MSCCH-05

VARDHMAN MAHAVEER OPEN UNIVERSITY, KOTA

PRACTICAL CHEMISTRY

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VARDHMAN MAHAVEER OPEN UNIVERSITY, KOTA

PRACTICAL CHEMISTRY

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LABORATORY'S RULES

1. Practicians must wear laboratory uniform in every laboratory activities including during the discussion time.
2. Practicians must prepare the report, and other tasks before practice begin.
3. Practicians are not allowed eating, drinking and smoking in laboratory.
4. Practicians are not allowed entering assistant room, storage and the research laboratory without permission from the assistant.
5. Except journal and laboratory kit, other should not be placed on the practice table.
6. Practice is done in definite workday and practicians are not allowed working outside these days without permission from the assistant.
7. Practicians should pay attention to sign (bell sound) at the beginning and at the end of practice time.
8. The fill up of attendance list will be done every workday including in every laboratory activities.
9. Practicians are not allowed to left the laboratory during the work hour without pennission from the assistant. Leaving laboratories more than 15 minute should be with written permission.
10. During the experiment activities, all windows should be opened.
11. Practicians that have finished the practice should asked for the signature of assistant.
12. Practicians are not allowed to take chemical compound from storage, the assistant will prepare the chemicals. Every chemical compound bottle should be clean and dry.
13. Liquid reagents must be taken by droper.
14. Solid reagents must be applied by spatula.
15. Reagents should be placed on reagents table and are not allowed to remove.
16. Every tool should be used according to its utility.
17. Laboratory kit contains boiling, pipette, spatula, vial, matches, and stirring stick.
18. Cleanness kit contains napkin, brush and detergent.

19. Each tool must be clean and dry before the storage.
20. Practicians are not allowed chemical compounds in the drawer except with the permission from assistant.
21. Before leaving the laboratory, fume hood, weight room, laboratory, floor, washing stand, table and seat should be neat and clean. Water, gas, electricity and windows should be shut down.
22. Contents are experiment's number, procedure, chemical and physical properties of matter which are used in the experiment, mechanism of reaction, characterstives of the reaction, theory, reference, and table of result.
23. Report and tasks must be wrote on A4 paper and contents are practician code, experiment's number, name, 2 no. of experiment, date of experiment, name of the assistant.
24. Each must. have assigned from assistant otherwise practician are not allowed to do the experiment.
25. Report and tasks should be handed over before the experiment begins. Practician who don't hand over the report and tasks on time won't be allowed to do the experiment.
26. Report and tasks that have been handed over can't be taken back by practicians.
27. In everything related with Organic Laboratory practicians are not allowed to cheat. Any violation related to this rule, will caused restriction of practician back to his/her own department and will not allow to practice for 1 or 2 semester, or the case will be handle by the university.
28. Repeated warning that caused by repeated violation will affect to practice point.
29. Practician must obey the rules without any exception.

NOTES

1. Practicians can have final exam after completion of all experiment, report, and tasks, collect all journals and finished all problems of tools and tables.
2. Each tool that returns to laboratory should be in good and clean condition.
3. Tables should be returned in neat and clean condition and so as the laboratory.
4. Anything related to the laboratory's rules that have not been written will be arranged later.

LABORATORY PRECAUTIONS

1 Safety Equipment

A set of safety rules is written on the inside behind cover of this book. Careful observation of these rules will help to prevent accidents in the laboratory. However, from time to time accidents can occur. Therefore, safety equipment is installed for this eventuality in the laboratory. Safety equipment should include:

- An eye wash
- A safety shower
- Fire extinguishers
- Hoods
- First-aid kit.

1.1 Eye Wash

The eyewash is designed to flush irritating chemicals from the eyes. It should be capable of providing a stream of water for at least 15 minutes. In the event of an eye accident, you should proceed to the eyewash at once and wash the eye for at least 15 minutes. During this process, the eye should be kept open. The eyes are the most vulnerable part of the body. In the event of any eye injury report the instructor at once. All eye injuries should be immediately examined by a health professional.

Never use the eyewash for anything other than its intended purpose.

1.2 Safety Shower

The safety shower is designed for two purposes, namely, to extinguish clothing fires and to provide a whole body wash if a large amounts chemical spills.

i. Clothing Fires: If your clothing catches fire, perhaps the best rule is to fall and roll. Never run to a shower with your clothes on fire, it will only fan the flames. Use the shower afterwards to squelch any residual embers.

ii. Large amount of Chemical Spills: Large amount of chemical spills on clothing or exposed parts of the body should be removed at once using the deluge shower. Affected clothing should be removed, and the affected body areas should be thoroughly washed to remove any chemical traces. Do not reuse affected clothing until it has been completely washed! Serious and avoidable injuries have resulted from wearing affected clothing.

1.3 Fire Extinguishers

In the laboratory, you will sometimes work with flammable materials. For most purposes, ABC fire extinguishers are adequate to extinguish most fires. Several of these extinguishers should be kept in the laboratory. Learn their location. Your instructor will demonstrate their use before you begin to work in the laboratory.

ABC-type extinguishers (e.g., lithium aluminium hydride or sodium) cannot extinguish some materials. In these circumstances, appropriate extinguishing materials will be provided and their use will be demonstrated before the experiment begins.

1.4 Hoods

If possible, do all experiments in a hood. The ventilation system draws the fumes generated by an experiment away from the experimenter. The walls of the hood enclose the experiment on five sides. Therefore, if on explosion or spill occurs, the experiment. A sliding transparent all these feature. The sash should always be kept between the individual's eyes and the experiment. In a modern organic laboratory, chemical reactions are always done in a hood.

1.5 First Aid Kits

First aid kits are used for minor injuries. Report all cuts and burns to the instructor, and at his/her discretion, visit the institute physician for further treatment.

i. **Cuts:** All cuts should be cleaned carefully to remove any chemical residue or broken glass before a Band-Aid is applied.

ii. **Burns:** Immediately flush burns under cold water for 15 to 20 minutes to reduce the magnitude of the injury. Do not rub the affected area or pack it in ice. If a seemingly minor injury appears worse, consult a physician.

2 Personal Protective Equipment

Wearing the proper clothing during an experiment is as important to an individual's safety as any other safety feature of the laboratory. This protective clothing should include the following.

2.1 Safety Glasses

Safety glasses or goggles must be worn from the time you enter the laboratory you leave the laboratory. There are no exceptions to this regulation!

Some individuals wear contact lenses rather than corrective glasses. This practice is not recommended in the laboratory. Soft contact lenses actually accumulate organic vapours and hold them against the eye. Serious injury can result. Hard contact lenses are somewhat better, however, in the event of a splash, the material can be drawn under the lens by capillary action. If during an experiment any irritation of the eye occurs, remove the contact lenses, wash the eye by the eyewash, report the instructor, and leave the laboratory. A physician should be consulted as soon as possible. Ordinary glasses are not safety glasses. In the event of a splash, they do not provide lateral protection. In additions, street glasses are frequently made of plastic, and they can be ruined easily by the solvents in the laboratory.

2.2 Lab Coats

Lab coats are designed to remove quickly in case of a fire or chemical spill. Lab coats provide protection against the minor spills and splashes of the laboratory reagents. The coat should at least protect the upper body from the neck to the waist, and preferably, it should protect up to the knees. The lab coat should be made of cotton and not of synthetic materials. During a clothing fire, a synthetic material melts and becomes incorporated into the burn. Synthetic lab coats tend to dissolve in organic solvents, therefore, they are not as durable as cotton ones.

2.3 Shoes

Proper laboratory footwear completely covers the foot. It may be either a street shoe or a sneaker, but sandals or open-toed shoes should not be worn. It is advisable to have a pair of sneakers in your locker and change them before the lab period begins.

2.4 Gloves

If toxic or colored (dyes) substances are used in the laboratory, the instructor may advise wearing gloves. Disposable gloves are preferred, and they should be worn only for as long as necessary.

3 Good Laboratory Practice

1. Food and drink should not be brought into the laboratory. Packaged materials (including lunches) can absorb materials from the air. Food consumed in the laboratory can easily become contaminated.
2. Also, beverages can easily absorb toxic vapours from the air. Serious cases of poisoning have resulted from this type of occurrence.

3. Smoking: Cigarette smoking is banned from the laboratory for two important reasons.

   i. As with food consumption, material from the air, hands, and desk can be carried to the mouth during smoking.

   ii. Cigarettes represent an unacceptable ignition hazard in the laboratory Cleanliness: During a laboratory experiment, you are exposed to a wide variety of chemicals. They can be retained on the hands, especially under the fingernails. It is a good laboratory practice to make sure your hands are clean before you leave the laboratory.

4 Safe Handling of Laboratory Equipment

Heat Sources: Gas burners, heating mantles, and steam baths are used as heat sources in the laboratory. Each source has its appropriate use and precautions.

4.1 Gas Burners

These devices provide instant high temperature (up to 1100 °C). However, the open flame represents a serious ignition hazard. For this reason, gas burners should not be used near volatile and easily ignited materials Furthermore, glass should not be heated directly in an open flame because the concentrated heat may cause it to crack.

4.2 Bunsen Burners

Bunsen burners are used frequently in student labs. However, when they are used, a ceramic heating pad should be placed between the flame and the flask. Never leave a lit burner unattended.

4.3 Heating Mantles

These devices heat more slowly than a gas burner, and thus give a lower temperature. Heating mantles use electricity as a source of heat, therefore, they should be kept dry, when used they should be connected to power only through a ground fault interrupter.

4.4 Steam baths

Steam baths provide a convenient source of heat for temperatures ranging from room temperature to 95°C. Steam, however, has a high heat of vaporization, and live steam can cause severe scalding.

5 Electrical Equipment

Electrical equipment represents two significant hazards in the organic laboratory.

5.1 Ignition Hazard

Electrical motors spark frequently during operation. These sparks can cause fires or explosions. For this reason In areas where solvents are located, only spark-free motors should be used. The problem of sparking also occurs with switches and plug connections. These devices should be on the outside of the hood where the concentration of solvent vapor is low and where the danger of igniting it is minimum.

5.2 Shock Hazard

Do not use poorly maintained equipment (e.g., frayed cords, loose plugs, etc.). Keep these devices dry and away from the puddles of water that may collect in a hood. All these devices should be connected through ground-fault interrupters to minimize shock hazards.

6 Waste Disposal

Every laboratory experiment generates products (e.g., spent solvents, pot residues, etc.) that must be disposed of the proper disposal of laboratory wastes is as much a part of the experiment as the synthesis and isolation of the product. Some general rules follow for disposing of chemical wastes.

6.1 Chemical Spills

Chemical spills should be cleanup as soon as they occur. The residues from the clean up should be placed in a properly labeled container for later disposal. Do not attempt to cleanup a large spill (i.e., 100 ml or more).

6.1.1 Solids

Sweep up solids and dispose of them in an appropriately labeled container.

6.1.2 Liquids

Spilled solvents can be absorbed on commercially available spill control materials such as vermiculite, clay, and so forth. Very small spills can be cleanup with take care paper towel. where the paper towel may react chemically with the spilled material (ie. oxidizing agents or reactive metals). Place the clean-up material. wet with the solvent, in a labeled waste bag for later disposal. Wear gloves when cleaningup the spill, unless you are absolutely certain that the spilled material is nontoxic. Neutralize spilled acids or bases and then rinse them down the drain.

6.1.3 Mercury

Broken thermometers are a common source of spilled mercury in the laboratory. Cleanup such spills immediately. Amalgamating agents are commercially available to remove such spills completely. Place the spent clean-up material and any free mercury in a separate waste container reserved for the disposal of mercury wastes. Dusting the spill with elemental sulphur is not an adequate clean-up procedure.

6.1.4 Broken Glass

Broken laboratory equipment often produces fragments razor-sharp edges and needlepoint. Place these broken glassware in a specially labeled container not in the common trash.

WARNING: Do not combine residues from chemical spills unless specifically told by the instructor. Violent chemical reactions can result from these mixtures.

7. Liquid Wastes

7.1. Chemical Reaction Wastes: Chemical reaction wastes are usually of known composition, and disposal can be planned ahead of time. Instructions for such disposal are found in the note column of each experiment. It is imperative that wastes be placed in the correct container. These containers should be used for only one experiment. The mixing of waste stream from various experiments should be used for only one experiment. Only the instructor should do the mixing of the waste streams from various experiments. Violent chemical reactions can result from the careless mixing of such waste streams.

7.2. Spent Acids and Bases: Carefully neutralizes these materials and pour them down the drain. This procedure should be followed only if the resulting salt is non hazardous. Otherwise, the spent material should be placed in a container for disposal.

8. Solid Wastes:

8.1 (a) Nonhazardous: If the materials are water soluble, dissolve them in water and flush them down the drain. Insoluble materials should be labeled and disposed of as nonhazardous solid waste.

b. Hazardous: Place these materials in a properly labeled container and save them for hazardous waste disposal.

COMMONLY USED LABORATORY EQUIPMENTS

Gas collecting tube	Measuring pipette	Stirring rod	Thermometer
Burette	Volumetric flask	funnel	Graduated cylinder
Test tube	Test tube rack	Spot plate	s-shaped test tube rack
Forceps	Dropper pipette	spatula	Triangular file
Erlenmeyer flask	Plastic wash bottle	Beaker	Gas-collecting bottle
Test tube brush	Pinch clamp	Test tube holder	Watch glass
Evaporating dish	Crucible and cover	Rubber stoppers	Pneumatic trough
Safety goggles	Crucible tongs	Clay triangle	Wire gauze
Utility clamp	Iron ring	Burette clamp	Wing tip
Burner	Ring stand		

UNIT-1

Inorganic Chemistry

EXPERIMENT 1

INORGANIC QUALITATIVE REACTION

Purpose

To study the reaction of metal ions with hydroxide ion and ammonia

Introduction

Metal cations react characteristically with base in the term of form and nature of product solubility, especially in water. Adding of base (strong) excessively often give more influences, according to the characteristic of cation in the term of amphoterism. often form complex compounds with ammonia. By this, identification of cation with strong base (NaOH) and weak base (NH_3) is an interesting activity in inorganic qualitative reaction.

Materials

- Apparatus - 0.5 M NaOH solution
- 2 M NaOH solution - 2 M NH_3 solution
- Chemicals - Mg^{2+}, Ba^{2+}, Al^{3+}, Cr^{3+} 0.1 M solution
- 2M NH_3/ NH_4Cl solution - Fe^{3+}, Mn^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, Ag^{2+}, Zn^{2+} Virote Solution

Procedure

1. Take nitrate cations (as mentioned above), 0.5M NaOH solution, 2 M NH_3 solution and NaOH 0.5 M solution in labeled-dropper bottle. These solutions are used as mother liquid.
2. Add drop by drop 1 ML (about 5 drops) of 0.5 MNaOH solution into 0.1M $Mg(NO_3)_2$ solution.

3. Divide the two parts, and put each to semi micro test tube. Centrifuge for 1 minute. Remove the supernatant with dropper pipette.

   a. In test tube 1, add 2 M NaOH solution (volume must not exceed of 1 mL) into the resulted precipitate.

   b. In test tube 2, add 2 M NH_3 (solution volume must not exceed of 1 mL) into the resulted precipitate.

4. Repeat step 2 to 3 for the 0.1 M solution of Ba^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Mn^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, Ag^{+} dan Zn^{2+}. Record the observation in the table on the worksheet

5. Identify which cations that form precipitate on the add on of NaOH

6. Identify which cations that form precipitate on the add on of NH_4OH

   a. Dissolves in the add on of excess NaOH

   b. Dissolves in the add on of excess NH_4OH

7. a. Add 0.1 M $Al(NO_3)_3$ solution slowly into 1 mL of 2MNaOH. Record your observation.

   b. Add 0.1 M $Fe(NO_3)_3$ solution slowly into 1 mL of 2MNaOH. Record your observation.

   c. Repeat the activities of (a) and (b) in opposite steps of reactant adding. Record your observation and explain.

EXPERIMENT 2

OXIDATION-REDUCTION REACTION (1)

Purpose

To study oxidation-reduction reaction of several compounds

Introduction

Oxidation is the releasing of electron and reduction is the capturing of electron. Oxidation and reduction reactions are always a pair reaction, in which transfer of electron occurres. Oxidizing agent is a species to that cause other species oxidized and itself reduced. Reducing agent is a species that cause other species to reduced and itself oxidized.

In this experiment, several general oxidation-reduction reactions are studied.

Table 2.1 Oxidizing and Reducing Agents

Oxidized form	Reduced form	Differentiation test or reaction character
M_NO_4 purple	Mn^{2+} uncolored	The colour changes, from purple to colourless
$Cr_2O_7^{2-}$ orange	Cr^{3+} green	The colour changes, from orange to green
I_2 brown	I^- colourless	The colour change, from brown to colourless Indicator sensitivity: starch solution changes to blue in the presence of I_2. If the blue color is not sharp, add 5 drops of $CHC1_3$, blue color will form on chloroform layer at the bottom of the tube.
Fe^{3+} brown	Fe^{2+} green	The colour changing of the two ions is difficult to be observed Test 1: add 1 drop of 0.1 M KSCN solution to make red blood color of $Fe(SCN)^{2+}$ for Fe^{3+} ion

		Test 2: Add 4 drops of 2 M solution of NaOH. The precipitate of $Fe(OH)_2$ is green, and $Fe(OH)_3$ is brown.
Sn^{4+}	Sn^{2+}	No colour changing Test: add 1 drop of 0.25 M $HgC1_2$ solution. White to purple precipitate of Hg_2C1_2 and Hg formed in the presence of Sn^{2+} ion.
SO_4^{2-}	SO_3^{2-}	No colour changing Test: add 2 drops of 0.1 M $BaCl_2$ solution and several drops of 2M HCl solution. White precipitate of $BaSO_4$ formed, whereas $BaSO_3$* dissolves in the addition of Hcl

*Generally, sulphite (SO_3^{2-}) ion is contaminated with sulphate because sulphite easily oxidized by dissolved oxygen.

Several compounds are oxidized and reduced in a reactions. The aims of this activity are to study oxidation-reduction reaction of several compounds and to test (special test) on it as seen in Table 2.1.

Each activity is conducted by using two reaction tubes. First tube for "test tube", as T and second one for "blank solution tube", labeled as B. Blank solution is a solution which contains (solvents) except compound that will be tested or studied. Use water or aquadest to replace the tested compound (in same volume).

Example:

Contents of tube T Contents of tube B ?

S.No.	Content of Tube T	Content of Tube B

5 drops of 0.1 M Fe^{2+} solution 5 drops of 0.1 M Fe^{2+} solution

2 drops of 2.5 M H_2SO_4 solution 2 drops of .5 M H_2SO_4 solution

5 drops of 3% H_2O_2 solution 5 drops of aquadest

The purpose of the blank solution making is to know the condition before and after reaction. Do the test to both tube T and tube B in order to know every change in the reaction clearly. In some cases, two blank solutions are needed. First blank solution for solvent one, and second solution for the other.

