ on **x**-axis.

Table 4.1 : Record of the Cell Potential Data

Sl. No.	[Cu ²⁺ (aq)]/mol L ⁻¹	log [Cu ²⁺ (aq)]/mol L ⁻¹	E _{cell} /V	E _(Cu²⁺/Cu) Experimental value
1.	0.2			
2.	0.1			
3.	0.05			
4.	0.025			
5.	0.0125			

Result

Write conclusion on the basis of data obtained.

Precautions

- Clean copper and zinc strips and connecting wires with sand paper before use.
- Place the salt bridge immediately in distilled water after its use.
- Carry out dilution of the solution to another concentration very carefully.
- Choose appropriate scales for plotting the graph.

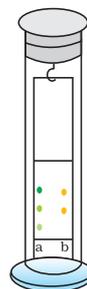
**Discussion Questions**

- For the reaction given below, apply Le-Chatelier principle to justify the results recorded by you and also bring out mathematical rationalisation of your results.

$$\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)},$$
- Determine the slope of the graph. Match experimental value with the theoretical value. On what factors does the value of slope depend?
- Devise another experiment to study the variation in cell potential with concentration of one of the ions involved in a cell reaction.
- What factor is kept in mind while selecting an electrolytic solution for the construction of a salt bridge?
- Is it possible to measure the single electrode potential?

UNIT-5

Chromatography



THE technique of chromatography is vastly used for the separation, purification and identification of compounds. According to IUPAC, chromatography is a physical method of separation in which the components to be separated are distributed between two phases, one of which is stationary while the other moves in a definite direction.

The stationary phase is usually in the form of a packed column (column chromatography) but may take other forms such as flat sheet or a thin layer adhering to a suitable form of backing material such as glass (thin-layer chromatography). In **column chromatography**, mobile phase flows through the packed column, while in **thin layer chromatography**, mobile phase moves by capillary action. In this the thin film stationary phase may be either a liquid or a solid and the mobile phase may be a liquid or a gas. Different possible combinations of these phases give rise to principal techniques of chromatography. Two of these are described below.

In **partition chromatography**, stationary phase is thin film of liquid adsorbed on an essentially inert support. Mobile phase may be a liquid or a gas. **Paper chromatography** is an example of partition chromatography in which liquid present in the pores of paper is stationary phase and some other liquid is movable phase. Separation depends upon partition of substance between two phases and the adsorption effects of inert support on compounds undergoing chromatographic separation.

In **adsorption chromatography**, the stationary phase is a finely divided solid adsorbent and the mobile phase is usually a liquid. Process of separation depends upon selective adsorption of components of a mixture on the surface of a solid.

In chromatography, substance equilibrates between a mobile and a stationary phase. The more the interaction of substance with the stationary phase, slower is its movement.

In this unit you will learn about the technique of separating the components of a mixture by using paper chromatography.

EXPERIMENT 5.1

Aim

Separation of pigments present in the leaves (spinach) and flowers (rose, marigold) by paper chromatography and determination of R_f value of components.

Theory

In paper chromatography, water molecules present in the pores of the filter paper act as the stationary phase and the moving phase can be a solvent like hexane, toluene, acetone or a mixture of solvents such as methanol-water mixture etc. As the moving phase passes through the spot on which sample has been adsorbed, it dissolves the components more or less readily; depending upon the solubility and carries them along with it while moving on the support.

At a given temperature and for a given solvent, it is possible to determine the characteristic rate of movement of each substance on the chromatographic paper, as the moving phase moves. This is represented by relative front or **retardation factor also called R_f value**. R_f values of different compounds are different even if the mobile phase (solvent) is same. Furthermore, R_f value of a compound may be different in different solvents. R_f values can be calculated by using the following expression:

$$R_f = \frac{\text{Distance travelled by the substance from reference line (cm)}}{\text{Distance travelled by the solvent front from reference line (cm)}}$$

Since solvent front moves faster than the compounds, the R_f value of a substance will always be less than one. Also note that R_f value has no unit.

If the compound is coloured then its position on the chromatographic paper may be easily located. However, if the substance is colourless, it may be treated with a reagent, which imparts it a characteristic colour. This reagent is given the name **developer**. Iodine is the most commonly used developer in paper chromatography. Several other techniques are available for locating the spots.

Material Required



- Whatman's filter paper No.1 of size 4 cm 17 cm : One
- Gas jar of size 5 cm 20 cm: One
- Rubber cork fixed with hook in the centre : One
- Test tubes : As per need



- Flower extract and extract of leaves : As per need
- Distilled water : As per need
- Methanol/Acetone : As per need
- Petroleum ether boiling range (60–80°C) : As per need
- Chloroform /Acetone : As per need

Methanol



Acetone



Petroleum ether



Chloroform



Procedure

- Grind flowers/leaves in a mortar and transfer the paste into a test tube.
- Add small amounts of methanol or acetone in the crushed material. Close the test tube with an appropriate cork and

shake it well. Filter it and collect the filtrate in a test tube and cork the test tube.

- (iii) Procure a Whatman filter paper No.1 of size 4 cm × 17 cm and mark a line at a distance of 3 cm from one of the ends of the paper with the help of a pencil [Fig. 5.1(a)].
- (iv) Using a finely drawn capillary, put one spot 'a' for the extract of leaves and one spot 'b' for the extract of flowers. Allow these spots to dry as shown in Fig. 5.1 (a).
- (v) Hang the filter paper in a jar containing 20 mL mixture of petroleum ether (boiling range 60–80°C) and chloroform containing 19 mL petroleum ether and 1 mL chloroform or a mixture of petroleum ether (boiling range 60–80°C) and acetone in the ratio 9:1 (18 mL petroleum ether + 2 mL acetone) so that the solvent does not touch the reference line as given in Fig. 5.1 (b).
- (vi) Keep this jar as such till the mobile phase (solvent) rises up to 2/3 of the length of the paper [Fig. 5.1(c)].
- (vii) Remove the filter paper from the jar, mark the solvent front, outline the spots with the help of a pencil and allow the filter paper to get dry.
- (viii) Measure the distance travelled by the solvent front and the centre of different spots with respect to the reference line as given in Fig. 5.1 (d).
- (x) Ascertain the number of pigments, which are present in the extract of leaves and flowers.
- (xi) Calculate the R_f value of different spots with the help of the expression mentioned earlier.

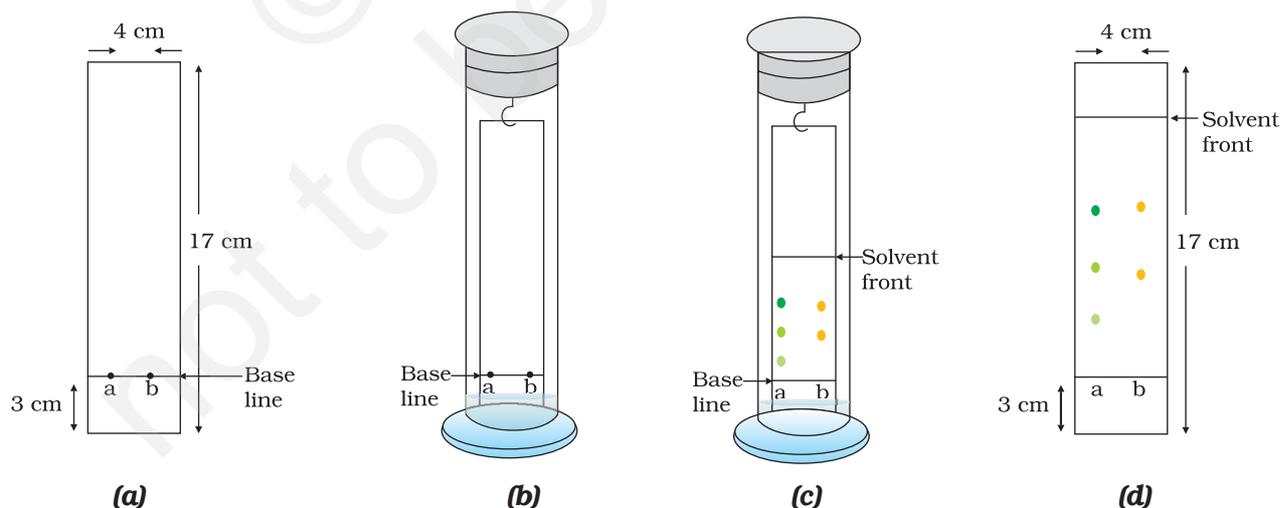


Fig. 5.1 : (a) Marked paper; (b) Dipping the filter paper in the solvent; (c) Developing chromatogram; and (d) Developed chromatogram

(xii) Record your observations as in Table 5.1.

Table 5.1: Separation of pigments of leaves and flowers

Sl. No.	Name of the extract	Colour of the spot	Distance travelled by the components of the spots 'a' or 'b' from the reference line in cm	Distance travelled by the solvent from reference line in cm	R_f value
1.					
2.					
3.					
4.					

Result

- (i) R_f values of components of flower are _____.
- (ii) R_f values of components of leaves are _____.

Precautions

- Use good quality pencil for drawing the reference line so that the mark does not dissolve in the solvent in which TLC is run.
- Dip the paper strip in the solvent in such a way that the spot of the mixture is above the solvent level and the movement of the solvent front is not zig-zag.
- While spotting the test solution on the paper, do not allow the spots to spread. Use finely drawn capillary to put the spot on the paper.
- Ensure that the filter paper strip hangs freely in the jar.
- Once the experiment is set, do not disturb the jar as long as the chromatogram is being developed.
- Keep the jar covered with the lid when the chromatogram is being developed.
- Make the paper strip perfectly dry before developing the spots.
- Handle the organic solvent/solvents, with care.

EXPERIMENT 5.2

Aim

Separation of the constituents of a mixture of inorganic compounds containing two cations, Pb^{2+} and Cd^{2+} , using chromatographic technique.

Theory

Principle for the separation of cations is same as has been explained in Experiment 5.1. In this case the two cations to be separated are colourless. therefore, a developer is needed. In the present case, ammonium sulphide $(\text{NH}_4)_2\text{S}^*$, can be used to locate the position of these ions on chromatographic paper or plate.

Material Required



- Whatman's filter paper No. 1 of size 4 cm × 17 cm : One
- Gas jar of size 5 cm × 20 cm : One
- Rubber cork fixed with hook in the centre : One
- Test tubes : As per need



- 1–2% solution of $\text{Pb}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2$: As per need
- Ethanol : As per need
- 6.0 M HNO_3 : As per need

Ethanol



Lead nitrate



Cadmium nitrate



Procedure

- Procure a Whatman No. 1 filter paper of size 4 cm × 17 cm. With the help of a pencil, mark a line at a distance of 3 cm from one of the ends of this paper.
- Put a spot of the mixture on the marked line with the help of a fine capillary.
- Hang the filter paper in a jar containing a mixture of ethanol, 6.0 M HNO_3 and distilled water, in the ratio 8:1:1.
- Keep the jar as such till the mobile phase (solvent) rises up to two third of the length of the paper.
- Remove the filter paper from the jar, mark the solvent front.
- Spray ammonium sulphide solution on the chromatography paper to obtain spots of yellow and black colour. Mark the position of spots with a pencil and allow the paper to dry.
- Measure the distance moved by the solvent front and the different spots of the cations with respect to the reference line. This distance is the shortest distance between the reference line and the centre of different spots.
- Record the observations in tabular form as in Table 5.2. Calculate the R_f value for each cation.

* Ammonium sulphide is prepared by passing H_2S gas through the mixture containing 100 mL water and 10 mL liquor ammonia for about 45 minutes.

Table 5.2 : Separation of Pb^{2+} and Cd^{2+} ions by paper chromatography

Sl. No.	Colour of the spot	Distance travelled by components from reference line/cm	Distance travelled by the solvent from reference line/cm	R_f value
1.				
2.				
3.				

Result

- (i) R_f values of Pb^{2+} ions is _____.
- (ii) R_f values of Cd^{2+} ions is _____.

Precautions

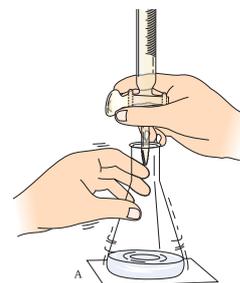
- Use good quality pencil for drawing the reference line so that the mark does not dissolve in the solvent in which TLC is run.
- Dip the paper strip in the solvent in such a way that the spot of the mixture is above the solvent level and movement of solvent front is not zig-zag.
- While spotting the test solution on the paper, do not allow the spots to spread. Use finely drawn capillary to put the spot on the paper.
- Ensure that the filter paper strip hangs freely in the jar.
- Once the experiment is set, do not disturb the jar as long as the chromatogram is being developed.
- Keep the jar covered with the lid when the chromatogram is being developed.
- Make the paper strip perfectly dry before developing the spots.
- Handle the organic solvent/solvents, with care.

**Discussion Questions**

- What is a chromatogram? Explain the principle on which the technique of chromatography is based.
- What are the essential characteristics of the substance used as a developer?
- How is the phenomenon of 'adsorption' applied in the separation of compounds by chromatography?

UNIT-6

TITRIMETRIC ANALYSIS (REDOX REACTIONS)



THE oxidation and reduction reactions in aqueous solutions involve the transfer of electrons from one species to another. In the oxidation of a substance electron(s) is (are) transferred from the species and in reduction, electron(s) is (are) gained by the species. Oxidation and reduction reactions occur simultaneously. A reaction, which involves simultaneous oxidation and reduction, is called a redox reaction. The titrations involving redox reaction are called redox titrations. You know that in acid-base titrations, indicators which are sensitive to pH change are employed to note the end point. Similarly, in redox titrations there is a change in oxidation potential of the system. The indicators used in redox reactions are sensitive to change in oxidation potential. The ideal oxidation-reduction indicators have an oxidation potential intermediate between the values for the solution being titrated and the titrant and these show sharp readily detectable colour change.

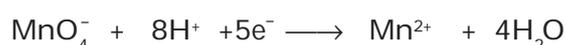
EXPERIMENT 6.1

Aim

To determine the concentration/molarity of KMnO_4 solution by titrating it against a 0.1 M standard solution of oxalic acid.

Theory

In the present experiment, potassium permanganate acts as a powerful oxidising agent. Although KMnO_4 acts as an oxidising agent in alkaline medium also, for quantitative analysis mostly acidic medium is used. The oxidising action of KMnO_4 in the acidic medium can be represented by the following equation:



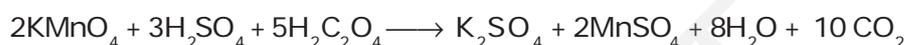
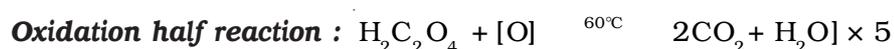
The acid used in this titration is dilute sulphuric acid. Nitric acid is not used as it is itself an oxidising agent and hydrochloric acid is usually avoided because it reacts with KMnO_4 according to the equation given below to produce chlorine and chlorine which is also an oxidising agent in the aqueous solution.



Since, oxalic acid acts as a reducing agent, it can be titrated against potassium permanganate in the acidic medium according to the following equation:

Reactions of oxalic acid

A. Chemical equations



B. Ionic equation



In these equations, MnO_4^- is reduced to Mn^{2+} and $\text{C}_2\text{O}_4^{2-}$ is oxidised to CO_2 . The oxidation number of carbon in $\text{C}_2\text{O}_4^{2-}$ changes from +3 to +4.

In these titrations, potassium permanganate acts as a self-indicator. Initially colour of potassium permanganate is discharged due to its reduction by oxalic acid. After complete consumption of oxalate ions, the end point is indicated by the appearance of a light pink colour produced by the addition of a little excess of unreacted potassium permanganate. Further, during the titration of oxalic acid against potassium permanganate, warming of oxalic acid solution ($50^\circ\text{--}60^\circ\text{C}$) along with dilute H_2SO_4 is required. This is essential because the reaction takes place at higher temperature. During the titration, first manganous sulphate is formed which acts as a catalyst for the reduction of KMnO_4 by oxalic acid. Therefore, in the beginning the reaction rate is slow and as the reaction proceeds, the rate of the reaction increases.

Material Required



- Measuring flask (250 mL): One
- Burette (50 mL) : One
- Burette stand : One
- Pipette : One
- Conical flask : One
- Funnel : One
- Weighing bottle : One
- Glazed tile(white) : One
- Burner : One
- Wire gauze : One
- Chemical balance : One



- Oxalic acid : As per need
- Potassium permanganate solution : As per need
- 1.0 M Sulphuric acid : As per need

Procedure

A. Preparation of 0.1 M standard solution of oxalic acid

Prepare 0.1M oxalic acid solution as mentioned in experiment 2.1(Unit 2, Class XI, Laboratory Manual)

B. Titration of oxalic acid solution against potassium permanganate solution

Oxalic acid



Potassium permanganate



Sulphuric acid



- (i) Rinse and fill a clean burette with potassium permanganate solution. Remove the air bubble, if any, from the nozzle of the burette by releasing some solution through it. The burette used in the permanganate titration must have a glass stop cock as rubber is attacked by permanganate ions.
- (ii) Take 10 mL of 0.1 M oxalic acid solution in a conical flask and add half of the test tube full (5 mL) of 1.0 M H_2SO_4 to it to prevent the formation of any precipitate of manganese dioxide during the course of the titration.
- (iii) Heat the oxalic acid solution upto $50^\circ - 60^\circ C$ before titrating it with potassium permanganate solution taken in the burette. To increase the visibility of the colour change, place the conical flask containing the solution to be titrated over a white glazed tile kept below the nozzle of the vertically fitted burette.
- (iv) Note the initial reading of the volume of permanganate solution in the burette and add it in small volumes to the hot oxalic acid solution while swirling the contents of the flask gently. The violet colour of permanganate solution is

discharged on reaction with oxalic acid. The end point is indicated by the appearance of permanent light pink colour due to a slight excess of permanganate solution.

- (v) Repeat the titration till three concordant readings are obtained. Since the solution of KMnO_4 is of dark colour, the upper meniscus should be considered for noting the burette readings.
- (vi) Record the readings as shown in observation Table 6.1 and calculate the strength of potassium permanganate solution in mols/litre.

Table 6.1 : Titration of potassium permanganate solution against standard oxalic acid solution

Sl. No.	Volume of Oxalic acid in mL	Burette readings		Volume (V) of KMnO_4 used $V = (y-x)$ mL
		Initial (x)	Final (y)	

Calculations

- (i) The strength of the unknown solution in terms of molarity may be determined by the following equation.

$$a_1 M_1 V_1 = a_2 M_2 V_2 \quad (6.1)$$

For oxalic acid vs potassium permanganate titration:

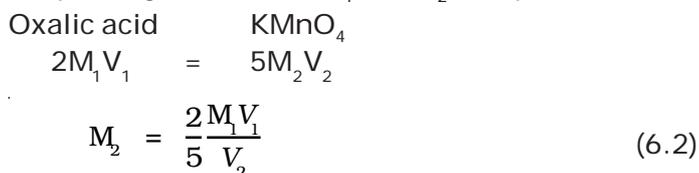
$a_1 = 2$, (the number of electrons lost per formula unit of oxalic acid in a balanced equation of half cell reaction)

$a_2 = 5$, (the number of electrons gained per formula unit of potassium permanganate in the balanced equation of half cell reaction)

M_1 and M_2 are the molarities of oxalic acid and potassium permanganate solutions used in the titration.

V_1 and V_2 are the volumes of oxalic acid and potassium permanganate solutions.

On putting the value of a_1 and a_2 in equation 6.1 we get



We can calculate the molarity of potassium permanganate solution by using equation 6.2. Strength of the solution is given by the following equation:

$$\text{Strength} = \text{Molarity} \times \text{Molar mass}$$

Result

- (i) Molarity of KMnO_4 solution is _____.
- (ii) Strength of KMnO_4 solution is _____.

Precautions

- Always rinse the burette and the pipette with the solutions to be taken in them.
- Never rinse the conical flask with the experimental solutions.
- Remove the air gaps if any, from the burette.
- Never forget to remove the funnel from the burette before noting the initial reading of the burette.
- No drop of the liquid should hang at the tip of the burette at the end point and while noting reading.
- Always read the upper meniscus for recording the burette reading in the case of all coloured solutions.
- Never use pipette and burette with a broken nozzle.
- Lower end of the pipette should always remain dipped in the liquid while sucking the liquid.
- Do not blow out the last drop of the solution from the jet end of the pipette.
- The strength of the solution must be calculated up to the fourth decimal place.
- Do not forget to heat the mixture of oxalic acid and H_2SO_4 solutions between $50^\circ\text{--}60^\circ\text{C}$ while titrating it against potassium permanganate.



