NATIONAL OPEN UNIVERSITY OF NIGERIA

FACULTY OF SCIENCE

DEPARTMENT OF PURE AND APPLIED SCIENCES

COURSE CODE: CHM292

COURSE TITLE: PRACTICAL CHEMISTRY IV (ORGANIC AND PHYSICAL)

CHM 292 PRACTICAL CHEMISTRY IV (ORGANIC AND PHYSICAL)
COURSE TEAM:

Course Team

Course Writer/Developer — **Dr. Uduak Aletan**
National Open University of Nigeria

Course Editor — **Dr. Akeem Abayomi**
Department of Chemistry
University of Lagos

Course Reviewer/ Revised — **Prof. Nnabuk Okon Eddy:**
Department of Pure and Industrial Chemistry
University of Nigeria, Nsukka,

NATIONAL OPEN UNIVERSITY OF NIGERIA

National Open University of Nigeria
Headquarters
Plot 91, Cadastral Zone,
Nnamdi Azikiwe Expressway,
Jabi - Abuja

Email: centralinfo@nou.edu.ng
URL: www.nou.edu.ng

Published by
National Open University of Nigeria,
First Printed 2015

Revised and Reprinted 2020
ISBN 978-058-582-6

INTRODUCTION

This course guide informs you about the course, the materials available and how to work with them to take full advantage of learning through effective time management.

Most organic lab courses are completed without incident, apart from minor cuts or burns, and serious accidents are rare. Nevertheless, the potential for a serious accident always exists. To reduce the likelihood of an accident, you must learn the following safety rules and observe them at all times. Additional safety rules or revisions of these rules may be provided by your instructor.

i. *Wear approved eye protection in the laboratory at all times*. Even when you aren't working with hazardous materials another student's actions could endanger your eyes, so never remove your safety goggles or safety glasses until you leave the lab. Do not wear contact lenses in the laboratory because chemicals splashed into an eye may get underneath a contact lens and cause damage before the lens can be removed. Determine the location of the eyewash fountain nearest to you during the first laboratory session, and learn how to use it.

ii. *Never smoke in the laboratory or use open flames in operations that involve low boiling flammable solvents*. Anyone found smoking in an organic chemistry laboratory is subject to immediate expulsion. Before you light a burner or even strike a match, inform your neighbors of your intention to use a flame. If anyone nearby is using flammable solvents, either wait until he or she is finished or move to a safer location, such as a fume hood. Diethyl ether and petroleum ether are extremely flammable, but other common solvents, such as acetone and ethanol, can be dangerous as well. When ventilation is inadequate, the vapors of diethyl ether and other highly volatile liquids can travel a long way; lighting a burner at one end of a lab bench that has an open bottle of ether at its other end has been known to start an ether fire. Learn the location and operation of the fire extinguishers, fire blankets, and safety showers at the first laboratory session.

iii. *Consider all chemicals to be hazardous and minimize your exposure to them.* Never taste chemicals, do not inhale the vapors of volatile chemicals or the dust of finely divided solids, and prevent contact between chemicals and your skin, eyes and clothing. Many chemicals can cause poisoning by ingestion, inhalation, or absorption through the skin. Strong acids and bases, bromine, thionyl chloride, and other corrosive materials can produce severe burns and require special precautions, such as wearing gloves and laboratory coat. Some chemicals cause severe allergic reactions, and others may be carcinogenic (tending to cause cancer) or teratogenic (tending to cause birth defects) by inhalation, ingestion (swallowing) or skin absorption. To prevent accidental ingestion of toxic chemicals, don't bring food or drink into the laboratory or use mouth suction for pipetting, and wash your hands thoroughly after handling any chemical. To prevent inhalation of toxic or carcinogenic chemicals, work under an efficient fume hood or use a gas trap to keep chemical fumes out of the laboratory atmosphere. To prevent contact with corrosive or toxic chemicals, wear appropriate gloves and a laboratory coat. Clean up chemical spills immediately – use a neutralizing agent a plenty of water for acids and bases, and an absorbent for solvents. In case of a major spill, or if the chemical spilled is very corrosive or toxic, notify your instructor before you try to clean it up.

iv. *Exercise great care when working with glass and when inserting or removing thermometers and glass tubing.* Among the most common injuries in a chemistry lab are cuts from broken glass and burns from touching hot glass. Protect your hands with gloves or a towel when inserting glass tubes or thermometers into stoppers or thermometer adapters, and when removing them. Grasp the glass close to the stopper or thermometer adapter and gently twist it in or out.

v. *Wear appropriate clothing in the laboratory.* Wear clothing that is substantial enough to offer some protection against accidental chemical spills, and shoes that can protect you from spilled chemicals and broken glass. Human hair is very flammable, to tie up your hair or wear a hair net while using a burner if you have long hair.

vi. *Dispose of chemicals properly.* For reasons of safety and environmental protection, most organic chemicals shouldn't be washed down the drain. Except when your instructor or an experiment's directions indicate otherwise, place used

organic chemicals and solutions in designated waste containers. Some aqueous solutions can be safely poured down the drain, but consult your instructor if there is any question about the best method for disposing of a particular chemical or solution.

vii. *Never work alone in the laboratory or perform unauthorized experiments.* If you wish to work in the laboratory when no formal lab period is scheduled, you must obtain permission from the instructor and be certain that others will be present while you are working.

Practical Chemistry IV is a second semester, two-credit unit compulsory course for all Bachelor of Science (B.Sc.) Chemistry students. It is a dual practical course addressing the practical aspects necessary for students offering Organic Chemistry II (CHM 203), as well as Physical Chemistry II (CHM 201). Being a practical based course, you are expected to carry out the experiments in your laboratory.

WHAT YOU WILL LEARN IN THIS COURSE

In module 1 of this course you will learn how to prepare common organic compounds, how to purify or analyse (paper layer chromatography) these compounds. Finally, you will learn how to determine the functional groups in organic compounds (qualitative analysis). In module 2, you will deal with experiments in physical chemistry. These include pH measurement, determination of relative molar mass from colligative properties (that is the boiling point, freezing point, vapor pressure, and osmotic pressure), demonstration of partition coefficient in two immiscible solvent, temperature measurement and heat of dissolution, ideal gas law (measuring the molar volume of a gas and the universal gas constant).

THE COURSE AIMS

Generally, the course is aimed at encouraging you to have a practical knowledge of important aspects of courses in organic and physical chemistry.

WORKING THROUGH THIS COURSE

Each unit has specific learning laboratory experiment with specific objectives. Endeavour to achieve these objectives when you go through these experiments. Attend the practical classes and make sure you participate fully. Also go through the objectives after completing the unit to see whether you have understood the concepts treated in the unit.

Read textbooks and other materials which may be provided by the National Open University of Nigeria. Make sure you do not miss the practical classes.