Materials

Apparatus - Test tube – H_2O_2 (3%), - H_2SO_4 (5 M), $5MH_2SO_4$

Chemicals - Semi micro test tube - ($SnCl_2$) (0.1 M) - KSCN (0.05M)

$O.1MSnCl_4$ 0.05MKSCN

- Dropper pipette - HCl (5 M) - KI (0.1 M)

5MHCl 0.1MKI

- Test tube shelf - MnO_4 (0.02 M) 0.02M MnO_4

- $H_2C_2O_4$ (0.1 M) – $K_2Cr_2O_7$ (0.02 M) $2.02MK_2Cr_20_7$

- $Fe(NH_4)_2(SO_4)_2$ (0.1 M) (must be fresh by prepared)

0.1 $MH_2C_2O_4$ ($COOH_1$ COOH) $O.1MFe(NHu)_2$ $(SOu)_2$

Procedure

Do the experiments according to the procedure in Table 2.2 in worksheet and refer to Table 2.1.

1. Preparation of fresh solution of Fe^{2+}

   a. Take 2 gram of Fe $(NH_4)_2(SO_4)_2 \cdot 6H_2O$ crystal into 250 ML Glass beaker.

   b. Add 5 mL of 5 M H_2SO_4 solution and 50 mL of aquadest in above beaker in point a.

   c. Mix the mixture until all crystals are dissolved (heat the mixture if necessary).

2. For each reaction in Table 2.2, use 5 drops of reagent (reactant) for tube T and tube B, as shown in Table 2.2.? Prepare blank solution for each system and check it with the assistant before doing the experiment.

3. If there is no reaction at room temperature, heat the solution by placing the test tube in hot water.

4. If it is necessary, appropriate tests must be conducted to both tube T and B.

Notes:

a. Conduct the redox tests to both tube T and B (see Table 2.1).

b. Use fresh solution of $Fe(NH_4)_2(SO_4)_2$ to get Fe^{2+} ion.

c. The KI solution must be coloured /in fresh condition, (replace the KI solution if the color is yellow).

EXPERIMENT 3

OXIDATION-REDUCTION REACTION (2)

THE INFLUENCES OF ACID AND BASE ON METALS

Purpose

To study the influences of acid and base on metals

Introduction

• Acid

Acid is a species that can donate proton (proton donor). Strong acid donate its entire proton. Mineral acids such as HCl, HNO_3 H_2SO_4 and H_3PO_4 are strong acids. Acid can act as oxidizing agent. H^+ is oxidizing agent (and reduced to H_2). Table 3.1 shows the influences of several acids on metals.

• Metal

Metal tends to form cation (positive ion) whether in solution or compound. Solid metal reacts with acid to produce cation and releases electron(s).

$$M\,(s) \longrightarrow M^{n+}\,(aq) + n\,e$$

The released electron is captured by oxidizing agent (H^+, NO_3^-, SO_4^{2-}) and gas is released. The series of metals listed in Table 3.1 is known as **activity series**. elements. Therefore, potassium (K) is the strongest reducer that can replace all Metal above in the series will reduce the metals below in the series. Metals below in the **activity series**, according to the reaction:

$$n\,K\,(s) + M^{n+}\,(aq) \longrightarrow n\,K+\,(aq) + M\,(s)$$

Vice versa, all metals above of hydrogen, can replace acid (for example replace with H^+) and all metals right (below) of hydrogen will react with oxidizing acids.

• Alkali

Alkali refers to strong base with the formula of M(OH)n, where M is alkali metals (such as Na, K) or alkaline earth metals (such as Ca, Mg) and the value

of n is 1 (for alkali) or 2 (for alkaline earth). Several metals react with alkali solution. The alkali reaction shows the "semi metal" nature of the elements. Semi metal nature is a combination of metal and non-metal nature. In some cases, metal oxide found react with acid and base. These metal oxides are called as amphoteric oxides. Elements that form amphoteric oxides are also able to react with alkali and acid to produce H_2 gas.

Zinc also reacts with acid and base in the same way, but slow and relatively difficult to observe the occurrence of H_2 gas. To prove that zinc has already dissolved, add sulphide ion to form white precipitate of zinc sulphide.

Table 3.1

Metals	Acid replacement		Oxidizing acids		
	HCl dilute / concentrated (up to 10 M)	H_2SO_4 dilute	H_2SO_4 concentrated (=18 M)	HNO_3 dilute	HNO_3 concent ed (= 15 M
K	Dissolve to form chloride with lower oxidation state and hydrogen gas.	Dissolve to form sulphate with lower oxidation state and hydrogen gas.	Dissolve to form sulphate with higher oxidation state and sulphur dioxide (SO_2)	Dissolve to form nitrate with lower oxidation state and nitrogen(II) oxide (NO) 1) 2) 3)	Dissolv to f nitrate with higher oxidati state nitroge (IV) ox (NO_2)
Na					
Ba					
Sr					
Ca					
Mg [1)]					
Al [2)]					
Zn					
Cd					
Fe					
Co					
Ni					
Sn					

Pb		No influence			
H					
Cu3)	No influence				
Hg					
Ag					
Pt			No influence	No influence	No influen
Au					

Notes:

1)With HNO_3 solution dilute (< 1M), Mg produces H_2)

2)HNO_3 react very slowly with Al in cold condition.

3) Co(II) nitrate formed with the addition of HNO_3, whereas Co(I) nitrate does not formed.

Materials

Apparantus :- Test tube - Fe, Zn, Cu, Al, Pb metals - NaOH (2 M)

Chemicals :- Test tube rack - Iron nail – HNO_3 (5 M) 2MNaOH

Dropper pipette – Na_2S solution - HCl (5 M)

Procedure

1. Prepare small pieces of Zn, Fe, Cu, Al and Pb metals. Clean these metals by using steel fiber (sandpaper) and place the samples in separate test tube rack separately.
2. Add 3 mL of solution to test tube and record the resulted-observation in Table 4.2 in worksheet. Write the reaction equation.
3. If the reaction does not occur, heat the test tube gently and record the resulted-observation.
4. Repeat steps 2 to 3 for other metals.
5. Replace 5 M HCl with 5MHNO_3 solution, and repeat step 1 to 4. Record the resulted-observation in Table 4.2. Write the reaction equation.

6. Repeat the step 1 to 4 with 5MNaOH If there is no resulted-observation after heating. Record the resulted-observation in Table 4.3. Write the reaction equation.

7. Add 2 mL of Na_2S solution into the test tube. Record the resulted-observation in Table 4.3. Write the reaction equation.

Attention.

1. Acid and alkali are corrosive substances. Use goggles during the experiment.

2. If the solution spilled out to clothes or skin, wash it with water immediately.

3. Poisonous gas may be resulted during the experiment. Do the experiment separately and use reagents in small amount to avoid or to minimize the produced-poisonous gas. If excess reagents are used, move rack and test tube to the fume hood.

4. Clean the residue with flowing water. Take the metal residue from washing vessel and throw to rubbish bin.

5. Sulphide solution is dangerous and poisonous compound. Store the solution in the fume hood. Throw residual solution into the washing vessel in fume hood.

EXPERIMENT 4

ELECTROCHEMISTRY CELL AND ELECTRODE POTENTIAL

Purpose

To study electrode potential of several metals in electrochemical cell

Introduction

Electrode potential of a metal illustrates the reduction-oxidation tendency of particular metal relatively to standard electrode, usually H_2 system (100 kPa) $|$ H^+(1 M) where the value of E^0 = 0.00 V. The measurement of electrode potential carried out simpler by using standard electrode Cu^{2+} (1 M) $|$ Cu. Of course, converting relative to hydrogen electrode, the value of standard electrode of Cu^{2+} $|$ Cu (E^0 = 0.34 V) must be subtracted.

Standard Electrode of Cu^{2+} (1M) | Cu and salt bridge

Standard electrode contains narrow glass tube and hollowed-bottom. The mixture contains of gel, $NaNO_3$ and cotton filled at the bottom of tube. The hollow bottom is plugged with cotton in order to restrain gel position. Add 1 M $CuSO_4$ solution above gel and immerse copper wire as terminal. This standard electrode circuit is called half cell circuit and salt bridge. If this standard electrode circuit is immersed in another half-cell contains standard solution, such as Zn^{2+}| Zn and both terminal (Cu and Zn) are connected to voltmeter, electromotive force of cell value is obtained. The electrolyte is used to keep charge balance during redox process occurred and gel to prevent the mixing of ions from the two half-cell areas. Standard electrode of Copper wire 1 M Cu^{2+} (aq) Gel + $NaNO_3$

Materials

- Standard electrode of Cu^{2+} | Cu
- Half cell system of $Fe^{2+|}$ Fe, Mg^{2+} | Mg, Zn^{2+} | Zn, Sn^{2+} | Sn, Pb^{2+} | Pb, Al^{3+} | Al
- Voltmeter

Procedure

1. Immerse the standard electrode into the solution of half-cell system.

2. Connect each terminal with voltmeter wire; turn the voltmeter button to DC position, read, and record the value of emf.
3. Lift the standard electrode; wash it with flowing water on glass part, use again for other half-cell systems.

EXPERIMENT 5

CORROSION OF METALS (1)

Purpose

To study the nature of corrosion of several metals in gel medium

Introduction

Spontaneous redox reaction in electrochemical cell is the sum of two half cell reaction with positive value of total electromotive force of the (emf). The level of corrosion of metal is studied by comparing oxidation level relative to O_2 in water. In base condition, reduction of oxygen in water yields OH^- ion, which forms pink-red color with phenolphthalein (pp) indicator. Iron oxidized to Fe^{2+} which forms blue color with ferricyanide ion. If such redox reactions take place in gel medium, the resulted-color localized in oxidation or reduction area. Due to the slow spreading of ions, it is possible to identify anode and cathode side. The active site of iron stick (such as iron nail), found at the end of nail. The electrons flow through the stick and then captured by oxygen. Therefore, oxidation occurres, at the end of nail, and reduction at the center.

Materials

- Test tube – $K_3[Fe(CN)_6]$ solution *
- Beaker Chemicals 250 mL - Gel
- Bunsen burner, wire gauze - Phenolphthalein (pp)
- Iron nail - Zink sheet
- Aluminium sheet - Tin sheet
- Copper sheet ***)**

Do not use $K_4[Fe(CN)_6]$

Procedure

A. Seaweed gel making

1. Boil 80 mL of aquadest in 250 mL beaker.
2. Pour 0.5 g seaweed into aquadest and stir it until the gel dissolves.
3. Add 5 g of NaCl into the solution and stir continuously
4. Add 2 mL of phenolphthalein (pp) indicator and 1 mL of 0.1 M $K_3[Fe(CN)_6]$ solution. Stir until homogeny and stop the heating. Cool down the gel. The color of the mixture must be yellow, not green, blue or colourless.

B. Cleaning of iron nail

5. Submerge five iron nails into 15 mL of 2 M H_2SO_4 solution in the test tube for five minutes.
6. Boil 50 mL of water in 250 mL beaker, clean the acid from the nails carefully, rinse nails with water and then put the nails gently into boiling water. Take the nails into test tube with clean pliers.

C. Working with cleaned nails

7. Label test tubes 1 to 5. Take a cleaned nail into test tube 1. Attention: for test tube 2 – 5, nails must be precisely fit in the hole of metals (see Figure 6.1)?
8. Make a hole on copper, zinc, tin and aluminium sheets with a nail. Put a cleaned nail through those holes. Ensure, there is a good contact between the two metals (alternative way: wrap the nail with the sheet).
9. Take these pairs of metals in the test tube 2 – 5. Pour gel indicator (that has been made) gently into test tube 1 – 5. Attention: there must be no bubble.
10. The test tubes on a shelf tube. After a while, observe the color changing around the gel.

Note:

If the colour changing is not observed the test tubes to beaker and observe it next day.

EXPERIMENT 6

CORROSION OF METALS (2)

Purpose

To study the corrosion character of metals (iron and copper)

Introduction

The amount of electron transferred during corrosion process is measured by using multimeter. The function of electrodes (anode species and cathode species) is confirmed by knowing the direction of electron flowing or potential gap. Sodium chloride acts as electrolyte to keep ions mobility.

Materials

Apparatus - Iron sheet 8 cm x 2 cm -0.1 M $K_3[Fe(CN)_6]$ solution

Chemicals - Copper sheet 8 cm x 2 cm - Phenolphthalein (pp)

- Sandpaper - 3% NaCl solution

- Multimeter or milliammeter - Acetone

Procedure

1. Clean the iron and copper sheets with sandpaper and acetone soaked-cotton to clean the fat.
2. Mix the solutions of 40 mL of 3 % NaCl solution and 20 mL of 0.1 M $K_3[Fe(CN)_6$ solution in 250 mL glass beaker to form feroxyl indicator. Add phenolphthalein indicator gently into the mixture and stir it. In this experiment, feroxyl indicator produces blue color with Fe^{2+} ion and pp produces pink colour with OH^- ion.
3. Place an iron sheet and a cooper sheet into white paper based-250 mL beaker glass. By using alligator clips, connect the two metals with milliammeter. Pour the feroxyl solution into the glass beaker until the electrode ends immersed. (Note: keep the alligator clip dry and two metals do not connect directly).
4. Observe the electric current indicator on milliammeter. To investigate the amount of electrons flow through the two metals. When the colour changed, observe the indicator on milliammeter?

5. Record the result of the observation on worksheet paper and compare with Experiment 5 that has been done.

EXPERIMENT 7

CORROSION OF METALS (3)

Purpose

To study the corrosion characters of metals (iron, magnesium and copper)

Introduction

The protection of metals from corrosion of on machineries is an important effort. Beside painting and platting, there is a method to prevent corrosion based on the characteristic of metals. In many cases, metal is becoming less reactive due to the protection of strong oxide layer from more reactive metal. By this, metal is protected from the corrosion process by sacrificed-electrode. The method is known as sacrificial anode.

Sacrificial anode means that anode is sacrificed to protect the cathode from further corrosion. The process is based on the chemical nature of the metals. The easily more oxidized metals will protect the lower less oxidized metals from the corrosion.

Materials

Apparatus - Iron sheet 8 cm x 2 cm - 3% NaCl solution

Chemicals - Copper sheet 8 cm x 2 cm - Acetone

- Magnesium ribbon - Sandpaper

- Multimeter or milliammeter -

Procedure

1. Clean the iron and copper sheets with sandpaper and acetone soaked-cotton to clean the fat.
2. Prepare 50 mL of 3% NaCl solution in 250 mL. beaker.
3. Immerse an iron sheet and a copper sheet into the beaker and then use alligator clips to connect the two metals to milliammeter. (Note: keep the alligator clips dry and two metals do not connect directly).
4. Observe the electric current indicator on milliammeter to investigate the amount of electrons flow through the two metals.

5. Change copper electrode with magnesium ribbon and then observe the electric current indicator on milliammeter to investigate the amount of electrons flow through the two metals.
6. Record the result of the observation on worksheet paper and compare the results with the rate of iron metals corrosion.

PREPARATION OF POTASSIUM-CHROMIUM ALUM, $KCr(SO_4)_2 \cdot 12H_2O$

Purpose

To study the preparation of potassium-chromium alum

Introduction

Alum is a double salt of $M^{I}M^{II}(SO_4)_2 \cdot nH_2O$, where M^{I} is alkali metas (Na, K); M^{II} is metals with oxidation state +3, such as Al, Cr and Fe. Alum of K/Na – Al – sulfate and K/Na – Cr – sulfate are good example of alum, whose its crystallization is easy to be studied.

Materials

Apparatus - Glass Beaker - Watch glass - Sodium dichromate

Chemicals - Stirring rod - Water bath - 3% Hydrogen peroxide

- Evaporating dish - (5 M) H_2SO_4- HNO_3(2 M)

- Filter paper - Ethanol - (5 M) NaOH

- Hirsch funnel , ICE bath

Procedure

1. Pour 25 mL of 5 M H_2SO_4 solution into a glass beaker and then add 4 g potassium dichromate. Stir the mixture and heat in a water bath to dissolve dichromate.
2. Cool the solution in ice bath for about 10 minutes and then add 4 mL of ethanol drop by drop into the mixture. Add ethanol carefully, because the reaction releases heat. Observe the changes occurred and record on worksheet paper.
3. Cover the glass beaker with watch glass and observe the changes occurred next day.
4. Collect the crystals formed in Hirsch funnel and move the residue from glass beaker by adding 5 mL of 60 % ethanol solution. If it is necessary, repeat the procedure until no more residue left in Hirsch funnel. Let the crystals dry at room temperature (called as air-drying) untill next day.

5. Weigh the crystal mass and calculate the yield percentage of potassium-chromium alum based on the amount of dichromate used.

6. Test of the chromium ion present in alum.

   In a test tube dissolve 0.056 g alum in about 5ML of water and add 5 M NaOH solution drop by drop with continuous shaking. (Add drop by drop of 5 M NaOH to sample (0.05 g alum in 2 mL of water) until no more change. (Every one drop of NaOH, shake and observe carefully before next adding). Then add 1 mL of 3% H_2O_2 solution and heat the mixture until the color change. The yellow color indicates the presence of chromate ion (CrO_4^{2}). Record the observation on worksheet paper and write the balanced ionic reaction of the oxidation of Cr^{3+}(aq) by H_2O_2 in base condition.

   Note: the test for Cr^{3+} must be undertaken in base condition.

7. Test of presence of sulphate ion in alum

   In a test tube, dissolve 0.05 g chromium alum in 5 mL of water. Add few drops of 0.1 M $Ba(NO_3)_2$ solution and 2 M HNO_3 solution. Record the observation on worksheet paper and write the balanced ionic reaction of the test.

   Formation of white precipitate confirms the presence of SO_4^{2-} in alum.

EXPERIMENT 9

PREPARATION OF POTASSIUM-ALUMINUM ALUM, $KAl(SO_4)_2 \cdot 12H_2O$

Purpose

To study the preparation of potassium-aluminium alum

Materials

Apparatus - 100 mL Beaker glass - Ethanol 60%

Chemicals - Stirring rod - Aluminium (soft drink cane)

- Filter paper - KOH (2M)
- Hirsch funnel – H_2SO_4(9 - 10 M)
- Graduated cylinder 10 mL - Watch glass
- Water bath - Glass wool

Procedure

1. Weigh 0.2 g of small pieces of aluminium on watch glass.

2. Pour 10 mL of 0.2 MKOH solutions into glass beaker.

3. Warm the solution on water bath and then add a piece of aluminium (do it in fume hood).

Note: **Do not warm the solution too hot and remove glass beaker from fume hood until all pieces of aluminium added to the solution. The reaction of aluminium and KOH releases hydrogen gas**.

4. As the reaction completed remove the beaker glass from water bath immediately. Move it back into water bath as the reaction slowed down (no more bubbles produced) and add other piece of aluminium.

5. Where all pieces of aluminium have been reacted, filter the mixture with a funnel that has plugged with glass wool. (Ask the assistant how to do it).

6. Add 20 mL of 9-10 M H_2SO_4 into filtrate solution carefully and check it with litmus paper. Ensure that the solution is acidic.

Note: **Concentrated (10 M) sulfuric acid irritates and burns the skin. If it happened, wash with flowing water and take medical care**.

7. Cover the glass beaker with watch glass and keep it for about 24 hours. After 24 hours, the crystal of potassium aluminium alum, $KAl(SO_4)_2 \cdot 12H_2O$, are formed. (The growing of crystal may be speedup by scraping the stirring rod to the inner part of solution while cooling or add 2-3 mL of ethanol).

8. Collect the formed-crystals on Hirsch funnel and move the residue from glass by adding 5 mL beaker of 60% ethanol. If it is necessary, repeat the procedure until no more residue left in Hirsch funnel.