Discussion Questions

- What specific name is given to the permanganate titrations?
- Which indicator is used in the permanganate titration?

- (iii) Why is a burette with pinch-cock regulator not used for the permanganate titration ?
- (iv) Why do we heat oxalic acid solution containing sulphuric acid up to 50–60°C in the permanganate titration?

EXPERIMENT 6.2

Aim

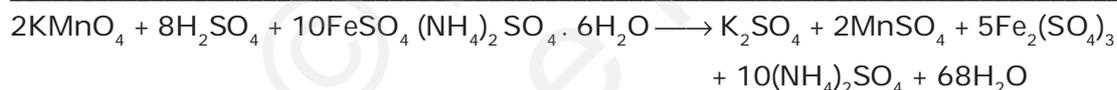
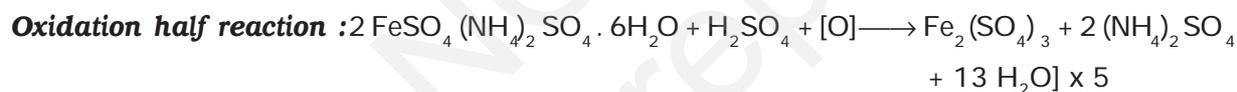
To determine the concentration/molarity of KMnO_4 solution by titrating it against standard solution of ferrous ammonium sulphate.

Theory

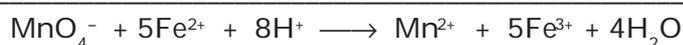
Like oxalic acid, ferrous ammonium sulphate also acts as a reducing agent in the titration against potassium permanganate.

The reaction which takes place is given below :

(a) Chemical equation



(b) Ionic equation



The oxidation number of iron in Mohr's salt is +2. Iron is oxidised during the reaction and its oxidation number changes from +2 to +3. In this titration heating of ferrous ammonium sulphate solution is not required because reaction rate is very high even at room temperature. Also, at high temperatures, ferrous ions may be oxidised to ferric ions by oxygen of air and error may be introduced in the experiment.

Material Required



- Measuring flask (250 mL) : One
- Burette (50 mL) : One
- Burette stand : One
- Pipette : One
- Conical flask : One
- Glazed tile (white) : One
- Funnel : One
- Weighing bottle : One



- Potassium permanganate solution : As per need
- Dilute sulphuric acid : As per need
- Ferrous ammonium sulphate : As per need

Procedure

Potassium permanganate



Sulphuric acid



A. Preparation of 0.05 M, standard solution of ferrous ammonium sulphate

(Molar mass of $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O} = 392 \text{ g mol}^{-1}$).

- (i) Weigh 4.9000 g of ferrous ammonium sulphate and transfer it into a 250 mL measuring flask through a funnel.
- (ii) Transfer the solid sticking to the funnel with the help of distilled water into the flask and add dilute H_2SO_4 into the flask drop wise to get the clear solution.
- (iii) Shake the flask till the substance dissolves and make the solution upto the mark.

B. Titration of ferrous ammonium sulphate against potassium permanganate solution

- (i) Rinse and fill the clean burette with potassium permanganate solution. Remove air bubbles if any, from the burette tip by releasing some solution through it.
- (ii) Take 10 mL of 0.05 M ferrous ammonium sulphate solution in a conical flask and add half test tube ($\approx 5 \text{ mL}$) full of (1.0 M) H_2SO_4 to it.
- (iii) Titrate the above solution with potassium permanganate solution till the colour of the solution changes to permanent pink. Swirl the content of the flask during the titration.
- (iv) Repeat the titration, until three concordant readings are obtained.
- (v) Record the readings as shown in observation Table 6.2 and calculate the strength of potassium permanganate solution in mols/litre.

Table 6.2 : Titration of potassium permanganate solution against standard ferrous ammonium sulphate solution

Sl. No.	Volume of ferrous ammonium sulphate solution used for each titration in mL	Burette Readings		Volume (V) of KMnO_4 used $V = (y-x)$ mL
		Initial (x)	Final (y)	

Calculations

The strength of unknown solution in terms of molarity may be determined by the following equation :

$$a_1 M_1 V_1 = a_2 M_2 V_2$$

M_1 and M_2 are the molarities of ferrous ammonium sulphate and potassium permanganate solutions and V_1 and V_2 are volumes of ferrous ammonium sulphate and potassium permanganate solutions, respectively.

$a_1 = 1$, (the number of electrons lost per formula unit of ferrous ammonium sulphate in the half cell reaction)

$a_2 = 5$, (the number of electrons gained per formula unit of potassium permanganate in a half cell reaction)

Strength can be calculated by the formula given below :

$$\text{Strength} = \text{Molarity} \times \text{Molar mass}$$

Result

The strength of the given potassium permanganate solution is ____ g/L.

Precautions

- Always use a fresh sample of ferrous ammonium sulphate to prepare its standard solution.
- Other precautions are same as that in Experiment 6.1.

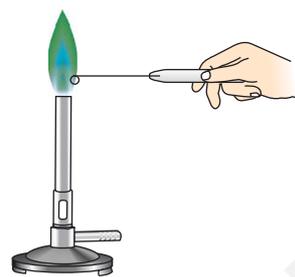


Discussion Questions

- (i) Why is ferrous ammonium sulphate solution not heated before titration?
- (ii) Why is nitric acid or hydrochloric acid not used in permanganate titration? Explain.
- (iii) Why is dilute sulphuric acid added while preparing a standard solution of ferrous ammonium sulphate?
- (iv) How will you prepare 100 mL of 0.1 M standard solution of ferrous ammonium sulphate?
- (v) Why is KMnO_4 not regarded as a primary standard?
- (vi) What type of titrations are given the name redox titrations? Name some other redox titrations?

UNIT-7

SYSTEMATIC QUALITATIVE ANALYSIS



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

- Formation of a precipitate
- Change in colour
- Evolution of gas etc.

Systematic analysis of an inorganic salt involves the following steps:

- Preliminary examination of solid salt and its solution.
- Determination of anions by reactions carried out in solution (wet tests) and confirmatory tests.
- Determination of cations by reactions carried out in solution (wet tests) and confirmatory tests.

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

Heating of dry salt, blow pipe test, flame tests, borax bead test, sodium carbonate bead test, charcoal cavity test etc. come under dry tests. Some of these tests are given later in this unit.

Solubility of a salt in water and the pH of aqueous solutions give important information about the nature of ions present in the salt. If a solution of the salt is acidic or basic in nature, this means that it is being hydrolysed in water. If the solution is basic in nature then salt may be some carbonate or sulphide etc. If the solution shows acidic nature then it may be an acid salt or salt of weak base and strong acid. In this case it is best to neutralise the solution with sodium carbonate before testing it for anions.

Gases evolved in the preliminary tests with dil. H_2SO_4 /dil. HCl and conc. H_2SO_4 also give good indication about the presence of acid radicals (See Tables 7.1 and 7.3). Preliminary tests should always be performed before starting the confirmatory tests for the ions.

EXPERIMENT 7.1

Aim

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

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

Anions - CO_3^{2-} , S^{2-} , SO_3^{2-} , SO_4^{2-} , NO_2^- , NO_3^- , Cl^- , Br^- , I^- , PO_4^{3-} , $\text{C}_2\text{O}_4^{2-}$,
 CH_3COO^- .

(Insoluble salts to be excluded)

Theory

Two basic principles of great use in the analysis are:

- (i) the Solubility product; and
- (ii) the Common ion effect.

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

Material Required



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



- Reagents : As per need

SYSTEMATIC ANALYSIS OF ANIONS

Step - I : Preliminary Test with Dilute Sulphuric Acid

In this test the action of dilute sulphuric acid (procedure is given below) on the salt is noted at room temperature and on warming.

Carbonate (CO_3^{2-}), sulphide (S^{2-}), sulphite (SO_3^{2-}), nitrite (NO_2^-) and acetate (CH_3COO^-) react with dilute sulphuric acid to evolve different gases. Study of the characteristics of the gases evolved gives information about the anions. Summary of characteristic properties of gases is given in Table 7.1 below.

Procedure

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

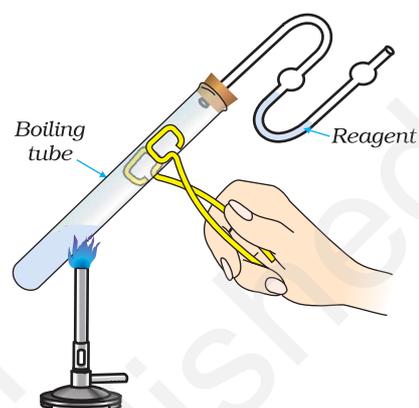


Fig. 7.1 : Testing a Gas

Table 7.1 : Preliminary test with dilute sulphuric acid

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

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

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

Preparation of sodium carbonate extract

Take 1 g of salt in a porcelain dish or boiling tube. Mix about 3 g of solid sodium carbonate and add 15 mL of distilled water to it. Stir and boil the content for about 10 minutes. Cool, filter and collect the filtrate in a test tube and label it as sodium carbonate extract.

Confirmatory tests for acid radicals, which react with dilute sulphuric acid are given below in Table 7.2.

Table 7.2 : Confirmatory tests for CO_3^{2-} , S^{2-} , SO_3^{2-} , NO_2^- , CH_3COO^-

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

* Like CO_2 sulphur dioxide also turns lime water milky. But CO_2 is odourless gas and SO_2 has a characteristic smell.

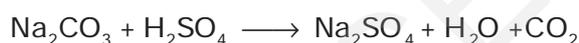
Acetate (CH_3COO^-)	<p>(a) Take 0.1 g of salt in a china dish. Add 1 mL of ethanol and 0.2 mL conc. H_2SO_4 and heat. Fruity odour confirms the presence of acetate ion.</p> <p>(b) Take 0.1 g of salt in a test tube, add 1-2 mL distilled water, shake well filter if necessary. Add 1 to 2 mL neutral** ferric chloride solution to the filtrate. Deep red colour appears which disappears on boiling and a brown-red precipitate is formed.</p>
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** **Preparation of neutral Ferric Chloride :** Add dilute NaOH solution to ferric chloride solution drop by drop with shaking until a small but permanent precipitate of ferric hydroxide is obtained. Filter the precipitate and use the filtrate for analysis.

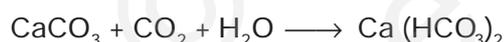
Chemistry of Confirmatory Tests

1. Test for Carbonate ion [CO_3^{2-}]

If there is effervescence with the evolution of a colourless and odourless gas on adding dil. H_2SO_4 to the solid salt, this indicates the presence of carbonate ion. The gas turns lime water milky due to the formation of CaCO_3 (Fig. 7.1)



If CO_2 gas is passed in excess through lime water, the milky appearance disappears due to the formation of calcium hydrogen carbonate which is soluble in water.



Hydrogen sulphide



2. Test for Sulphide ion [S^{2-}]

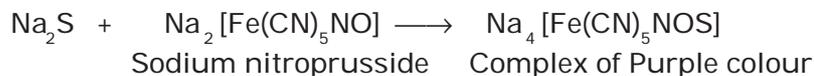
- (a) With warm dilute H_2SO_4 a sulphide gives hydrogen sulphide gas which smells like rotten eggs. A piece of filter paper dipped in lead acetate solution turns black on exposure to the gas due to the formation of lead sulphide which is black in colour.



Lead sulphide
Black precipitate

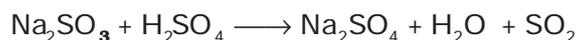
- (b) If the salt is soluble in water, take the solution of salt in water make it alkaline with ammonium hydroxide and add sodium nitroprusside solution. If it is insoluble in water take sodium carbonate extract and add a few drops of sodium nitroprusside solution. Purple or violet

colouration due to the formation of complex compound $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$ confirms the presence of sulphide ion in the salt.

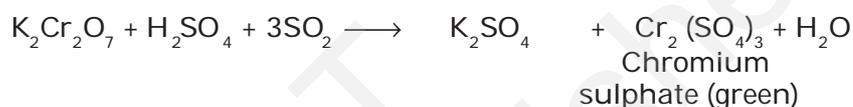


3. Test for Sulphite ion $[\text{SO}_3^{2-}]$

- (a) On treating sulphite with warm dil. H_2SO_4 , SO_2 gas is evolved which is suffocating with the smell of burning sulphur.



The gas turns potassium dichromate paper acidified with dil. H_2SO_4 , green.



Barium compounds



Potassium permanganate



- (b) An aqueous solution or sodium carbonate extract of the salt produces a white precipitate of barium sulphite on addition of barium chloride solution.



This precipitate gives following tests.

- (i) This precipitate on treatment with dilute HCl, dissolves due to decomposition of sulphite by dilute HCl. Evolved SO_2 gas can be tested.

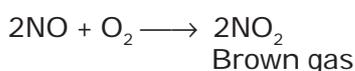
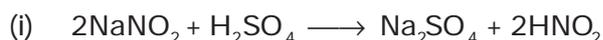


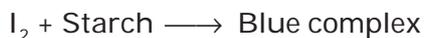
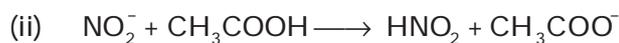
- (ii) Precipitate of sulphite decolourises acidified potassium permanganate solution.



4. Test for Nitrite ion $[\text{NO}_2^-]$

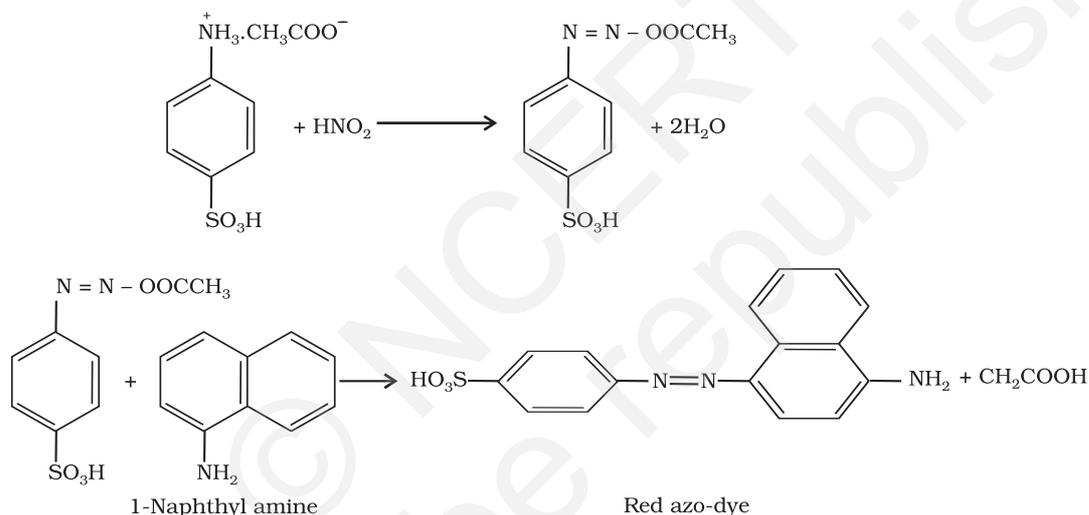
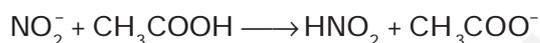
- (a) On treating a solid nitrite with dil. H_2SO_4 and warming, reddish brown fumes of NO_2 gas are evolved. Addition of potassium iodide solution to the salt solution followed by freshly prepared starch solution and acidification with acetic acid produces blue colour. Alternatively, a filter paper moistened with potassium iodide and starch solution and a few drops of acetic acid turns blue on exposure to the gas due to the interaction of liberated iodine with starch.





(b) Sulphanilic acid — 1-naphthylamine reagent test (Griss-Ilosvay test)

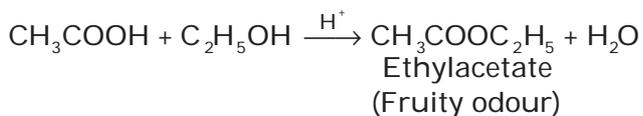
On adding sulphanilic acid and 1-naphthylamine reagent to the water extract or acidified with acetic acid, sulphanilic acid is diazotised in the reaction by nitrous acid formed. Diazotised acid couples with 1-naphthylamine to form a red azo-dye.



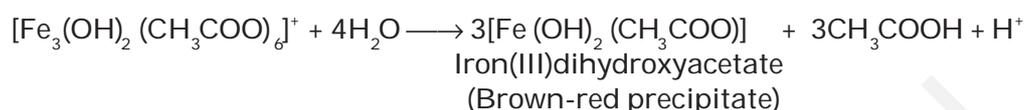
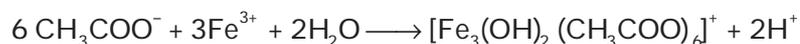
The test solution should be very dilute. In concentrated solutions reaction does not proceed beyond diazotisation.

5. Test for Acetate ion $[\text{CH}_3\text{COO}^-]$

(a) If the salt smells like vinegar on treatment with dil. H_2SO_4 , this indicates the presence of acetate ions. Take 0.1 g of salt in a china dish and add 1 mL of ethanol. Then add about 0.2 mL of conc. H_2SO_4 and heat. Fruity odour of ethyl acetate indicates the presence of CH_3COO^- ion.



- (b) Acetate gives deep red colour on reaction with neutral ferric chloride solution due to the formation of complex ion which decomposes on heating to give Iron (III) dihydroxyacetate as brown red precipitate.



Step-II : Preliminary Test with Concentrated Sulphuric Acid

If no positive result is obtained from dil. H_2SO_4 test, take 0.1 g of salt in a test tube and 3-4 drops of conc. H_2SO_4 . Observe the change in the reaction mixture in cold and then warm it. Identify the gas evolved on heating (see Table 7.3).

Table 7.3 : Preliminary examination with concentrated sulphuric acid

Observations	Inference	
	Gas/Vapours Evolved	Possible Anions
A colourless gas with pungent smell, which gives dense white fumes when a rod dipped in ammonium hydroxide is brought near the mouth of the test tube.	HCl	Chloride, (Cl^-)
Reddish brown gas with a pungent odour is evolved. Intensity of reddish gas increases on heating the reaction mixture after addition of solid MnO_2 to the reaction mixture. Solution also acquires red colour.	Br_2 vapours	Bromide, (Br^-)
Violet vapours, which turn starch paper blue and a layer of violet sublimate is formed on the sides of the tube. Fumes become dense on adding MnO_2 to the reaction mixture.	I_2 vapours	Iodide, (I^-)
Brown fumes evolve which become dense upon heating the reaction mixture after addition of copper turnings and the solution acquires blue colour.	NO_2	Nitrate, (NO_3^-)
Colourless, odourless gas is evolved which turns lime water milky and the gas coming out of lime water burns with a blue flame, if ignited.	CO and CO_2	Oxalate, ($\text{C}_2\text{O}_4^{2-}$)

Confirmatory tests for the anions which react with concentrated sulphuric acid are given in Table 7.4.