THE COURSE MATERIALS

The main components of the course are:

1. The Course Guide
2. Study Units
3. Laboratory Experiments
4. Tutor-Marked Assignments
5. References/Further Reading

Module 1

Study Section 1: Preparation of esters

Study Section 2: Preparation of aldehydes and ketones

Module 1

Study Section 3: Preparation of aspirin

Study Section 2: Quantitative analysis of common functional groups

1.0 Introduction

2.0 Learning Outcome

3.0 Main Content

3.1 Functional group identification test

3.2 Group Classification

3.3 Functional group classification test

4.0 (i) Self Assessment Questions and Answers

(ii) Class Activity

5.0 Conclusion

6.0 Summary

7.0 References

Module 3

Study Section 1: Verification of Arrhenius and Transition state equations

1.0 Introduction

2.0 Learning Outcome

3.0 Main Content

3.1 Verification of Arrhenius equation

3.2 Verification of Transition state equation

4.0 (i) Self Assessment Questions and Answers

(ii) Class Activity

5.0 Conclusion

6.0 Summary

7.0 References

Module 3

Study Section 2: Refractive index measurements

1.0 Introduction

2.0 Learning Outcome

3.0 Main Content

3.1 Experimental procedures

4.0 (i) Self Assessment Questions and Answers

(ii) Class Activity

Study Section 3: Determination of partition function

1.0 Introduction

2.0 Learning Outcome

3.0 Main Content

3.1 Determination of partition function for benzoic acid on CH_2Cl_2 and water

3.2 Microscale partitioning of a colour indicator

3.3 Macroscale separation of acid, base and neutral compound

4.0 (i) Self Assessment Questions and Answers

(ii) Class Activity

5.0 Conclusion

6.0 Summary

7.0 References

Module 4

Study Session 4: Temperature measurement and heat of dissolution

1.0 Introduction

2.0 Learning Outcome

3.0 Main Content

3.1 Experimental procedure

4.0 (i) Self Assessment Questions and Answers

(ii) Class Activity

5.0 Conclusion

6.0 Summary

7.0 References

PRESENTATION SCHEDULE

As you must have read earlier, this course is practical. It is important you attend the practical classes that will be organised by your study centres and participate. Submit your report on time. You should guard against falling behind in your work.

ASSESSMENT

There are three aspects assessing students' performance in this course. The first is made up practical assessment, second consists of the tutor-marked assignment and third is the written examination.

The practical work you do will account for 20% of your total course work. Your TMA will account for 30% of your total course work. At the end of the course you will need to sit for a final or end of course examination of about two-hour. This examination will count for 50% of your course mark.

SOURCES OF INFORMATION

Corey, E. J. and Cheng, X. (1998). The logic of chemistry synthesis. Wiley, New York
Leonard, J. Lygo, B. and Procter, G. (2013). Advanced practical organic chemistry. 3rd edition. CRC press, UK.

Li, J. J., Pflum, D. A. and Limberakis, C. (2007). Modern synthesis in the Laboratory. CRC press, UK

Richard, O. C., Norman, C. and Coxon, J. M. (2010). Principles of organic synthesis. CRC press, UK

Vogel, A. I. (2011). Tectbook of practical organic chemistry. 3rd edition. Lonoman, UK.

Vogel, A. I., Tatchell, A. R and Furnis, B. S. (1996). Vogel's textbook of practical organic chemistry. 5th Edition. Pearson Edition, UK

http://swc2.hccs.edu/pahlavan/

http://web.me.com/dbyrum/Ris/ChmY2InClassS2/

http://course1.winona.edu/tnalli/spring05/209labs

http://www.sep.alquds.edu/chemistry/scripts/student/

http://cemca.org/andcollege/andcwebsite/subject01/

http://chemistry.slss.ie/resources/downloads/

http://www.chem.wisc.edu/courses

http://www.bc.edu/schools/cas/chemistry/undergrad/org

http://orgchem.colorado.edu/Technique/Procedures/

http://webs.anokaramsey.edu/chemistry/Chem1062

http://www.xula.edu/chemistry/documents

http://www.uncp.edu/home/mcclurem/courses

MAIN COURSE

CONTENTS

MAIN COURSE

CONTENTS **PAGE**

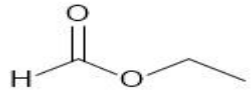
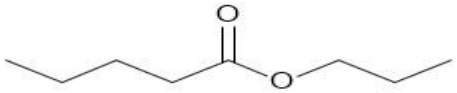
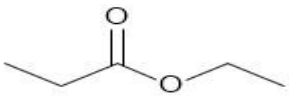
MODULE 1

UNIT 1 PREPARATION OF ESTERS

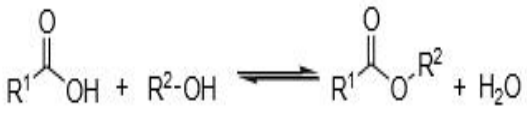
CONTENTS

1.0 INTRODUCTION

Esters are derived from carboxylic acids. A carboxylic acid contains the -COOH group, and in an ester the hydrogen in this group is replaced by a hydrocarbon group such as, CH_3, C_2H_5, etc. This could be an alkyl group like methyl or ethyl, or one containing a benzene ring like phenyl. Esters are widespread in nature and are widely used in industry, notably for flavourings. Example of esters are shown below

	
Ethyl methanoate (ethyl formate) rum flavouring	Propyl pentanoate (n-propyl n-valerate): pineapple flavouring
	
Ethyl butanoate (ethyl butyrate) apple odour	Octyl ethanoate (n-octyl acetate) orange odour

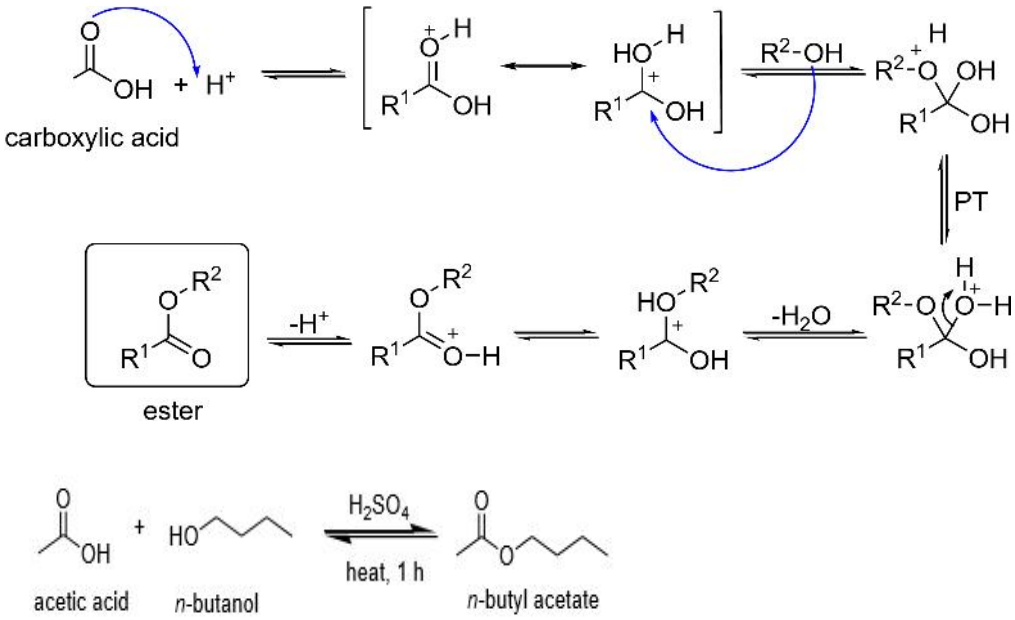
Classical approach to synthesis of an ester is the is the Fischer esterification method, which involves treating a carboxylic acid with an alcohol in the presence of a dehydrating agent:



Strong acids, such as tetraoxosulphate (VI) acid catalyze this reaction. Many other acids are also used. Esterification is highly reversible. The simple reaction of one equivalent each of acid and alcohol gives a mixture of starting materials and products. The yield of the product may be improved using Le Chatelier's principle, which involves,

- using excess of the alcohol (i.e. as a solvent)
- using a dehydrating agent. Tetraoxosulphate (V) acid does not only catalyzes the reaction but sequesters water (a reaction product)
- removal of water by physical means such as an azeotropic distillation with cyclohexane or toluene.