9. Keep the crystals to dry till next day.

10. Weigh the crystal mass and calculate the yield percentage based on the amount of aluminium used.

11. Do the re-crystallization to the impure yield with water as solvent.

12. For students who have synthesized both alum (chromium and aluminium), both alums have the same structure, therefore it is possible to grow mix crystals. Hang up a small part of aluminium alum with yarn and immerse it into saturated solution of chromium alum. By this, the alternate layers are formed, colourless of aluminium alum and purple to reddish of chromium alum.

Re-crystallization technique

The purpose of re-crystallization is to purify resulted-solid. The resulted-solid is dissolved in minimum amount of solvent in an erlenmeyer flask or glass beaker . The solid must has high solubility in hot solvent, but low in cold one. If undissolved- solid impurities found in hot solution, filter it with funnel and filter paper in hot condition to avoid early crystallization. If crystals found on filter paper, wash it with hot solvent. If the filtrate is too dilute, concentrate it by heating till crystallization point. Pure crystals grow during the cooling process. The growing of crystal may be speed up by scraping the stirring rod to inner part of beaker. The pure crystals filtered and washed with solvent in minimum amount.

EXPERIMENT 10

PREPARATION OF COORDINATION COMPOUND, $[Ni(NH_3)_6]I_2$

Purpose

To study the preparation of coordination compound of $[Ni(NH_3)_6]I_2$

Introduction

Complex (coordination) compounds are characteristic compounds of transition metals that correspond to the existence of d orbital. The existence of d orbital cause transition metals not only to have various oxidation states but also the capability to interact coordinately with other donor atom. Complex compound of $[Ni(NH_3)_6]I_2$ is an example of Ni^{2+}compound with coordination number 6 where its crystallization is relatively easy to study. The success of the compound preparation is easily tested qualitatively to Ni^{2+}.

Materials

Apparatus - 100 mL Beaker 1 M Ammonia

Chemicals - Stirring rod - Ethanol

- Filter paper - Nickel chloride hexahydrate
- Hirsch funnel - Potassium iodide
- Graduated cylinder 10 mL - Starch indicator
- Labeled-test tube – H_2O_2(3%)

Procedure

1. Dissolve 1 g of nickel chloride hexahydrate into 5 mL water in a beaker.

2. Place the beaker in the fume hood and add 10 mL of concentrated NH_3 solution.

3. Add 2.6 g of potassium iodide to the mixture. Keep the mixture for several minutes.

4. Collect the formed-crystal on Hirsch funnel, wash it twice with 2 mL of ethanol solution 1:1 and then add 2 mL of ethanol.

5. Dry the crystals in for several minutes.

6. The dried-crystals filter paper. Ask the assistant how to move crystals from Hirsch funnel to filter paper.

7. Remove the excees solvent by pressing the crystals between two filter papers.

8. The resulted crystal to the weighed and labeled-tube. Weigh the tube mass with the crystals. Calculate mass percentage of the product based on the amount of nickel chloride hexahydrate taken.

9. Test of the presence existence of nickel ion in the compound.

Dissolve a small amount of the sample (about 0.001 g of compound in 0.5 mL of water), add 5MNH_3 solution, and then add 5 drops of dimethyl glyxyi solution. Red strawberry solid produced if there is Ni^{2+} ion.

10. Test of the presence of iodide ion in the compound.

Dissolve a small amount of compound (about 0.001 g of compound in 0.5 mL of water), acidify with 2 drops of 5 M sulfuric acid solution and then add 3% H_2O_2 solution.

EXPERIMENT 11

PURIFICATION OF KITCHEN SALT BY RE-CRYSTALLIZATION METHOD

Purpose

To study the crystallization method on the purification of kitchen salt by evaporation and precipitation

Introduction

High-level compound is an important thing in chemistry. The usual method of solid purification is re-crystallization (the formation of repeating crystal). Re-crystallization is based on the difference of solubility capacity of solid and impurities in particular solvent. If it possible, use alternate solvent that only dissolves the impurities. Such purification is widely used in industrial and laboratory to improve the quality of particular substance.

Requisites of a solvent in re-crystallization process are:

1. Give a significant solubility differences between purified-substance and impurities.

2. The solubility of substance in solvent is a temperature function. The solubility usually decreases with the decreasing temperature.

3. Easily separates from the crystals.

4. Does not leave the impurities in the purified crystals.

5. Does not react with purified substance.

Kitchen salt contains sodium chloride as major component, and Ca^{2}+, Mg^{2+}, Al^{3+}, $Fe^{3+,}$ SO_4^{2}-, I^- and B^- r as impurities. These impurities are easily dissolved in water. Re-crystallization method with water as a solvent is a general method to get high-level sodium chloride from kitchen salt. Particular ions are needed to eliminate the presence of impure ions. These ions will bind the impure ions to form low-level solubility compound in water. By this, the purified and impure substances are easily separated.

Materials

Apparatus - Burner - Kitchen salt and CaO crystal

Chemicals - Beaker -0.5 M $Ba(OH)^2$ or $BaCl^2$ solution

- Graduated cylinder - $(NH_4)_2CO_3$ solution (6 gram in 200 mL)
- Funnel - 0.1 M HCl solution
- Gas adapter - Concentrated H_2SO_4
- Filter paper and litmus paper

Procedure

1. In a beaker, dissolve about 16 g of kitchen salt in 50 mL water. Boil and stir the mixture. Divide the solution into 2 parts in equal amount and called as solution A and B.

2. Crystallization of solution A

a. Add about 0.2 g of CaO in the solution A

b. Add $Ba(OH)_2$ solution drop by drop until no more precipitate formed at the last drop.

c. Add $(NH_4)_2CO_3$ solution drop by drop and stir continuously.

d. Filter the mixture in a cleaned and weighed beaker. Neutralize filtrate by adding dilute HCl solution drop by drop. (Test the neutrality of the solution with litmus paper in every drop).

e. Evaporate the solution until relatively dry.

f. Weigh the resulted NaCl (which is brighter and whiter than original kitchen salt) and calculate the percentage filed.

3. Crystallization of solution B

a. Saturate the solution B by passing HCl gas. Hydrochloric acid gas obtained from the reaction of kitchen salt and concentrated sulfuric acid. (Do the reaction in fume hood). The flowing of HCl gas is stopped when no more NaCl crystal grows in the solution.

b. Separate the crystal by filtering, dry it and then weigh the product and compare with solution A.

EXPERIMENT 12

TOTAL HARDNESS OF WATER

Purpose:

To determine the total hardness of water samples from (1) the corporation water supply and (2) the college well.

Introduction:

Hardness of water is caused by the presence of Ca^{2+} and Mg^{2+} ions. Total hardness is defined as the sum of Ca^{2+} and Mg^{2+} ion concentrations, expressed in milligrams of $CaCO_3$ per litre. If Eriochrome Black T (= EBT) is added to an aqueous solution containing Ca^{2+} and Mg^{2+} ions at a pH of 10.0 ± 0.1, the solution becomes wine red. Both will be complexed by EDTA. When all the Ca^{2+} and Mg^{2+} ions present are complexed by EDTA, the solution changes to blue. Mg^{2+} ions must be present to yield a satisfactory end point. [If Mg^{2+} is not present in the sample water, small amounts of complexometrically neutral Mg salt of EDTA is added to the buffer]. The titration should be completed in less than 5 minutes to minimize the tendency of $CaCO_3$ precipitation.

Note: (1) If mureoxide is used as indicator, the titration gives hardness due to Ca^{2+} alone. A dilute solution of NaOH is used instead of ammonia buffer in this case. The colour change is from pink to purple.

(2) Publications in the area of water analysis still use 'mL' instead of 'cm^3' and 'L' instead of 'dm^3'. The same terminology is used here.

Apparatus required:

(1) One 50 mL burette.

(2) One 250 mL beaker.

(3) Two 250 mL and one 1000 mL few volumetric flasks.

(4) One 500 mL Beaker.

(5) One 100 mL measuring cylinder.

Chemicals required: (per student)

(1) EDTA disodium salt hydrate, Analar, 1 gram.

(2) Calcium carbonate powder, anhydrous, Analar, 1 gram.

(3) Eriochrome Black T indicator, a few crystals.

(4) Methyl orange indicator 1 ml

(5) Ammonium chloride, 17 g.

(6) Dropper and glass rod. (6) Concentrated NH_3 solution, 150 mL

(7) Hydrochloric acid, 1:1, about 50 mL.

Preparation of reagents:

Note: Prepare all reagents using distilled water only! Reagents 1 and 2 may be used in common by all students. All preparations are to be prepared by students.

1. **Standard $CaCO_3$ solution** :Accurately weigh out 1.000g of analar anhydrous $CaCO_3$ powder in a clean 500 mL beaker. Add carefully just sufficient 1:1 HCl to dissolve the powder completely. Add 200 mL distilled water, cover with a watch glass and boil for a few minutes to expel CO_2. Cool and add a few drops of methyl orange indicator and adjust to the intermediate orange colour by adding drops of dilute ammonia or HCl as required. Transfer quantitatively into a 1000 mL volumetric flask and make up the volume using distilled water. 1 mL of this solution ≡ 1.00 mg of $CaCO_3$.

2. Buffer solution: Dissolve 17g of NH_4Cl in 150 mL concentrated NH_3 solution in a 250 mL volumetric flask and make up the volume with distilled water. Keep it in a clean stopper bottle.

3. EDTA solution: Weigh out about 0.93g of EDTA disodium salt hydrate into a 250 mL volumetric flask, add a little ammonia solution and about 200 mL of distilled water and swirl gently to dissolve completely (presence of ammonia makes dissolution of EDTA faster). Make up the volume to the mark to get approximately 0.01 M solution. Standardise against standard $CaCO_3$ solution. Obtain result in the form "1 mL EDTA solution ≡ ____ mg $CaCO_3$. (Note: Standardisation to be recorded in the usual form).

Procedure:

(1) Standardisations of EDTA: Pipette out 20 mL of standard $CaCO_3$ solution in a 250 mL beaker and add 1 to 2 mL of buffer solution. Add 2 or 3 small crystals. Do not use more indicator than necessary to get pale colour) of EBT and stir using a glass rod to get wine red colour. Titrate with EDTA solution, stirring after each addition, till the colour just changes to blue. Repeat.

(2) Estimation of hardness in sample: Measure out 100 mL of sample water (using cylinder) in a clean 250 mL beaker and titrate using EDTA exactly as above. Repeat.

Calculation:

Standardisation of EDTA: V mL of EDTA ≡ 20 mL $CaCO_3$ solution ≡ 20 mg $CaCO_3$. Therefore 1 mL of EDTA = _____ mg $CaCO_3$.

Estimation of hardness in sample: 100 mL water ≡ V mL EDTA ≡ _____ mg $CaCO^3$. Therefore 1000 mL water = _____ mg $CaCO_3$.

Result:

(1) Total hardness in corporation tap water = _____ mg $CaCO_3$/L

(2) Total hardness in college well water = _____ mg $CaCO_3$/L

EXPERIMENT 13

ESIMATION OF CALCIUM

Purpose:

To determine the mass of calcium in the whole of the given solution.

Introduction:

Eriochrome Black T (= EBT) forms a wine-red coloured complex with Ca^{2+} ions in solution at a pH of about 10 (obtained by adding ammonia solution). EDTA forms a stronger complex with the Ca^{2+} ions and liberates free EBT, which has a blue colour. One mole of EDTA complexes with one mole of Ca^{2+} ions.

$Na_2H_2EDTA + Ca^{2+} \longrightarrow CaH_2EDTA(complex) + 2\ Na+$

Apparatus required:

(1) One 50 ml burette.

(2) One 250 ml conical flask.

(3) Two 100 ml and one 250 ml volumetric

(4) One 250 ml Beaker.

(5) One 100 mL measuring cylinder.

(6) Dropper, glass rod and watch glass.

(7) Hydrochloric acid, 1:1, about 10 mL.

Chemicals required: (per student)

(1) EDTA disodium salt hydrate, Analar, 5 grams.

(2) Calcium carbonate powder, anhydrous, Analar, 1 gram.

(3) Eriochrome Black T indicator, a few crystals.

(4) Methyl orange indicator solution, 1 mL.

(5) Ammonium chloride, 2 g.

(6) Concentrated NH_3 solution, 15 mL

Preparation of reagents:

Note: Prepare all reagents using distilled water only. All preparations are to be done by students.

Buffer solution: Dissolve 17g of NH_4Cl in 150 ml concentrated NH_3 solution in a 400 ml beaker and dilute to 250 ml with distilled water. Keep it in a clean stopper bottle. (Enough for all students)

EDTA solution: Weigh out about 4.65g of EDTA disodium salt hydrate in a 250 mL volumetric flask, add a little ammonia solution and about 200 mL of distilled water and swirl gently to dissolve completely (presence of ammonia makes dissolution of EDTA faster). Make up to the mark to get approximately 0.05 M EDTA solution.

Procedure:

Preparaion of standard 0.05M $CaCO_3$ solution: Accurately weigh out about 500 mg of analar anhydrous $CaCO_3$ powder in a clean 250 ml beaker. Add about 20 ml distilled water. Carefully add just sufficient 1:1 HCl in drops and sir to dissolve the powder completely. Cover with a watch glass and boil for a few minutes to expel CO_2. Cool and add a few drops of methyl orange indicator and adjust to the intermediate orange colour by adding drops of dilute ammonia or HCl as required. Transfer quantitatively into a 100 ml volumetric flask and make up the volume distilled with water. Calculate molarity of the solution.

Standardisation of EDTA: Pipette out 20 cm^3 of standard $CaCO_3$ solution into a 250 ml conical flask and add 1 to 2 ml of buffer solution. Add 2 or 3 small crystals of EBT and stir using a glass rod to get wine red colour. Titrate with EDTA solution, stirring after each addition, till the colour just changes to blue. Repeat to get concordant reading.

Estimation of calcium: Make up the given calcium solution to 100 ml. Pipette out 20 ml of the solution a clean 250 ml conical flask and titrate using EDTA exactly as above. Repeat to get concordant reading. Calculate molarity, and hence mass of Ca^{2+} in the whole of the given solution.

Calculation:

Standardisation of EDTA: Mass of $CaCO_3$ weighed out = w^2.

Molar mass of $CaCO_3$ = 100g

Therefore molarity M_1 = w/100 x 1000/100= $\frac{Wx1200}{100 \times 100} = \frac{10}{10}$

V_1 ml of EDTA ≡ 20 ml $CaCO_3$ solution.

Therefore molarity M_2 of EDTA = $20xM_1/V_1$=20 x m1 _____.

Estimation of Ca^{2+} in sample: V_2 cm^3 of EDTA ≡ 20 cm^3 $CaCO_3$ solution.

Therefore molarity M_3 of the Ca^{2+}soluion = V_2*M_2/20= _____.

Molar mass of Ca^{2+} = 40.078

Therefore mass of Ca^{2+} in the whole of the given solution = M_3*40.078/10= _____.

Result:

Mass of Ca^{2+} in the whole of the given solution = _____ g.

EXPERIMENT 14

QUALITATIVE ANALYSIS OF CATIONS

Purpose:

To Identify cations present in unknown solutions.

Introduction:

The most common cations have been placed into five groups based upon solubility in aqueous solutions when different reagents are added. The reactions which occur are useful in identifying the presence of these cations in unknown samples. The process of identifying the cations is called **qualitative analysis**. The purpose of this experiment is to identify which cations are present in unknown solutions.

The separation scheme used to identify the cations in solution is based on their reactions. The five groups into which the cations are placed are as follows:

Group	Property	Ions
I	Insoluble chlorides	Ag^{+} Pb^{2+} Hg_2^{2+}
II	Acid-insoluble sulfides	Cu^{2+} Bi^{3+} Cd^{2+} Pb^{2+} Hg^{2+} Sb^{3+} Sn^{2+} Sn^{4+}
III	Base-insoluble sulfides and hydroxides	Al^{3+} Cr^{3+} Co^{2+} Fe^{3+} Mn^{2+} Ni^{2+} Zn^{2+}
IV	Insoluble phosphates	Ba^{2+} Ca^{2+} Mg^{2+} Sr^{2+}
V	Soluble salts	Li^{+} Na^{+} K^{+} NH_4^{+}

A series of flowcharts are used to summarize the steps involved in the procedure of separating and identifying the ions. These flowcharts are given at the end of the procedure.

Although more ions are listed above, we will concentrate on the separation of ten cations. These cations will provide you with an understanding of the process of qualitative analysis and allow you to perform the experiment in the alloted time.

The cations you will learn to identify are:

Ag^{+} Pb^{2+} Cu^{2+} Fe^{3+} Mn^{2+} Zn^{2+} Ba^{2+} Na^{+} K^{+} NH_4^{+}

Chemicals and Apparatus

Chemicals:

0.10 **M** solutions of nitrate salts of the cations

various reagents required for the experiment

Apparatus: test tubes, eyedroppers, test tube brushes, stirring rods, litmus paper, ALKACID paper, centrifuges, hot plates, 400-mL beakers (for hot water baths)

Safety Equipment: goggles, gloves, hood.

Objectives:

In this experiment you will learn to:

1. observe the results of precipitation reactions and color changes during the separation of a mixture of ions.
2. observe different color flames associated with the different metal ions.
3. identify ions present in an unknown sample mixture by comparing the results with those of the known solutions.

Procedure

NOTE: Unless otherwise indicated, all reactions should be performed using the medium-sized test tubes, 13 x 100 mm.

1. Take 5 mL each of the "Group I & II", "Group III & IV", and "Group V" solutions containing the ten ions in approximately 0.10 **M** concentrations in three 6-inch test tubes. Label the test tubes according to the solutions.
2. Use the Group V solution to identify the ammonium ion first.

Identification of ammonium ion, NH_4^{+}

Salts of ammonium ions are extremely soluble in water. Therefore, whenever possible, determination of the presence or absence of ammonium ion should be done at the beginning of a qualitative analysis scheme. This will allow you to

use ammonium salts as reagents whenever possible without affecting your results.

1. To test the presence of ammonium ion, take 1 mL of solution in a 50-mL beaker. Add 5 drops of 1 **M** NaOH to this solution.

2. Wet a piece of red litmus paper with water. Place the litmus paper on the bottom side of a watch glass.

3. Cover the beaker with the watch glass, so that the litmus paper can react with the fumes generated by heating the solution slowly. (DO NOT BOIL THE SOLUTION.) The ammonia gas generated by the ammonium ion will cause the damp litmus paper to turn **blue**. This represents a positive test for the ammonium ion.

The reactions which occur in solution are:

(a) $NH_4^+ + OH^- \xrightarrow{\Delta} NH_{3\,(g)} + H_2O_{\,(g)}$

(b) $NH_{3\,(g)} + H_2O_{\,(l)} \longrightarrow NH_4^+ + OH^-$

(c) OH^- + red litmus 〉 blue litmus

Identification of Group I Cations (Chart 1)

1. Take 2 ml of group I & II Solution prepared earlier in a 10 cm test tube. In a 10-cm test tube, place 2 mL of the "Group I & II" solution which you obtained earlier. Add 10 drops of 6 **M** HCl. Stir well and centrifuge. Remember to use a test tube with an equal volume of water to balance the centrifuge.

2. Add three additional drops of 6 **M** HCl to the test tube. If additional solid forms, centrifuge again. Repeat this step until no additional precipitation is observed.