Table 7.4 : Confirmatory tests for Cl^- , Br^- , I^- , NO_3^- and $\text{C}_2\text{O}_4^{2-}$

Anion	Confirmatory Test
Chloride (Cl^-)	<p>(a) Take 0.1 g of salt in a test tube, add a pinch of manganese dioxide and 3-4 drops of conc. sulphuric acid. Heat the reaction mixture. Greenish yellow chlorine gas is evolved which is detected by its pungent odour and bleaching action.</p> <p>(b) Take 1 mL of sodium carbonate extract in a test tube, acidify it with dil. HNO_3 or take water extract and add silver nitrate solution. A curdy white precipitate is obtained which is soluble in ammonium hydroxide solution.</p> <p>(c) Take 0.1 g salt and a pinch of solid potassium dichromate in a test tube, add conc. H_2SO_4, heat and pass the gas evolved through sodium hydroxide solution. It becomes yellow. Divide the solution into two parts. Acidify one part with acetic acid and add lead acetate solution. A yellow precipitate is formed. Acidify the second part with dilute sulphuric acid and add 1 mL of amyl alcohol followed by 1 mL of 10% hydrogen peroxide. After gentle shaking the organic layer turns blue.</p>
Bromide (Br^-)	<p>(a) Take 0.1 g of salt and a pinch of MnO_2 in a test tube. Add 3-4 drops conc. sulphuric acid and heat. Intense brown fumes are evolved.</p> <p>(b) Neutralise 1 mL of sodium carbonate extract with hydrochloric acid (or take the water extract). Add 1 mL carbon tetrachloride (CCl_4)/chloroform (CHCl_3)/carbon disulphide. Now add an excess of chlorine water dropwise and shake the test tube. A brown colouration in the organic layer confirms the presence of bromide ion.</p> <p>(c) Acidify 1 mL of sodium carbonate extract with dil. HNO_3 (or take 1 mL water extract) and add silver nitrate solution. A pale yellow precipitate soluble with difficulty in ammonium hydroxide solution is obtained.</p>
Iodide (I^-)	<p>(a) Take 1 mL of salt solution neutralised with HCl and add 1 mL chloroform/carbon tetrachloride/carbon disulphide. Now add an excess of chlorine water drop wise and shake the test tube. A violet colour appears in the organic layer.</p> <p>(b) Take 1 mL of sodium carbonate extract acidify it with dil. HNO_3 (or take water extract). Add, silver nitrate solution. A yellow precipitate insoluble in NH_4OH solution is obtained.</p>

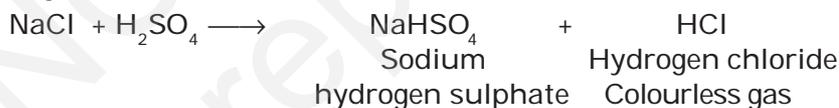
*Nitrate (NO_3^-)	Take 1 mL of salt solution in water in a test tube. Add 2 mL conc. of H_2SO_4 and mix thoroughly. Cool the mixture under the tap. Add freshly prepared ferrous sulphate along the sides of the test tube without shaking. A dark brown ring is formed at the junction of the two solutions.
Oxalate ($\text{C}_2\text{O}_4^{2-}$)	(a) Take 1 mL of water extract or sodium carbonate extract acidified with acetic acid and add calcium chloride solution. A white precipitate insoluble in ammonium oxalate and oxalic acid solution but soluble in dilute hydrochloric acid and dilute nitric acid is formed. (b) Take the precipitate from test (a) and dissolve it in dilute H_2SO_4 . Add very dilute solution of KMnO_4 and warm. Colour of KMnO_4 solution is discharged. Pass the gas coming out through lime water. The lime water turns milky.

Chemistry of Confirmatory Tests

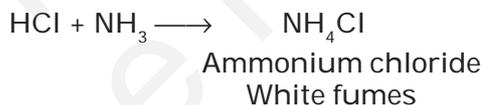
1. Test for Chloride ion [Cl^-]

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

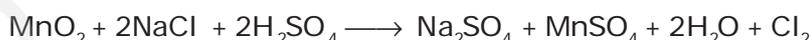
Manganese dioxide



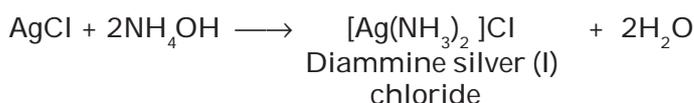
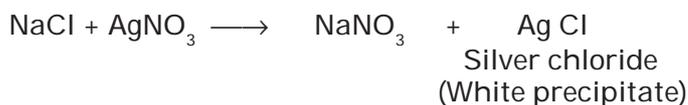
Silver nitrate



- (b) If a salt gives effervescence on heating with conc. H_2SO_4 and MnO_2 and a light greenish yellow pungent gas is evolved, this indicates the presence of Cl^- ions.

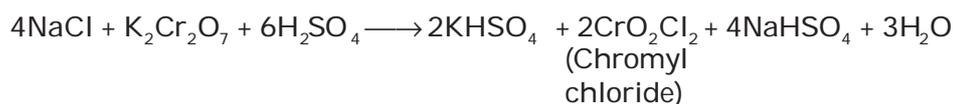


- (c) Salt solution acidified with dilute HNO_3 on addition of silver nitrate solution gives a curdy white precipitate soluble in ammonium hydroxide solution. This indicates the presence of Cl^- ions in the salt.



* This test can also be performed by adding first ferrous sulphate solution and then conc. H_2SO_4 .

- (d) Mix a little amount of salt and an equal amount of solid potassium dichromate ($K_2Cr_2O_7$) in a test tube and add conc. H_2SO_4 to it. Heat the test tube and pass the evolved gas through sodium hydroxide solution. If a yellow solution is obtained, divide the solution into two parts. Acidify the first part with acetic acid and then add lead acetate solution. Formation of a yellow precipitate of lead chromate confirms the presence of chloride ions in the salt. This test is called **chromyl chloride test**.*



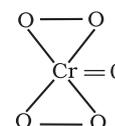
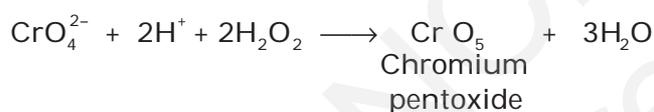
Chromyl chloride



Lead chromate



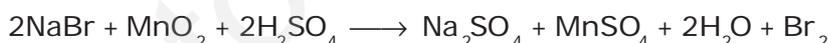
Acidify the second part with dilute sulphuric acid and add small amounts of amyl alcohol and then 1 mL of 10% hydrogen peroxide solution. On gentle shaking organic layer turns blue. CrO_4^{2-} ion formed in the reaction of chromyl chloride with sodium hydroxide reacts with hydrogen peroxide to form chromium pentoxide (CrO_5) (See structure) which dissolves in amyl alcohol to give blue colour.



Structure of chromium pentoxide

2. Test for Bromide ion (Br^-)

If on heating the salt with conc. H_2SO_4 reddish brown fumes of bromine are evolved in excess, this indicates the presence of Br^- ions. The fumes get intensified on addition of MnO_2 . Bromine vapours turn starch paper yellow.



Bromine
very toxic by
inhalation
corrosive



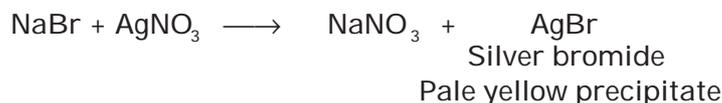
- (a) Add 1 mL of carbon tetrachloride (CCl_4)/chloroform ($CHCl_3$)** and excess of freshly prepared chlorine water dropwise to the salt solution in water or sodium carbonate extract neutralised with dilute HCl. Shake the test tube vigorously. The appearance of an orange brown colouration in the organic layer due to the dissolution of bromine in it, confirms the presence of bromide ions.



* Chromyl chloride test should be performed with minimum amount of substance to avoid pollution by Cr^{3+} ions.

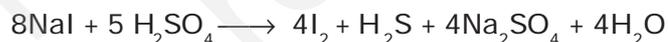
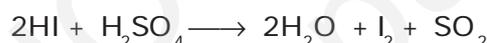
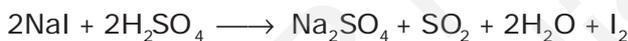
** In place of carbon tetrachloride or chloroform, carbon disulphide or dichloromethane (CH_2Cl_2) can also be used.

- (b) Acidify the sodium carbonate extract of the salt with dil. HNO_3 . Add silver nitrate (AgNO_3) solution and shake the test tube. A pale yellow precipitate is obtained which dissolves in ammonium hydroxide with difficulty.

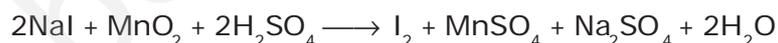


3. Test for Iodide ion (I^-)

- (a) If on heating the salt with conc. H_2SO_4 , deep violet vapours with a pungent smell are evolved. These turns starch paper blue and a violet sublimate is formed on the sides of the test tube, it indicates the presence of I^- ions. Some HI, sulphur dioxide, hydrogen sulphide, and sulphur are also formed due to the following reactions.



On adding MnO_2 to the reaction mixture, the violet vapours become dense.

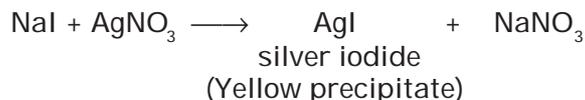


- (b) Add 1 mL of CHCl_3 or CCl_4 and chlorine water in excess to the salt solution in water or sodium carbonate extract neutralised with dil. HCl and shake the test tube vigorously. Presence of violet colouration in the organic layer confirms the presence of iodide ions.



Iodine dissolves in the organic solvent and the solution becomes violet.

- (c) Acidify sodium carbonate extract of the salt with dil. HNO_3 and add AgNO_3 solution. Appearance of a yellow precipitate insoluble in excess of NH_4OH confirms the presence of iodide ions.



Iodine,
harmful by
inhalation
and contact
with skin



Chlorine,
toxic by
inhalation

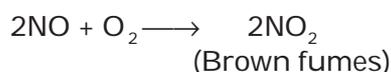
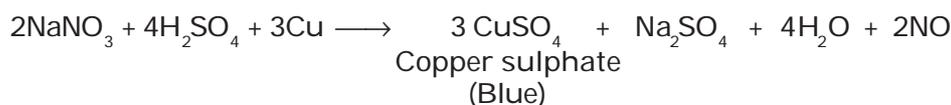


Chloroform,
harmful and
toxic by
inhalation



4. Test for Nitrate ion $[\text{NO}_3^-]$

- (a) If on heating the salt with conc. H_2SO_4 light brown fumes are evolved then heat a small quantity of the given salt with few copper turnings or chips and conc. H_2SO_4 . Evolution of excess of brown fumes indicates the presence of nitrate ions. The solution turns blue due to the formation of copper sulphate.



- (b) Take 1 mL of an aqueous solution of the salt and add 2 mL conc. H_2SO_4 slowly. Mix the solutions thoroughly and cool the test tube under the tap. Now, add freshly prepared ferrous sulphate solution along the sides of the test tube dropwise so that it forms a layer on the top of the liquid already present in the test tube. A dark brown ring is formed at the junction of the two solutions due to the formation of nitroso ferrous sulphate (Fig. 7.2). Alternatively first ferrous sulphate is added and then concentrated sulphuric acid is added.

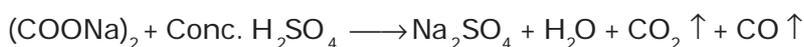


Fig. 7.2 : Formation of brown ring



5. Test for Oxalate ion $[\text{C}_2\text{O}_4^{2-}]$

If carbon dioxide gas along with carbon monoxide gas is evolved in the preliminary examination with concentrated sulphuric acid, this gives indication about the presence of oxalate ion.



Copper
sulphate



Nitric
acid

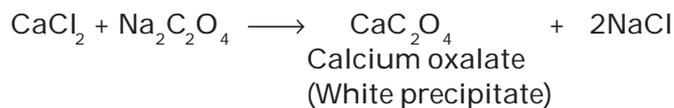


Oxalates



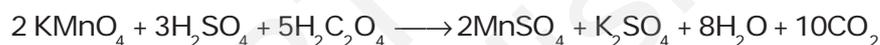
Oxalate is confirmed by the following tests:

- (a) Acidify sodium carbonate extract with acetic acid and add calcium chloride solution. A white precipitate of calcium oxalate, insoluble in ammonium oxalate and oxalic acid solution indicates the presence of oxalate ion.



- (b) KMnO_4 test

Filter the precipitate from test (a). Add dil. H_2SO_4 to it followed by dilute KMnO_4 solution and warm. Pink colour of KMnO_4 is discharged:



Pass the gas evolved through lime water. A white precipitate is formed which dissolves on passing the gas for some more time.

Step-III : Test for Sulphate and Phosphate

If no positive test is obtained in Steps-I and II, then tests for the presence of sulphate and phosphate ions are performed. These tests are summarised in Table 7.5.

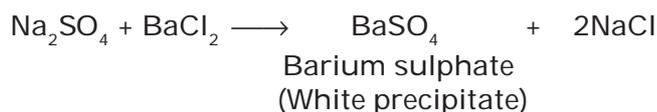
Table 7.5 : Confirmatory tests for Sulphate and Phosphate

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

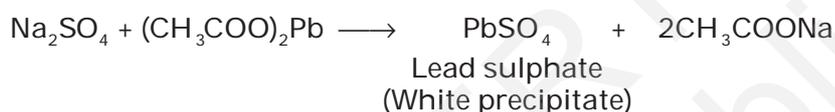
Chemistry of Confirmatory Tests

1. Test of Sulphate ions $[\text{SO}_4^{2-}]$

- (a) Aqueous solution or sodium carbonate extract of the salt acidified with acetic acid on addition of barium chloride gives a white precipitate of barium sulphate insoluble in conc. HCl or conc. HNO_3 .

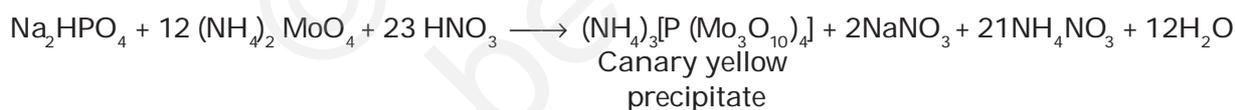


- (b) Sulphate ions give white precipitate of lead sulphate when aqueous solution or sodium carbonate extract neutralised with acetic acid is treated with lead acetate solution.



2. Test for Phosphate ion $[\text{PO}_4^{3-}]$

- (a) Add conc. HNO_3 and ammonium molybdate solution to the test solution containing phosphate ions and boil. A yellow colouration in solution or a canary yellow precipitate of ammonium-phosphomolybdate, $(\text{NH}_4)_3[\text{P}(\text{Mo}_3\text{O}_{10})_4]$ is formed. Each oxygen of phosphate has been replaced by Mo_3O_{10} group.



SYSTEMATIC ANALYSIS OF CATIONS

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

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

1. Colour Test

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

Table 7.6 : Characteristic colours of some metal ions

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

2. Dry Heating Test

- (i) Take about 0.1 g of the dry salt in a clean and dry test tube.
- (ii) Heat the above test tube for about one minute and observe the colour of the residue when it is hot and also when it becomes cold. Observation of changes gives indications about the presence of cations, which may not be taken as conclusive evidence (see Table 7.7).

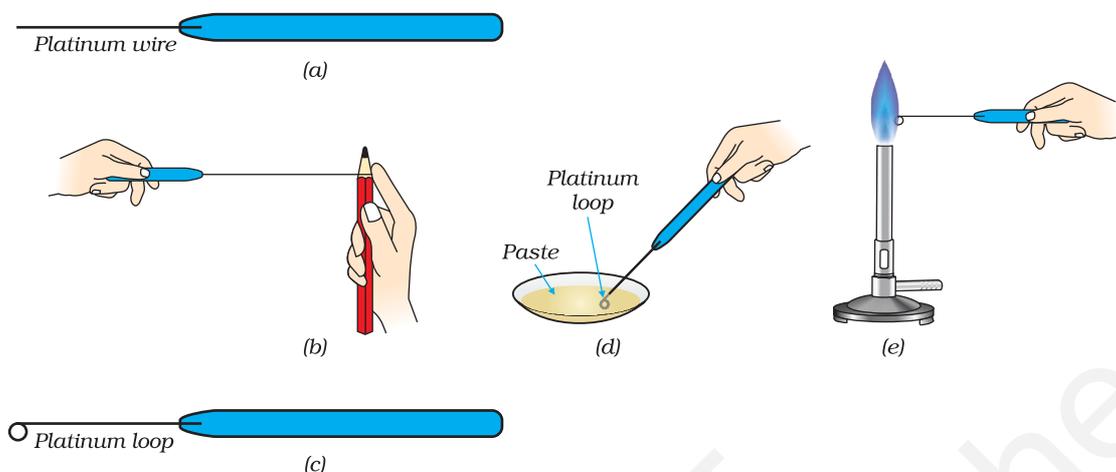
Table 7.7 : Inferences from the colour of the salt in cold and on heating

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

3. Flame Test

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

- (i) Make a tiny loop at one end of a platinum wire.
- (ii) To clean the loop dip it into concentrated hydrochloric acid and hold it in a non-luminous flame (Fig. 7.3).
- (iii) Repeat step (ii) until the wire imparts no colour to the flame.
- (iv) Put 2-3 drops of concentrated hydrochloric acid on a clean watch glass and make a paste of a small quantity of the salt in it.
- (v) Dip the clean loop of the platinum wire in this paste and introduce the loop in the non-luminous (oxidising) flame (Fig. 7.3).
- (vi) Observe the colour of the flame first with the naked eye and then through a blue glass and identify the metal ion with the help of Table 7.8.

**Fig. 7.3 : Performing flame test****Table 7.8 : Inference from the flame test**

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

4. Borax Bead Test

This test is employed only for coloured salts because borax reacts with metal salts to form metal borates or metals, which have characteristic colours.

- To perform this test make a loop at the end of the platinum wire and heat it in a flame till it is red hot.
- Dip the hot loop into borax powder and heat it again until borax forms a colourless transparent bead on the loop. Before dipping the borax bead in the test salt or mixture, confirm that the bead is transparent and colourless. If it is coloured this means that, the platinum wire is not clean. Then make a fresh bead after cleaning the wire.
- Dip the bead in a small quantity of the dry salt and again hold it in the flame.
- Observe the colour imparted to the bead in the non - luminous flame as well as in the luminous flame while it is hot and when it is cold (Fig. 7.4).
- To remove the bead from the platinum wire, heat it to redness and tap the platinum wire with your finger. (Fig. 7.5).

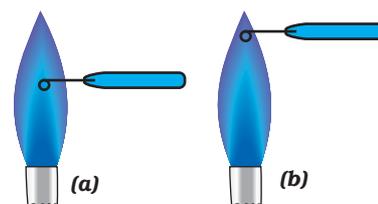
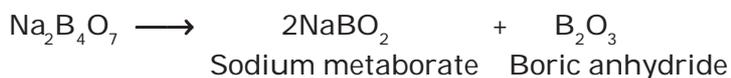


Fig. 7.4 : Borax bead test
(a) Heating in reducing flame (b) Heating in oxidising flame

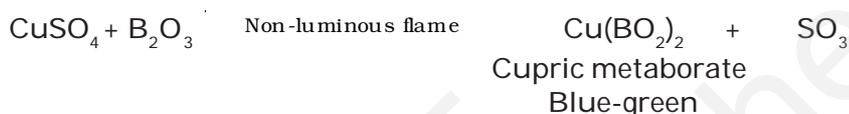
On heating, borax loses its water of crystallisation and decomposes to give sodium metaborate and boric anhydride.



Borax



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

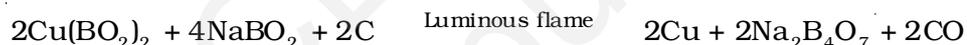


Two reactions may take place in the reducing flame:

(i) The blue $\text{Cu}(\text{BO}_2)_2$ is reduced to colourless cuprous metaborate as follows:



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



The preliminary identification of metal ion can be made from Table 7.9.

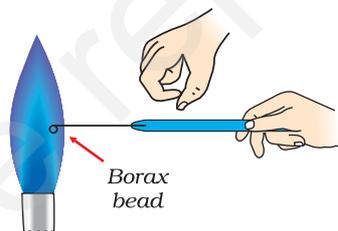


Fig. 7.5 : Removing borax bead

Table 7.9 : Inference from the borax bead test

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

5. Charcoal Cavity Test

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

- (i) Make a small cavity in a charcoal block with the help of a charcoal borer. Do not apply pressure otherwise it will crack [Fig.7.6 (a)].
- (ii) Fill the cavity with about 0.2 g of the salt and about 0.5 g of anhydrous sodium carbonate.

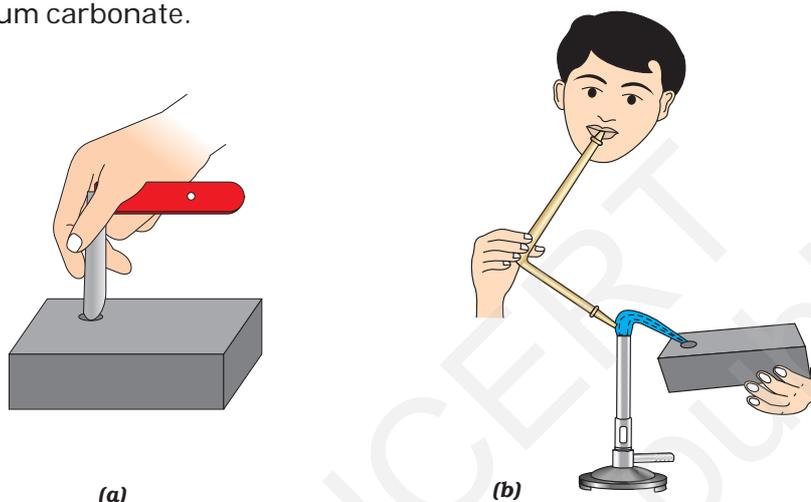
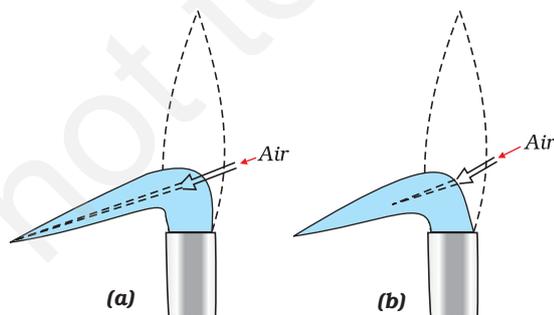


Fig. 7.6 : (a) Making charcoal cavity (b) Heating salt in the cavity

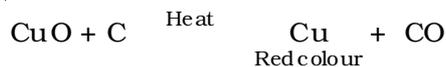
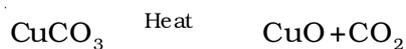
- (iii) Moisten the salt in the cavity with one or two drops of water, otherwise salt/mixture will blow away.
- (iv) Use a blowpipe to heat the salt in a luminous (reducing) flame and observe the colour of oxide/ metallic bead formed in the cavity both when hot and cold [Fig. (7.6 b)]. Obtain oxidising and reducing flame as shown in Fig. 7.7 a and b.
- (v) Always bore a fresh cavity for testing the new salt.