The General mechanism for the reaction is shown below



When an organic acid, R-COOH, is heated with an alcohol, R'-OH, in the presence of a strong mineral acid, the chief organic product is a member of the family of organic compounds known as esters.
The general reaction for the esterification of an organic acid with an alcohol is:
R-COOH + HO-R' ↔ R-CO-OR' + H_2O

In the general reaction, R and R' represent hydrocarbon chains, which may be the same or different. As a specific example, suppose acetic acid, CH_3COOH, is heated with ethyl alcohol, CH_3CH_2OH, in the presence of a mineral acid catalyst. The esterification reaction will be:

CH_3-COOH + HO-CH_2CH_3 ↔ CH_3 -COO-CH_2 CH_3 + H_2O

The ester produced by this reaction (CH_3-COO-CH_2 CH_3) is named *ethyl acetate,* indicating the acid and alcohol from which it is prepared. Esterification is an equilibrium reaction, which means that the reaction does *not* go to completion on its own. Frequently, however, the esters produced are extremely volatile and can be removed from the system by distillation. If the ester is not very easily distilled, it may be possible instead of adding a desiccant to the equilibrium system, thereby removing water from the system and forcing the equilibrium to the right.

Unlike many organic chemical compounds, esters often have very pleasant, fruitlike odors. Many of the odours and flavourings of fruits and flowers are due to the presence of esters in the essential oils of these materials. Table 1 gives some esters with pleasant fragrances, as well as indicating from what alcohol and which acid the ester may be prepared. A fruit or flower generally contains only a few drops of ester, giving a very subtle odour. Usually, the ester is part of some complex mixture of substances, which, taken as a whole, have the aroma attributed to the material. When prepared in the laboratory in relatively large amounts, the ester may seem to have a pronounced chemical odour, and it may be difficult to recognize the fruit or flower that has this aroma. Other examples of esters, their aroma and constituents are shown in Table 1 below

Table 1: Common Esters and their Constituents

Ester	**Aroma**	**Constituents**
n-propyl acetate	Pears	n-propyl alcohol/acetic acid
methyl butyrate	Apples	methyl alcohol/ butyric acid
isobutyl	Rum	isobutyl alcohol/propionic
octyl acetate	Oranges	n-octyl alcohol/acetic acid
methyl	Grapes	Methyl alcohol/2-aminobenzoic
isoamyl acetate	Bananas	isoamyl alcohol/acetic acid
ethyl butyrate	Pineapples	ethyl alcohol/butyric acid
benzyl acetate	Peaches	benzyl alcohol/acetic acid

2.0 OBJECTIVES

By the end of this unit, you should be able:

- what is an ester
- what is esterification
- how to prepare and ester
- how to calculate the amount of ester produced

3.0 MAIN CONTENT

3.1 Preparation of esters

3.1.1 Apparatus/reagents required

Acetic acid (15 ml), n-butanol (11.45 ml), concentrated. sulfuric acid (2 mL) 10 % sodium hydrogenocarbonate solution (10 mL) and anhydrous sodium sulphate (1 g)	heating mantle, Boy elevator 100 mL), round bottle flask, water condenser distillation kit, Buchner funnel, filter paper, separating funnel, boiling chips, grease, gloves.

3.1.3 Experimental procedures

In a 100 mL round-bottom flask, introduce successively acetic acid (15 mL), *n*-butanol (11.5 mL) and concentrated sulfuric acid (~ 2 mL). Next, add a few boiling chips and fit a water condenser lubricated with grease (**Figure 1.1**). The mixture is refluxed by means of a heating mantle for 1 hour, after which the reaction mixture is transferred into a separating flask containing 30 mL of water (**Figure 1.2**). The aqueous layer is isolated and the organic layer is washed first with a 10 % solution of sodium hydrogen trioxocarbonate, $NaHCO_3$ (1 x 10 mL) and then with water (2 x 10 mL). Then, the organic layer is dried over anhydrous sodium sulphate Na_2SO_4 (~ 1 g) and filtered over a Büchner funnel. Finally, the filtrate is distilled slowly and the boiling point recorded (**Figure 1.3**). **Weigh the mass of product (n-butyl acetate) obtained.**