3. Centrifuge the test tube again. Then use an eyedropper to transfer the supernatant liquid above the solid to another test tube. This solution contains the Cu^{2+} ion. Label this as "Group II", and set the test tube aside.

4. The precipitate from step 3 is a mixture of AgCl and $PbCl_2$. Add 2 mL of distilled water to the precipitate. Stir and heat the test tube in a hot-water bath for 3 minutes. Centrifuge and transfer the liquid to a clean test tube.

5. Add 2 drops of 6 **M** acetic acid and 5 drops of 0.10 **M** K_2CrO_4 to the liquid. **The formation of a yellow precipitate confirms the presence of lead, Pb^{2+}.** Discard the contents of the test tube in the chromate waste container.

Rinse the test tube twice with small amounts of water and add the rinses to the chromate waste.

6. Wash the precipitate from step 4 with 3 mL of distilled water. Centrifuge and test for Pb^{2+}. Continue until no positive test for lead is observed.

7. Once the lead is absent, wash the precipitate with 2 mL of water. Discard the washes. Then add 2 mL of 6 **M** NH_3 to the precipitate. The AgCl will dissolve the diamminesilver (I) complex ion $[Ag(NH_3)_2^+]$.

8. Add 2 mL of 6 **M** HNO_3 to the solution. **A white to off-white precipitate confirms the presence of silver ion, Ag^+.**

Discard the silver solid in the "AgCl waste" container.

Identification of Group II Cations (Chart 2)

9. The solution in the test tube from step 3 contains the Cu^{2+} ions. To this solution, add 1 mL of 3% H_2O_2. Boil the solution to reduce the volume of about 1 mL. Now add 6 **M** HCl until the pH reaches. Once the pH has been lowered to, add 1 mL of 1 **M** CH_3CSNH_2 (thioacetamide) to the test tube.

10. Heat the test tube in a Boiling Water Bath **under a fume hood** for at least 5 minutes. The reactants will generate H_2S , a toxic gas, in small quantities, so you should avoid breathing the fumes as much as possible. The reaction will produce a precipitate which will get darker as heating continues. Continue heating for two minutes until no color change occurs stopped changing. Put a cork stopper on the test tube and cool it under the water tap; then allow the test tube stand for a minute or so before centrifuging.

Note: Because H_2S gas generated, you must centrifuge these samples under a fume hood.

11. Decant the solution above the precipitate and transfer to a clean test tube. Add 1 mL of 1 **M** NH_4Cl and 1 mL water to the precipitate and set aside.

12. Check the pH of the solution; if it is below 0.5, add 1 **M** CH_3COONH_4, ammonium acetate, to bring the pH up to 0.5. A brown or yellow precipitate may form. Add 1 mL of 1 **M** thioacetamide, and heat for three minutes in the BWB. Centrifuge and decant the liquid into a clean test tube for future use. (NOTE: If you have a general unknown that contains Group III, IV, or V cations, they will be in the solution. If you are only working with Group II cations, you may discard the liquid.)

13. Add 1 mL of 1 **M** NH_4Cl and 1 mL water to the precipitate and combine with the precipitate of step 11. Add 2 mL of 1 **M** NaOH and heat with stirring

for two minutes. Centrifuge and discard the solution. Wash the precipitate twice with 2 mL of water and 1 mL of 1 **M** NaOH, stir, centrifuge, and discard the washes.

14. Add 2 mL of 6 **M** HNO_3, nitric acid, to the precipitate. This will dissolve the CuS and precipitates. Then add 6 **M** NH_3 until the solution is basic to litmus. Add an additional 10 – 15 drops of 6 **M** NH_3. **The presence of copper ion, Cu^{2+}, is confirmed by a deep royal blue solution.** Formation of a deep boyal blue solution confirms the process of CU^{2+}

Identification of Group III Cations(Chart 3)

The identification of Group III cations is determined from the solution obtained from step 17 of the procedure (during separation of Group II cations from other cations). If you did not have a mixture, you should start the procedure using 2 mL of a general stock solution containing Group III & IV cations.

15. Pour 2 mL of the Group III & IV cations in a test tube. Boil the solution to reduce the volume to 1 mL. Then add 1 mL of 1**M**NH_4Cl to the solution. Swirl to dissolve any crystallized salts.

16. Make the solution basic to litmus by adding 6**M**NH_3; then add an additional 0.5 mL NH_3. Add 1 mL 1 **M** thioacetamide, stir well, and heat in a BWB **under a fume hood** for 5 minutes, or at least two minutes until no color changes. A black solid with a yellow solution on top is informed.

17. Centrifuge and separate the solid from the solution. Add more thioacetamide to the solution and repeat the heating and centrifugation steps. Save the solution for analysis of the Group IV cations, Ba^{2+}.

Note: Because you have generated H_2S, you must centrifuge these samples under a fume hood.

18. Wash the precipitate twice with 1 mL 1**M**NH_4Cl, 2 mL water, and 5 drops of 6 **M** NH_3. Centrifuge and discard the washes.

19. Add 1 mL 6**M**HCl and 1 mL water to the precipitate. Mix thoroughly and pour in a 30-mL beaker. Boil gently for about one minute. Add 1 mL water, stir, and pour the slurry into a test tube. Centifuge and decant the liquid into a clean test tube..

The solid material may be discarded since Fe^{3+}, Mn^{2+}, and Zn^{2+} dissolved when the HCl was added.

20. To the solution from step 19, add 6 **M**NaOH until it is basic to litmus, then add an additional 10 – 15 drops of NaOH. Pour the resulting slurry in a 30-mL beaker and boil gently for two minutes with stirring. Cool to room

temperature and add 1mL 1**M**NaOCl, sodium hypochlorite (bleach). Swirl for about 30 seconds, then boil the liquid gently, reducing the volume to about 2 mL, If Mn^{2+} is present, the foam will have a purple color. Add 0.5 mL of 6**M**NH_3, swirl for 30 seconds, and boil for 1 minute. Transfer to a test tube and centrifuge the solid. Decant the liquid into a clean test tube. The iron and manganese ions have precipitated from solution; the Zn^{2+} ion is in solution as $Zn(OH)_4^{2-}$.

21. Make the solution acidic to litmus with 6**M**HCl. Add three drops of HCl in excess. Then add 5 drops of 0.2 **M** $K_4Fe(CN)_6$, potassium ferrocyanide. **A light green precipitate of $K_2Zn[Fe(CN)_6]$ confirms the presence of Zn^{2+}.**

22. Add 1 mL water and 1 mL 3**M**H_2SO_4 to the solid precipitate from step 20. Stir and heat the test tube in the BWB for 3 minutes. Centrifuge and decant the liquid, which contains Fe^{3+}; the MnO_2 will not dissolve.

23. Add 2 mL water and 5 drops of 1 **M** NH_4SCN to the solution. **A deep "blood red" color, due to the formation of $[Fe(SCN)_6^{3-}]$, is a positive test for the Fe^{3+}.**

24. Add 1 mL water, 1 mL 3**M**H_2SO_4, and 1 mL 3% H_2O_2 to the precipitate of MnO_2. The precipitate will dissolve. Then take 1 mL of the solution into a clean test tube, and add 1 mL 6**M**HNO_3 to the test tube. Finally, add 0.3 - 0.4 g of sodium bismuthate with spatula in the test tube. Let the mixture stand for two minutes before centrifuging. **A purple solution is due to the presence of MnO_4^- and confirms the presence of Mn^{2+}.**

Identification of Group IV & Group V Cations(Chart 4)

25. Use the solution from step 17 to identify the presence of the Groups IV and V cations. Transfer the liquid to a 50 mL beaker and boil down to 2 mL. Centrifuge and discard any solid matter. Add 1 mL of 6**M**HCl to the liquid. take the liquid in a beaker, and boil essentially to dryness.Transfer the beaker to the hood, and carefully heat the dry solid to drive off any ammonium salts produced in previous steps. Stop heating when no visible smoke is being evolved.

26. Let the beaker cool to room temperature, then add 2 mL water and 1 mL 6**M**HCl in the beaker. Warm gently to dissolve any remaining salts. Transfer the liquid in a test tube and centrifuge. Decant the liquid in a clean test tube. Discard the insoluble material.

27. To the above solution add 1 mL 1 **M**$(NH_4)_2CO_3$ and 1 mL 6**M** NH_3. Stir and let it stand for 10 minutes. Barium carbonate or barium hydroxide will

precipitate out of the solution. Centrifuge and separate the solution from the precipitate.

If you have a general unknown, the Na^+, K^+, and NH_4^+ will be left in solution. Identification of these unknowns should be done after you complete step 29.

28. Wash the precipitate with a few drops of 1 **M** $(NH_4)_2CO_3$ and 6**M** NH_3. Discard the washes. Then add 0.5 mL 6 **M** HCl. The solid will dissolve. Add 1 mL 1 **M** Na_2SO_4. Barium will precipitate out as a fine white solid. Then add 2 mL 0.10 **M** K_2CrO_4 and 0.5 mL 6 **M** NaOH to the precipitate, with stirring. The $BaSO_4$ will be converted to $BaCrO_4$, a yellow solid. Centrifuge and discard the liquid. Wash the solid several times with water until the solution is no longer yellow.

29. To the solid remaining after washing, add 1 mL 6 **M** HCl and stir. The $BaCrO_4$ will dissolve and produce an orange solution. Add 0.5 mL 3**M** H_2SO_4. **A white precipitate of $BaSO_4$ confirms the presence of Ba^{2+}.**

Flame Tests for Analysis of Sodium and Potassium

One of the most common methods of identifying cations is by using a flame test. The flame color is due to excitation of valence-shell electrons upon heating, followed by relaxation of the electrons with the emission of photons of light.

Sodium ion can be identified by a very intense yellow-orange flame. Potassium ion is identified by a lavender-pink flame. However, if both ions are present together, the intense flame of Na^+ hides the color of the K^+ flame. It is therefore necessary to use a blue cobalt glass plate to absorb the color of the sodium ion, so that the flame of potassium ion can be seen.

The ammonium ion will not interfere with the flame tests.

30. Take a flame test wire from the instructor. Light a bunsen burner and place the wire in the flame to clean the wire. The wire will be clean when the color of the flame above the wire is blue.

To assist in cleaning the wire, you may dip the wire in 6 M HCl before placing the wire in the flame.

31. Dip the wire into a test tube containing the "Group V" ions. You should obtain a small drop of solution in the loop of the wire. Place the wire in the flame. You should observe the yellow-orange flame of Na^+ almost immediately.

32. Repeat step 31, except this time you should place a blue cobalt glass plate in front of your eyes. Here you will observe a slight color change of the

flame, which will appear almost pinkish-purple behind the cobalt glass plate which confirms the presence of K^+ ions.

Chart 1 below shows the separation of the Group I cations Ag^{+} and Pb^{2+} from the other cations.

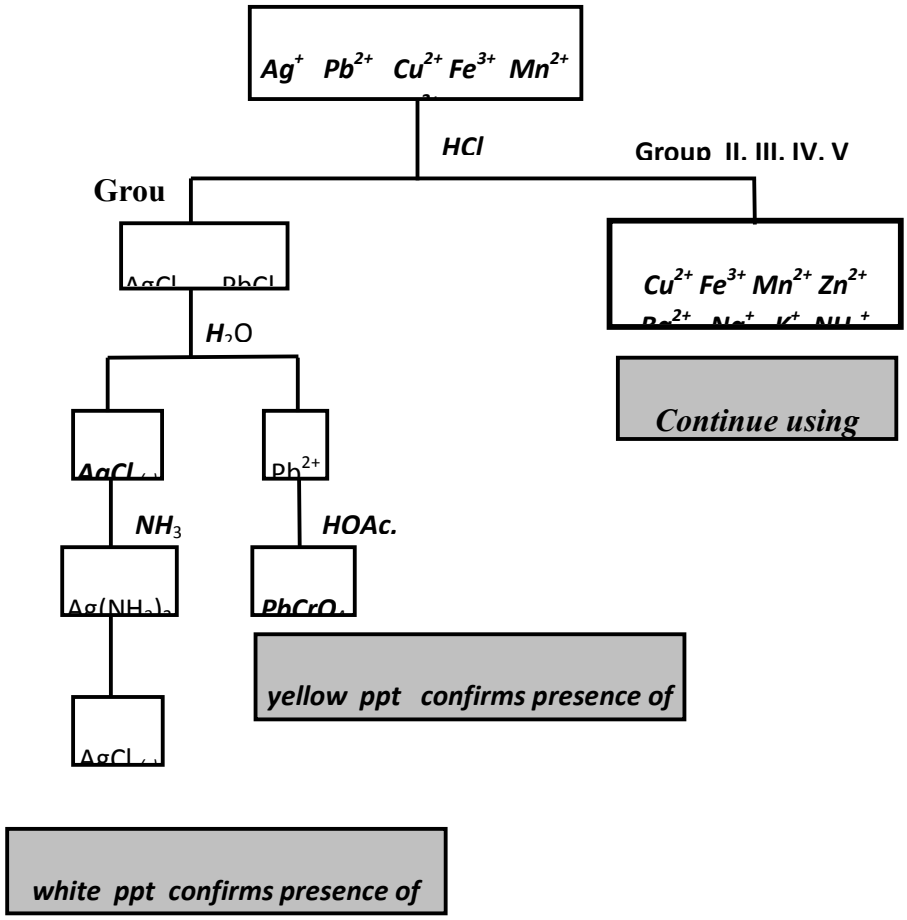


Chart 2 below shows the separation of the Group II cation Cu^{2+} from the remaining cations of Group III, IV, and V.

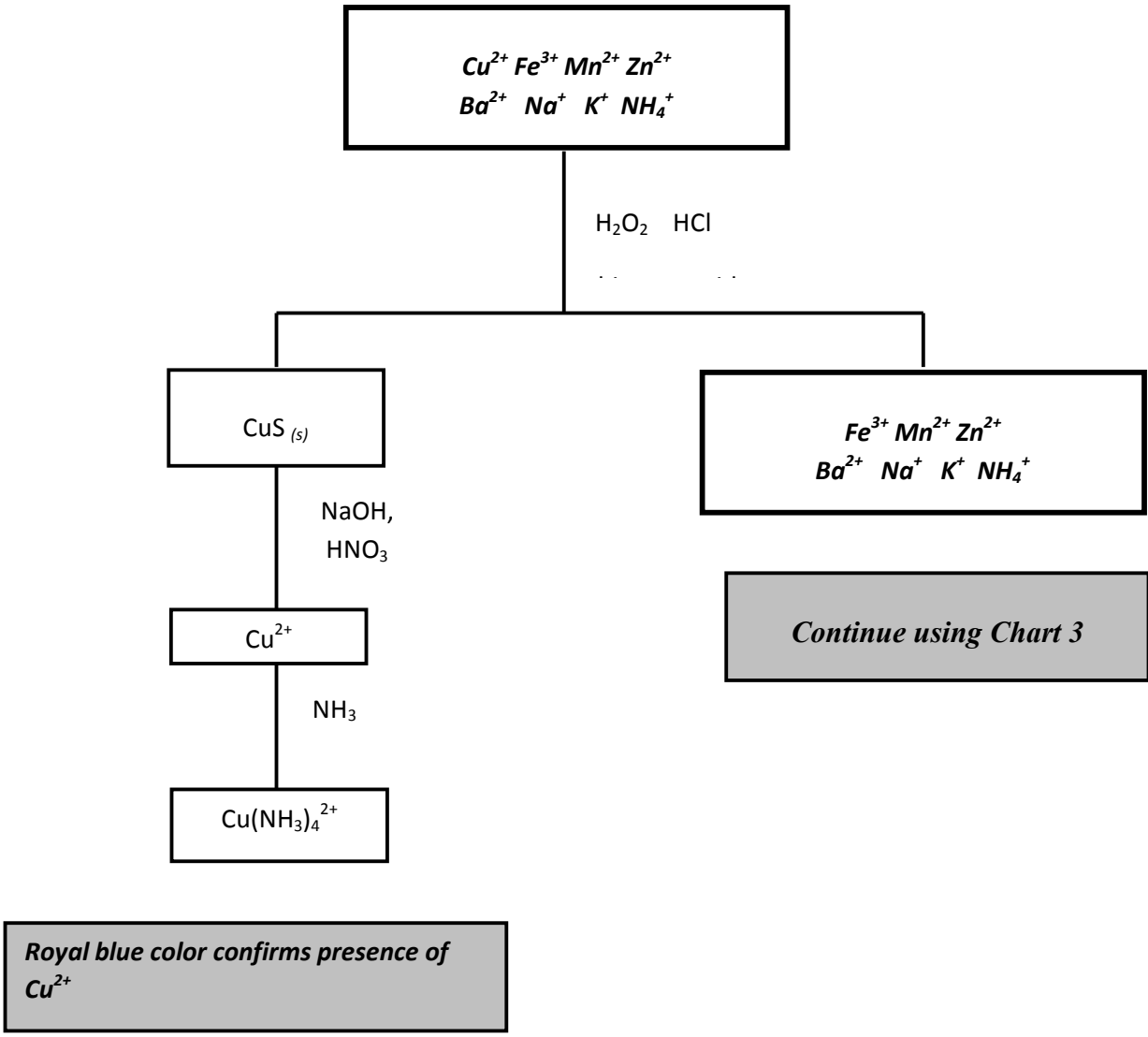
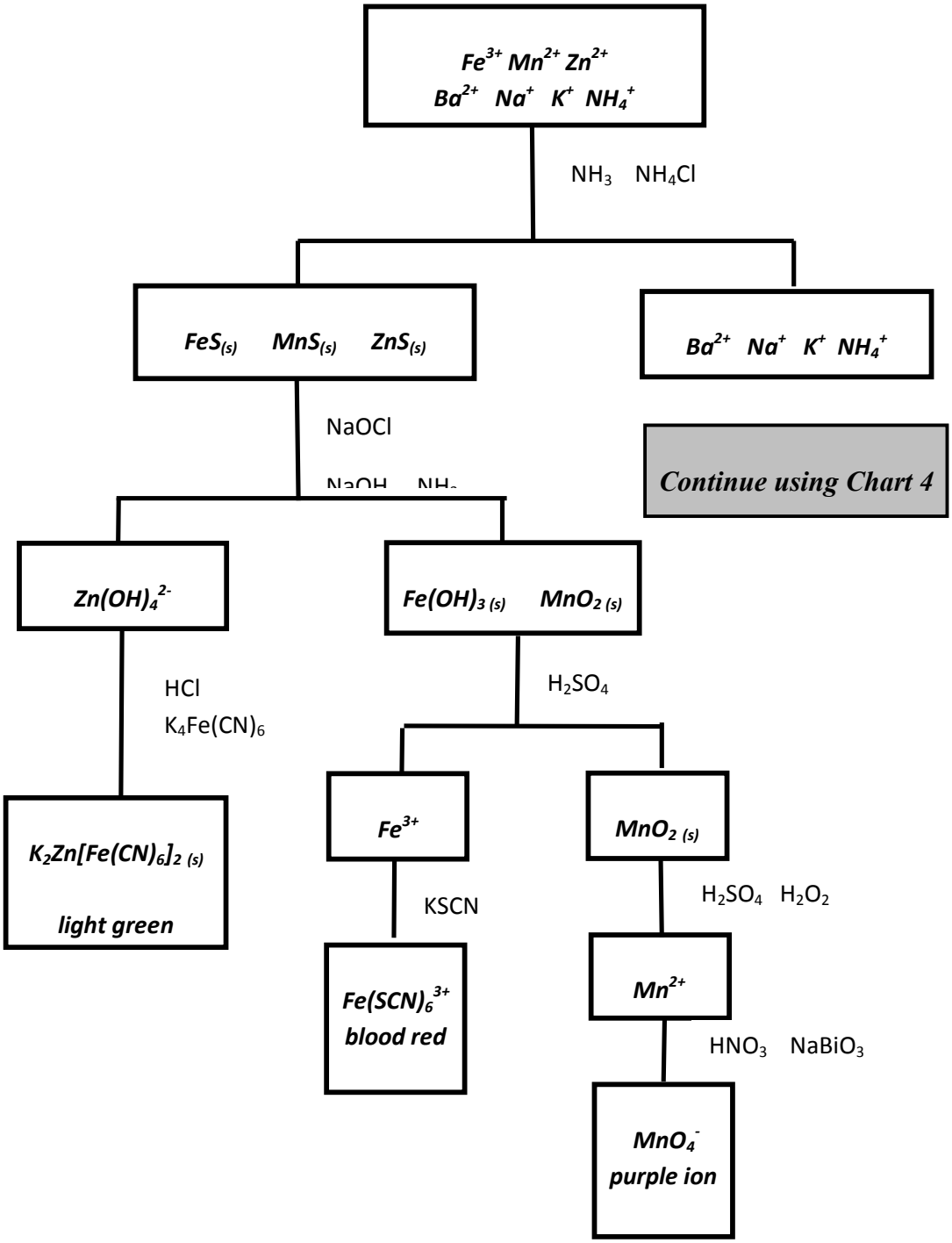


Chart 3 Below shows the separation of the Group III cations Fe^{3+}, Mn^{2+}, and Zn^{2+} from the cations of Group IV and V.