**Fig. 7.7 : Obtaining oxidising and reducing flame
(a) Oxidising flame; and (b) Reducing flame**

- Note :**
- To obtain oxidising flame hold the nozzle of the blowpipe about one third within the flame.
 - To obtain reducing flame place nozzle of the blowpipe just outside the flame.

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



In case of ZnSO_4 :



Yellow when hot,
White when cold

The metal ion can be inferred from Table 7.10.

Table 7.10 : Inference from the charcoal cavity test

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

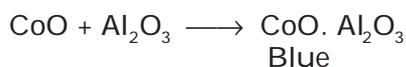
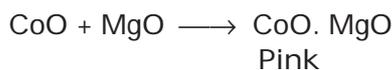
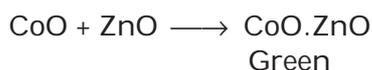
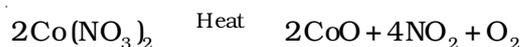
6. Cobalt Nitrate Test

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

- Treat the residue with two or three drops of cobalt nitrate solution.
- Heat it strongly in non-luminous flame with the help of a blow pipe and observe the colour of the residue.

On heating, cobalt nitrate decomposes into cobalt (II) oxide, which gives a characteristic colour with metal oxide present in the cavity.

Thus, with ZnO , Al_2O_3 and MgO , the following reactions occur.



Step-II : Wet Tests for Identification of Cations

The cations indicated by the preliminary tests given above are confirmed by systematic analysis given below.

The first essential step is to prepare a clear and transparent solution of the salt. This is called **original solution**. It is prepared as follows:

Preparation of Original Solution (O.S.)

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

The following solvents are tried:

1. Take a little amount of the salt in a clean boiling tube and add a few mL of distilled water and shake it. If the salt does not dissolve, heat the content of the boiling tube till the salt completely dissolves.
2. If the salt is insoluble in water as detailed above, take fresh salt in a clean boiling tube and add a few mL of dil.HCl to it. If the salt is insoluble in cold, heat the boiling tube till the salt is completely dissolved.
3. If the salt does not dissolve either in water or in dilute HCl even on heating, try to dissolve it in a few mL of conc. HCl by heating.
4. If salt does not dissolve in conc. HCl, then dissolve it in dilute nitric acid.
5. If salt does not dissolve even in nitric acid then a mixture of conc. HCl and conc. HNO₃ in the ratio 3:1 is tried. This mixture is called aqua regia. A salt not soluble in aqua regia is considered to be an insoluble salt.

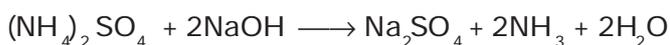
Group Analysis

(I) Analysis of Zero group cation (NH₄⁺ ion)

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

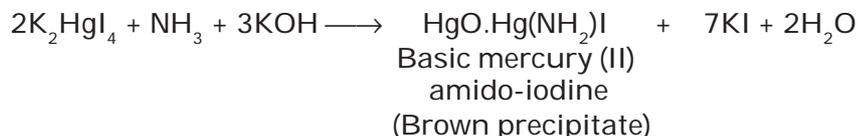
Chemistry of Confirmatory Tests for NH₄⁺ ion

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



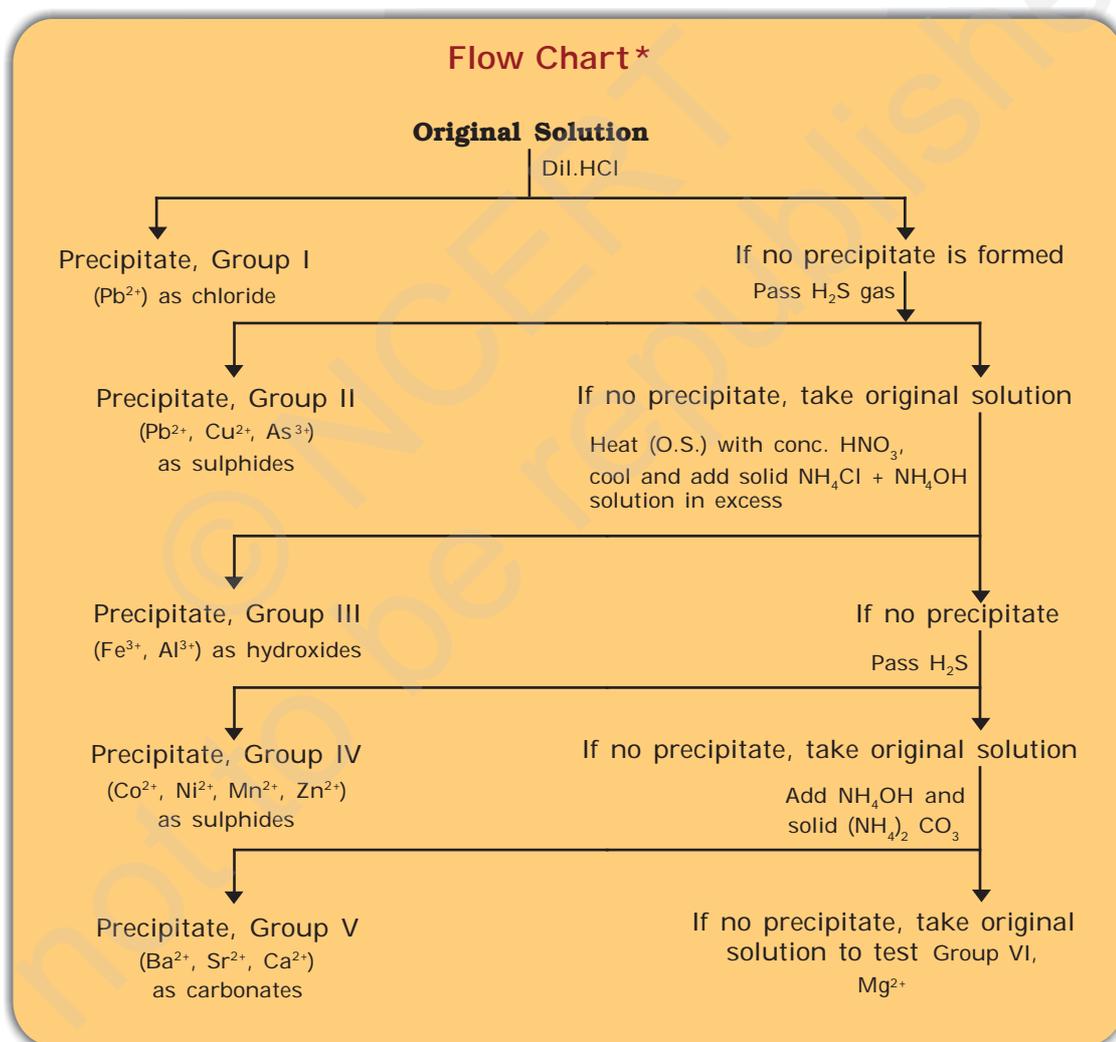
Mercury
Salts

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



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

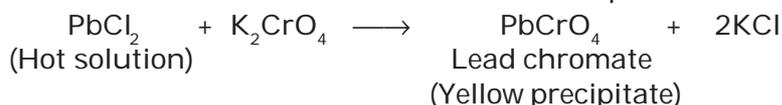
The separation of all the six groups is represented as below:



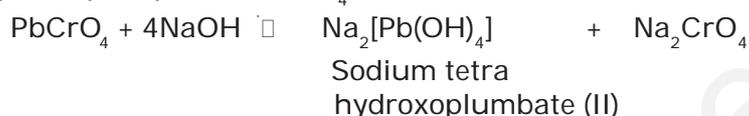
* This flow chart is for the detection of one cation only. For detection of more than one cation modification will be required.

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

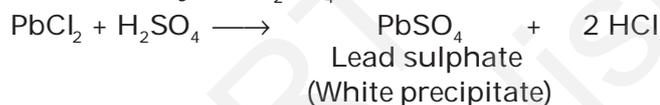
2. On addition of potassium chromate (K_2CrO_4) solution a yellow precipitate of lead chromate is obtained. This confirms the presence of Pb^{2+} ions.



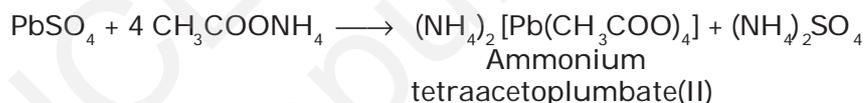
The yellow precipitate (PbCrO_4) is soluble in hot NaOH solution.



3. A white precipitate of lead sulphate (PbSO_4) is formed on addition of alcohol followed by dil. H_2SO_4 .



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



Hydrogen
sulphide



(III) Analysis of Group-II cations

If group-I is absent, add excess of water to the same test tube. Warm the solution and pass H_2S gas for 1-2 minutes (Fig. 7.6). Shake the test tube. If a precipitate appears, this indicates the presence of group-II cations. Pass more H_2S gas through the solution to ensure complete precipitation and separate the precipitate. If the colour of the precipitate is black, it indicates the presence of Cu^{2+} or Pb^{2+} ions. If it is yellow in colour, then presence of As^{3+} ions is indicated.

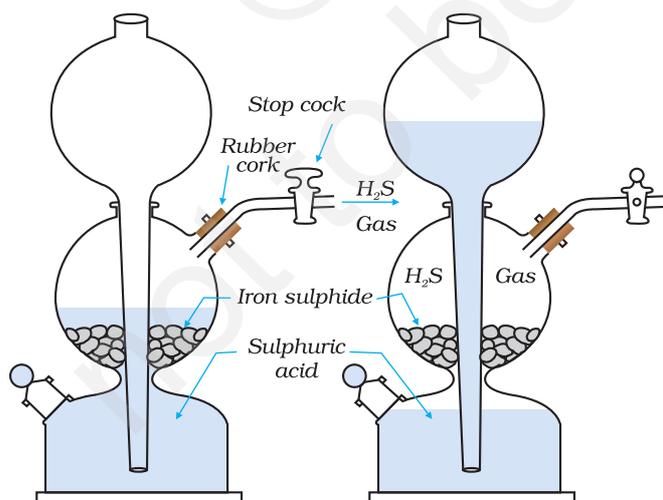


Fig. 7.8 : Kipp's apparatus for preparation of H_2S gas

Take the precipitate of group-II in a test tube and add excess of yellow ammonium sulphide solution to it. Shake the test tube. If the precipitate is insoluble, **group II-A (copper group)** is present. If the precipitate is soluble, this indicates the presence of **group-II B (arsenic group)**.

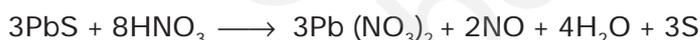
Confirmatory tests for the groups II A and II B are given in Table 7.13.

Table 7.13 : Confirmatory tests for Group-II A and II B cations

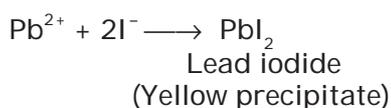
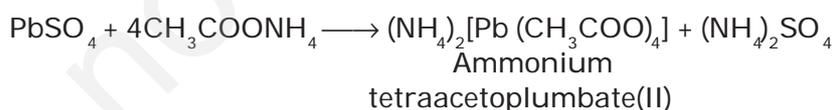
Black precipitate of Group II A ions (Pb^{2+} , Cu^{2+}) insoluble in yellow ammonium sulphide is formed.	If a yellow precipitate soluble in yellow ammonium sulphide is formed then As^{3+} ion is present.
Boil the precipitate of Group II A with dilute nitric acid and add a few drops of alcohol and dil.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

Group-II A (Copper Group)**Chemistry of confirmatory tests of Group-II A cations****1. Test for Lead ion (Pb^{2+})**

Lead sulphide precipitate dissolves in dilute HNO_3 . On adding dil. H_2SO_4 and a few drops of alcohol to this solution a white precipitate of lead sulphate appears. This indicates the presence of lead ions.



The white precipitate dissolves in ammonium acetate solution on boiling. When this solution is acidified with acetic acid and potassium chromate solution is added, a yellow precipitate of PbCrO_4 is formed. On adding potassium iodide solution, a yellow precipitate of lead iodide is formed.

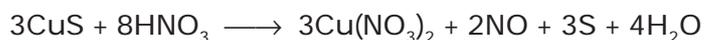


Alcohol

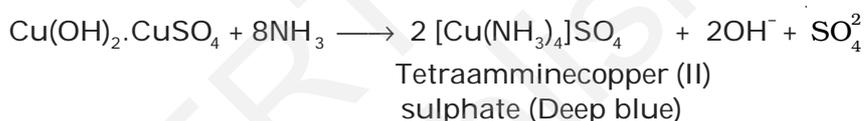
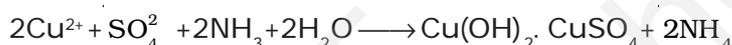
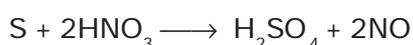


2. Test for Copper ion (Cu²⁺)

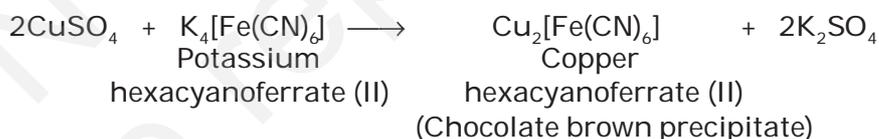
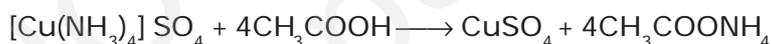
- (a) Copper sulphide dissolves in nitric acid due to the formation of copper nitrate.



On heating the reaction mixture for long time, sulphur is oxidised to sulphate and copper sulphate is formed and the solution turns blue. A small amount of NH₄OH precipitates basic copper sulphate which is soluble in excess of ammonium hydroxide due to the formation of tetraamminecopper (II) complex.

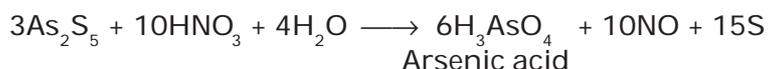
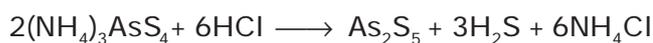


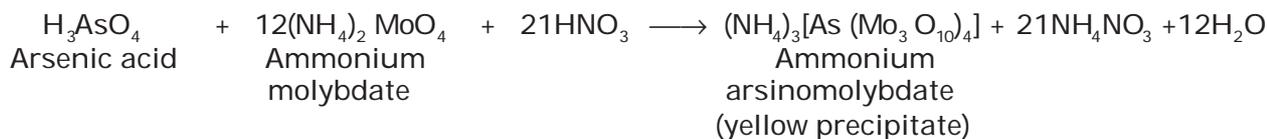
- (b) The blue solution on acidification with acetic acid and then adding potassium ferrocyanide [K₄Fe(CN)₆] solution gives a chocolate colouration due to the formation of copper ferrocyanide i.e. Cu₂[Fe(CN)₆].



Group-II B (Arsenic Group)

If group- II precipitate dissolves in yellow ammonium sulphide and the colour of the solution is yellow, this indicates the presence of As³⁺ ions. Ammonium thioarsenide formed on dissolution of As₂S₃ decomposes with dil. HCl, and a yellow precipitate of arsenic (V) sulphide is formed which dissolves in concentrated nitric acid on heating due to the formation of arsenic acid. On adding ammonium molybdate solution to the reaction mixture and heating, a canary yellow precipitate is formed. This confirms the presence of As³⁺ ions.





(IV) Analysis of Group-III cations

If group-II is absent, take original solution and add 2-3 drops of conc. HNO_3 to oxidise Fe^{2+} ions to Fe^{3+} ions. Heat the solution for a few minutes. After cooling add a small amount of solid ammonium chloride (NH_4Cl) and an excess of ammonium hydroxide (NH_4OH) solution till it smells of ammonia. Shake the test tube. If a brown or white precipitate is formed, this indicates the presence of group-III cations. Confirmatory tests of group-III cations are summarised in Table 7.14.

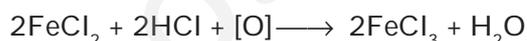
Observe the colour and the nature of the precipitate. A gelatinous white precipitate indicates the presence of aluminium ion (Al^{3+}). If the precipitate is brown in colour, this indicates the presence of ferric ions (Fe^{3+}).

Table 7.14 : Confirmatory test for Group-III cations

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

Chemistry of confirmatory tests of Group-III cations

When original solution is heated with concentrated nitric acid, ferrous ions are oxidised to ferric ions.

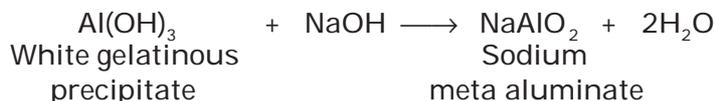


Third group cations are precipitated as their hydroxides, which dissolve in dilute hydrochloric acid due to the formation of corresponding chlorides.

1. Test for Aluminium ions (Al^{3+})

- (a) When the solution containing aluminium chloride is treated with sodium hydroxide, a white gelatinous precipitate of aluminium hydroxide is formed

which is soluble in excess of sodium hydroxide solution due to the formation of sodium meta aluminate.



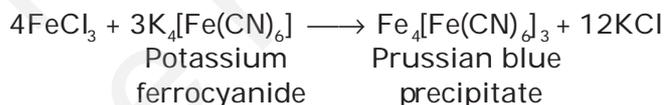
- (b) In the second test when blue litmus is added to the solution, a red colouration is obtained due to the acidic nature of the solution. On addition of NH_4OH solution drop by drop the solution becomes alkaline and aluminium hydroxide is precipitated. Aluminium hydroxide adsorbs blue colour from the solution and forms insoluble adsorption complex named 'lake'. Thus a blue mass floating in the colourless solution is obtained. The test is therefore called **lake test**.

2. Test for ferric ions (Fe^{3+})

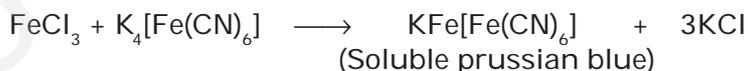
Reddish brown precipitate of ferric hydroxide dissolves in hydrochloric acid and ferric chloride is formed.



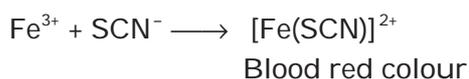
- (a) When the solution containing ferric chloride is treated with potassium ferrocyanide solution a blue precipitate/colouration is obtained. The colour of the precipitate is Prussian blue. It is ferric ferro-cyanide. The reaction takes place as follows:



If potassium hexacyanoferrate (II) (i.e. potassium ferrocyanide) is added in excess then a product of composition $\text{KFe}[\text{Fe(CN)}_6]$ is formed. This tends to form a colloidal solution ('soluble Prussian blue') and cannot be filtered.



- (b) To the second part of the solution, add potassium thiocyanate (potassium sulphocyanide) solution. The appearance of a blood red colouration confirms the presence of Fe^{3+} ions.



(V) Analysis of group-IV cations

If group-III is absent, pass H_2S gas in the solution of group-III for a few minutes. If a precipitate appears (white, black or flesh coloured), this indicates

the presence of group-IV cations. Table 7.15 gives a summary of confirmatory tests of group-IV cations.