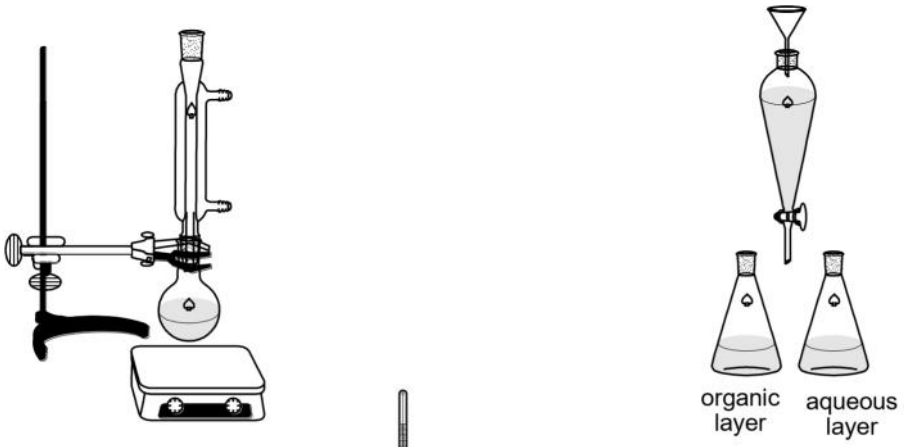


Figure 1.2

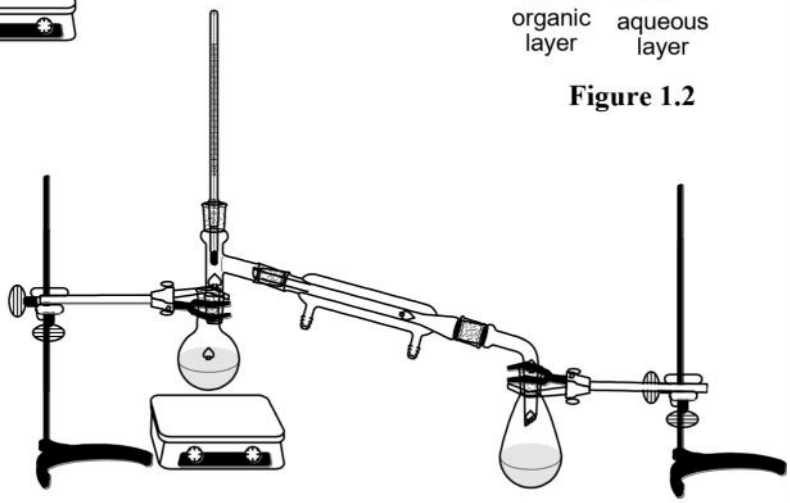
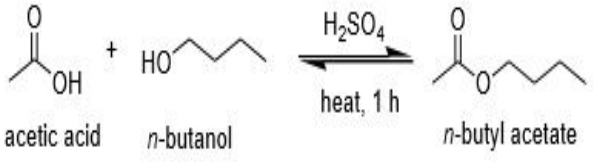


Figure 1.3

Equation for the reaction



Properties of reactants and products are contained in the Table presented below

Compound	**M.W. (g/mol)**	**Density (g/mL)**	**b.p (ºC)**
Acetic acid	60.05	1.049	117-118
n-Butanol	74.12	0.81	116-118
Sulfuric acid, 98 %	98.08	1.84	~ 290
n-Butyl acetate	116.16	0.88	124-126

Mass of product expected (calculated from stoichiometry) = --------
Mass of product obtained = ----------

$$\textbf{Percentage yeild} = \frac{\textbf{Mass of product obtained}}{\textbf{Mass of product expected}} \times \frac{\mathbf{100}}{\mathbf{1}}$$

$= - - - - - - - - -$

SELF-ASSESSMENT EXERCISE

1. Which of the following compounds is an ester?
2. Which of the following is used as catalyst for the esterification of carboxylic acid and alcohol?

    a) Nitrous acid
    b) Sulphuric acid
    c) Sulphurous acid
    d) Nitric acid
3. What will be the product for the given reaction?
    $CH_3OH + CO \rightarrow ?$
    a) Ethyl formate
    b) Methyl formate
    c) Ethyl acetated) Methyl acetate

4. Hydrolysis of ester leads to the formation of which of the following products in basic medium?
    a) Ether and alcohol
    b) Alcohol and sodium carboxylate
    c) Aldehyde and alcohol
    d) Sodium carboxylate

4.0 CONCLUSION

Esters can be prepared by heating an acid with alcohol in the presence of mineral acid as a catalyst.

5.0 SUMMARY

Esters can be found as both natural and artificial products. Esters can be prepared in the laboratory using different materials. In this unit, attempts have been made to explain what esters are and how you can prepare a sample in the laboratory.

6.0 TUTOR-MARKED ASSIGNMENT

Answer the following questions

(1) Why do we use a small amount of mineral acid?
(2) What is the reactant in excess? Justify your answer.
(3) What is the role of sodium hydrogen trioxocarbonate (IV)?
(4) Write the equation of the chemical reaction and the associated mechanism.
(5) What is the role of the distillation?

(6) Compare the recorded boiling point with the literature data. 8) Propose another synthetic method for the preparation of n-butyl acetate.

7.0 REFERENCES/FURTHER READING

Corey, E. J. and Cheng, X. (1998). The logic of chemistry synthesis. Wiley, New York

Leonard, J. Lygo, B. and Procter, G. (2013). Advanced practical organic chemistry. 3rd edition. CRC press, UK.

Li, J. J., Pflum, D. A. and Limberakis, C. (2007). Modern synthesis in the Laboratory. CRC press, UK

Richard, O. C., Norman, C. and Coxon, J. M. (2010). Principles of organic synthesis. CRC press, UK

Vogel, A. I. (2011). Textbook of practical organic chemistry. 3rd edition. Lonoman, UK.

Vogel, A. I., Tatchell, A. R and Furnis, B. S. (1996). Vogel's textbook of practical organic chemistry. 5th Edition. Pearson Edition, UK

UNIT 2 PREPARATION OF ALDEHYDES AND KETONES

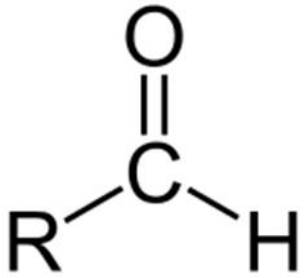
CONTENTS

1.0 INTRODUCTION

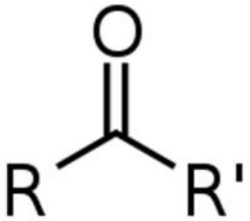
Ketone are very useful organic compounds and occurs naturally in many living organisms. Ketone generation in the form of ribulose-1,5-bisphosphate is one of the steps in photosynthesis and help in the formation of the necessary organic compounds during photosynthesis. Ketones are present as sugars (in living things) and are called ketoses. It is also present in most vertebrates including humans as ketone bodies.

Aldehydes and Ketones are simple organic compounds containing a carbonyl group. Carbonyl group contains carbon-oxygen double bond. These organic compounds are simple because the carbon atom presents in the carbonyl group lack reactive groups such as OH or Cl.

An aldehyde is one of the classes of carbonyl group-containing alkyl group on one end and hydrogen on the other end. The R and Ar denote alkyl or aryl member respectively. In the condensed form, the aldehyde is written as –CHO while its structural formula can be drawn as shown below



On the other hand, ketone is a member of the carbonyl group-containing alkyl or aryl group on both the end of the carbonyl group. The general formula of ketone is RC(=O)R’. In this case, R and R’ are the different carbon containing substituents.



2.0 OBJECTIVES

By the end of this unit, you should be able to:

- know how to prepare aldehyde and ketone
- know the mechanism of the synthesis
- know some properties of aldehyde and ketone
- differentiate between aldehyde and ketones

3.0 MAIN CONTENT

3.1 Preparation methods for Aldehydes and Ketones

i. By oxidation of alcohols

Oxidation of primary and secondary alcohols leads to the formation of aldehydes and ketones. The oxidation is possible with the help of common oxidizing agents are $KMnO_4$, $K_2Cr_2O_7$, and CrO_3. Strong oxidizing agents helps in the oxidation of the primary alcohol to aldehyde then to a carboxylic acid.