EXPERIMENT 15

QUALITATIVE ANALYSIS OF ANIONS

Purpose:

Identification of anions from unknown solution

Introduction:

In qualitative analysis we test determine which chemical substance is present (whereas in quantitative analysis we determine how much of a given chemical substance is present). The qualitative analysis, or identification, of the common anions is markedly simpler than the analysis of the cations. One reason is that there are only few possibilities for the anions, another is that analysis of anions usually relies on spot tests of the anions rather than separations followed by confirmatory tests. For these reasons, the study of qualitative analysis often begins with the anions. The common anions you will test for are carbonate, phosphate, sulphate, bromide, chloride, iodide, acetate, thiocyanate, and nitrate. (Before begin this experiment, you should review the formulas and structures of these ions from your textbook.

Qualitative analysis of anions

The anions to be analyzed can be categorized into four groups.

I. The Acid Volatile Group

This group includes the carbonate and sulphide ions. Upon addition of strong acid, these anions form gases that are readily evolved from solution. For carbonate:

$$CO_3^{2-}(aq) + 2\,H^+(aq) \longrightarrow H_2CO_3(aq)$$

Carbonic acid, H_2CO_3, is unstable and is rapidly decomposed to carbon dioxide and water.

$$H_2CO_3(aq) \longrightarrow CO_2(g) + H_2O(l)$$

Sulfide ion, when acidified, produces the foul-smelling hydrogen sulphide gas: $S^{2-}(aq) + 2H^+(aq) \longrightarrow H_2S(g)$

The H_2S is usually unavoidably detected by the odor of rotten eggs, but since

the gas is toxic, you should not inhale it. For reasons of laboratory safety in these experiments we will not include sulphide ion. We will only use carbonate in this experiment.

II. The Barium Precipitate Group.

This group includes sulphate and phosphate ions. These are the only ions on our list that form precipitates upon the addition of excess Ba^{+2} ion.

$$Ba^{2+} + SO_4^{2-} \square BaSO_4$$

$$Ba^{2+} + PO_4^{3-} \square Ba_3(PO_4)_2$$

Sulphate can be differentiated from phosphate in that the barium phosphate is soluble in HCl, while barium sulphate is insolvable.

III. The Silver Precipitate Group.

This group includes the halides: iodide, bromide, and chloride, and also the thiocyanate ion, which is often called a pseudohalide. All of these form light-colored precipitates with excess Ag^+ ion. The precipitates vary slightly in appearance, which helps to distinguish them.

$Ag^+(aq) + X^-(aq) \Longrightarrow AgX(s)$ $(X^- = Br^-, Cl^-, I^-, SCN^-)$

The thiocyanate ion is readily confirmed by the blood-red complex it forms with Fe^{+3}.

The halides can be oxidized to the halogens, then extracted into an organic layer and identified by color. For example, when reacting with "chlorine water (Cl_2 dissolved in water), the Cl_2 oxidizes (takes away an electron) the Br^- to Br_2 which can be extracted into hexane layer.

$$2Br^-_{(aq)} + Cl_{2(aq)} \rightarrow Br_{2(hex)} + 2Cl^-_{(aq)}$$

IV. The Soluble Group.

The fourth group is made up of the last two of the anions you will encounter, nitrate and acetate. Nitrate ion is identified by the very specific brown ring test. Acetate ion is identified by the vinegar odor of acetic acid.

Brown Ring Test: The qualitative test for nitrate has traditionally been the "brown ring" test. The brown color is caused by the formation of $Fe(NO)^{+2}$ in the presence of NO and excess Fe^{2+} in a two-step reaction:

$$3\ Fe^{2+}(aq) + NO3^-(aq) + 4\ H^+(aq) \rightarrow 3\ Fe^{3+}(aq) + NO(aq) + 2\ H2O$$

$$NO(aq) + Fe^{2+}(aq) \rightarrow Fe(NO)^{2+}(aq)\ (brown)$$

The H^+ is provided by concentrated sulfuric acid. Because of its density, H_2SO_4 will form a lower layer when added to an aqueous solution. The solutions are layered rather than mixed because the heat of dilution of sulfuric acid is enough to destroy the brown Fe complex. The "brown ring" forms at the interface between the two layers.

Like nitrate, most compounds of acetate are soluble. Although the test is sometimes inconclusive, the simplest test is the conversion of acetate to acetic acid, which can be confirmed by a sweet fruity smell.

Materials and Equipment

Dropping bottles of

Solutions -1 M Solutions of Nano, NaCi, NaScN,

1 M $NaNO_3$, 1 M NaCl, 1 M NaSCN or KSCN, 1 M Na_3PO_4, 1 M NaBr, 1 M $NaC_2H_3O_2$ (sodium acetate), 1 M Na_2SO_4,1 M NaI, 1 M Na_2CO_3,conc. H_2SO_4 6 M H_2SO_4, 6 M HNO_3, 6 M HCl 0.1 M $Fe(NO_3)_3$, bleach (5.25% NaClO),1 M $BaCl_2$, 0.2 M $FeSO_4$, $AgNO_3$ solution, saturated KNO_2, hexane, copper wool or fine Cu wire and starch solution.

Apparatus

Test tubes, test tube rack, test tube holder, stirring rods, pH paper, Bunsen burner, lead acetate paper, centrifuge, 10-mL graduated cylinder, ring stand and clamp, boiling water bath, ice water bath.

Procedure

GROUP I. The Acid Volatile Group

1. Test for CO_3^{2-}

Take 10 drops of 1 M Na_2CO_3 in a small test tube. Dilute with distilled water to about double the volume and mix with a clean stirring rod. Add 6MH_2SO_4, 1 drop by drop, and continue until the effervescence (bubbles) ceases. The bubbling is only barely detectable under dilute conditions, so observe very carefully.

GROUP II. The Barium Precipitate Group

2. Test for SO_4^{2-}

Take 10 drops of 1 M Na_2SO_4 solution in a small test tube and dilute slightly. Add 4 drops of 1 M $BaCl_2$ and mix well. The precipitate may form slowly, especially if the sulphate solution is very dilute. Allow the precipitate to settle and decant the supernatant.

Confirmatory test: Add 6 drops of 6MHCl to the above precipitate and stir. Does The precipitate does not dissolve? This conferms the presence of SO_4^{-2} ion.

3. Test for PO_4^{3-}

Take 10 drops of 1 M Na_3PO_4 solution in a small test tube and dilute slightly. Add 6 drops of 1 M$BaCl_2$ and mix well. Allow the precipitate to settle and decant the supernatant.

Confirmatory test: Add 7 drops of 6 M HCl to the above precipitate and stir. Is the solid

soluble in HCl? Record all observations, The precipitate dissolves. This confirms the presence of phosphate ion.

GROUP III. The Silver Precipitate Group

4. Test for SCN^-

In a test tube mix 5 drops of 1 M KSCN (or NaSCN) with 2 drops of $AgNO_3$. Precipitate is formed the results. Save the precipitate for later comparison to unknown.

Confirmatory test: Take 5 drops of 1 M KSCN (or NaSCN) in a test tube and slightly dilute it. Add 2 drops of 0.1 M $Fe(NO_3)3$ and blood red coloured complex is formed. Dilute the complex with water until the test tube is nearly full. Notice that the color is still detectable, even at very dilute concentrations. This confirms presence of Scn^- ion.

5. Test for Cl^-

Take 12 drops of 1 M NaCl in a test tube and add 8 drops of 0.2 M $AgNO_3$. White coloured precipitate is formed.

Confirmatory test for Cl^-.

In another test tube add 12 drops of 1 M NaCl and acidify with 8 drops of 6 MHCl

Dilute with 6 drops of distilled water. Add 2 mL hexane gently over the aqueous solution. Add chlorine water drop by drop. After adding about 2 mL of chlorine water, shake vigorously and observe any colour change. The color will be extremely pale, if it is visible at all. (You are not actually producing chlorine here, only trapping the free $Cl2$ present in the chlorine water). Stopper the test tube and set it aside for later comparison.

6. Test for I^-

Take 10 drops of 1 M NaI solution in a test tube and add 8 drops of 0.2 M $AgNO_3$. Note the appearance of the precipitate and set it aside. yellow coloured precipitate is formed.

Confirmatory test for I^-:

In another test tube take 10 drops of 1 MNaI, add 10 drops of 6 M acetic acid,

CH_3COOH. Dilute the solution with 5 drops of distilled water. Add 2 mL of hexane gently down the side of the test tube. Add 4 drops of chlorine water. The $Cl2$ reacts with the I^- to form free iodine, I_2. The nonpolar I_2 will dissolve readily in the upper organic layer. Shake or agitate briefly. The appearance colour of organic layer confirms the presence of I ion.

7. Test for Br^-

Take 12 drops of 1 M NaBr solution in a test tube and add 8 drops of 0.2 M $AgNO_3$. Note the appearance of the precipitate, and set it aside for later comparison. A pale yellow precipitate is formed.

Confirmatory test for Br^- : Perform this experiment in the fumehood take 12 drops of 1 M NaBr in a test tube and acidify with 8 drops of 6 M HCl. take dilute slightly 5 drops of distilled water. Check with pH paper that the solution is strongly acidic. Add 2 mL of hexane gently down the side of the test tube. Add 4 drops of chlorine water to the test tube with NaBr and hexanes and note the yellow appearance as Br_2 is absorbed into the upper, organic hexane layer. Shake the test tube gently. Continue adding the chlorine water dropwise and stir vigorously or agitate. A darker color will develop in the hexane layer as the reaction continues. The presence of Br^- ion this confirm.

GROUP IV. The Soluble Group.

8. Test for NO^3- Ring test

Take 10 drops of 1 M NaNO3 in a test tube and add 10 drops of 0.5 M iron(II) sulfate, $FeSO_4$. Mix well. and take 2 mL of **concentrated** H_2SO_4 (i.e., not the 6M solution you have used earlier) in a separate test tube and place in ice water. Keep both the test tubes in ice water bath for 3-5 minutes.

Hold the test tube with the $NO3^-/Fe^{+2}$ solution at an angle of abut 30^o (check with the TA or instructor for correct technique). Now pour 1 to 1.5 mL of the chilled sulfuric acid gently down the side of the test tube, to avoid mixing the layers. Let the mixture stand undisturbed for a few minutes. A brown ring in formed at the junction of two layers which confirms the presence of No3-ion.

9. Test for acetate, $CH3COO^-$

Take 12 drops of 1 M $NaC_2H_3O_2$ (sodium acetate) solution in a small test tube and add 4 drops of **concentrated** sulfuric acid, H_2SO_4. Heat it in a hot water bath for 1 to 2 minutes. Smell the vapors from the test tube by gently wafting them to your nose. Does it smell like vinegar? If not, add 2 more drops of sulfuric acid and heat a little longer.If the test for acetate is inconclusive, add 10 drops of ethanol to the mixture and heat for 2 minutes in a boiling water bath (heat water to boiling in a beaker). Remove and small the odor of this preparation, ethyl acetate, which has a sweet, fruity smell. Thi confirms the presence of CH3 Co ion.

Unit-2

Organic Chemistry

EXPERIMENT 16

EXTRACTION

Introduction

There are two main applications of extraction in organic chemistry: (1) the separation and isolation of substances from mixtures of solids, typically those that occur in nature and (2) the selective isolation of substances from solutions of mixtures that arise in synthetic chemistry.

Extraction of Solids. Examples of extractions of solid mixtures are the extraction of alkaloids from leaves and bark, flavoring extracts from seeds, perfume essence from flowers, and sugar from sugar cane. Solvents commonly used for this purpose are ether, dichloromethane, chloroform, acetone, various alcohols, and water. In the laboratory, a common form of apparatus for continuous extraction of solids by means of volatile solvents is the Soxhlet extractor (Figure 16.1), meanwhile discontinuous one is Maceration extractor.

Extraction of Solutions. A more common application of extraction is in "liquid-liquid" extraction, which is used to isolate a substance dissolved in one solvent by shaking the solution with another solvent, immiscible with the first, in a separatory funnel (figure 16.2) and continuous extractors (Figure 16.1).In this course, the term "extraction" refers to the process whereby a component in a mixture is transferred into another solvent phase: The operation involves shaking an immiscible pair of liquids, whereby a solute passes from one liquid to the other. Commonly, one of the liquids will be an aqueous (water) solution and the other, an organic solvent (e.g.diethyl ether or CH_2CI_2) or a solution involving an organic solvent).Before using the separating funnel, apply a thin coat of grease or, when dichloromethane is used as solvent, a film of water, to the glass tap (DO NOT grease Teflon taps). Check for leaks by adding a small volume of the solvent to be used to the separating funnel with the tap inserted and closed.

Using the separating funnel (Figure 16.2):

1. Close the tap.

2. With the separating funnel supported in a ring clamp, add the two liquid phases and insert the stopper.

3. Remove funnel from ring clamp and, holding the stopper firmly with the palm of one hand, invert the funnel and release pressure through the tap.

4. After closing the tap, shake the funnel several times whilst holding both the stopper and the tap.

5. At frequent intervals during an extraction, release excess pressure through the tap. Take care not to point the stem, at your neighbor during this operation.

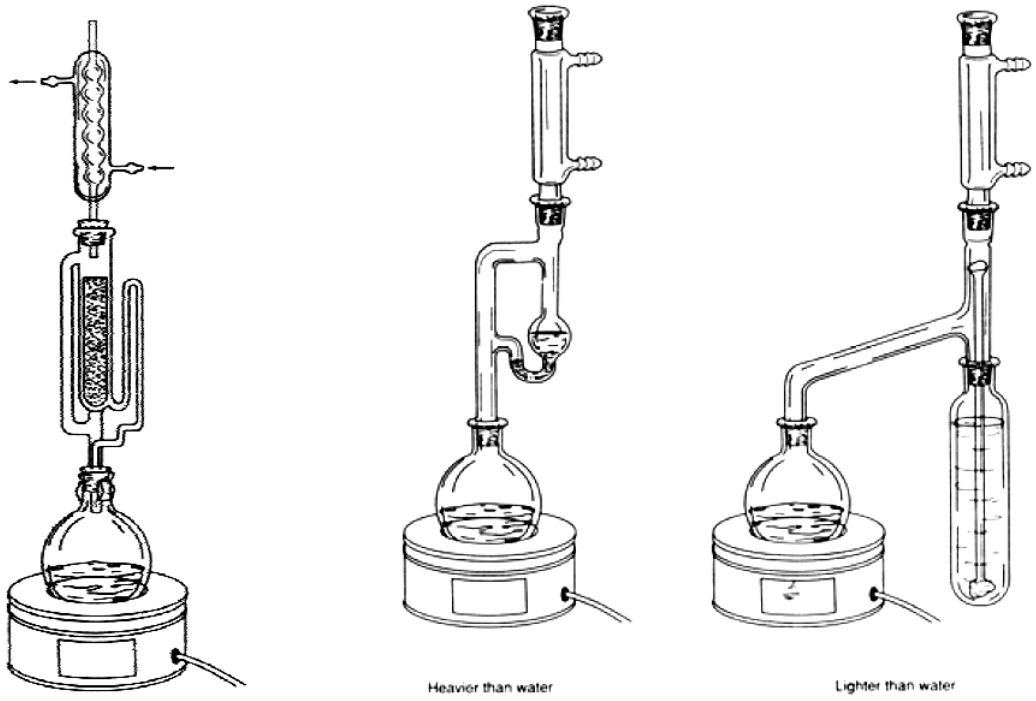


Figure 16.1 Soxhlet Extractor and Continuous Extractor Assembly

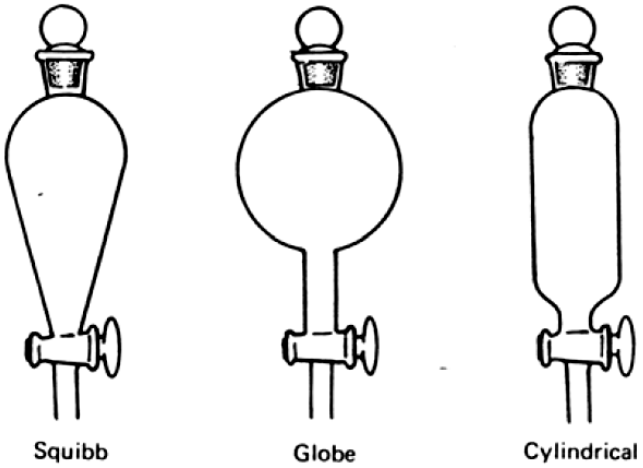


Figure 16.2 Separatory Funnel

6. When the extraction is completed, replace the separating funnel in the ring clamp, remove the stopper and allow the phases to settle.

7. Drain the lower phase in an appropriate container, and then pour out the upper phase through the neck of the funnel into another container.

Principal Extraction is based on the differential solubility of compounds in various solvents. The solvents (used in pairs) for extraction must be immiscible. Water is frequently used as one of the pair because its solvent ability can be dramatically altered by changing its pH during the course of an extraction sequence. It has further advantage of being insoluble (immiscible) in most organic solvents.In a typical extraction, a mixture of two compounds is dissolved one solvent taken in a separatory funnel, and then shaken (extracted) with a second, immiscible solvent. Ideally, one of the compounds in the mixture will be preferentially extracted into the new solvent leaving the other compound behind in the original solvent. The new solvent can then be separated from its immiscible partner. Solvent removal from the two layers will yield two separate compounds in a reasonably pure state.

Procedure

In a 500 mL Erlenmeyer flask take 30 g of ordinary dry tea, 300 mL of water and 0.5 g of powdered calcium carbonate. After boiling the mixture gently with occasional swirling for 20 minutes, add 5 g of Celite or other filter aid, filter the hot mixture on a Buchner funnel and press the filter cake firmly with a large cork to obtain as much as possible of the liquid. Cool the aqueous extract to 15-20°C, transfer it to a separatory funnel and extract the caffeine with three successive 25 mL portions of methylene chloride (Chloroform).