Table 7.15 : Confirmatory test for Group-IV cations

White precipitate (Zn²⁺)	Flesh coloured precipitate (Mn²⁺)	Black precipitate (Ni²⁺, Co²⁺)
<p>Dissolve the precipitate in dilute HCl by boiling. Divide the solution into two parts.</p> <p>(a) To the first part add sodium hydroxide solution. A white precipitate soluble in excess of sodium hydroxide solution confirms the presence of Zn²⁺ ions.</p> <p>(b) Neutralise the second part with ammonium hydroxide solution and add potassium ferrocyanide solution. A bluish white precipitate appears.</p>	<p>Dissolve the precipitate in dilute HCl by boiling, then add sodium hydroxide solution in excess. A white precipitate is formed which turns brown on keeping.</p>	<p>Dissolve the precipitate in aqua regia. Heat the solution to dryness and cool. Dissolve the residue in water and divide the solution into two parts.</p> <p>(a) To the first part of the solution add ammonium hydroxide solution till it becomes alkaline. Add a few drops of dimethyl glyoxime and shake the test tube. Formation of a bright red precipitate confirms the presence of Ni²⁺ ions.</p> <p>(b) Neutralise the second part with ammonium hydroxide solution. Acidify it with dilute acetic acid and add solid potassium nitrite. A yellow precipitate confirms the presence of Co²⁺ ions.</p>

Chemistry of confirmatory tests of Group-IV cations

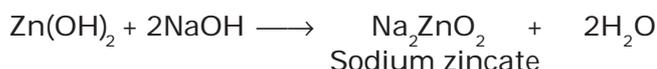
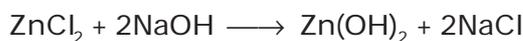
Fourth group cations are precipitated as their sulphides. Observe the colour of the precipitate. A white colour of the precipitate indicates the presence of zinc ions, a flesh colour indicates the presence of manganese ions and a black colour indicates the presence of Ni²⁺ or Co²⁺ ions.

1. Test for Zinc ion (Zn²⁺)

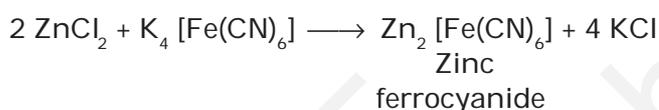
Zinc sulphide dissolves in hydrochloric acid to form zinc chloride.



- (a) On addition of sodium hydroxide solution it gives a white precipitate of zinc hydroxide, which is soluble in excess of NaOH solution on heating. This confirms the presence of Zn^{2+} ions.

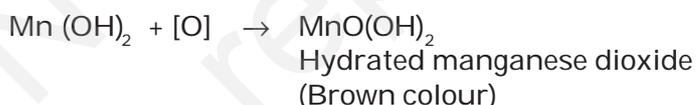


- (b) When potassium ferrocyanide $K_4Fe(CN)_6$ solution is added to the solution after neutralisation by NH_4OH solution, a white or a bluish white precipitate of zinc ferrocyanide appears.



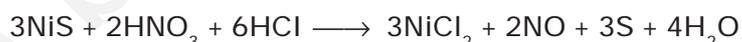
2. Test for Manganese ion (Mn^{2+})

Manganese sulphide precipitate dissolves in dil. HCl on boiling. On addition of NaOH solution in excess, a white precipitate of manganese hydroxide is formed which turns brown due to atmospheric oxidation into hydrated manganese dioxide.

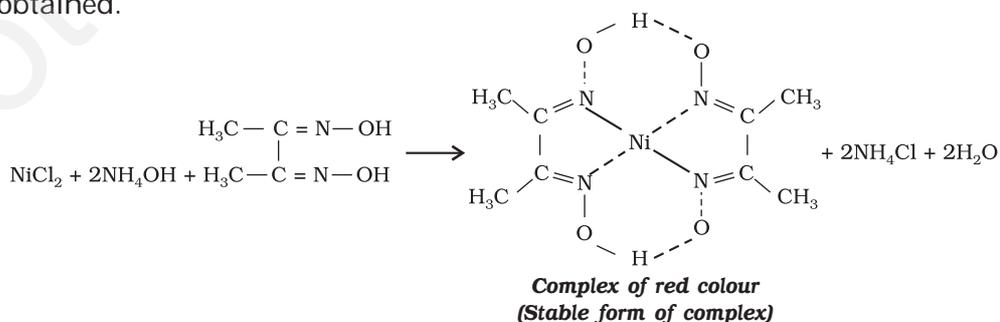


3. Test for Nickel ion (Ni^{2+})

The black precipitate of nickel sulphide dissolves in aqua regia and the reaction takes place as follows:

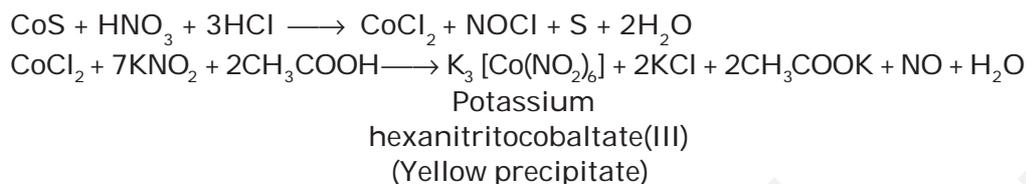


After treatment with aqua regia nickel-chloride is obtained which is soluble in water. When dimethyl glyoxime is added to the aqueous solution of nickel chloride, made alkaline, by adding NH_4OH solution, a brilliant red precipitate is obtained.



4. Test for Cobalt ion (Co^{2+})

Cobalt sulphide dissolves in aqua regia in the same manner as nickel sulphide. When the aqueous solution of the residue obtained after treatment with aqua regia is treated with a strong solution of potassium nitrite after neutralisation with ammonium hydroxide and the solution is acidified with dil. acetic acid, a yellow precipitate of the complex of cobalt named potassium hexanitritocobaltate (III) is formed.



(VI) Analysis of Group-V cations

If group-IV is absent then take original solution and add a small amount of solid NH_4Cl and an excess of NH_4OH solution followed by solid ammonium carbonate ($\text{NH}_4)_2\text{CO}_3$. If a white precipitate appears, this indicates the presence of group-V cations.

Dissolve the white precipitate by boiling with dilute acetic acid and divide the solution into three parts one each for Ba^{2+} , Sr^{2+} and Ca^{2+} ions. **Preserve a small amount of the precipitate for flame test.** Summary of confirmatory tests is given in Table 7.16.

Table 7.16 : Confirmatory test for Group-V cations

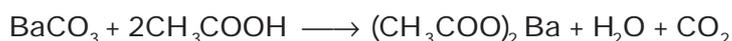
Dissolve the precipitate by boiling with dilute acetic acid and divide the solution into three parts one each for Ba^{2+} , Sr^{2+} and Ca^{2+} ions		
Ba^{2+} ions	Sr^{2+} ions	Ca^{2+} ions
(a) To the first part add potassium chromate solution. A yellow precipitate appears. (b) Perform the flame test with the preserved precipitate. A grassy green flame is obtained.	(a) If barium is absent, take second part of the solution and add ammonium sulphate solution. Heat and scratch the sides of the test tube with a glass rod and cool. A white precipitate is formed. (b) Perform the flame test with the preserved precipitate. A crimson-red flame confirms the presence of Sr^{2+} ions.	(a) If both barium and strontium are absent, take the third part of the solution. Add ammonium oxalate solution and shake well. A white precipitate of calcium oxalate is obtained. (b) Perform the flame test with the preserved precipitate. A brick red flame, which looks greenish-yellow through blue glass, confirms the presence of Ca^{2+} ions.

Chemistry of Confirmatory Tests of Group-V cations

The Group-V cations are precipitated as their carbonates which dissolve in acetic acid due to the formation of corresponding acetates.

1. Test for Barium ion (Ba^{2+})

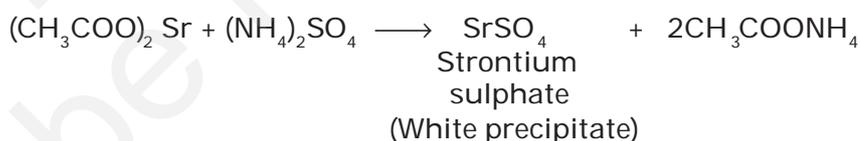
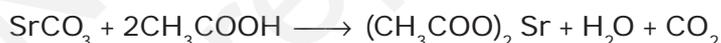
- (a) Potassium chromate (K_2CrO_4) solution gives a yellow precipitate of barium chromate when the solution of fifth group precipitate in acetic acid is treated with it.



- (b) **Flame test :** Take a platinum wire and dip it in conc. HCl. Heat it strongly until the wire does not impart any colour to the non-luminous flame. Now dip the wire in the paste of the (Group-V) precipitate in conc. HCl. Heat it in the flame. A grassy green colour of the flame confirms the presence of Ba^{2+} ions.

2. Test for Strontium ion (Sr^{2+})

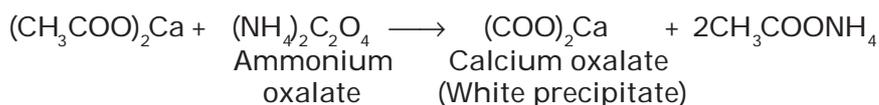
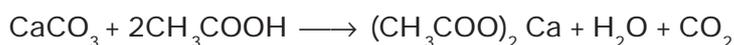
- (a) Solution of V group precipitate in acetic acid gives a white precipitate of strontium sulphate with ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$, solution on heating and scratching the sides of the test tube with a glass rod.



- (b) **Flame test :** Perform the flame test as given in the case of Ba^{2+} . A crimson red flame confirms the presence of Sr^{2+} ions.

3. Test for Calcium ion (Ca^{2+})

- (a) Solution of the fifth group precipitate in acetic acid gives a white precipitate with ammonium oxalate solution.



- (b) **Flame test :** Perform the flame test as mentioned above. Calcium imparts brick red colour to the flame which looks greenish-yellow through blue glass.

(VII) Analysis of Group-VI cations

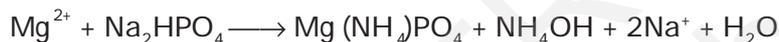
If group-V is absent then perform the test for Mg^{2+} ions as given below.

Chemistry of Confirmatory Tests of Group-VI cations**Test for Magnesium ion (Mg^{2+})**

- (a) If group-V is absent the solution may contain magnesium carbonate, which is soluble in water in the presence of ammonium salts because the equilibrium is shifted towards the right hand side.



The concentration of carbonate ions required to produce a precipitate is not attained. When disodium hydrogenphosphate solution is added and the inner walls of the test tube are scratched with a glass rod, a white crystalline precipitate of magnesium ammonium phosphate is formed which indicates the presence of Mg^{2+} ions.



Magnesium ammonium
phosphate (White precipitate)

Note down the observations and the inferences of the qualitative analysis in tabular form as given in the specimen record given in pages 114-115.

Note :
Some times precipitate of magnesium ammonium phosphate appears after some time. So warm the solution and scratch the sides of test tube after adding sodium hydrogen phosphate solution.

Precautions

- Always use an apron, an eye protector and hand gloves while working in the chemistry laboratory.
- Before using any reagent or a chemical, read the label on the bottle carefully. Never use unlabelled reagent.
- Do not mix chemicals and reagents unnecessarily. Never taste any chemical.
- Be careful in smelling chemicals or vapours. Always fan the vapours gently towards your nose (Fig. 7.9).
- Never add sodium metal to water or throw it in the sink or dustbin.
- Always pour acid into water for dilution. Never add water to acid.
- Be careful while heating the test tube. The test tube should never point towards yourself or towards your neighbours while heating or adding a reagent.



Fig. 7.9 : How to smell a gas



- (h) Be careful while dealing with the explosive compounds, inflammable substances, poisonous gases, electric appliances, glass wares, flame and the hot substances.
- (i) Keep your working surroundings clean. Never throw papers and glass in the sink. Always use dustbin for this purpose.
- (j) Always wash your hands after the completion of the laboratory work.
- (k) Always use the reagents in minimum quantity. Use of reagents in excess, not only leads to wastage of chemicals but also causes damage to the environment.



Discussion Questions

- (i) What is the difference between a qualitative and a quantitative analysis?
- (ii) Can we use glass rod instead of platinum wire for performing the flame test? Explain your answer.
- (iii) Why is platinum metal preferred to other metals for the flame test?
- (iv) Name the anions detected with the help of dilute H_2SO_4 ?
- (v) Why is dilute H_2SO_4 preferred over dilute HCl while testing anions?
- (vi) Name the anions detected by conc. H_2SO_4 .
- (vii) How is sodium carbonate extract prepared ?
- (viii) What is lime water and what happens on passing carbon dioxide gas through it?
- (ix) Carbon dioxide gas and sulphur dioxide gas both turn lime water milky. How will you distinguish between the two?
- (x) How will you test the presence of carbonate ion?
- (xi) What is the composition of dark brown ring which is formed at the junction of two layers in the ring test for nitrates?
- (xii) Name the radical confirmed by sodium nitroprusside test.
- (xiii) What is chromyl chloride test ? How do you justify that CrO_2Cl_2 is acidic in nature?
- (xiv) Why do bromides and iodides not give tests similar to chromyl chloride test?
- (xv) Describe the layer test for bromide and iodide ions.

- (xvi) Why is silver nitrate solution stored in dark coloured bottles?
- (xvii) How do you test the presence of sulphide ion?
- (xviii) Why does iodine give a blue colour with starch solution?
- (xix) What is Nessler's reagent?
- (xx) Why is original solution for cations not prepared in conc. HNO_3 or H_2SO_4 ?
- (xxi) Why cannot conc. HCl be used as a group reagent in place of dil. HCl for the precipitation of 1st group cations?
- (xxii) How can one prevent the precipitation of Group-IV radicals, with the second group radicals?
- (xxiii) Why is it essential to boil off H_2S gas before precipitation of radicals of group-III?
- (xxiv) Why is heating with conc. nitric acid done before precipitation of group-III?
- (xxv) Can we use ammonium sulphate instead of ammonium chloride in group-III?
- (xxvi) Why is NH_4OH added before $(\text{NH}_4)_2\text{CO}_3$ solution while precipitating group-V cations?
- (xxvii) Why do we sometimes get a white precipitate in group-VI even if the salt does not contain Mg^{2+} radical?
- (xxviii) What is aqua regia?
- (xxix) Name a cation, which is not obtained from a metal.
- (xxx) How can you test the presence of ammonium ion?
- (xxxi) Why are the group-V radicals tested in the order Ba^{2+} , Sr^{2+} and Ca^{2+} ?
- (xxxii) Why does conc. HNO_3 kept in a bottle turn yellow in colour?
- (xxxiii) Why should the solution be concentrated before proceeding to group-V?
- (xxxiv) Why is the reagent bottle containing sodium hydroxide solution never stoppered?
- (xxxv) What do you understand by the term common ion effect?
- (xxxvi) Why is zinc sulphide not precipitated in group-II?

SPECIMEN RECORD OF SALT ANALYSIS

Aim

To analyse the given salt for one anion and one cation present in it.

Material required



- Boiling tubes, test tubes, test tube holder, test tube stand, delivery tube, corks, filter papers, reagents

Sl. No.	Experiment	Observation	Inference
1.	Noted the colour of the given salt.	White	Cu^{2+} , Fe^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+} are absent.
2.	Noted the smell of the salt.	No specific smell.	S^{2-} , SO_3^{2-} , CH_3COO^- may be absent.
3.	Heated 0.5 g of the salt in a dry test tube and noted the colour of the gas evolved and change in the colour of the residue on heating and cooling.	(i) No gas was evolved. (ii) No particular change in colour of the residue is observed when heated and when cooled.	(i) CO_3^{2-} may be present, NO_3^- , NO_2^- , Br^- may be absent. (ii) Zn^{2+} may be absent.
4.	Prepared a paste of the salt with conc. HCl and performed the flame test.	No distinct colour of the flame seen.	Ca^{2+} , Sr^{2+} , Ba^{2+} , Cu^{2+} may be absent.
5.	Borax bead test was not performed as the salt was white in colour.	—	—
6.	Treated 0.1 g of salt with 1 mL dil. H_2SO_4 and warmed.	No effervescence and evolution of vapours.	CO_3^{2-} , SO_3^{2-} , S^{2-} , NO_2^- , CH_3COO^- absent.
7.	Heated 0.1 g of salt with 1 mL conc. H_2SO_4 .	No gas evolved.	Cl^- , Br^- , I^- , NO_3^- , $\text{C}_2\text{O}_4^{2-}$ are absent.
8.	Acidified 1 mL of aqueous salt solution with conc. HNO_3 . Warmed the contents and then added 4-5 drops of ammonium molybdate solution.	No yellow precipitate	PO_4^{3-} absent.

9.	Acidified water extract of the salt with dil. HCl and then added 2mL of BaCl ₂ solution.	A white ppt. is obtained which is insoluble in conc. HNO ₃ and conc. HCl.	SO ₄ ²⁻ present.
10.	Heated 0.1 g of salt with 2 mL NaOH solution.	Ammonia gas is not evolved.	NH ₄ ⁺ absent.
11.	Attempted to prepare original solution of the salt by dissolving 1g of it in 20 mL water.	Clear solution formed	Water soluble salt is present.
12.	To a small part of the above salt solution added 2 mL of dil. HCl.	No white precipitate formed.	Group-I absent.
13.	Passed H ₂ S gas through one portion of the solution of step 12.	No precipitate formed.	Group-II absent.
14.	Since salt is white, heating with conc. HNO ₃ is not required. Added about 0.2 g of solid ammonium chloride and then added excess of ammonium hydroxide to the solution of step 12.	No precipitate formed.	Group-III absent.
15.	Passed H ₂ S gas through the above solution.	No precipitate formed.	Group-IV absent.
16.	Added excess of ammonium hydroxide solution to the original solution and then added 0.5 g of ammonium carbonate.	No precipitate formed.	Group-V absent.
17.	To the original solution of salt added ammonium hydroxide solution, followed by disodium hydrogen phosphate solution. Heated and scratched the sides of the test tube.	White precipitate.	Mg ²⁺ confirmed.

Result

The given salt contains:

Anion : SO₄²⁻

Cation : Mg²⁺

UNIT-8

TESTS FOR FUNCTIONAL GROUPS IN ORGANIC COMPOUNDS



EXPERIMENT 8.1

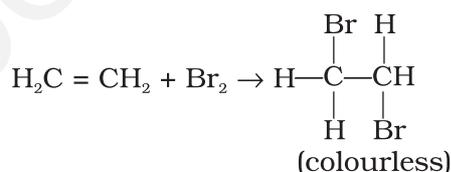
Aim

To identify the functional groups present in an organic compound.

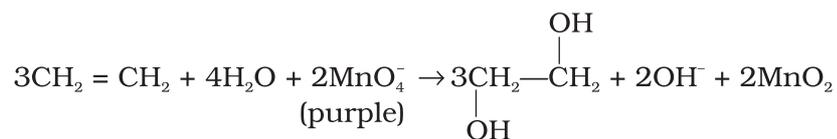
I. TESTS FOR UNSATURATION

Theory

Organic compounds containing $>C=C<$ and / or $-C\equiv C-$ bonds are called unsaturated compounds. These compounds undergo addition reaction with bromine water or the solution of bromine in carbon tetrachloride, chloroform or glacial acetic acid. Addition of bromine to an alkene results in the formation of vicinal dibromide. The reddish orange colour of the solution of bromine in carbon tetrachloride disappears on reaction with an alkene. The reaction is as follows :



Alkenes decolourise the neutral/alkaline KMnO_4 solution and vicinal glycols are formed (**Bayer's test**). Reaction takes place as follows :



Both the above reactions are used as tests for unsaturation.

Material Required



- Test tubes : Two
- Test tube holder : One



- Potassium hydroxide solution : 1–2 mL
- Carbon tetrachloride/ chloroform : 2 mL
- Bromine water/solution of bromine in CCl₄ or chloroform : 2 mL
- Potassium permanganate solution : As per need
- Compound to be tested : As per need

Procedure

A. Bromine water test

Dissolve 0.1 g or 5 drops of organic compound in 2 mL of carbon tetrachloride in a test tube and add 2% solution of bromine in carbon tetrachloride or bromine water drop by drop with continuous shaking. Decolourization of bromine solution indicates the presence of unsaturation in organic compound.

Potassium hydroxide 

Carbon tetrachloride 

Chloroform 

Bromine 

Potassium permanganate  

B. Bayer's test

Dissolve 25-30 mg of organic compound in 2 mL of water or acetone (free of alcohol) and add 1% potassium permanganate solution containing equal volume of 1% sodium carbonate solution. The discharge of the colour of more than one drop of potassium permanganate indicates the presence of unsaturation in the organic compound. Carrying out the reaction under alkaline conditions removes the possibility of confusion due to substitution in aromatic compounds.