Primary alcohols having low molecular weight can undergo oxidation and form aldehydes. The reaction mixture after aldehyde formation can avoid further oxidation if the reaction temperature is modulated so that the boiling point of the aldehyde is lower than the alcohol which helps in the distillation of aldehyde from the reaction mixture soon after its formation. Hence, it is important to maintain the reaction temperature slightly more than 349K (see example below)

$$CH_3CH_2CH_2OH \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3CH_2CH_2CHO$$

Aldehyde and ketone preparation are possible by oxidation of primary and secondary alcohol by agents such as PCC (pyridinium chlorochromate), Collins reagents (Chromium trioxide-pyridine complex), and Cu at 573 K.

$$R - CH_2 - OH \xrightarrow{Collins\ reagent/PCC/Cu\ at\ 573\ K} RCHO$$

$$R - CH(OH) - R' \xrightarrow{Collins\ reagent/PCC/Cu\ at\ 573\ K} RCOR'$$

Collin's reagent or chromium trioxide-pyridine complex is a good oxidizing reagent for conversion of primary alcohol to aldehydes. Additionally, an advantage of Collins reagent is that it helps to cease further

oxidation of aldehydes to carboxylic acids. However, the reaction with Collins reagent is possible in a non-aqueous medium such as CH_2Cl_2. PCC is pyridinium chlorochromate. The mixture of pyridine along with CrO_3 and HCl in dichloromethane leads to the formation of Pyridine chlorochromate or PCC ($C_5H_5NH^+CrO_3\ Cl^-$).
Ketones can be prepared by using similar oxidizing agents from secondary alcohols.

$$RCH(OH)R' + [O] \rightarrow RCOR' + H_2O$$

ii. Dehydrogenation of alcohols

This preparation method applies in case of conversion of volatile alcohols to aldehydes. It is generally used in industrial application. Vapours of alcohol are passed through heavy metal catalysts such as Cu or Ag in this technique. Primary alcohol produces aldehyde whereas secondary alcohol produces ketones, respectively.

For example, alcohols undergo dehydrogenation when vapours of primary alcohol or secondary alcohol pass through copper gauze at a temperature of 573 K. For example, n-propyl alcohol can be converted to propionaldehyde in the dehydrogenation process, as shown below,

$$CH_3CH_2CH_2OH \xrightarrow{Cu/573\ K} CH_3CH_2CH_2CHO + H_2$$

It is possible to use different metal catalysts such as copper or silver under heating conditions during dehydrogenation of alcohol.

This is one of the better methods for preparation of aldehydes and ketones because further oxidation to carboxylic acids is not possible.

iii. Preparation from hydrocarbons

This method is further divided into two separate methods. They are

- By ozonolysis of alkenes
- By hydration of alkynes

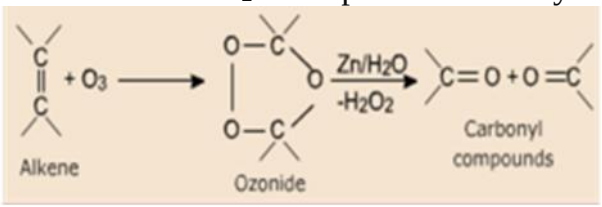
(iv) Ozonolysis of alkenes

Formation of aldehyde and ketone is possible by ozonolysis of alkenes. Ozonolysis is a reaction method in which addition of ozone molecules or O_3 to an alkene compound leads to the formation of ozonide. Reduction of the ozonide compound with the help of zinc dust and water produces the smaller molecules, which in this case will be the respective aldehydes and ketones.

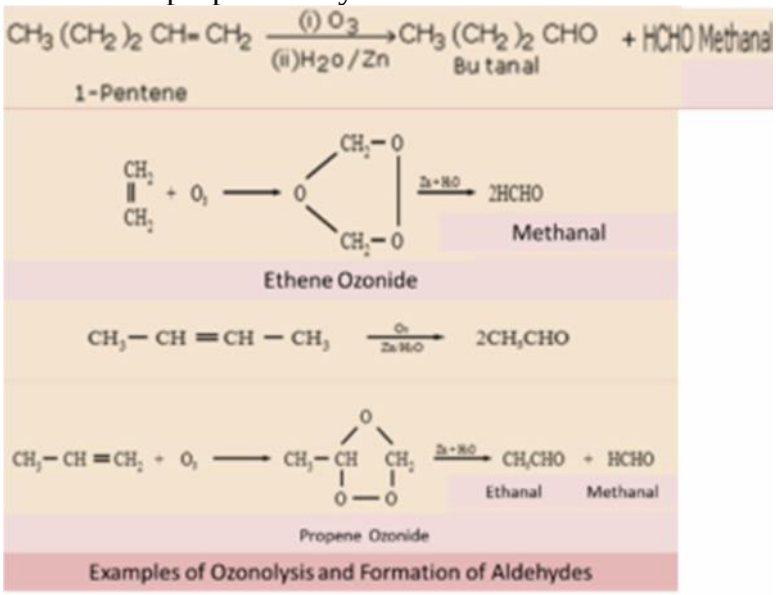
The reaction produces aldehydes, ketones and in some cases both the compounds on the basis of the substitution arrangement of the alkene compounds.

Refer to the example below to observe how an alkene on ozonolysis leads to the formation of the ozonide compound. This compound

further undergoes subsequent reductive cleavage with Zn dust and water or H_2/Pd to produce carbonyl compounds.

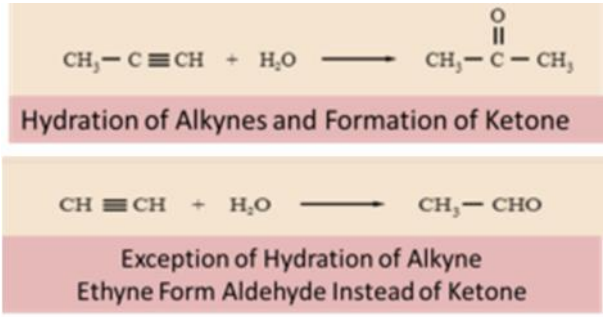


Zinc Dust helps in removing the H_2O_2 thereby ceasing the chances of further oxidation of carbonyl compounds to acids. Refer to the examples below to see how choosing a suitable alkene for this method helps to achieve the proper aldehyde or ketone.



(v) **Hydration of alkynes**

Alkynes follow Markovnikov's rule in the presence of a proper catalyst to produce ketones. All alkynes react with water in the presence of $HgSO_4$ and H_2SO_4 to form ketones. However, the reaction of ethyne with water in the presence of the catalyst ($HgSO_4$ and H_2SO_4) leads to the formation of acetaldehyde. This is an only exception where alkyne on hydration produces acetaldehyde. Rest all the alkyne on hydration produces ketones.

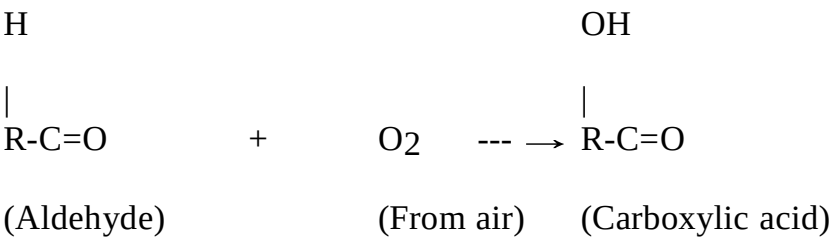


Physical properties

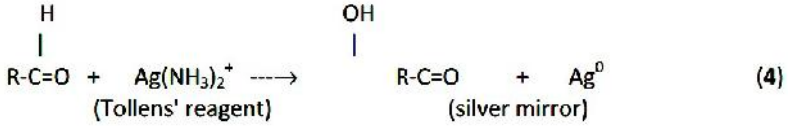
Because they contain the polar carbonyl group, aldehydes and ketones are polar compounds. However, they cannot form hydrogen bonds one to another, as do alcohols. Therefore, the boiling points of aldehydes and ketones are less than those of alcohols of similar molecular weight, but greater than those of hydrocarbons of similar molecular weight. The solubility of aldehydes and ketones in H_2O is significant if they contain less than five carbons. This is because hydrogen bonds to the water molecules are formed. Acetaldehyde (ethanal, CH_3CHO) and acetone are miscible with water in all proportions.