Pour the combine chloroform extract into an Erlenmeyer flask and add 0,5 g sodium sulphate. Decant the chloroform solution from sodium sulfate indicant flask. Evaporate the solvent on the steam bath. Scrape the dry product from the flask and weight the crude caffeine.

EXPERIMENT 17

RECRYSTALLIZATION

Introduction

Recrystallization of a crystalline material is carried out in order to remove impurities. Briefly, the procedure involves dissolving the material in an amount of solvent that will produce a saturated solution at a temperature close to the boiling point of the solvent. Insoluble impurities are removed by gravity filtration of the hot solution and the purified compound crystallizes as the filtrate cools. Suction filtration is used to isolate the purified crystals.

The steps involved in recrystallization may be summarised as follows:

1. Select the solvent.
2. Dissolve the material in minimum amount of the hot solvent.
3. FiIter the solution if necessary.
4. Allow crystallization to take place.
5. Collect the crystals.
6. Wash the crystals.
7. Dry the crystals.

Procedure

Dissolve the crude caffeine in a minimum amount of acetone by warming the mixture on steam bath. Add drop wise just enough mixed "hexane" to turn the warmed solution faintly cloudy,then allow the solution to cool and allow the product to crystallize. Collect the green-tinged crystals on a small vacuum filter and wash them with a little mixed 'hexane".

EXPERIMENT 18

CHROMATOGRAPHY

Introduction

Chromatography is an exceptionally versatile separation technique that in one or more of its numerous forms is used by just about every research chemist. In any chromatographic separation there are two phases (solid, liquid, or gas); these move relative to each other while maintaining intimate contact. The sample is introduced into the moving phase, and the sample components distribute themselves between the stationary phase and the mobile one. The components spend different times in the stationary phase as determined by the structures of the components and the two phases. If one component spends a larger fraction of the time in the mobile phase, it will move along quickly; if it spends more time in the stationary phase it will move slowly. As with extraction, the relative amounts in the two phases is determined by a distribution coefficient, which is related to the same structural factors that control solubility. The degree of separation of a mixture is controlled by the differences in the distribution coefficient of the components.

Laboratory Practice

Thin-Layer Chromatography(TLC)

A convenient type of commercial TLC plate comes as 20x20-cm sheets consisting of a 100-μm layer of adsorbent bound to a 200 μm sheet of plastic. With reasonable care these can be cut with ordinary (sharp) scissors or a paper cutter into 2x 10-cm strips suitable for analytical separations.

A convenient developing chamber for TLC plates can be prepared from an ordinary wide-mouthed, screw-cap bottle. The inside of the bottle is lined with a folded circle of filter paper, which acts as a wick to transfer the developing solvent to the upper portions of the chamber. As shown in Figure 18.1, the circle of filter paper is folded to form a rectangle, which is inserted in the wide- mouthed bottle with the folds against the walls of the bottle. The size of filter paper should be chosen so that the folded paper comes close to the top of the bottle, but there must be a gap between the paper and the top of the bottle so that the approach of the solvent front to the upper line on the plate can be seen without removing the cap. Sufficient solvent is added to the bottle to saturate the liner and leave a layer 2-4 mm deep at its shallowest point. The spotted end of the plate is centered in the bottom of the chamber with its upper edge leaning against the wall; the spotted face of the plate should

face the gap in the filter paper lining so that the rising spots will be visible. The bottle is capped and gently set aside until the rising solvent front has just reached the upper line. The plate is then removed and the solvent is allowed to evaporate from it. Since the solvent vapors may be harmful, it is good practice to do the evaporation in a hood.

If one or more of the components to be identified is colorless, a convenient visualization technique is to place the plate in another screw-cap bottle containing a few crystals of iodine mixed with about. a table spoon of sand which serves to disperse the iodine. The capped bottle is held horizontally and rotated for a few seconds to bring the plate in contact with the iodine and sand mixture. Iodine vapour is adsorbed on the plate wherever there is a concentration of organic material and produces a brown spot (commercial plastic plates do not adsorb a significant amount of iodine under these conditions; some organic compounds also do not adsorb iodine vapor). After the color has developed, the plate is removed and a circle in made with pencil around each spot. On exposure to air, the brown iodine spots gradually evaporate. Another method for visualization, which works with compounds that adsorb ultraviolet (UV) light, is to use thin-layer plates that have been impregnated with a fluorescent dye. When the plate is exposed to UV light, the dye will glow; if the organic compound absorbs UV light, it will prevent the light from reaching the dye and make a dark spot at that point against the glowing background. While the plate is glowing, the dark spots should be circled carefully with a pencil so that their positions can be measured and recorded after the ultraviolet light has been withdrawn. When handling the UV lamp, take care to avoid looking directly at the light source because unfiltered UV light could damage your eyes.

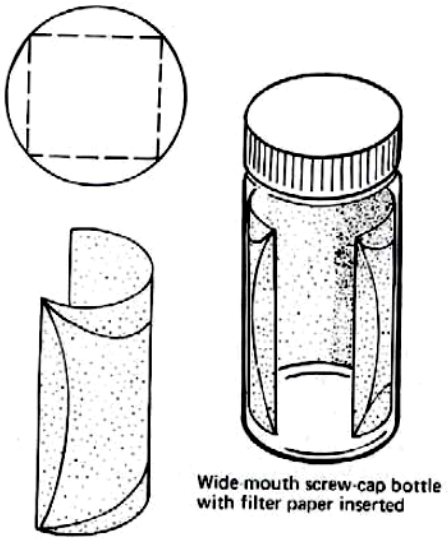


Figure 18.1Developing Chamber for Thin-Layer Chromatography

Column Chromatography

A simple apparatus for liquid-solid column chromatography is a glass tube that has been constricted at one end (Figure 18.2). For separation of 0.1- to 0.5-g samples, a convenient tube size is 60 cm of 15-mm diameter tubing. This size will hold about 50 g of solid support and give a 100: 1 ratio of packing to sample. Other sample sizes may be used with appropriately scaled apparatus.

Pencil Columns

When you are working with only a few milligrams of sample, the column just described is much too large. TLC could be used, but an interesting option is to do column chromatography with a Pasteur pipet for the column. A small wad of glass wool is pushed into the constricted neck of the pipet, followed by enough adsorbent to produce a column about 3-5 cm high. The sample and solvent are added in the way described previously. Frequently, the solvent will not flow through the column on its own and must be forced through (slowly) with a rubber bulb.

Procedure

Separation of Ink Pigments by Thin-Layer Chromatography

Prepare two 2x 10-cm thin-layer plates by drawing two horizontal pencil lines across each plate 7 mm from each end. On the bottom line of each plate, about 5 mm from the left-hand edge, make a single, sharp dot of ink from a black Flair pen; in the center of the line make a second spot about 2 mm in diameter by momentarily holding the pen tip on the plate; on the right-hand side of the line, about 5 mm from the edge, make a third spot about 5 mm in diameter. Add sufficient acetone to an 8-oz, wide-mouth, screw-cap bottle containing a filter paper lining until a 3-mm-deep layer is produced. Center one of the spotted plates in the bottle with the upper edge leaning against the side and screw the cap tightly onto the bottle. When the solvent front reaches the upper pencil line, remove the plate and allow the solvent to evaporate. While the first plate is developing, repeat the process with the other plate and a second 8-oz bottle using a 1 : 1 mixture of acetone and 95% ethanol. Determine and record the Rf values for all of the colored spots. Determine which spots, if any, are UV active. Determine which spots are stained by I_2. Make a sketch of the two plates in your laboratory notebook showing the location and shape of the spots with side notes on their response to UV and I_2 . The experiment can be repeated with other colors of Flair pens to determine if the same dyes are used that were found in the analysis of the pen with black ink.

Separation of Plant Pigments by Thin-Layer Chromatography

In a mortar take 1 g of spinach, 1 g of clean sand, 5 mL of acetone, and 5 mL of mixed "hexanes." Grind the spinach until the green chlorophyll appears to have been extracted completely. Decant the solution into a small beaker.

Prepare two thin-layer plates as described above and in the center of each bottom line place a microdrop of the chlorophyll extract. Blow gently on the spot so that the solvent evaporates quickly. Repeat the addition of the extract several times until a distinct green spot is visible. The additions should superpose as closely as possible.

Develop one plate with 1: 4 (v: v) mixture of acetone and mixed "hexanes" as described in (A). Develop the second plate with a 1: 6: 1 (v: v: v) of aceton, mixed hexanes and etalon 95%.

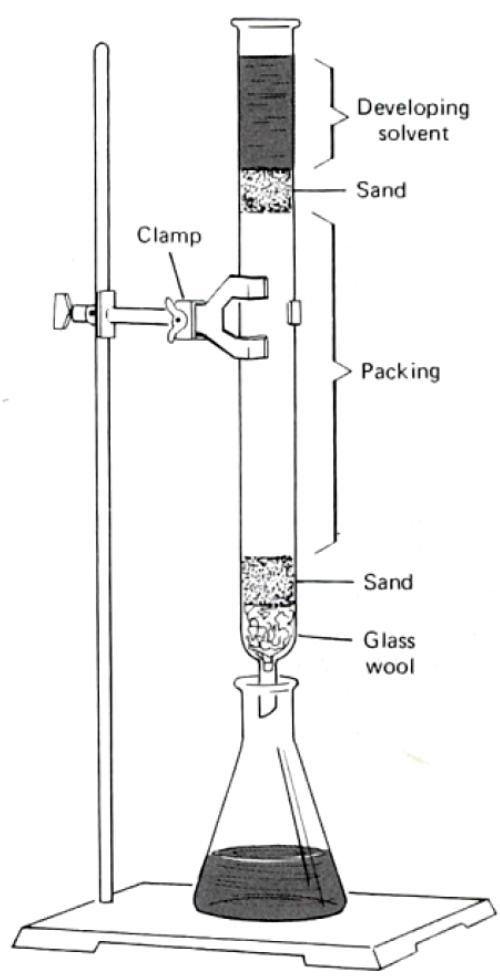


Figure 18.2Apparatus for Column Chromatography

Separation of a Dye Mixture by column chromatography

Insert a small wad of glass wool into the constricted end of a 30-cm length of 10-mm diameter tubing and clamp the tube in an upright position (see Figure 18.2). Add a 5-mm

layer of coarse sand to the tube. In a 100-mL beaker, prepare a slurry of 6 g of aluminum oxide in 10 mL of hot water, and transfer the slurry in small batches to the tube (swirl between additions). The water that filters through the sand and glass wool should be collected and used to transfer any column material that remains in the beaker. After the packing has settled, add a second 5-mm layer of sand, followed by a small filter paper circle.

When the last drop of water penetrates the column, add 4 drops of the dye solution to the top of the column. When the dye solution has penetrated, add a few drops of water to wash down any dye adhering to the walls. After the wash water has penetrated, fill the tube with water and allow the chromatogram to develop.

EXPERIMENT 19

DISTILLATION

Introduction

Distillation is the most important means of separating and purifying liquid compounds on a large scale. It consist of vaporizing the liquid and condensing the vapor in a separate receiver. There are several kinds of distillation processes ; simple**,** fractional, steam and distillation under reduced pressure. Simple distillation will be discussed first since it depends upon principles and concepts which will be needed to understand the other techniques.

Simple distillation. Distillation consists of boiling a liquid and condensing the vapor in such a manner that the condensate (distillate) is collected in a separate container. A simple apparatus assembly for this operation is shown in Figure 19.1. When a pure substance is distilled at constant pressure, the temperature of the distilling vapor will remain constant throughout the distillation provided that sufficient heat is supplied to ensure a uniform rate of distillation and superheating is avoided. In actual practice these ideal conditions are not obtained; drafts in the laboratory can cause momentary condensation of vapors before they reach the thermometer, which lowers the temperature sensed by the thermometer. On the other hand, after they leave the surface of the liquid the distilling vapors may be heated above the liquid's boiling point (superheating), which increases the temperature sensed by the thermometer. Because of these two contrary effects, a distillation range of 1-20 aocctually represents an essentially constant boiling point. With somewhat more refined apparatus and technique, a distillation range of 0.10 occan be observed for a pure compound.

The temperature reading of a thermometer in the distilling vapor represents the boiling point of that particular portion of the distillate. This temperature will be the same as the boiling point of the liquid in the distilling flask only if the distilling vapor and the boiling liquid are identical in composition. Since a pure liquid fulfills this condition, a constant thermometer reading is sometimes used as a criterion of purity of a liquid. It should be noted, however, that certain mixtures (such as azeotropes) also give constant thermometer readings. Occasionally two liquids have such similar boiling points that no appreciable change in the thermometer readings will be observed when a mixture of them is distilled.

Fractional Distillation

The common use of the term fractional distillation refers to a distillation operation in which a fractionating column has been inserted between the boiler and the vapor takeoff to the

condenser. The effect of this column is to give in a single distillation a separation equivalent to several successive simple distillations (Figure 19.2).

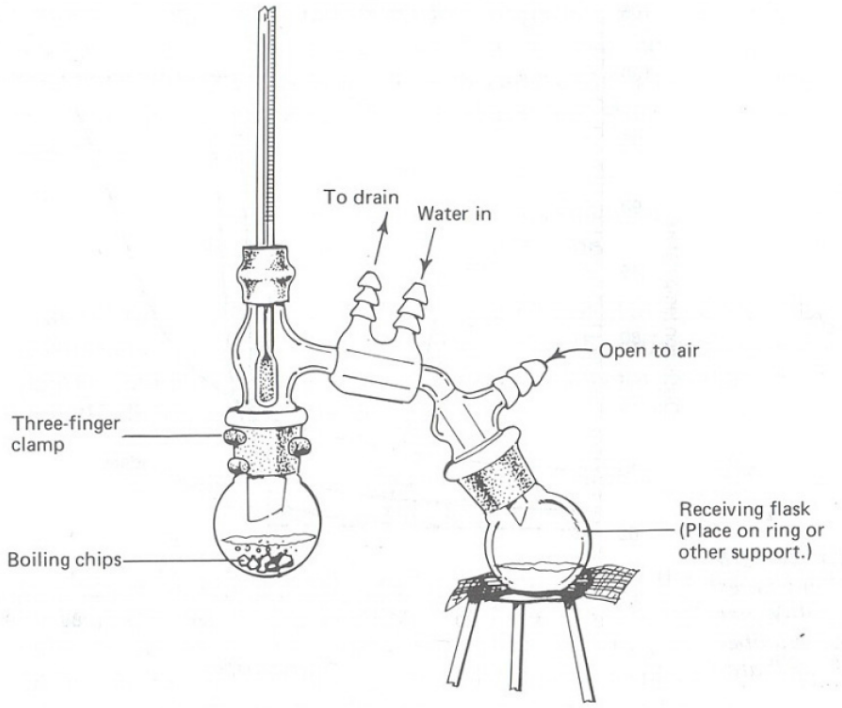


Figure 19.1 Apparatus for Simple Distillation

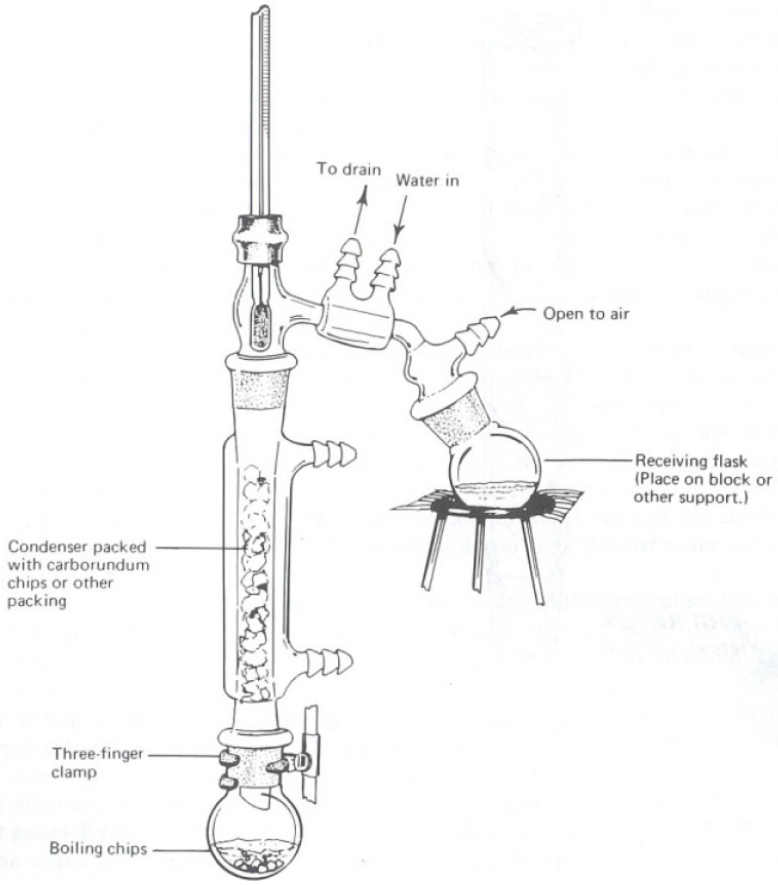


Figure 19.2 Apparatus for Fractional Distillation

Vacuum Distillation

Since the boiling temperature of a liquid is decreased by diminishing the pressure on its surface, you can distill a liquid below its boiling point at a lower temperature by using an apparatus that is connected to a vacuum pump that maintains a lower inside pressure. This procedure is useful for purifying liquids (or low-melting solids) that decompose at elevated temperature.

Steam Distillation

Steam distillation consists of distilling a mixture of water and an insoluble or partly soluble substance. The practical advantage of steam distillation is that the mixture usually distills at a temperature below the boiling point of the lower-boiling component. Consequently, it is possible to steam distill a high boiling organic compound at a temperature much below its boiling point (in fact, below 100°) without resortin, to vacuum distillation. Steam distillation is useful also in separating mixtures when one component has an appreciable vapor pressure (at least 5 mm) in the vicinity of 100° and the other has a negligible vapor pressure. The

process of steam distillation is widely employed in the laboratory and in industry; e.g., for the isolation of pinene, aniline, nitrobenzene, and many natural essences and flavoring oils.

Laboratory Practice

The purpose of this section is to provide sufficient practice in purification of liquids by distillation so that this operation can subsequently be carried out skillfully and without reference to detailed directions. Usually only one or two of these procedures will be assigned.

Simple Distillation

Arrange a distillation assembly similar to the one shown in Figure 19.1.

Distillation of a Pure Compound

In a 250-mL boiling flask take 100 mL of pure methanol (caution- flammable liquid) by means of a clean and dry funnel. Add one or two tiny boiling chips, attach the boiling flask with condensor thermometer, and make certain that all connections are tight. Place a graduated cylinder beneath the drip tip to serve as receiver. Heat the flask gently until the liquid begins to boil. Adjust the heating rate until the ring of vapor condensation moves up the wall of the flask and past the thermometer into the condenser. Record the temperature when the first few drops of distillate are collected. Continue to distill the liquid slowly (not over 2 mL/min) and record the distilling temperature at regular intervals during the distillation when the total distillate amounts to 1, 2, 3, etc., mL. Discontinue the distillation (and turn off the heat source) when all but 1 mL of the liquid has distilled. Record the temperature range from the beginning to the end of the distillation; this is the observed boiling point. If the boiling point differs from the literature value, record the correction in your laboratory notebook for future reference.