Note: (i) *Unsaturation in an organic compound is confirmed only when both of the above tests are positive.*

(ii) *In place of CCl₄ any other solvent such as CHCl₃/dioxan and even water can be used to dissolve the organic compound for carrying out the reaction.*

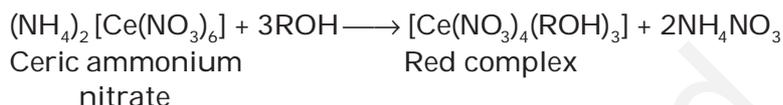
Precautions

- (a) The tests should be performed at room temperature.
- (b) Handle bromine solution carefully. Do not inhale the vapours and also avoid its contact with the skin.

II. TEST FOR ALCOHOLIC (R—OH) GROUP

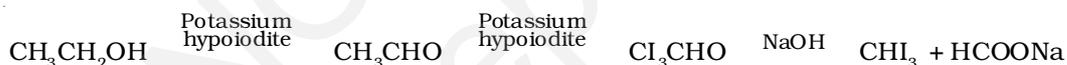
Theory

Alcoholic compounds on reaction with ceric ammonium nitrate give a red colouration due to the formation of a complex.



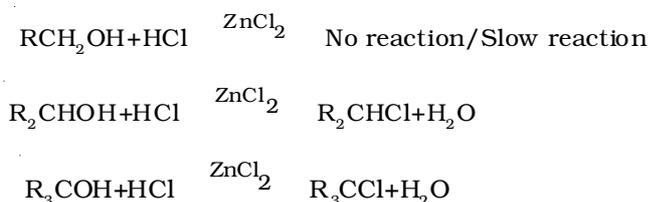
Distinction between primary, secondary and tertiary alcohols can be done on the basis of iodoform test and Lucas test.

Ethanol and secondary alcohols which contain $\text{CH}_3\text{—CH}(\text{OH})\text{R}$ group (iodoform reaction) give positive iodoform test. To carry out reaction, potassium iodide and sodium hypochlorite solution are added to the compound in the presence of sodium hydroxide solution. Probably sodium hypochlorite first oxidises potassium iodide into potassium hypoiodite, which oxidises $\text{CH}_3\text{—CH}(\text{OH})\text{R}$ group to CH_3COR group and then iodates it in the alkaline medium of the reaction mixture by replacing the α -hydrogen attached to the carbon atom adjacent to carbonyl group by iodine. Iodoform is formed after cleavage of C—C bond.



Lucas Test

Lucas reagent contains zinc chloride and concentrated hydrochloric acid. This reagent reacts with primary, secondary and tertiary alcohols at different rates. Tertiary alcohols react almost instantaneously, secondary alcohols react in about 1-5 minutes and primary alcohols react very slowly. The reaction may take 10 minutes to several days.



Alcohols are soluble in Lucas reagent but the formed alkyl halides are not soluble. Therefore, formation of two layers in the reaction medium indicate the occurrence of the reaction.

- Primary alcohols - Layers do not separate
- Secondary alcohols - Layers separate within 1-5 minutes
- Tertiary alcohols - Layers separate immediately

Material Required



- Test tube holder : One
- Test tubes : As per need



- Ceric ammonium nitrate solution : As per need
- Sodium hydroxide : As per need
- Iodine solution : As per need
- Lucas reagent : As per need
- Dioxan : As per need

Procedure

A. Ceric ammonium nitrate test

Take 1 mL solution of organic compound dissolved in a suitable solvent. Add a few drops of ceric ammonium nitrate solution. Appearance of red colour shows the presence of alcoholic – OH group.

Note : *The red colour disappears after keeping the reaction mixture for sometime. The colour also disappears if excess of ceric ammonium nitrate solution is added. Therefore, use of excess of ceric ammonium nitrate solution should be avoided.*

B. Iodoform test

First method

Take 0.2 mL of the compound in a test tube, add 10 mL of 10% aqueous KI solution and 10 mL of freshly prepared NaOCl solution. Warm gently; yellow crystals of iodoform separate.

Second method

Dissolve 0.1 g or 4 to 5 drops of compound in 2 mL of water. If it does not dissolve, add dioxane drop by drop to get a homogeneous solution. Add 2 mL of 5% sodium hydroxide solution followed by potassium iodide-iodine reagent* dropwise with continuous shaking till a definite dark colour of iodine persists. Allow the reactants to remain at room temperature for 2-3 minutes. If no iodoform separates, warm the reaction mixture in a water bath at 60°C. Add more drops of potassium iodide-iodine reagent. If colour of iodine disappears continue addition of reagent till the colour of iodine persists even after two minutes of heating at 60°C. Remove excess iodine by adding a few drops of sodium hydroxide solution with shaking. Dilute the mixture with equal volume of water and keep it at room temperature for 10-15 minutes. A yellow precipitate of iodoform is obtained if test is positive.

Sodium hydroxide 

Iodine 

* Potassium iodide-iodine reagent is prepared by dissolving 20 g of potassium iodide and 10 g of iodine in 100 mL of water.

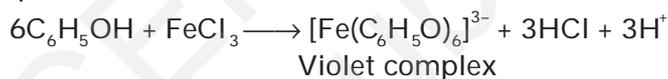
C. Lucas test

Take 1 mL of compound in a test tube. Add 10 mL of Lucas reagent. Shake well and note the time for the separation of two distinct layers.

Note : Lucas test is applicable to only those alcohols which are soluble in the reagent because the test is based on separation of alkyl halides as separate layer.

III. PHENOLIC (AR-OH) GROUP**Theory**

The -OH group attached directly to the ring carbon of an aromatic ring is called phenolic -OH group. Phenols are weakly acidic, therefore they are soluble in NaOH solution but at the same time they are not sufficiently acidic to be soluble in sodium hydrogencarbonate solution. Phenols give coloured complex with neutral ferric chloride solution. For example, phenol gives a complex of violet colour as follows :



Resorcinol, *o*-, *m*- and *p*-cresol give violet or blue colouration, catechol gives green colour which rapidly darkens. 1 and 2-Naphthol do not give characteristics colours. Phenols condense with phthalic anhydride in the presence of concentrated H_2SO_4 . Phenol condenses to give phenolphthalein which gives a dark pink colour with NaOH solution. This is called phthalein dye test.

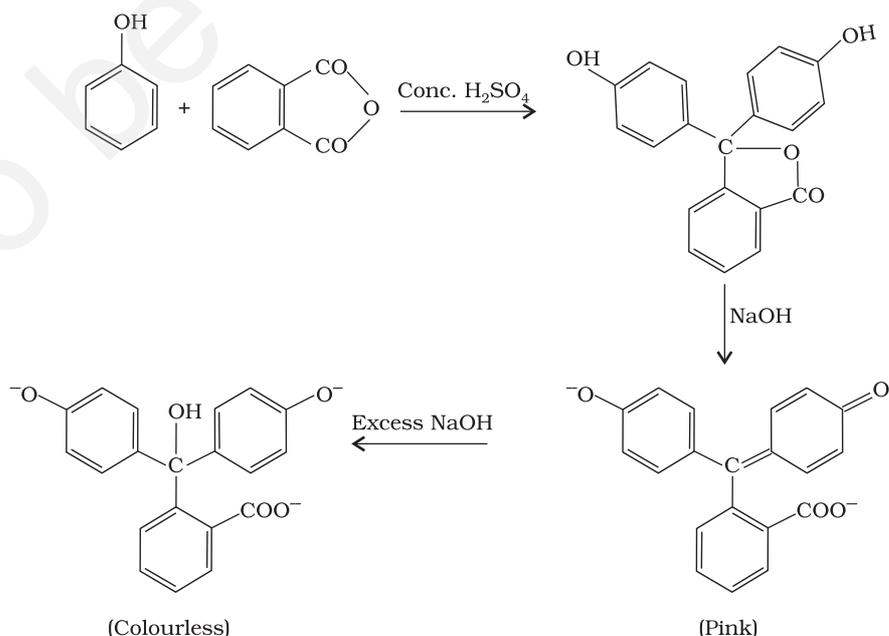


Table 8.1 : Colours produced by some other phenolic compounds in phthalein dye test

Compound	Colour	Compound	Colour
<i>o</i> -Cresol	red	Catechol	Usually blue takes longer time to appear
<i>m</i> -Cresol	bluish-purple	Resorcinol	Green fluorescent colour of fluorescein
<i>p</i> -Cresol	No colour		

Material Required

	<ul style="list-style-type: none"> • Test tube holder : One • Test tubes : As per need 		<ul style="list-style-type: none"> • Blue litmus paper • Ferric chloride solution • Conc. sulphuric acid • Sodium hydroxide • Phthalic anhydride • Organic compound containing phenolic -OH group 	According to requirement
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Procedure**A. Ferric chloride test**

Take 2 mL of aqueous or alcoholic solution of the organic compound in a test tube, add neutral ferric chloride solution dropwise and note the colour change. Appearance of a blue, green, violet or red colour indicates the presence of phenolic -OH group.

Sulphuric acid 

Sodium hydroxide 

Phthalic anhydride 

B. Phthalein dye test

Take 0.1 g of organic compound and 0.1 g of phthalic anhydride in a clean dry test tube and add 1-2 drops of conc. H_2SO_4 . Heat the test tube for about 1 minute in an oil bath. Cool and pour the reaction mixture carefully into a beaker containing 15 mL of dilute sodium hydroxide solution. Appearance of pink, blue, green, red etc. colours indicates the presence of phenolic -OH group in the compound. However, the colour disappears on addition of large excess of sodium hydroxide solution.

Note : (i) Neutral ferric chloride solution is prepared by adding dilute sodium hydroxide solution to ferric chloride solution drop by drop till a small but permanent brown precipitate appears. Solution is filtered and the clear filtrate is used for the test.

(ii) Some phenols like 2,4,6 - trinitrophenol and 2,4 - dinitrophenol, which contain electron withdrawing groups are strong acids and dissolve even in sodium hydrogencarbonate solution.

Precautions

- Always use freshly prepared, neutral and very dilute solution of ferric chloride.
- Phenol is toxic and corrosive in nature and should be handled with care.

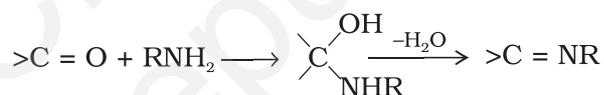
IV. ALDEHYDIC AND KETONIC GROUPS ($-\text{CHO}$ and $-\overset{\text{O}}{\parallel}{\text{C}}-$)

Theory

Both aldehydes and ketones contain carbonyl group ($>\text{C} = \text{O}$) and are commonly known as carbonyl compounds. Identification of aldehydes and ketones is done by two important reactions of carbonyl group i.e.

- addition reaction on double bond of $>\text{C} = \text{O}$ group and
- oxidation of carbonyl group.

Addition reactions of derivatives of ammonia are important from the point of view of identification of carbonyl compounds. Addition is generally followed by elimination resulting in the formation of unsaturated compound.



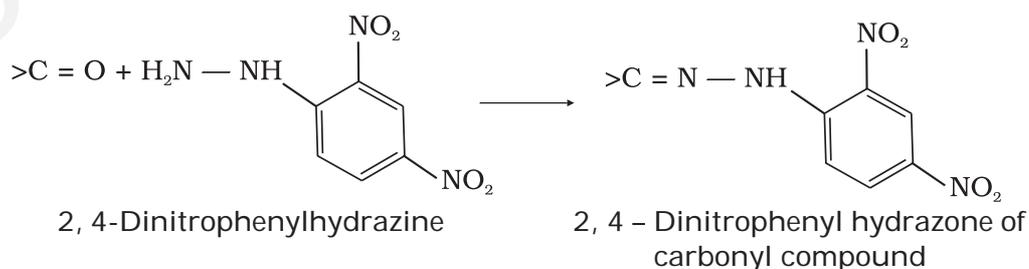
(R = alkyl, aryl or $\text{C}_6\text{H}_5\text{NH}$ etc.)

These reactions are catalysed by an acid or a base and do not occur under strongly acidic or basic conditions. Each reaction requires an optimum pH for its occurrence. Therefore, maintenance of pH is very important while carrying out these reactions.

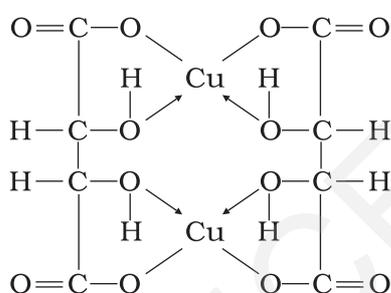
As far as oxidation is concerned, aldehydes are easily oxidised to carboxylic acids while ketones require relatively stronger oxidising agents. Distinction can be made between these two types of carbonyl compounds on the basis of difference in their reactivity.

Following tests are performed for the identification of aldehydic and ketonic groups:

- On reaction with 2,4-dinitrophenylhydrazine (2,4-DNP), they form the respective 2,4-dinitrophenyl hydrazones.



These two carbonyl compounds (aldehydes and ketones) are distinguished on the basis of tests using mild oxidising reagents, like Tollen's reagent and Fehling's reagent or Benedict's reagent. Tollen's reagent is an alkaline solution of silver cation complexed with ammonia, and Fehling's and Benedict's reagents are alkaline solutions containing cupric ions complexed with tartarate and citrate ions respectively. Fehling's reagent is freshly prepared by mixing equal amounts of Fehling's solution A and Fehling's solution B. Fehling's reagent deteriorates on keeping while Fehling's solutions A and B are quite stable. Fehling's solution A is an aqueous copper sulphate solution while Fehling's solution B is an alkaline solution of sodium potassium tartarate (Rochelle's salt). The reagent contains Cu^{2+} ion complexed with tartarate ions. The structure of the complex is given below :



Copper tartarate complex

Benedict modified the original Fehling's test by using a single solution which is more convenient for the test. Benedict's solution is more stable than Fehling's reagent and can be stored for a long time. It is an alkaline solution containing a mixture of copper sulphate and sodium citrate ($2\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 11\text{H}_2\text{O}$).

Complex formation decreases the cupric ion concentration below that necessary for precipitation of cupric hydroxide. These two reagents oxidize aldehydes while ketones remain unaffected. The chemistry of these tests is as follows:



However, aromatic aldehydes do not give positive Fehling's test. In Benedict test also, Cu^{2+} ions are reduced to Cu^+ ions in the same manner as in the case of Fehling's reagent.

Aldehydes also give pink colour with Schiff's reagent (the reagent is prepared by decolourising aqueous solution of *p*-rosaniline hydrochloride dye by adding sodium sulphite or by passing SO_2 gas). Ketones do not respond to this test.

Material Required



- Beaker (250 mL) : One
- Test tube holder : One
- Test tubes : As per need



- Schiff's reagent : As per need
- Fehling's solutions A and B : As per need
- Silver nitrate : As per need
- Dilute ammonium hydroxide solution : As per need
- 2,4-Dinitrophenylhydrazine reagent : As per need

Silver nitrate



Ammonia solution



Ammonia gas



Procedure

A. Test given by both aldehydes and ketones

2,4-Dinitrophenylhydrazine test (2,4-DNP test)

Take 2-3 drops of the liquid compound in a test tube or in case of solid compound, dissolve a few crystals of it in 2-3 mL alcohol. Add a few drops of an alcoholic solution of 2,4-dinitrophenylhydrazine. Appearance of yellow, orange or orange-red precipitate confirms the presence of carbonyl group. If precipitate does not appear at room temperature, warm the mixture in a water bath for a few minutes and cool.

B. Tests given by aldehydes only

Following tests namely Schiff's test, Fehling's test and Tollen's test are given by aldehydes only.

Schiff's test

Take 3-4 drops of the liquid compound or dissolve a few crystals of organic compound in alcohol and add 2-3 drops of the Schiff's reagent. Appearance of pink colour indicates the presence of an aldehyde.

Fehling's test

Take nearly 1 mL of Fehling's solution A and 1 mL of Fehling's solution B in a clean dry test tube. To this add 2-3 drops of the liquid compound or about 2 mL of the solution of the solid compound in water or alcohol. Heat the content of the test tube for about 2 minutes in a water bath. Formation of brick red precipitate of copper (I) oxide indicates the presence of an aldehyde. This test is not given by aromatic aldehydes.

Benedict's test

Add 5 drops of the liquid compound or the solution of the solid organic compound in water or alcohol to 2 mL Benedict's reagent. Place the test tube in boiling water bath for 5 minutes. An orange-red precipitate indicates the presence of an aldehyde.

Tollen's test

- (i) Take 1 mL of freshly prepared (~ 2 %) silver nitrate solution in a test tube. Add 1-2 drops of sodium hydroxide solution to it and shake, a dark brown precipitate of silver oxide appears. Dissolve the precipitate by adding ammonium hydroxide solution drop-wise.
- (ii) To the above solution, add an aqueous or an alcoholic solution of the organic compound.
- (iii) Heat the reaction mixture of step (ii) in a water bath for about 5 minutes. Formation of a layer of silver metal on the inner surface of the test tube which shines like a mirror, indicates the presence of an aldehyde.

Precautions

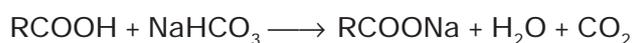
- (a) Always use freshly prepared reagents to perform the tests.
- (b) Do not heat the reaction mixture directly on a flame.
- (c) After performing the test, destroy the silver mirror by adding dilute nitric acid and drain off the solution with excess of water.

V. CARBOXYL GROUP (—COOH)**Theory**

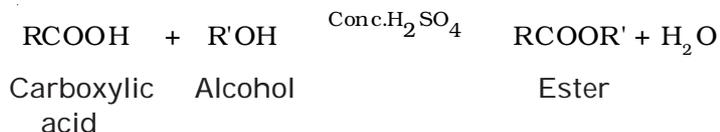
Organic compounds containing carboxyl functional groups are called carboxylic acids.

The term carboxyl, derives its name from the combination of words carbonyl and hydroxyl because carboxylic functional group

contains both of these groups ($\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—OH}$). These acids turn blue litmus red and react with sodium hydrogencarbonate solution to produce effervescence due to the formation of carbon dioxide. This is a test that distinguishes carboxylic acids from phenols.



These react with alcohols in the acidic medium to produce esters.



Material Required



- Test tube holder : One
- Glass rod : One
- Test tubes : As per need



- Blue litmus paper /solution : As per need
- Ethyl alcohol : As per need
- Sodium hydrogencarbonate solution : As per need

Procedure

A. Litmus test

Ethyl alcohol



Put a drop of the liquid compound or a drop of the solution of the compound with the help of a glass rod on a moist blue litmus paper. If the blue colour of the litmus paper changes to red, the presence of either a carboxylic group or a phenolic group is indicated.

B. Sodium hydrogencarbonate test

Take 2 mL of saturated aqueous solution of sodium hydrogencarbonate in a clean test tube. Add a few drops of the liquid compound or a few crystals of solid compound to it. The evolution of brisk effervescence of CO_2 indicates the presence of carboxyl group.

C. Ester test

Take about 0.1 g compound in a test tube, add 1 mL ethanol or methanol and 2-3 drops of concentrated sulphuric acid. Heat the reaction mixture for 10-15 minutes in a hot water bath at about 50°C . Pour the reaction mixture in a beaker containing aqueous sodium carbonate solution to neutralise excess sulphuric acid and excess carboxylic acid. Sweet smell of the substance formed indicates the presence of carboxyl function in the compound.

Precaution

Add the compound in sodium hydrogencarbonate solution slowly so that effervescence is visible clearly.

VI. AMINO GROUP ($-\text{NH}_2$)

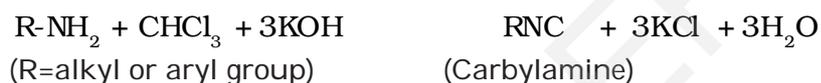
Theory

Organic compounds containing amino group are basic in nature. Thus they easily react with acids to form salts, which are soluble in water.

Both, aliphatic and aromatic amines are classified into three classes namely- primary ($-\text{NH}_2$), secondary ($-\text{NH}-$) and tertiary ($-\text{N}<$), depending upon the number of hydrogen atoms attached to the nitrogen atom. Primary amine has two hydrogen atoms, secondary has one while tertiary amine has no hydrogen atom attached to nitrogen.

(i) Carbylamine test

Aliphatic as well as aromatic primary amines give carbylamine test in which an amine is heated with chloroform.

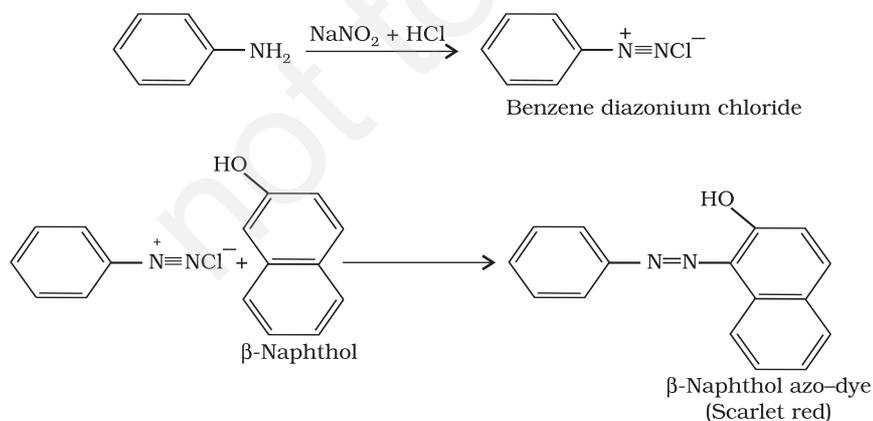


Caution!