Chemical properties

Aldehydes are easily oxidized a fact due to the presence of the hydrogen attached to the carbonyl group (this is not present in ketones, which are less easily oxidized). Oxidation of aldehydes yields carboxylic acids. Even air will oxidize an aldehyde (eq. 3).

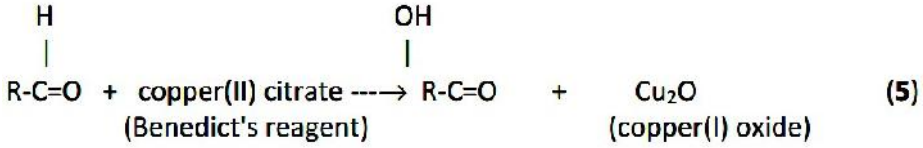


Other weak oxidizing agents can bring about this reaction. One of these is **Tollens' reagent**, a basic (OH^-) solution of the silver complex ion, $Ag(NH_3)^+$. The reaction produces metallic silver (Ag^0), which often forms a shiny "mirror" on the sides of the container (eq. 4).



Tollens' reagent is used to detect the presence of aldehydes. A solution of Benedict's reagent can also oxidize aldehydes. This solution consists

of a basic (OH^-) solution of copper (II) citrate (whose complex composition cannot be represented by a simple formula):



The conversion of the clear, blue copper (II) citrate to insoluble, reddish copper(I)oxide indicates a positive test. The reaction occurs not only with simple aldehydes but also with "reducing sugars" such as glucose.

3.1 Preparation of acetone from 2-propanol

Acetone, or propanone, is the organic compound with the general formula, $(CH_3)_2CO$. It is a colouless, volatile, flammable liquid and is the simplest and smallest ketone.
Acetone is miscible with water and serves as an important solvent for various purposes including cleaning purposes in laboratories. Acetone is a common building block in organic chemistry. Familiar household uses of acetone are as the active ingredient in nail polish removal and as paint thinner.

3.1.1 Materials

- 20 mL 70% 2-propanol (isopropyl alcohol)
- Distilled water
- 100 mL acidic dichromate ($K_2Cr_2O_7/H_2SO_4$) solution
- Distillation apparatus including thermometer
- Ice/water bath.

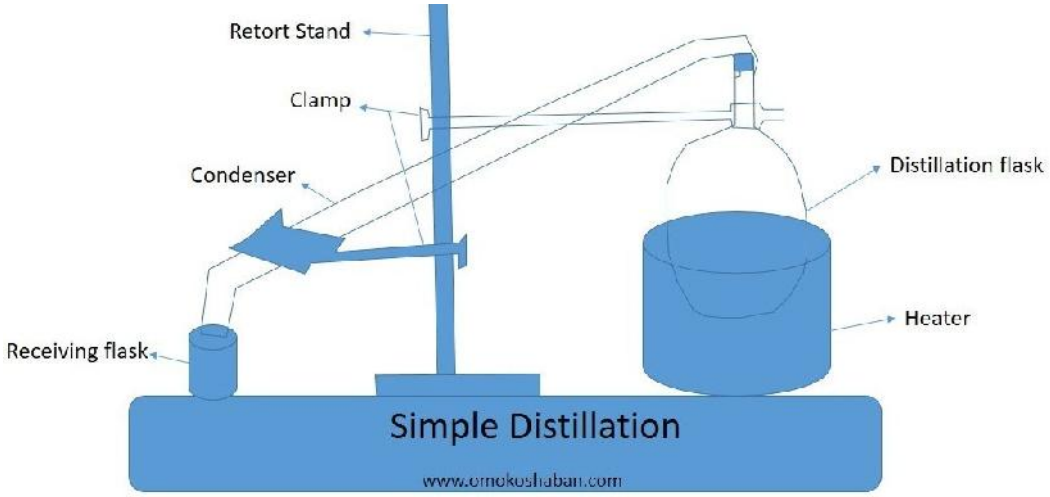
3.1.2 Experimental procedure

Measure 20 ml of 70% of 2-propanol into 250 ml beaker, add 20 ml of distilled water stir the mixture, on the process the mixture will raise in temperature, then cool the temperature by place the 250 ml beaker mixture on the 500 ml prepared ice bath, allow the temperature to cool to 10 °C.

Without removing the prepared mixture from the water bath, add 100 ml of dichromate ($K_2Cr_2O_7/H_2SO_4$) solution, wait in a few second the solution will turn dark, with sudden increase of the temperature to about 56 to 65 °C.

(Caution: the solution is corrosive)
Now stir the mixture with stirring rode while still on the ice bath until the temperature fall to 50 °C. The mixture is now set to distilled acetone out.

Turn the mixture into a 250 ml beaker or a larger distilling flask using funnel to avoid the mixture been spilled away.
Now set up a distillation apparatus as show bellow to distilled out the acetone



Heat the mixture gently, the liquid should start boiling after 10 to 15 minutes, and acetone will start dropping on the receiver. Take note of the temperature at which first drop appear and record it down, continue with the distillation until 5ml of acetone is collected and recorded

3.2 Oxidation of Ethanol to Ethanal

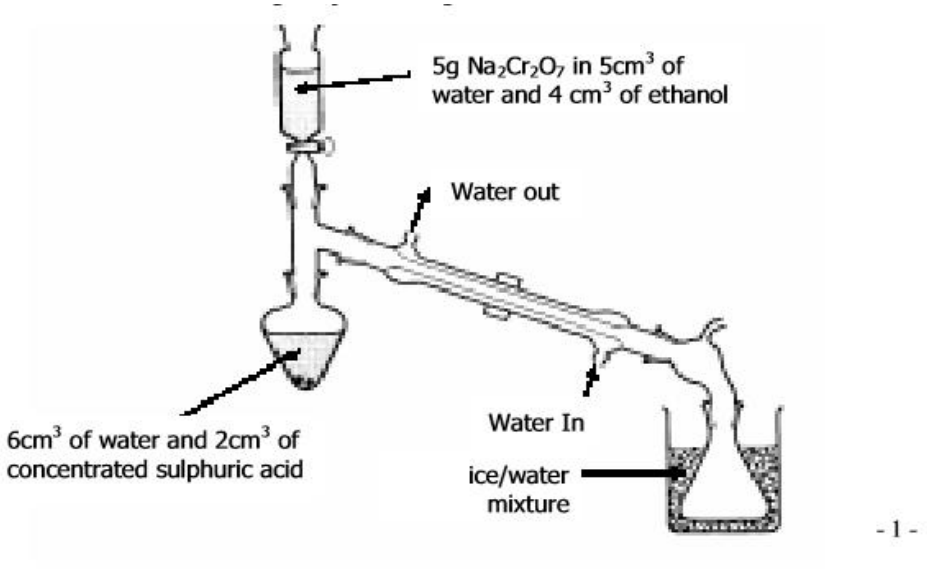
In this experiment, you will study how to prepare acetaldehyde from ethanol

3.2.1 Materials:

- 10 ml Ethanol C_2H_5OH
- Cu wire

3.2.2 Experimental procedure

To 6 cm^3 of water in the pear-shaped flask, add 2 cm^3 of concentrated sulphuric acid and set up the apparatus as shown below, but with a stopper in place of the dropping funnel. Make sure that all the glass joints are greased.