Transfer the used methanol to a bottle provided for this purpose. From your data, draw a distillation graph for pure methanol, plotting distilling temperatures on the vertical axis against total volume of distillate on the horizontal axis.

Fractional Distillation

Arrange an assembly for fractional distillation as shown in Figure 19.2.

(A) Methanol and Water

For the separation of a 50:50 mixture (by volume) of methanol and water, the following temperature ranges are satisfactory for the fractions: A, 64-70; B, 70-80; C, 80-90; D, 90-95; and E, residue. Plot your data for the distilation temperature versus volume distilled and by selecting the curve closest to your data estimate the number of theoretical plates obtained.

(B) Acetic Acid and Water

In this experiment you will fractionally distill a mixture of glacial acetic acid and water (100: 31.5 by volume, 1: 1 mole ratio) and follow the progress of separation by titrating 0.5-mL portions of several fractions against standard aqueous sodium hydroxide with phenolphthalein indicator to determine the acetic acid content. The acetic acid content of the original mixture should be determined in the same way before the material is fractionated. If a column having a large number of plates is used, it will be desirable to use larger portions of the early fractions.

Obtain a 35-mL of a 1 : 1 molar solution of acetic acid and water. Fill a 50-mL burette with 1.0 N sodium hydroxide solution. With the aid of pipet, take 0.5 mL of the 1 : 1 molar solution of acetic acid and water in a 50-mL Erlenmeyer flask and add 10 mL of water and a few drops of phenolphthalein indicator. Titrate to a slightly pink end point and record the volume of titrant. Repeat the titration on two more 0.5-mL samples of the 1 : 1 molar solution of acetic acid and water and compute the average titer.

Assemble a fractional distillation apparatus using a 50-mL round-bottomed flask for the boiler and a 25-mL graduated cylinder for the receiver. take 30 mL of the 1 : 1 mixture in the flask and add few boiling chip. You will need a small test tube that has been marked to show the liquid level when it contains exactly 0.5 mL of liquid.

Heat the mixture until it boils and then adjust the heating rate so that the mixture distills at a maximum rate of 1 drop/sec. Note the temperature at which the first drop distills. Collect the first 0.5 mL of distillate in your marked test tube and the next 4.5 mL in the graduated cylinder. Record the distillation temperatures at each 1-mL interval. Transfer the 0.5-mL sample to a 50-mL Erlenmeyer flask (rinse the tube with a total of 10 mL of distilled water and add the rinse to the Erlenmeyer flask). Mark the flask to indicate the sample it contains.

When the volume of distillate reaches 5 mL, collect another 0.5-mL sample in the test tube and transfer it in the same manner to another Erlenmeyer flask. Collect the next 4.5 mL of distillate in the graduated cylinder, recording the distillation temperatures at each 1-mL interval. Repeat this process at 10 mL, 15 mL, 20 mL, and 25 mL of distillate. Titrate the six samples with the sodium hydroxide solution (the early samples will require very little titrant) and calculate the mole fraction of acetic acid present. In the calculations assume that the volumes of acetic acid and water are additive so that the mole fraction in any sample is simply proportional to the titer value obtained for the initial 0.5 mole fraction mixture.

Prepare a plot of boiling point (ordinate) versus the total volume of distillate (abscissa) and a second plot of the mole fraction of acetic acid versus the total volume of distillate.

EXPERIMENT 20

FUNCTIONAL GROUP ANALYSIS IDENTIFICATION

Introduction

Any compound other than a saturated hydrocarbon has at least one functional group, which can be identified by carrying out a series of "classification tests" that serve to narrow the range of possibilities until only one remains. When the functional group is identified, an appropriate table of characterized compounds containing this group is consulted, and those compounds having chemical and physical properties consistent with the sample are selected. In favorable cases only a few compounds will be found; rarely will there be more than 10.

The lists of compounds containing each functional group give not only the physical properties of the molecules but also the properties of solid substances (derivatives) that can be prepared from it by tested procedures. Since the melting points of these derivatives are usually distinctive, the combination of properties of the original substance and of its derivatives is sufficient to identify it. The list of functional groups is restricted but does include the most commonly encountered types.

In the laboratory it is important to perform the classification tests in a sequence consistent with the accumulated evidence, never at random. A good guide is the solubility classification scheme (Figure 20.1), which lists the possible functional groups for each solubility class. For example, if the elemental analysis reveals nitrogen and the compound falls in solubility class B**,** the amine tests should be performed directly.

As a second example, if a neutral compound falls in class S or N and does not contain nitrogen, sulfur, or halogens, the functional group must be one of the following: alcohol, aldehyde, ketone, or ester. In this case, the recommended next step is to test with 2,4-dinitrophenylhydrazine for an aldehyde or ketone. If the test result is positive, further structural distinctions can be made with the tests described in the procedures for aldehydes and ketones. A negative 2,4-dinitrophenylhydrazone test should be followed by the hydroxamate test for esters. If that test is negative, only the alcohol class remains, and this can be confirmed by the classification tests for alcohols. Functional groups of compounds that fall into other solubility classes can be identified by analogous strategies.

To ensure satisfactory results for the tests, we recommend that the specified quantities of liquid reagents be measured in a graduated cylinder or a calibrated dropper. If a test is being done for the first time, it is a good idea to practice on materials of known structure.

Infrared (IR) analysis is a powerful tool for identifying functional groups because a single IR spectrum reveals much about the nature of all of the fuctional groups present. However, the IR spectrum usually does not provide a total answer and one must resort to either other instrumental techniques or the chemical methods described here.

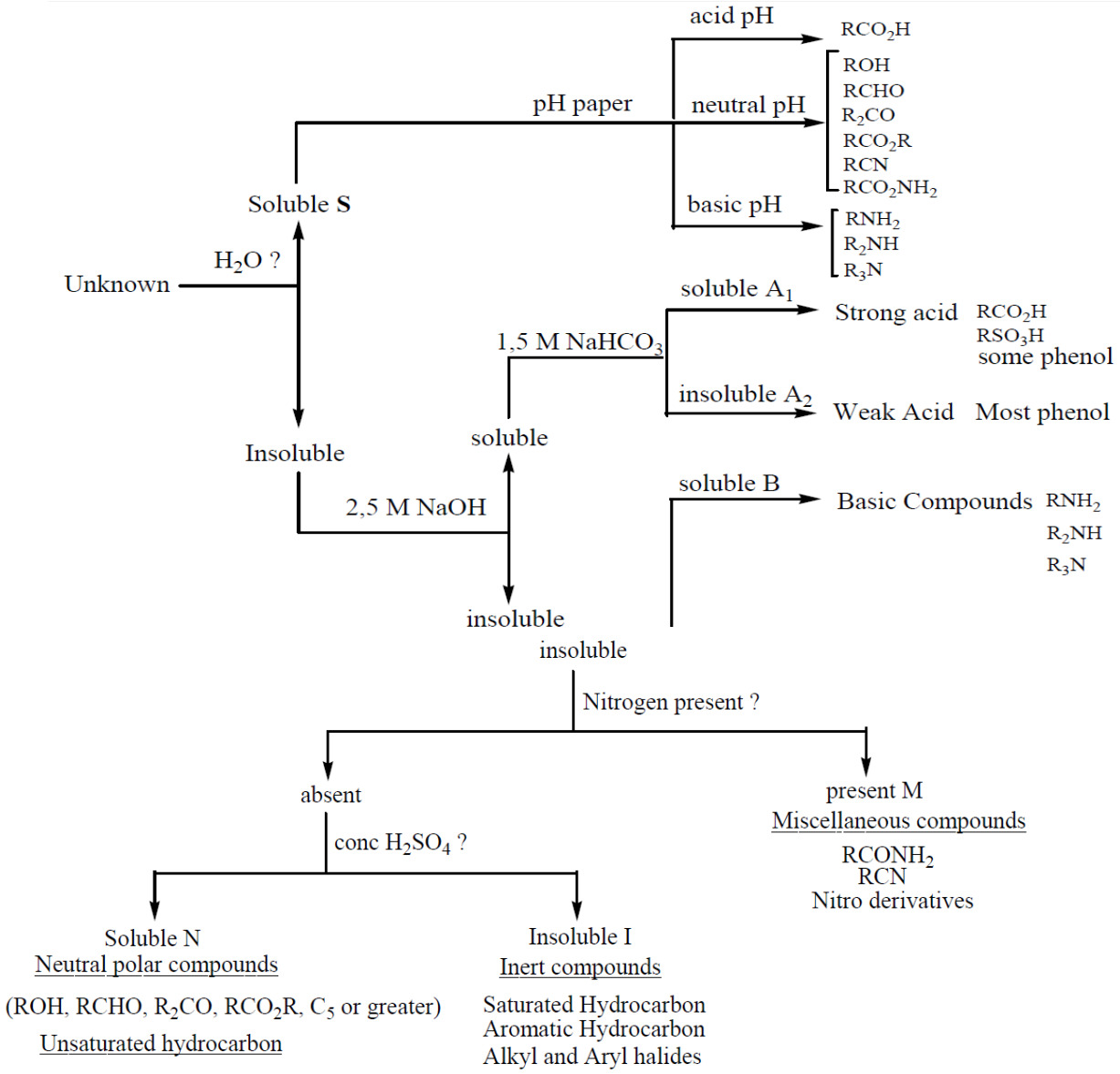


Chart 20.1 The Solubility Classification Scheme of functional group organic compounds.

Test of extra elements in an organic compound- identification of functional groups in organic compounds it is necessary to test the presence of extra elements (N,S and holograms) in the given organic compound to test an extra element in an organic compound test an extra element in an organic compound lassar method in most earlier method .

In this test the organic compounds in first heated with sodium metal to form sodium self of the extra element present in the organic compound which is soluble in water and thus can be tested as as anion.

Test of Nitrogen: Take about 2 Ml ofd L.S. in a test tube add few crystals of $FeSO_4$ A dirty green precipitrate will form of ppt is not formed add few droups of dilute NaOH Boil for two minutes cool and add few drops of dil H_2SO_4

Alcohols

The tests described are used to distinguish among primary, secondary, and tertiary alcohols. The tests also can yield information about the structure surrounding the carbon bearing the alcoholic functional group. The Ritter test is a general test for alcohols or other readily oxidizable functional groups such as aldehydes. The Lucas test and the iodoform test provide further structural information about the alcohol.

Ritter Test

This test, based on the ability of primary and secondary alcohols to be oxidized by an acetic acid solution of potassium permanganate, distinguishes these alcohols from tertiary alcohols. The permanganate ion is purple, but when reduced the color changes to brown; a positive test is the disappearence of the purple color. To 3 mL of glacial acetic acid (caution-corrosive!) contained in a small test tube, add 2 drops of your unknown liquid (or about 20 mg of a solid) and mix thoroughly. Add dropwise, with swirling to mix the contents after each addition, a saturated aqueous solution of potassium permanganate and note any change in the color of the solution. If the alcohol is tertiary, the purple permanganate color will persist as a rose color after 1 or 2 drops have been added. If the alcohol is primary or secondary, the solution will decolorize the permanganate and remain clear until sufficient permanganate has been added to oxidize all of the alcohol. Remember that the Ritter test probes the oxidizability of the unknown; if the unknown contains another readily oxidized functional group such as an aldehyde or alkene, the test will also be positive even in the absence, of an alcohol. As with all chemical reaction tests it is prudent to try the test on compounds I known to give both a positive (a primary or secondary alcohol) and a negative (tertiary alcohol) result.

Lucas Test

The reagent used is concentrated hydrochloric acid containing 1 mole of anhydrous zinc chloride to 1 mole of the acid. The Lucas test distinguishes between primary, secondary, and tertiary alcohols and is based on the rate of formation of the insoluble alkyl chloride. To be reliable the alcohol should be soluble in water (class S). The ease of conversion of alcohol to chloride follows the stability of the corresponding carbocation, modified by the solubility of the alcohol in the test reagent. Allyl alcohol, CH_2=CH-CH_2OH, which yields a stabilized charge delocalized cation acts like a tertiary alcohol. Isopropyl alcohol sometimes fails to give a positive test because the chloride product is volatile (36°) and may escape from the solution. To 0.5 mL of the alcohol add quickly 3 mL of the hydrochloric acid-zinc chloride reagent at ,room temperature. Close the tube with a cork and shake it; then allow the mixture to stand. Tertiary alcohols give an immediate separation (emulsion) of the chloride, secondary alcohols require about 5 min, but most primary alcohols do not react significantly in less than an hour. If the result is positive, carry out a second test using concentrated hydrochloric acid alone, instead of the test reagent. This less reactive reagent will give chloride emulsions within 5 min only with tertiary alcohols.

Iodoform Test

This is a test for the specific structural feature R-CHOH-CH_3 (R may also be H). The test depends on initial oxidation of the alcohol to R-CO-CH_3, which is iodinated and then cleaved to give a bright yellow precipitate of iodoform. In a clean (acetone-free) 150-mm test tube mix 3 drops of the liquid (or about 50 mg of solid) with 2 mL of water and 2 mL of 10% aqueous sodium hydroxide solution. Add dropwise, with shaking, a 10% solution of iodine in potassium iodide until a definite brown color persists (indicating an excess of iodine).

With some compounds a precipitate of iodoform appears almost immediately in the cold. If it does not appear within 5 minute, warm the solution to 60° in a water bath. If the brown color is discharged, add more of the iodine solution until the iodine color persists for 2 minute. Add a few drops of sodium hydroxide solution to remove excess iodine, dilute the mixture with 5 mL of water, and allow it to stand for 5 minute at room temperature. For compounds that are not appreciably soluble in water, the sample may be dissolved in pure methanol instead of water. Before starting the test the solvent should be tested to see if iodoform-producing impurities are present. Iodoform crystallizes as lemon yellow hexagons having a characteristic odor. Their identity can be confirmed by collecting it with suction and taking the melting point (119°).

Aldehydes and Ketones

The 2,4-dinitrophenylhydrazone test is positive for both aldehydes and ketones. These may be distinguished by either the silver mirror test, which depends on the easy oxidation of aldehydes, or the Schiffs fuchsin test, which depends on the ease of formation of SO_2 adducts of aldehydes but not ketones. Another test that will distinguish aldehydes from ketones is the chromic acid test, described earlier under alcohols.. Aromatic aldehydes take about 60 sec to give a positive test. The iodoform test, also described earlier under alcohols, is specific for molecules containing a methyl group adjacent to a carbonyl group or to any other structure that can form such a methyl carbonyl combination. The only aldehyde that gives a positive iodoform test is acetaldehyde.

2,4-Dinitrophenylhydrazone Test

Most aldehydes and ketones react with 2,4-dinitrophenylhydrazine reagent to give precipitates of the 2,4-dinitrophenylhydraones. Esters and amides generally do not respond and can be eliminated on the basis of this test. The color of the precipitate depends on the degree of conjugation in the aldehyde or ketone. Unconjugated aliphatic carbonyl groups such as butanal or cyclohexanone give yellow participates. Conjugated carbonyls, such as benzaldehyde or methyl vinyl ketone, give red precIpItates. Unfortunately, the reagent is orange-red; one should establish that a reddish precipitate is really a new product and not just the starting reagent that has been made insoluble by the addition of the unknown.

In a clean small test tube, take 1 mL of 2,4-dinitrophenyl-hydrazine reagent and add a few drops of liquid (or about 50 mg of solid dissolved in the minimum amount of 95% ethanol). A positive test is the formation of a yellow to red precipitate. Most aldehydes and ketones will give a precipitate immediately, although some sterically hindered ones may take longer. If no precipitate appears within 15 min, heat the solution gently for 5 min; examine the test tube after it has cooled to room temperature.

Tollens' Reagent (Silver Mirror) Test

This test involves reduction of an alkaline solution of silver ammonium hydroxide to metallic silver and oxidation of the aldehyde, but not a ketone, to the carboxylic acid. This is an extremely mild oxidation and alcohols do not respond. Fehling's or Benedict's solution (alkaline cupric tartrate or citrate) also may be used as a test for aldehydes but the Tollens' test is more sensitive.

In a thoroughly clean 75-mm test tube, take 1 mL of a 5% solution of silver nitrate and add a drop of 10% aqueous sodium hydroxide. Add a very dilute solution of ammonia (about 2%) drop by drop, with constant shaking until the precipitate of silver oxide just dissolves. To obtain a sensitive reagent it is necessary to avoid a large excess of ammonia.

(CAUTION !!! The silver ammonium hydroxide reagent should be freshly prepared just before use and should not be stored. On standing, the solution may decompose and deposit an explosive precipitate of silver nitride, Ag_3N.)

Add 2 drops of the unknown to be tested, shake the tube and allow it to stand for 10 min. If no reaction has occurred in this time, place the tube in a beaker containing of water that has been heated to about 40^0 or and allow it to stand for 5 min. A positive test is the formation of a silver mirror (if the tube is clean) or a black precipitate of finely divided silver. Water-insoluble compounds give weak or negative tests. With such unknowns it is helpful to dissolve them in 0.5 mL of analytical reagent (AR)-grade acetone.

Schiff's Fuchsin Test

The intensely colored triphenylmethane dye fuchsin reacts with bisulfite (a source of SO_2) to produce the colorless "leuco" form of the dye. Aldehydes, but not ketones, react with this "leuco" dye to produce a new triphenylmethane dye possessing a similar fuchsin color. To a take few drops of the unknown to be tested, in 4-5 mL of water, add about 1 mL of the fuchsin test reagent and observe any development of purple color. Ketones do not respond to this test when perfectly pure, but the color reaction is very sensitive and responds to mere traces of an aldehyde.

Nonaromatic Hydrocarbons

There are four classes of hydrocarbons: (1) the saturated hydrocarbons, (2) the alkenes (olefins), (3) the alkynes (acetylenes), and (4) the aromatic hydrocarbons. Of these, only the alkenes and alkynes are in cold sulfuric acid (class N); the saturated hydrocarbons will fall in class I. A test for an aromatic hydrocarbon was described earlier in this section. There are no simple chemical tests for saturated hydrocarbons; these substances must be detected by their failure to give positive tests for either an aromatic ring or unsaturation. Saturated hydrocarbons are best detected by nuclear magnetic resonance. The suspected presence of un saturation can be confirmed by the cis hydroxylation with aqueous permanganate (Baeyer test) and by the trans addition of bromine in carbon tetrachloride. Almost all alkenes and alkynes react with these reagents. The only exceptions are molecules with strongly electron-withdrawing groups on the multiple bond, which fail to react with bromine because the intermediate bromonium ion is formed too slowly. Another complication of the bromine test is the tendency of C-H bonds adjacent to a double bond to discharge the bromine color by a free-radical substitution reaction that is accompanied by the evolution of hydrogen bromide. The Baeyer permanganate test is superior to the bromine test, but it also has complications. All easily oxidized molecules, such as aldehydes and phenols, give positive Baeyer tests.

Fortunately, the two tests are largely complementary. It is recommended that the permanganate test be tried first; then, if it is positive, the bromine test should be tried.