Carbylamine so formed is highly toxic and should be destroyed immediately after the test. For this cool the test tube and add carefully an excess of conc. HCl.

(ii) Azo dye test

Aromatic primary amines can be confirmed by azo dye test. Primary amine e.g. aniline reacts with nitrous acid generated *in situ* by the reaction of sodium nitrite with HCl at $0-5^\circ\text{C}$ to produce diazonium salt. This couples with β -naphthol to give a scarlet red dye, which is sparingly soluble in water.



Material Required

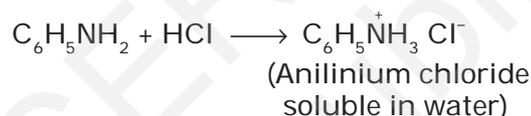
	<ul style="list-style-type: none"> • Test tubes : As per need • Test tube holder : One • Bunsen burner : One 		<ul style="list-style-type: none"> • Chloroform • Potassium hydroxide • Sodium nitrite solution • Aniline • β-Naphthol • Dilute hydrochloric acid • Sodium hydroxide solution • Ice 	} As per need
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Procedure

Chloroform Aniline Potassium hydroxide Sodium nitrite   β -naphthol 

A. Solubility test

Take 1 mL of given organic compound in a test tube and add a few drops of dilute HCl to it. Shake the contents of the test tube well. If the organic compound dissolves, it shows the presence of an amine.



B. Carbylamine test

Take 2-3 drops of the compound in a test tube and add 2-3 drops of chloroform followed by addition of an equal volume of 0.5 M alcoholic potassium hydroxide solution. Heat the contents gently. An obnoxious smell of carbylamine confirms the presence of primary amino group in the compound.

Caution!

Do not inhale the vapours. Destroy the product immediately by adding concentrated hydrochloric acid and flush it into the sink.

C. Azo dye test

- (i) Dissolve nearly 0.2 g of the compound in 2 mL of dilute hydrochloric acid in a test tube. Cool the content of the test tube in ice.
- (ii) To the ice cooled solution add 2 mL of 2.5% cold aqueous sodium nitrite solution.
- (iii) In another test tube, dissolve 0.2 g of β -naphthol in dilute sodium hydroxide solution.
- (iv) Add diazonium chloride solution prepared in step (ii) into the cold β -naphthol solution slowly with shaking.

The formation of a scarlet red dye confirms the presence of aromatic primary amine.

Precautions

- Do not expose yourself to the vapours while performing carbylamine test because isocyanide is highly poisonous. Destroy it immediately as described above.
- Maintain the temperature of the reaction mixture below 5°C during diazotisation, as diazonium chloride is unstable at higher temperatures.
- Always add diazonium chloride solution into the alkaline solution of β -naphthol and not vice-versa.

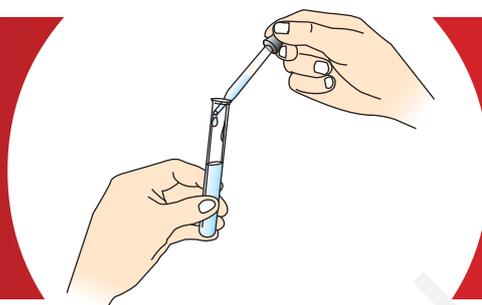


Discussion Questions

- What is Bayer's reagent?
- Why do alkenes and alkynes decolourize bromine water and alkaline KMnO_4 ?
- Explain why for the confirmation of unsaturation in a compound both the tests namely test with bromine water and test with Bayer's reagent should be performed.
- Why does phenol decolourize bromine water?
- How will you distinguish between phenol and benzoic acid?
- Why does benzene not decolourise bromine water although it is highly unsaturated?
- Why does formic acid give a positive test with Tollen's reagent?
- Outline the principle of testing glucose in a sample of urine in a pathological laboratory?
- Why is Benedict's reagent more stable than Fehling's reagent?
- How would you distinguish an aldehyde from a ketone by chemical tests?
- How would you separate a mixture of phenol and benzoic acid in the laboratory by using chemical method of separation?
- Write the chemistry of diazotisation and coupling reactions.
- How can you distinguish between hexylamine ($\text{C}_6\text{H}_{13}\text{NH}_2$) and aniline ($\text{C}_6\text{H}_5\text{NH}_2$)?
- How can you distinguish between ethylamine and diethylamine?
- How can CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ be distinguished chemically?
- Why is solution of iodine prepared in potassium iodide and not in water?
- What is haloform reaction? What type of compounds generally give this reaction?
- How can you distinguish the compounds $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_2\text{H}_5$ and $\text{C}_2\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_2\text{H}_5$ by simple chemical test?

UNIT-9

PREPARATION OF INORGANIC COMPOUNDS



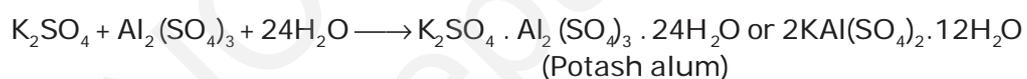
EXPERIMENT 9.1

Aim

To prepare double salts: ferrous ammonium sulphate (Mohr's salt) and potash alum.

Theory

When a mixture containing equimolar proportions of potassium sulphate and aluminium sulphate or ferrous sulphate and ammonium sulphate is crystallised from its solution, a double salt is formed. The formation of double salt may be shown as follows:



Ferrous ammonium sulphate (Mohr's salt)

Fe^{2+} and Al^{3+} ions undergo hydrolysis, therefore, while preparing aqueous solutions of ferrous sulphate and aluminium sulphate in water, 2-3 mL dilute sulphuric acid is added to prevent the hydrolysis of these salts.

Material Required



- Beaker (50 mL) : One
- Conical flask (50 mL) : One
- Trough : One
- Glass rod : One
- Tripod stand : One
- Funnel : One
- Wire gauze : One



- Potassium sulphate : As per need
- Aluminium sulphate : As per need
- Ferrous sulphate : As per need
- Ammonium sulphate : As per need
- Dilute sulphuric acid : As per need
- Ethanol : As per need

Procedure

(a) Preparation of Double Salt: Potassium Aluminium Sulphate (Potash Alum)

- (i) Take 10 mL of distilled water in a 50 mL beaker and heat it to about 40°C. Dissolve 6.6 g of aluminium sulphate in it and add about 0.4 mL of dilute sulphuric acid.

- (ii) Weigh 2.4 g of powdered potassium sulphate and transfer it to the above solution.
- (iii) Heat the solution with constant stirring till potassium sulphate dissolves completely.
- (iv) Allow the solution to cool to room temperature slowly.
- (v) On cooling, white crystals of potash alum separate out.
- (vi) Decant the mother liquor and wash the crystals by gently shaking with 1:1 cold water and alcohol mixture.
- (vii) Filter the crystals, dry these between the folds of a filter paper and note the yield.

Ethanol



Sulphuric acid



(b) Preparation of Double Salt: Ferrous Ammonium Sulphate

- (i) Dissolve 3.5 g of ferrous sulphate and 1.7 g of ammonium sulphate (weighed separately), in 5 mL of distilled water contained in a 50 mL conical flask by heating. Add about 0.5 mL of dilute sulphuric acid to the flask and concentrate the solution by heating till the crystallization point is reached.
- (ii) Allow the mixture to cool to room temperature slowly.
- (iii) On cooling, light green crystals of ferrous ammonium sulphate separate out.
- (iv) Decant the mother liquor and wash the crystals by shaking with very small amounts of 1:1 cold water and alcohol mixture to remove sticking mother liquor.
- (iv) Separate the crystals by filtration wash with alcohol, dry between the folds of a filter paper and record the yield.

Result

Yield of potash alum/Mohr's salt is _____ g.

Precautions

- (a) Cool the solution slowly to get good crystals. Avoid rapid cooling.
- (b) Do not disturb the solution while cooling.
- (c) Avoid prolonged heating while preparing crystals of ferrous ammonium sulphate, as it may oxidise ferrous ions to ferric ions and change the stoichiometry of the crystals.



Discussion Questions

- (i) Why do we take equimolar quantities of reacting compounds in the preparation of double salts?
- (ii) In the preparation of ferrous ammonium sulphate, can concentrated sulphuric acid be used in place of dilute sulphuric acid? Explain.
- (iii) What is the difference between iron compounds; $K_4[Fe(CN)_6]$ and $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$?

- (iv) What is the action of heat on potash alum?
- (v) Why does an aqueous solution of potash alum turn blue litmus red?
- (vi) What are the isomorphous substances?
- (vii) Give the name of some of the alums where cations are other than Al^{3+} .
- (viii) What is the difference between a complex compound and a double salt?

EXPERIMENT 9.2

Aim

To prepare potassium trioxalatoferate(III).

Theory

When hydrated ferric chloride is dissolved in aqueous solution of oxalic acid containing potassium hydroxide, green crystals of potassium trioxalatoferate(III) are obtained. The reaction involved in the formation of these green crystals is as follows:

**Material Required**

- Beaker (50 mL) : One
- Porcelain dish : One
- Water bath : One
- Glass rod : One
- Funnel : One



- Ferric chloride : 2.5 g
- Potassium hydroxide : 3.8 g
- Oxalic acid : 3.0 g
- Ethanol : As per need

Procedure

Potassium hydroxide



Ethanol



Oxalic acid



- (i) Prepare a solution of 3.0 g of oxalic acid in 12.5 mL of hot water contained in a clean 50 mL beaker.
- (ii) To the above solution, add 3.8 g of potassium hydroxide gradually in lots, with stirring so that it dissolves completely.
- (iii) Add 2.5 g of ferric chloride into the above solution with constant stirring till it is completely dissolved.
- (iv) Filter the solution and concentrate the green filtrate by heating in a porcelain dish over a water bath and cool the mixture slowly.
- (v) Filter the crystals so formed, wash with 1:1 mixture of cold water and alcohol and dry them by pressing between the folds of a filter paper.

Result

Yield of potassium trioxalatoferrate (III) is _____ g.

Precautions

- Do not evaporate the entire solvent when the solution is being concentrated.
- Weigh the desired quantities of different substances accurately.
- Maintain the temperature of hot water around 40°C .
- Add potassium hydroxide to oxalic acid solution in small lots.

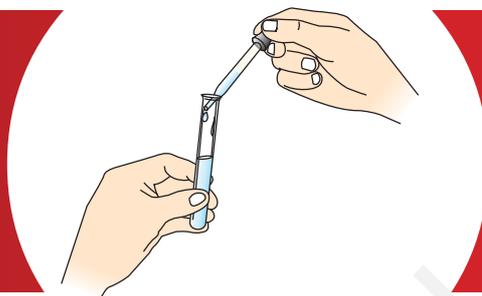


Discussion Questions

- Give IUPAC name of the compound called potassium ferrioxalate.
- What is the coordination number of iron in potassium trioxalatoferrate(III)?
- Give two examples of bidentate ligands other than oxalate ion.
- Why does the compound, potassium trioxalatoferrate(III), not give tests for ferric ions?
- What are chelates ?

UNIT-10

PREPARATION OF ORGANIC COMPOUNDS



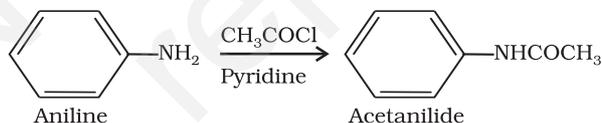
EXPERIMENT 10.1

Aim

To prepare acetanilide.

Theory

The replacement of one hydrogen atom of the —NH_2 group of aniline by $\text{CH}_3\text{CO—}$ group in the presence of glacial acetic acid. Gives acetanilide. In the laboratory, acetylation is usually carried out with acetic anhydride. Acetyl chloride may also be used for the purpose of acetylation if acetic anhydride is not available. Acetylation with CH_3COCl is usually carried out in the presence of pyridine.



Material Required



- Funnel : One
- Round bottomed flask (100 mL) : One
- Beaker (250 mL) : One
- Air condenser : One
- Sand bath : One
- Clamp and iron stand : One
- Pumice stone : As per need
- Melting point assembly : One



- Aniline : 5 mL
- Acetic anhydride / Acetyl chloride : 5 mL
- Acetic acid / Pyridine : 5 mL

Procedure

- (i) Take 5 mL of aniline in a 100 mL round bottom flask and add acetylating mixture containing 5 mL acetic anhydride and 5 mL glacial acetic acid. Alternatively, you can use 5 mL of acetyl chloride and 5 mL of dry pyridine as the acetylating mixture.

- (ii) Fit an air condenser on the mouth of the round bottom flask after adding a few pumice stones and reflux the mixture gently for 10-15 minutes on a sand bath.
- (iii) Cool the reaction mixture and pour it slowly in 150-200 mL of ice cold water with stirring.
- (iv) Filter the solid, wash it with cold water and recrystallise a small amount of sample from hot water containing a few drops of methanol or ethanol.
- (v) Report the yield and the melting point of the compound.

Aniline**Acetic anhydride****Acetyl chloride****Acetic acid causes serious burn****Pyridine****Result**

- (a) Yield of acetanilide _____ g.
- (b) Melting point of acetanilide is _____ °C.

Precautions

- (a) Handle acetic anhydride and acetyl chloride carefully as they cause irritation to the eyes and acetyl chloride also strongly fumes in air.
- (b) Store acetylchloride under dry conditions.
- (c) Handle pyridine with extreme caution. Dispense it in an efficient fume cupboard and wear disposable glasses while using it.
- (d) Distil pyridine before use because it absorbs moisture and the reaction does not take place under moist conditions.
- (e) Wash the solid 2-3 times with cold water till the filtrate is neutral to litmus.
- (f) Determine the melting point of perfectly dried and recrystallised sample.

ALTERNATIVE METHOD FOR THE PREPARATION OF ACETANILIDE

If acetic anhydride or pyridine is not available then the following method can be used for the preparation of acetanilide.

Material Required

- Boiling tube : One
- Water bath : One
- Melting point assembly : One
- Funnel : One



- Aniline : 1 mL
- Glacial acetic acid : 1 mL
- Acetyl chloride : 1 mL

Procedure

- (i) Take 1 mL of aniline in a dry boiling tube, add 1 mL of glacial acetic acid to it and mix the two thoroughly.
- (ii) To the above mixture add 1 mL of acetyl chloride in lots (0.3 mL at a time). The mixture becomes warm. If the boiling tube becomes unbearable to touch, cool it under tap water.
- (iii) After addition of whole amount of acetyl chloride, heat the mixture for five minutes in a boiling water bath.
- (iv) Cool the boiling tube and add ice-cold water (~10 mL) into the tube with constant stirring.
- (v) Filter the acetanilide separated as white powder and wash with water till filtrate is neutral to litmus.
- (vi) Crystallise the crude acetanilide with hot water. White shining needle shaped crystals are obtained.
- (vii) Report the yield and melting point of the compound.

Precautions

- (a) If aniline sample is too much coloured, distill it before carrying out the experiment, because yield is lowered with impure aniline.
- (b) Use perfectly dry apparatus.
- (c) Do not inhale the vapours coming out during the addition of acetyl chloride.
- (d) Determine the melting point of perfectly dried and recrystallized sample.

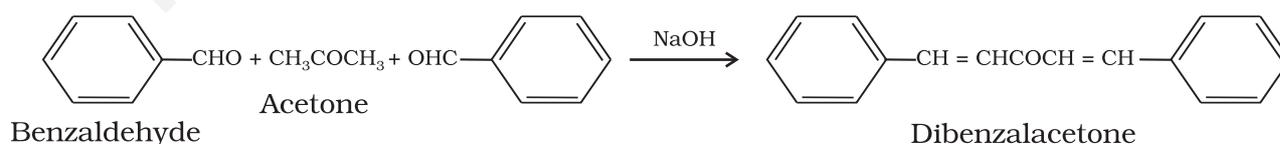
EXPERIMENT 10.2

Aim

To prepare dibenzalacetone (Dibenzylideneacetone)

Theory

α -Hydrogen atom of aliphatic aldehydes and ketones is acidic in nature, therefore, in the presence of dilute alkali, such an aldehyde or ketone condenses with an aromatic aldehyde to give α , β -unsaturated aldehyde or ketone. This reaction is called **Claisen - Schmidt reaction**. For example, benzaldehyde undergoes condensation with acetone in the presence of aqueous sodium hydroxide (NaOH) to give dibenzalacetone.



Material Required



- Conical flask(250 mL) : One
- Beaker(250 mL) : One
- Funnel : One
- Melting point assembly : One



- Ethanol : 25 mL
- NaOH : 3.15 g
- Benzaldehyde : 3.2 mL
- Acetone : 2.3 mL
- Ice : As per need
- Ethylacetate : As per need

Procedure

- (i) Prepare a solution of 3.15 g sodium hydroxide in a mixture of 25 mL ethanol and 30 mL distilled water taken in a 250 mL beaker. Cool the beaker in an ice bath maintained at a temperature of about 20–25°C.
- (ii) Prepare a mixture of 3.2 mL of benzaldehyde and 2.3 mL of acetone and add half of this mixture slowly in ice cooled NaOH solution prepared in step (i) with vigorous stirring. A fluffy precipitate is formed within 1-2 minutes. Stir the mixture gently for about fifteen minutes.
- (iii) After 15 minutes add remaining mixture of benzaldehyde and acetone and stir for 30 minutes more.
- (iv) Filter the pale yellow solid so obtained and wash with cold water. Dry it and recrystallise its small amount from ethanol or ethyl acetate.
- (v) Report the yield and the melting point of the compound.

Ethanol



NaOH



Benzaldehyde



Acetone



Ethyl acetate



Result

- (a) Yield of dibenzalacetone is _____ g.
- (b) Melting point of dibenzalacetone _____ °C.

Precautions

- (a) Maintain the temperature around 20°C while shaking the reaction mixture.
- (b) Always use freshly distilled benzaldehyde or the sample from a freshly opened bottle.

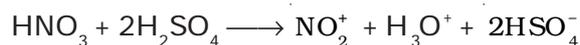
EXPERIMENT 10.3

Aim

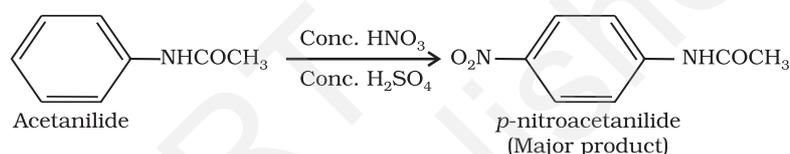
To prepare *p*-nitroacetanilide.

Theory

p-Nitroacetanilide is prepared by the nitration of acetanilide by using a mixture of conc. nitric acid and conc. sulphuric acid as nitrating reagent. The mixture of the two acids releases nitronium ion (NO_2^+), which acts as an electrophile in the reaction.



Nitronium ion attacks the benzene ring containing anilide group, mainly at the para position to give *p*-nitroacetanilide as a major product. This is an example of aromatic electrophilic substitution reaction.



Material Required



- Beaker (100 mL) : One
- Funnel : One
- Glass rod : One
- Ice bath : One



- Acetanilide : 2 g
- Glacial acetic acid : 2 mL
- Conc. H_2SO_4 : 5 mL
- Conc. HNO_3 : 1.5 mL
- Ice : As per requirement
- Ethanol/methanol : As per requirement

Acetic acid causes severe burns



Hazard Warning

- **Acetanilide may cause cyanosis.**

Procedure

- (i) Dissolve 2 g of acetanilide in 2 mL of glacial acetic acid taken in a 100 mL beaker.
- (ii) Add 4 mL of conc. H_2SO_4 gradually with stirring to the above mixture. The mixture becomes hot and clear solution is obtained. Cool the reaction mixture in an ice bath maintained at $0-5^\circ\text{C}$.
- (iii) Add a cold mixture of 1.0 mL conc. HNO_3 and 1.0 mL conc. H_2SO_4 to the viscous reaction mixture drop by drop with constant stirring, so that the temperature of the mixture does not rise above 10°C .
- (iv) Remove the beaker from the ice bath and allow the reaction mixture to attain room temperature. Let it stand at room temperature for about 30 minutes. Stir the reaction mixture continuously and pour it on 100g of crushed ice.
- (v) Stir the mixture well and filter the compound so obtained.