- 1 -

- Make up a solution containing 5 g of sodium dichromate in 5 cm^3 of water, add 4 cm^3 of ethanol and pour the mixture into the dropping funnel.
- Warm the acid in the pear-shaped flask until it is almost boiling and turn off the electrothermal mantle
- Carefully remove the stopper and put the dropping funnel in position, as shown in the diagram below.
- Add the mixture containing the ethanol at such a rate as to maintain the boiling of the mixture in the pear-shaped flask. Collect the distillate and write down all observation
- Carry out the following tests on the distillate and record your observation.

Put 5 cm^3 of 2,4-dinitrophenylhydrazine in a test tube and cautiously add 5 drops of the distillate. Record your observation.

SELF ASSESSMENT EXERCISE

i. What is the general structure and identify the functional group in each
ii. Give reasons why aldehydes is more reactive than ketones
iii. What is aldehyde and ketones simple organic compounds?

4.0 CONCLUSION

Aldehydes and ketones can be prepared by oxidation of alcohol, dehydrogenation of alcohol, from hydrocarbon or by ozonolysis of alkene

5.0 SUMMARY

Aldehydes and ketones are polar compounds which you can prepare in your laboratory.

In this unit, attempt has been made to explain some properties of aldehydes and ketones and some methods of preparing these compounds in the laboratory.

6.0 TUTOR-MARKED ASSIGNMENT

1. Identify and name the reagents that are useful in carrying out the following reactions
   - Cyclohexanol to cyclohexanone-
   - Hexan-1-ol to hexanal
   - But-2-ene to ethanol
   - Allyl alcohol to propanal
2. Under what condition can the ethanal be oxidized further?
3. If the ethanal is oxidized, what is the IUPAC name of the new product. Hence write a chemical reaction for both possibilities., i.e. oxidation of ethanol to ethanal and for further oxidation of ethanal
4. What was your observation in the test experiment involving 2,4-dinitrophenyl hydrazine. Explain the findings.

7.0 REFERENCES/FURTHER READING

Corey, E. J. and Cheng, X. (1998). The logic of chemistry synthesis. Wiley, New York

Leonard, J. Lygo, B. and Procter, G. (2013). Advanced practical organic chemistry. 3rd edition. CRC press, UK.

Li, J. J., Pflum, D. A. and Limberakis, C. (2007). Modern synthesis in the Laboratory. CRC press, UK

Richard, O. C., Norman, C. and Coxon, J. M. (2010). Principles of organic synthesis. CRC press, UK

Vogel, A. I. (2011). Tectbook of practical organic chemistry. 3rd edition. Lonoman, UK.

Vogel, A. I., Tatchell, A. R and Furnis, B. S. (1996). Vogel's textbook of practical organic chemistry. 5th Edition. Pearson Edition, UK

UNIT 3 PREPARATION OF ASPIRIN

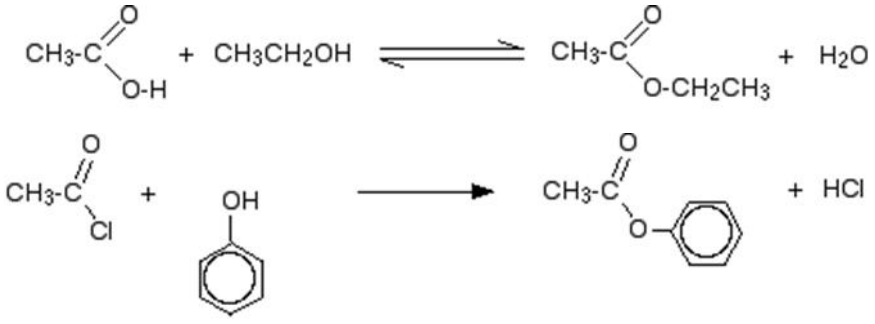
CONTENTS

1.0 INTRODUCTION

The classic synthesis of esters is the Fischer-Speier esterification, employed in experiment 1. However, several other methods are available, one being often favoured other another depending on the problems needing to be tackled. The method used in this experiment is the alcoholysis of an acid anhydride. Alternative methods include the following:

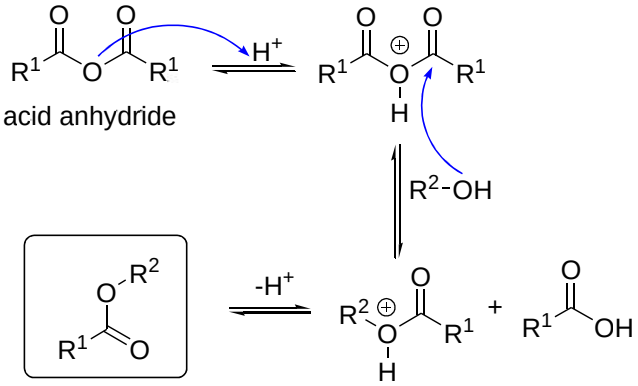
- alcoholysis of acyl chlorides
- Steglish esterification
- transesterification
- Favorskii rearrangement of α-haloketones in presence of base
- nucleophilic displacement of alkyl halides with carboxylic acid salts
- Baeyer-Villiger oxidation of ketones with peroxides
- Pinner reaction of nitriles with an alcohol

Alcohols react with acyl chlorides or acid anhydrides to give esters:

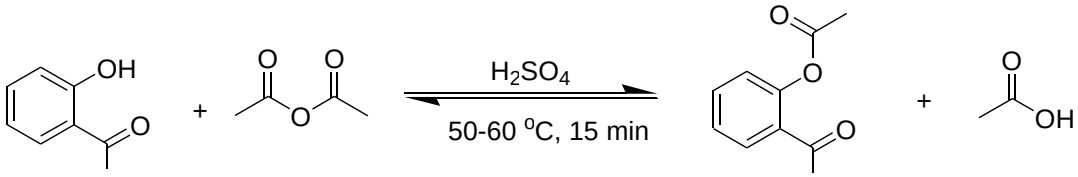


These reactions are irreversible, thus simplifying workup. Since acyl chlorides and acid anhydrides react also with water, anhydrous conditions are preferred. The analogous acylation of amines that produces amides is less sensitive towards water because amines are stronger nucleophiles and react more rapidly.