Permanganate Test (Baeyer Test)

In a small test tube dissolve 3 drops of the liquid (or 30 mg of a solid) unknown in 1 mL of pure alcohol-free acetone. The solvent must be tested for purity before use. Add dropwise, with vigorous shaking, a 1% alkaline aqueous solution of potassium permanganate. A positive test is the loss within 1 min of the purple permanganate ion color and formation of the insoluble brown hydrated oxides of manganese. Record the number of drops necessary to develop a persistent purple color; do not be deceived by a slight reaction caused by impurities in the unknown.

Bromine Test

This test should be carried out in the hood. In a small test tube dissolve 3 drops of the liquid (or 30 mg of a solid) unknown in 1 mL of carbon tetrachloride and add dropwise, with shaking, a 2% solution of bromine in carbon tetrachloride. Record the number of drops necessary to develop a persistent (for 1 min) bromine color. A positive test is the loss of brown colour of bromine.

CAUTION!!! Bromine can cause painful burns. If any of the solution is spilled on the skin, wash the area quickly and thoroughly with water and apply a dressing soaked in 10% sodium thiosulfate solution; consult a physician. Prolonged exposure to carbon tetrachloride vapor should be avoided because of its toxicity.

Aromatic Hydrocarbons

Molecules falling into solubility class I include saturated hydrocarbons, aromatic hydrocarbons and their derivatives. The flame test carried out in the 1 preliminary examination may have suggested the presence of an aromatic ring by the appearance of a yellow, sooty flame. Confirmation can be obtained from the Friedel-Crafts alkylation test described here. Aromatic hydrocarbons (and many of their derivatives) react serially with chloroform in the presence of anhydrous aluminum chloride to produce triarylmethanes. The intermediate chlorohydrocarbons react with aluminium chloride to produce carbocations that abstract a hydride ion from the triarylmethane to yield highly colored triarylmethyl cations. The color depends on the number of rings in the hydrocarbon. Benzene and its derivatives give an orange-red color; naphthalene and phenanthrene as well as their derivatives give blue-purple colors; an anthracene ring produces a green color. In general, the observed color depends on the nature of the substituents, but in the classification scheme described here the substituents will be either alkyl groups or halogens, which do not change

the colors significantly. In carrying out the test it is essential that the aluminum chloride be completely anhydrous. This is accomplished in the test procedure by freshly subliming a sample of aluminum chloride, which drives off any water that may be present.

Friedel-Crafts Test

Take about 100 mg of anhydrous aluminium chloride in a small, dry Pyrex test tube and heat it strongly with the tube held almost horizontally so as to sublime the chloride onto the cooler wall of the tube. While the tube is cooling, prepare in the hood in another small test tube a solution of about 20 mg of unknown in 10 drops of chloroform (caution-chloroform is toxic). Add this solution to the test tube containing the freshly sublimed aluminium chloride by dropping it directly onto the salt and note the color, if any, where they meet.

Phenols

Many phenols and related compounds form colored coordination complexes with ferric iron, in which six molecules of a monohydric phenol are combined with one atom of iron to form a complex anion. Most phenols produce red, blue, purple, or green colors. Sterically hindered phenols give negative tests. Aliphatic enols (ethyl acetoacetate, acetylacetone) give a positive test.

Ferric Complex To 2 mL of ethanol in a test tube, add 2 drops of liquid (or 20 mg of solid) unknown and a few drops of a 3% aqueous solution of ferric chloride. Shake well and observe the color.

C A U T I O N Phenol, the cresols, and other phenolic compounds in the pure state or in concentrated solution are toxic and cause painful bums. If any of these come in contact with the skin, wash the area quickly and thoroughly with soap and water.

Alkyl and Aryl Halides

Alkyl halides can be distinguished from aryl halides by a combination of two tests. The first is with alcoholic silver nitrate, which forms a precipitate of silver halide with alkyl halides that undergo SN_1 reactions. The order of reactivity for R groups is allyl and benzyl > tertiary > secondary » primary. The order for the halide-leaving group is I > Br > Cl. Secondary and primary halides give no reaction within 5 min; secondary halides react only when the solution is boiled. Primary, aromatic, and vinyl halides usually do not react even after 5 minutes of heating under reflux. Primary chlorides and bromides can be distinguished from the aromatic and vinyl halides by the reaction with sodium iodide in acetone. Primary bromides undergo SN_2 displacement reactions within 5 minutes at room temperature to produce sodium bromide, which is insoluble in acetone. The same reaction occurs with

primary chlorides at 50° to produce sodium chloride, which also precipitates. Secondary and tertiary bromides and some secondary chlorides also react at 50°C.

Alcoholic Silver Nitrate Test

In a small test tube take 2 mL of 2% solution of silver nitrate in ethanol and add 1 drop of liquid (or 10 mg of solid) unknown. A positive test is a precipitate of whitish silver halide within 5 min. If no reaction occurs in that time, boil the solution gently for 5 more min. If a precipitate forms, either at room temperature or on heating, it is advisable to verify that it is not the silver salt of an organic acid by adding 2 drops of dilute nitric acid (20: 1 water: acid). The acid salts will dissolve; the halides will not.

Sodium Iodide in Acetone Test

In a small test tube dissolve 2 drops of liquid (or 20 mg of solid) unknown in the minimum volume of acetone and add 1 mL of the sodium iodide solution (15 g of sodium iodide in 100 mL of AR-grade.-acetone). A positive test is white precipitate within 5 minutes at room temperature. If no reaction occurs, place the test tube in a beaker containing water at 50° C and after 5 minute cool the test tube to room temperature and note if a precipitate has formed.

UNIT-3

PHYSICAL CHEMISTRY

EXPERIMENT 21

pH METRY

Prupose

Determination the pH of water by a pH meter.

Apparatus and Materials

A 0.1 pt. (50 mL), wide-mouth glass beaker with a watch glass for cover, A pH meter, suitable for laboratory , Standard buffer solutions of known pH values of 4.0, 7.0, and 10.0, Distilled water, A glass stirring rod.

Procedure

1 Take about 50 ML sample water in a beaker and cover it with water glass.

2 Stir the water sample vigorously using a clean glass stirring rod.

3 Pour a 40 mL $\pm$ 5 mL sample into the glass beaker using the watch glass for a cover.

4 Let the sample stand for a minimum of one hour to allow the temperature to stabilize, stirring it occasionally while waiting. Measure the temperature of the sample and adjust the temperature controller of the pH meter to that of the sample temperature. This adjustment should be done just prior to testing On meters with an automatic temperature control, follow the manufacturer's instructions.

5 Standardize the pH meter by means of the standard solutions provided. Temperature and adjustments must be performed as stated under 3.

6 Immerse the electrode(s) of the pH meter in the water sample and turn the beaker slightly to obtain good contact between the water and the electrode(s).

7 The electrode(s) require immersion for 30 seconds or longer in the sample before reading to allow the meter to stabilize. If the meter has an auto read system, it will automatically signal when stabilized.

8 Read and record the pH value to the nearest tenth of a whole number. If the pH meter reads to the hundredth place, a round off rule will apply as follows: If the hundredth place digit is less than 5, leave the tenth place digit as is. If it is greater than 5, round the tenth place digit

up one unit. If the hundredth place digit equals 5, round the tenth place digit to the nearest even number.

9 Rinse the electrode(s) well with distilled water, then press lightly with tissue paper to remove any film formed on the electrode(s). Caution: Do not wipe the electrodes, as this may result in polarization of the electrode and consequent slow response.

EXPERIMENT 22

CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE

Purpose :

Determination of the rate of hydrogen peroxide decomposition catalyzed by manganese dioxide.

Theory :

Inhibitor free hydrogen peroxide solution decomposes spontanouosly librating oxygen in accordance with the following equation:

$$H_2O_2\ (aq) = H_2O\ (aq) + \tfrac{1}{2}\ O_2\ (g)$$

The decomposition rate is markedly accelerated by solids such as manganese dioxide or colloidal platinum, which act as catalysts. The course of reaction may be followed either by titrating the peroxide with potassium permanganate in acid medium, or by collecting the oxygen gas evolved.

Procedure :

1. Prepare 250 ml of 0.1 N $KMnO_4$ and 100 ml of 0.1 NH_2O_2 solution (Ten- volume hydrogen peroxide is approximately 3%). Thermostat the peroxide solution at 25 ^oC. Add about 0.03 g manganese dioxide and record the time.
2. After about 3 minutes pipette out 10 ml of the decomposing mixture into a flask containing about 10 ml of about 2.0 N sulphuric acid and titrate rapidly with potassium permanganate recording the main time of titration.
3. Repeat the above step at increasing time intervals extending for about 80 minutes, i.e. 5, 8, 13, 20, 30, 45, 60 and 80 minutes.

Calculations:

1. Tabulate the results in the following order:

   t, (a-x), log (a-x)

   where, t is the main time of titration in minutes and **(a-x)** the amount of undecomposed peroxide expressed in volume (ml) of $KMnO_4$.
2. Plot **log (a-x)** against **t** to identify the order of reaction, then deduce the

value of k (reaction rate constant) and $t_{1/2}$ (half-live time).

Results:

t(Minute)	(a-x)	log (a-x)
3		
5		
8		
12		
20		
30		
45		
60		
80		

EXPERIMENT 23

HYDROLYSIS (SAPONIFICATION) OF ETHYL ACETATE IN ALKALINE MEDIUM

Purpose:

Determination of the saponification rate constant of ethyl acetate in alkaline medium.

Theory :

In the presence of alkali ethyl acetate undergoes saponification in accordance With the reaction.

$CH_3COOC_2H_5$ + OH- = CH_3COO^- + C_2H_5OH

The rate of saponification is directly proportional to both concentrations of ester and alkali, and the reaction therefore, is a second order one, i.e.

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

where in the initial equal concentrations of ester and alkali, respectively (a = b in this case) and **k** is the reaction rate constant. t= time, a-x constitution at time t.

Procedure :

1. Prepare the following solutions:

100 ml of exactly 0.1 N **Na_2CO_3,**

100 ml of about 0.1 N HCl,

100 ml of exactly 0.1 N NaOH.

2. Standardize the acid against the carbonate and the hydroxide against the acid.

3. By appropriate dilution prepare 100 ml of exactly 0.025 N HCl and 100 ml of each of exactly 0.05 N and 0.025 N NaOH.

4. Prepare 100 ml of exactly 0.05 N ethyl acetate (density is 0.901 g/ml).

5. By means of a pipette, transfer 50 ml of 0.05 N ethyl acetate in a clean dry flask and 50 ml of 0.05 N NaOH, record the mixing time (note that the mixture will become 0.025 N with respect to each of alkali and ester).

6. Withdraw 10 ml portion of the reacting mixture, record the time (about 10 minutes from the start) and run immediately into a flask containing about 100 ml distilled water and exactly 10 ml of 0.025 N HCl. Titrate back the excess HCl with 0.025 N NaOH using phenolphethalin as an indicator.

7. Repeat step (6) at increasing time intervals making a total about eight titrations over a period extending for about 90 minutes.

Calculations :

1. If **a** is the amount of HCl equivalent to the original concentration of alkali which equivalent to the consumed alkali titrant and consumed ester (0.025) and **x** the amount of alkali equivalent to the excess HCl after time **t, (a-x)** gives, hence, the amount of each of alkali and ester remaining (the two are equal).

2. Tabulate the results in the following order:

t, x, (a-x), x/(a-x)

3. Plot **x/(a-x)** against **t** to identify the order of reaction.

4. Knowing the original concentration **a**, the reaction rate constant **k** in (dm3mol-1 min-1) may be calculated from the slope of the curve obtained.

Results:-

T (minute)	**X**	**(a-x)**	**x / (a-x)**
10			
20			
30			
40			
50			
60			
70			
90			

EXPERIMRNT 24

HYDROGEN PEROXIDE - HYDROGEN IODIDE REACTION

Purpose I:

Determination of the order of the veaction between hydrogen peroxide and hydrogen iodide.

Purpose II:

Determination of the rate constant and the energy of activation of the reaction between hydrogen peroxide and hydrogen todide.

Theory:

The overall reaction between $\mathbf{H_2O_2}$ and HI which represented by the equation

$$\mathbf{H_2O_2 + 2\ HI = 2\ H_2O + I2}$$

is kinetically of second order -not, as might be expected, third order. The suggested mechanism is probably as

$$\mathbf{H_2O_2 + I^- = H_2O + IO^-} \quad \text{(slow)},$$

$$\mathbf{IO^- + 2\ H^+ + I^- = H_2O + I_2} \quad \text{(fast)}$$

The rate-determining step is the slow stage, (first order with respect to both $[H_2O_2]$ and $[I^-]$). The order of the reaction with respect to H_2O_2 can be studied conveniently by choosing conditions such that there is practicallyconstant excess of HI. Then, the rate of the reaction depends only on $[H_2O_2]$ and temperature and, hence, the kinetics then follows the first order law, $\mathbf{Rate\ \alpha\ [H_2O_2]}$.This is achieved experimentally by continually adding small volumes ofsodium thiosulphate solution to remove the iodine as soon as it is liberated and to regenerate iodide according to the reaction

$$2S_2O_3^{--} + I_2 = S_4O_6^{--} + 2I^-$$

Note that: by using a large volume of solution and adding small amounts of concentrated thiosulphate solution, one can neglect the small increase of volume of the solution and take the concentration of I^- ions as constant.

The course of the reaction can readily be followed by timing the appearance of iodine (indicated by starch solution) after the addition of a small known volume of thiosulphate solution. The amount of iodine librated by the reaction at a series of times corresponds to

the volume of thiosulphate added. The total amount of iodine librated at infinite time can be determined from a standardization of the hydrogen peroxide used. Thus, it is possible to determine the concentration of hydrogen peroxide at any time, since 1 mol of iodine is librated for every mol of hydrogen peroxide destroyed. The order of the reaction with respect to HI can be determined by determining the first order velocity constant of the reaction with different concentrations of HI. Generally, the rate equation of the overall reaction is

Rate = k $[H_2O_2]^a$ $[HI]^b$

where, **k** is the rate constant, **a** and **b** are the order with respect to H_2O_2 and **HI**, respectively.

The rate of this reaction can be determined by allowing the reaction to proceed in the presence of thiosulphate and determining the time taken between mixing of the reactants and the appearance of iodine. The reciprocal of the time interval is a measure of the rate of reaction.

Procedure :

1. Prepare the following solutions

500 ml of 1.0 N H_2SO_4 ,

250 ml of 0.10 M KI ,

100 ml of 0.01 N $Na_2S_2O_3$. 5 H_2O,

50 ml of 1 vol. H_2O_2 ,

Freshly prepared starch solution.

- **To get the order with respect to H_2O_2:**

2. In dry small flat bottom flasks make up the following series of mixtures

(volumes in ml):

	Mixture				
	I	II	III	IV	V
1.0 N H_2SO_4	25	25	25	25	25
0.10 M KI	25	25	25	25	25
0.01 N $Na_2S_2O_3$. 5 H_2O	5	5	5	5	5
Starch + distilled water	4	3	2	1	--

3. To each mixture add respectively and separately: 1, 2, 3, 4 and 5 ml of H_2O_2 (making a total volume of 60 ml), mix thoroughly and meanwhile start a clock on. Determine the time period (**t**, sec.) indicated by the sudden appearance of the blue color. The results are tabulated as follows:

VH_2O_2 (ml), t, 1/t , log (1/t), log VH_2O_2 .

4. At constant [I-], the rate law of the reaction can be written as follows:

Rate = = k [H_2O_2]a

Then, **log Rate = log k + a log [H_2O_2]**

Considering the rate of reaction is measured as **1/t** and [H_2O_2] is represented by V_{H2O2}

log (1/t) = log k + a log V_{H2O2}

Plot **log (1/t)** against **log V_{H2O2}** . This gives a straight line, the slope of which is **a** and the intercept is **log k.**

- **To get the order with respect to HI:**

5. In dry small flate bottom flasks make up the following series of mixtures

(volumes in ml):

	Mixture				
	I	II	III	IV	V
1.0 N H_2SO_4	25	25	25	25	25
0.01 N $Na_2S_2O_3$. 5 H_2O	5	5	5	5	5
H_2O_2	2	2	2	2	2
Starch + distilled water	23	18	13	8	3

6. To each mixture add respectively and separately: 5, 10, 15, 20 and 25 ml of

0.1 M KI solution (making a total volume of 60 ml), mix thoroughly and meanwhile start a clock on. Determine the time period (**t**, sec.) between addition of KI solution and the sudden appearance of the blue color. The results are tabulated as follows:

V_{KI} (ml), t, 1/t , log (1/t) , log V_{KI} .

7. Similarly,

log (1/t) = log k + b log V_{KI}

Plot **log (1/t)** against **log V_{H2O2}** . This gives a straight line, the slope of which is **b** and the intercept is **log k.**

Purpose II:

Determination of the rate constant and the energy of activation of the reaction between hydrogen peroxide and hydrogen iodide.

Procedure:

1. Prepare 250 ml of the following solutions:

2.0 N H_2SO_4 , 0.4 M KI solution , 0.1 M $Na_2S_2O_3$. 5 H_2O, 1 vol. H_2O_2,

Freshly prepared starch solution.

2. In a clean dry conical flask take 20 ml of the hydrogen peroxide solution, add about 2 g solid potassium iodide and 10 ml of sulfuric acid. Leave the mixture for about five minutes in a dark place, then titrate the librated iodine with standard sodium thiosulphate solution, and, hence, standardize the hydrogen peroxide solution.

Note that: the consumed volume of $Na_2S_2O_3$ is equivalent to the librated I_2, equivalent to [H_2O_2] destroyed and equals **a**.

3. To 50 ml of potassium iodide solution in a dry bottle, add 20 ml of the diluted sulfuric acid and place in a thermostat at about 25 ^oC. At the same time have 20 ml of hydrogen peroxide solution and 10 ml of the starch solution (in separate boiling tubes) at the same temperature.

4. Arrange the 50 ml burette containing the sodium thiosulphate solution above the flask in the thermostat so that it will deliver directly into the solution, add the starch and hydrogen peroxide solutions (with vigorously shaking) and record the time at which a blue color appears, then add immediately 1 ml of the thiosulphate solution from the burette to discharge the color.

5. Continue the addition of 1 ml aliquots of sodium thiosulphate until the blue color appears until the blue color takes five to six times the initial time to reappear (it is essential that the reaction mixture be shaken continuously).

6. Repeat the experiment at various temperatures in the range 25 to 50 ^oC.

7. To determine the order of the reaction with respect to hydrogen iodide, repeat the experiment (at 25 ^oC) now using half and double the amounts of sulfuric acid and potassium iodide in the same total volume of the reaction mixture.

Treatment of the experimental data and discussion :

1. The total amount of librated iodine at infinite time can also be determined from the preliminary standardization. Thus, it is possible to determine the concentration of hydrogen peroxide in mole per liter, $[H_2O_2]$ at each time, **(a-x)**. Note that: **x** is the volume of $Na_2S_2O_3$ added.

2. Plot a graph of **log $[H_2O_2]$** (ln (a-x)) against **t**, at each temperature to obtain a straight line with a slope of **k** (rate constant) at constant iodide ion concentration (first order reaction) according to the equation:

ln $[H_2O_2]$ = -k t + B

3. From the values of the rate constant at different temperatures, calculate the activation energy of the reaction from the equation:

ln k = -Ea/RT + const.

by plotting the values of **ln k** against **1/T** to get a straight line with a slope of, then calculate **Ea** (activation energy).

From the values of the rate constant at different iodide concentrations determine the order of the reaction with respect to hydrogen iodide. The overall reaction will be of a second order.