- (vi) Wash the compound with cold water and dry it.
- (vii) Recrystallise a small amount of the pale yellow solid from alcohol. Colourless crystals of *p*-nitroacetanilide are obtained. Yellow ortho-nitroacetanilide formed in the small amount remains dissolved in the mother liquor.
- (viii) Record the yield and melting point of the pure compound.

Result

- (a) Yield of *p*-nitroacetanilide is _____ g.
- (b) Melting point of *p*-nitroacetanilide is _____ °C.

Precautions

- (a) Do not allow the temperature of the reaction mixture to exceed 10°C during addition of nitrating mixture.
- (b) Add mixture of concentrated nitric acid and sulphuric acid into the solution of acetanilide slowly and carefully.

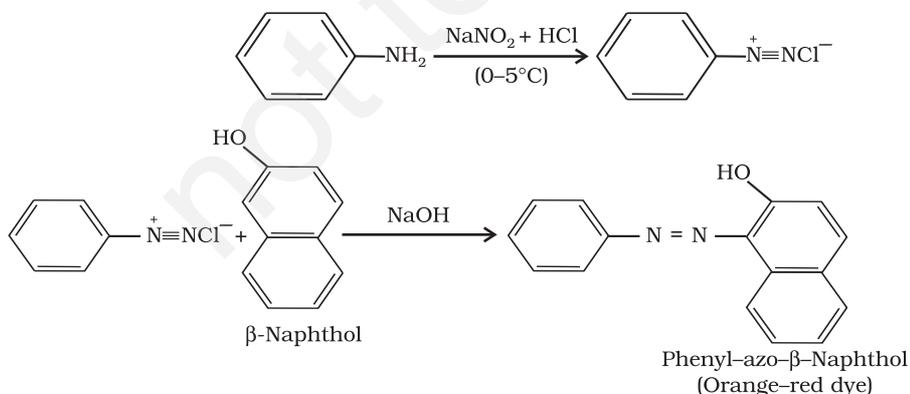
EXPERIMENT 10.4

Aim

To prepare phenyl-azo-β-naphthol (an azo dye).

Theory

Aniline is an aromatic primary amine. It forms diazonium salt when treated with nitrous acid at 0-5°C. Nitrous acid is generated *in situ* by the reaction of sodium nitrite with hydrochloric acid. The process is called **diazotisation**. The diazonium salt is coupled with an alkaline solution of β-naphthol to form an orange-red azo dye.



Material required

	• Beaker (250mL)	: One		• Aniline	: 2 mL
	• Conical flask (100mL)	: One		• Conc. HCl	: 6.5 mL
	• Glass rod	: One		• Sodium nitrite	: 1.6 g
	• Thermometer (210°C)	: One		• β-naphthol	: 3.2 g
	• Filter paper	: As per need		• Sodium hydroxide	: 2.0 g
	• Funnel	: One		• Glacial acetic acid	: 12.0 mL
	• Melting point assembly	: One		• Ice	: As per need
				• Distilled water	: As per need

Procedure

- Aniline** 
- HCl** 
- Sodium nitrite**  
- Sodium hydroxide** 
- β-naphthol** 
- Acetic acid causes severe burns**  
- Take 6.5 mL of concentrated hydrochloric acid in a 100 mL beaker. Dilute it with 6.5 mL of water and dissolve 2 mL of aniline in it.
 - Cool the above mixture by placing the beaker in an ice bath maintained at 0-5 °C temperature.
 - Diazotise the above mixture by adding a solution of 1.6 g of sodium nitrite in 8 mL water.
 - Dissolve 3.2 g β-naphthol in 18 mL of 10% sodium hydroxide solution. Add about 25 g of crushed ice to it.
 - Stir the β-naphthol solution well and add chilled diazonium chloride solution very slowly to it with constant stirring.
 - An orange red dye of phenyl-azo-β-naphthol is formed.
 - Allow the mixture to stand in the bath for 30 minutes with occasional shaking.
 - Filter the crystals obtained and wash them well with cold water.
 - Recrystallise about one-fourth of the crude product from glacial acetic acid.
 - Filter the recrystallised sample, wash with a little alcohol to remove acetic acid. Dry the recrystallised sample between the folds of a filter paper.
 - Record the yield and the melting point of the compound.

Result

- Yield of phenyl-azo-β-naphthol is _____g and its
- Melting point of phenyl-azo-β-naphthol is _____ °C.

Precautions

- Maintain the temperature in the range of 0-5°C during diazotisation.
- Always add diazonium chloride solution in alkaline β -naphthol for dye formation and not vice versa.
- Dry the recrystallised sample perfectly for determining the melting point.

Note : Azo-dye synthesis are mostly so nearly quantitative that one should use amounts of reactants closely agreeing with equations. Any excess of certain reactants may cause decomposition of unused material and tar may appear.

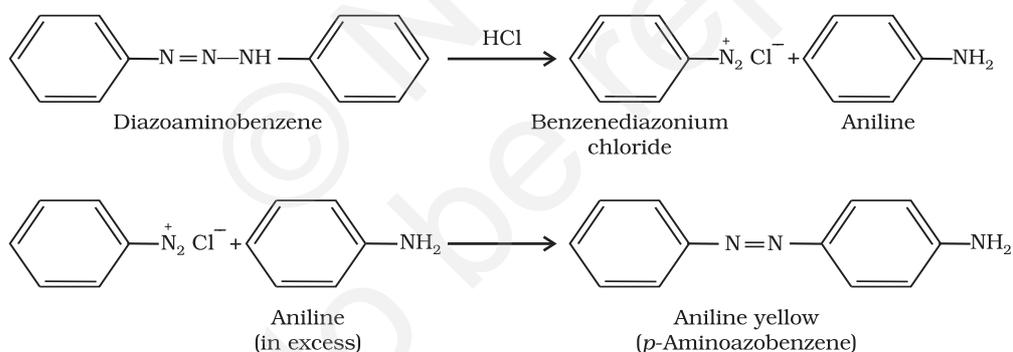
EXPERIMENT 10.5

Aim

To prepare aniline yellow (*p*-amino-azobenzene).

Theory

p-aminoazobenzene can be prepared in a good yield by rearrangement reaction of diazoaminobenzene with a small quantity of aniline hydrochloride in the presence of aniline as solvent. The chemistry of this conversion is as follows:



The above reaction is carried out only in weakly acidic conditions.

Material Required



- Conical Flask (100 mL) : One
- Thermometer : One
- Funnel : One
- Melting point assembly : One
- Waterbath : One



- Diazoaminobenzene : 3 g
- Aniline : 7 mL
- Aniline hydrochloride : 1.5 g
- Glacial acetic acid : 9 mL
- Carbon tetrachloride : 9 mL

Procedure

Aniline



Acetic acid
causes
severe burns



Carbon
tetrachloride



- (i) Dissolve 3 g of finely powdered diazoaminobenzene in 7 mL of aniline in a 100 mL conical flask.
- (ii) Add 1.5 g of finely powdered aniline hydrochloride to the above mixture.
- (iii) Warm the mixture with occasional shaking on a water bath at about 40-45°C, for a period of about one hour.
- (iv) Remove the flask from the water bath and allow the reaction mixture to stand at room temperature for about 30 minutes.
- (v) Add 9 mL of glacial acetic acid diluted with an equal volume of water and shake the reaction mixture thoroughly to convert excess aniline to its acetate, which is water-soluble.
- (vi) Allow the mixture to stand for 15 minutes with occasional stirring.
- (vii) Filter *p*-aminoazobenzene, wash with a little cold water and dry between the folds of a filter paper.
- (viii) Recrystallise a small portion of crude *p*-aminoazobenzene from carbon tetrachloride.
- (ix) Report the yield and melting point of *p*-aminoazobenzene.

Result

Yield of *p*-aminoazobenzene is _____ g and its melting point is _____°C.

Precautions

- (a) Maintain the temperature of the reaction mixture at about 40-50°C.
- (b) Wash the crude product with a small volume of water repeatedly.
- (c) Note the melting point of the perfectly dry sample.

AN ALTERNATIVE PROCEDURE FOR PREPARING ANILINE YELLOW

Theory

Aniline yellow can also be prepared by direct diazotisation and coupling as followed for phenyl-azo- β -naphthol dye. However, coupling of the diazonium salt with aniline or any other aromatic amine is carried out in a weakly acidic medium.

Material Required



- Funnel : One
- Conical flask (100 mL) : One
- Thermometer : One
- Melting point assembly : One



- Aniline : 6 mL
- 1.0 M HCl : 4 mL
- Carbon tetrachloride : As per need

Procedure

- (i) Prepare a solution of benzene diazonium chloride using 2 mL of aniline according to the method described for the preparation of phenyl-azo- β -naphthol dye (see experiment 10.4).
- (ii) Prepare a solution of 4 mL aniline in 4 mL 1.0 M HCl.
- (iii) Add the cold solution of aniline hydrochloride slowly into the cold solution of benzene diazonium chloride.
- (iv) Filter the yellow compound and dry it between the folds of a filter paper.
- (v) Recrystallise the small amount of crude sample from carbon tetrachloride and report the yield and melting point.

Aniline



Carbon tetrachloride



HCl



Discussion Questions

- (i) Why is acetic anhydride preferred over acetyl chloride for acetylation reaction?
- (ii) In the preparation of *p*-nitroacetanilide another minor product is formed. What is this compound and how can this be separated from *p*-nitroacetanilide?
- (iii) Is it necessary to recrystallise the compound obtained from the reaction? Explain why.
- (iv) How is an organic compound recrystallised?
- (v) What is the role of acetic acid or pyridine in acetylation?
- (vi) How is crude solid compound purified?
- (vii) Which of the following compounds on diazotisation followed by coupling with β -naphthol will form an azo dye?
 - (a) *p*-Toluidine
 - (b) Benzylamine
 - (c) N-Methylaniline.
- (viii) Why are diazonium chlorides usually soluble in water?
- (ix) How is methyl orange prepared in the laboratory?
- (x) How can phenol and aniline be distinguished chemically?
- (xi) Why is aniline soluble in hydrochloric acid while it is insoluble in water?
- (xii) Why is aniline a weaker base than ammonia?
- (xiii) In contrast to aromatic primary amines, aliphatic primary amines do not form stable diazonium salts. Why?

PROJECTS

Project 1

Title

Study the variation in the amount of oxalate ions in guava fruit at different stages of ripening.

Objective

The objective of this project is to investigate the variation in the amount of oxalate ions present in guava at different stages of its ripening (i.e. unripe, partially ripe and fully ripe).

Brief Procedure

Collect different samples of guava fruit (green, pale-green, yellowish-white and yellowish, i.e. from unripe to fully ripe variety). Take 100 grams of one of the sample of guava fruit, crush it into a mortar and transfer the paste in 100 mL of water. Boil the contents for 10-15 minutes and filter. Take the filtrate, add about 5 mL of dilute sulphuric acid and titrate it against 0.001M KMnO_4 solution. Repeat the procedure with other samples of guava and draw conclusion.

Project 2

Title

A study to compare the quantity of casein present in different samples of milk.

Objective

To compare the quality of different samples of milk by finding out quantity of casein present in them.

Brief Procedure

Take 200 mL of each sample of milk in separate 500 mL beakers. Heat the milk samples upto 50 – 60°C. Add a few drops of dilute hydrochloric acid slowly with constant stirring for 5-10 minutes. Casein coagulates as an amorphous substance. Filter the substance and wash the precipitate several times with tap water. Remove the fat by using a suitable organic solvent. Weigh casein so obtained after drying.

Project 3**Title**

Preparation of soyabean milk and its comparison with natural milk.

Objective

To prepare soyabean milk and compare it with natural milk with respect to curd formation, effect of temperature, taste etc.

Brief Procedure

Prepare soyabean milk by first soaking soyabean seeds in warm water and keeping them overnight in water. Make a paste of seeds by crushing and finely grinding them. Mix the pasty mass with warm water to get soya milk. Filter the mixture and discard the undissolved portion. Compare soya milk with natural milk and conclude whether soya milk can be a substitute for natural milk. The comparison may be made with respect to the nutrients present, colour, smell, taste, effect of temperature, curd formation, etc.

Project 4**Title**

Study the effect of potassium metabisulphite as a food preservative under various conditions.

Objective

To study the effect of concentration of potassium metabisulphite (preservative), temperature and time on preservation of food.

Brief Procedure

Collect amla fruits and wash these with water. Cut these into small pieces and dry in the sunlight for a few hours. Mix the salt and the spices to the pieces. Pour 25g of amla pieces into each of the six boiling tubes numbered as 1, 2, 3...etc. Weigh 500 mg of potassium metabisulphite and dissolve it in 20 mL of distilled water. Keep the boiling tube No. 1 without mixing preservative and oil. In boiling tube No. 2 and 3 add 1 mL of the preservative solution and 2 mL of oil and mix the mixture with the glass rod. Keep the boiling tube No. 2 at the room temperature (25-35°C) and the boiling tube No. 3 at a temperature of 40°C. In boiling

tube No. 4, 5 and 6, add 2 mL, 4 mL and 8 mL of the preservative solution respectively and 2 mL of mustard oil. Keep these boiling tubes at the room temperature. Prepare again the fresh mixtures in boiling tubes No. 4, 5 and 6 and keep them at 40°C temperature.

Keep all these boiling tubes for 3 to 5 days. Note the growth of fungi, if any, in these tubes. Record your observations and draw conclusion.

Project 5

Title

A Study of enzymatic hydrolysis of starch

Objective

Study the hydrolysis of starch by salivary amylase and the effect of pH and temperature on it.

Brief Procedure

Take about 20-30 mL of warm distilled water (30°C– 40°C) in the mouth and mix it with the saliva by gargling in the mouth. Collect the saliva mixed water in a beaker.

Digestion of Starch by Saliva Solution

Take 10 mL of the starch solution in a boiling tube and add 2 mL of 1% sodium chloride solution in it. Keep the boiling tube in a water bath, maintained at 30° – 40°C, for at least 15 minutes. Pour 2 mL of the saliva solution in the boiling tube and start the stopwatch immediately. Take out 2-3 drops of the mixture after one minute and pour it in the test tube containing iodine solution. Shake the contents of the test tube and note the colour of the solution, if any. Similarly, take out 2-3 drops of the mixture from the boiling tube after every one-minute and add to iodine solution contained in the test tubes. Record the colour of the solution in each case. Stop taking readings when there is no change in colour. Record the readings in a tabular form.

In order to study the effect of temperature on the digestion of starch by saliva, perform the above experiment at 50°C.

The effect of pH of reaction medium can also be studied by using small quantities of dilute HCl and dilute NaOH in the separate experiments carried out in the same manner as above.

Project 6**Title**

A comparative study of the rate of fermentation of the following substances: (a) Wheat flour, (b) Gram flour, (c) Potato juice, (d) Carrot juice, (e) Orange juice, (f) Apple juice, and (g) Sugar-cane juice.

Objective

To determine the rate of fermentation of different substances and study the effect of concentration, time and temperature on the rate of fermentation of these substances.

Brief Procedure

Take a conical flask (100 mL) fitted with a delivery tube as shown in Fig. 12.1. Remove the delivery tube and add 10 g of wheat flour and about 80 mL of the distilled water into the flask. Stir the contents of the flask with a glass rod and add 2 g of yeast. Stir the contents again. Fit the delivery tube into the mouth of the flask. Tie a balloon with the help of a thread to the upper end of the delivery tube as shown in Fig. 12.1. As the fermentation proceeds, carbon dioxide gas is evolved and the balloon inflates. The extent to which the balloon inflates in the given time is the measure of the rate of reaction. Repeat the experiment with other materials such as potato juice, orange juice, apple juice and sugar-cane juice.



Fig. 12.1 : Determination of rate of fermentation

Effect of concentration of yeast

Study the effect of concentration of yeast on the rate of fermentation of any one of the above materials. For this, carry out the reaction using 2, 3 and 4 grams of yeast and note the extent of inflation of balloon in each case in a fixed time interval.

Effect of time

Carry out the reaction using the same ingredients for different intervals of time and observing the extent of inflation of balloon.

Effect of temperature

Carry out the reaction using the same ingredients for a fixed interval of time but at three different temperatures (25°C, 30°C, and 35°C). Note the extent of reaction by observing the inflation of balloon in these reactions.

Project 7

Title

Extraction of essential oils present in saunf (aniseeds), Ajwain (carum) and illaichi (cardamom)

Objective

To extract essential oils from aniseeds, carum, and cardamom by using petroleum ether as a solvent.

Brief Procedure

Take 100 g of crushed aniseed in a conical flask and add 100 mL of petroleum ether (of boiling range 60°-80°) in it. Close the mouth of the flask with a rubber cork and shake it for sometime. Keep the flask for a day. Filter the solution and collect in a distillation flask. Distill off the petroleum ether at 60°C - 80°C. Petroleum ether is a highly inflammable liquid. Do not bring any flame near it. Use heating mantle for heating the flask. Do not heat it directly on flame. Transfer the liquid (oil) which is left in the flask to a boiling tube and close the mouth of the boiling tube with a rubber cork. Note the colour, odour and volume of the essential oil so collected.

Similarly, extract essential oils of carum and cardamom.

Project 8

Title

Study of common food adulterants.

Objective

To identify the food adulterants in fat, oil, butter, sugar, turmeric powder, chilli powder and pepper.

Background information

Adulteration of food means substitution of the genuine food material wholly or in part with any cheaper or inferior substance or removal of any of its constituents, wholly or in part, which affects adversely the nature, substance or quality of the food. According to the Indian Preservation of Food Adulteration Act (PFA) 1954, any ingredient which when present in food, is injurious to health is an adulterant.

Some of the foods commonly adulterated in India and the adulterants found in them are as follows ; corresponding form of Khesari dal (grain/bean/flour) is mixed with pulses like masoor, bengal gram dal, red gram dal, black gram, and channa. Consumption of khesari dhal for a long time results in paralysis of the lower limbs.

Sometimes seeds, barks, leaves and other matter are dressed up to look like genuine foodstuffs and are used to adulterate pure ones. For example exhausted tea leaves or coloured sawdust are mixed into fresh tea. Powdered bran and sawdust may be present in ground spices. Easily obtainable seeds are substituted for cumin, cardamom, black pepper, mustered seeds etc.

Edible oils and fats are adulterated with cheap edible and non edible oils. Seeds of Argemone maxicana resemble mustered and are used to mix with mustard seeds and oil extracted from seeds is used to adulterate oils such as coconut, mustard, sesame and groundnut. Argemone oil is poisonous and its use results in dropsy in human beings. Oils and fats are also adulterated with petroleum products which cause gastrointestinal disorders.

Talc and chalk powder are used to adulterate wheat flour, Arrowroot powder and confectionary, starch is used as a filler in milk and milk products.

Coaltar dyes and mineral pigments like lead chromate and red or yellow earth are common food adulterants used for colouring milk products, confectionary, soft drinks, beverages, tea, spices, bakery products, fruits and vegetables to give better look.

Brief procedures for testing food adulterants in some of the food materials are given below :

Brief Procedure

Vanaspati ghee in butter

Take 0.5g of butter sample in a test tube and melt it by heating gently. To this liquid add a small amount of sugar and a few drops

of HCl and shake the mixture for 5 minutes. Appearance of pink colour indicates the presence of vanaspati ghee in the butter.

Dyes in fats and oils

Take 1 mL of fat/oil in a test tube and add 1 mL of the mixture of sulphuric acid and glacial acetic acid in the ratio 1:4. Heat the mixture. Appearance of pink colour indicates the presence of dyes in fats and oils.

Chalk in sugar

Take 1 g of sugar in a test tube and add 2 mL of dilute H_2SO_4 in it. Evolution of effervescence indicates the presence of chalk in sugar.

Artificial colour in red chillies

Take a glass tumbler filled with distilled water and pour a few grams of red chilli powder in it. Stir the mixture with the glass rod and allow it to stand for a few minutes. Appearance of brick red colour in water shows the presence of artificial colour in red chilli.

Coloured chalk powder in turmeric powder

Take about 0.5g of turmeric powder in a test tube and add 1 mL of dilute H_2SO_4 . Evolution of effervescence shows the presence of coloured chalk powder in turmeric.

Sawdust coloured with coaltar dye in turmeric powder

Take about 1.0 g turmeric powder in a test tube add a few drops of conc. HCl . Instant appearance of violet colour which persists on dilution with distilled water indicates the presence of sawdust coloured with metanil yellow, a coaltar dye.

Pappaya seeds in black pepper

Take a beaker filled with distilled water and add one spoon full of pepper. Papaya seeds float over water while pepper settles down.