1.1 Mechanism of reaction



1.2` Reaction



Compound	M.W. (g/mol)	Density (g/mL)	b.p (°C)
Salicylic acid	138.12	/	211
Acetic anhydride	102.09	1.08	138-140
Sulfuric acid, 98 %	98.08	1.84	~ 290
Aspirin	180.16	/	/

2.0 OBJECTIVES

By the unit of this, you should be able to:

- Synthesize aspirin from its corresponding acid anhydride and alcohol
- Compare two different synthetic routes for the preparation of esters

3.0 MAIN CONTENT

3.1 Preparation of aspirin

3.1.2 Apparatus and reagents required

Reagents	Apparatus
salicylic acid (2 g) acetic anhydride (3 mL) conc. sulfuric acid (1 drop) methanol or ethanol (6 mL) anhydrous sodium sulphate (1 g)	50 mL beaker thermometer glass rod Büchner funnel, filter paper bain-marie melting point apparatus

3.2 Experimental procedures

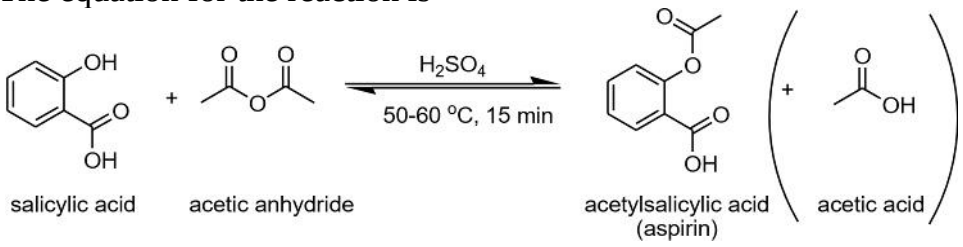
In a 50 mL beaker, introduce salicylic acid (2 g) and acetic anhydride (3 mL). Then, add 1 drop of concentrated sulfuric acid and stir the mixture. Heat by means of a bain-marie for 15 min while stirring continually with a glass rod.

Add 35 mL of water, swirl the mixture and carry out a vacuum filtration. **Weigh the mass of crude product (aspirin) obtained.**

The crude acetylsalicylic acid is purified by recrystallisation. It is dissolved in hot methanol or ethanol (6 mL). The resulting solution is poured into 20 mL of hot water. If a precipitation occurs, heat the mixture until complete dissolution and then let it cool down slowly (in the air, next water, then ice water). After recrystallisation, the solid is filtered and dried. **Weigh the mass of pure product (aspirin) obtained.**

3.3 Reporting

The equation for the reaction is



Compound	M.W. (g/mol)	Density (g/mL)	volume (mL)	mass (g)	n (mmol)
Salicylic acid	138.12	/	/	2.00	14.5
Acetic anhydride	102.09	1.08	3	3.24	31.7
Aspirin	180.16	/	/	**2.61**	14.5

SELF-ASSESSMENT EXERCISE

i. For the synthesis of aspirin, how do you calculate the percent yield if the reaction produces 4.70 grams of aspirin. The reaction, using molecular formulas is $C_7H_6O_3 + C_4H_6O_3 \rightarrow C_9H_8O_4 + C_2H_4O_2$. The relevant molecular weights are 180 grams per mole for aspirin, and 138 grams per mole for salicylic acid. An excess of acetic anhydride is used in this preparation. The limiting reagent for this reaction will be salicylic acid.

4.0 CONCLUSION

Aspirin can be prepared by the reaction of salicylic acid with acetic anhydride

5.0 SUMMARY

The percentage yield of aspirin synthesized from the reaction of salicylic acids and acetic anhydride depends on several reaction conditions such as temperature, concentration, etc.

Aspirin is one of the most common analgesic and can be prepared by esterification reaction as explained in this experiment. One of the most challenging tasks involved in converting the laboratory prepared product into consumable one is purification process.

6.0 TUTOR-MARKED ASSIGNMENT

From your experimental results, complete the following information

Mass of pure product expected: _____ g

Mass of crude product obtained: _____ g

Mass of pure product obtained: _____ g

$$Percentage\ yeild\ in\ crude\ product = \frac{Mass\ of\ crude\ product\ obtaine}{Mass\ of\ pure\ product\ expected} d \times \frac{100}{1}$$

$$\boldsymbol{Percentage\ yeild\ in\ pure\ product} = \frac{Mass\ of\ pure\ product\ obtained}{Mass\ of\ pure\ product\ expected} \times \frac{100}{1}$$

7.0 REFERENCES/FURTHER READING

Corey, E. J. and Cheng, X. (1998). The logic of chemistry synthesis. Wiley, New York

Leonard, J. Lygo, B. and Procter, G. (2013). Advanced practical organic chemistry. 3rd edition. CRC press, UK.

Li, J. J., Pflum, D. A. and Limberakis, C. (2007). Modern synthesis in the Laboratory. CRC press, UK

Richard, O. C., Norman, C. and Coxon, J. M. (2010). Principles of organic synthesis. CRC press, UK

Vogel, A. I. (2011). Tectbook of practical organic chemistry. 3rd edition. Lonoman, UK.

Vogel, A. I., Tatchell, A. R and Furnis, B. S. (1996). Vogel's textbook of practical organic chemistry. 5th Edition. Pearson Edition, UK

UNIT 4 PAPER CHROMATOGRAPHY

CONTENTS

1.0 INTRODUCTION

Paper chromatography has proved to be very successful in the analysis of chemical compound and lipid sample in particular. In paper chromatography, the sample mixture is applied to a piece of filter paper, the edge of the paper is immersed in a solvent, and the solvent moves up the paper by capillary action. It is the simplest and commonest form of liquid-liquid chromatography. Whatman filter paper or commercially prepared cellulose plates are used for chromatographic separation.

The paper commonly used consists of highly purified cellulose. Cellulose, a homopolysaccharide of glucose. Contains several thousand anhydro-glucose units-linked through oxygen atoms. The paper exhibits weak ion exchange and adsorptive properties.

Modified forms of paper have been produced in which the paper has been impregnated with alumina, silica gel, and an ion-exchange resin, etc.
The chemical composition of Whatman filter paper no: 1 is: a-cellulose (98 to 99%), b-cellulose (0.3 to 1%), Pentosans (0.4 to 0.8%), Ash (0.07 to 0.1%) & ether soluble matter (0.015 to 0.1%).

There are two main techniques, which may be employed for the development of paper Chromatograms. Ascending techniques, descending techniques, radial development and two-dimensional chromatography.

The ratio of the distance travelled by a component (i.e. amino acid) to that travelled by the solvent front, both measured from the marked point of the application of the mixture, is called the "Resolution front (Rf)" value for that component.

$$R_f = \frac{Distance\ from\ origin\ run\ by\ the\ compund}{Distance\ from\ origin\ run\ by\ the\ solvent}$$

The filter paper strip may be sprayed with ninhydrin and heated so that the coloured spots showing the location of amino acids may develop. The colour densities of these spots may be measured with a recording(or) reflectance photometer device.

2.0 OBJECTIVES

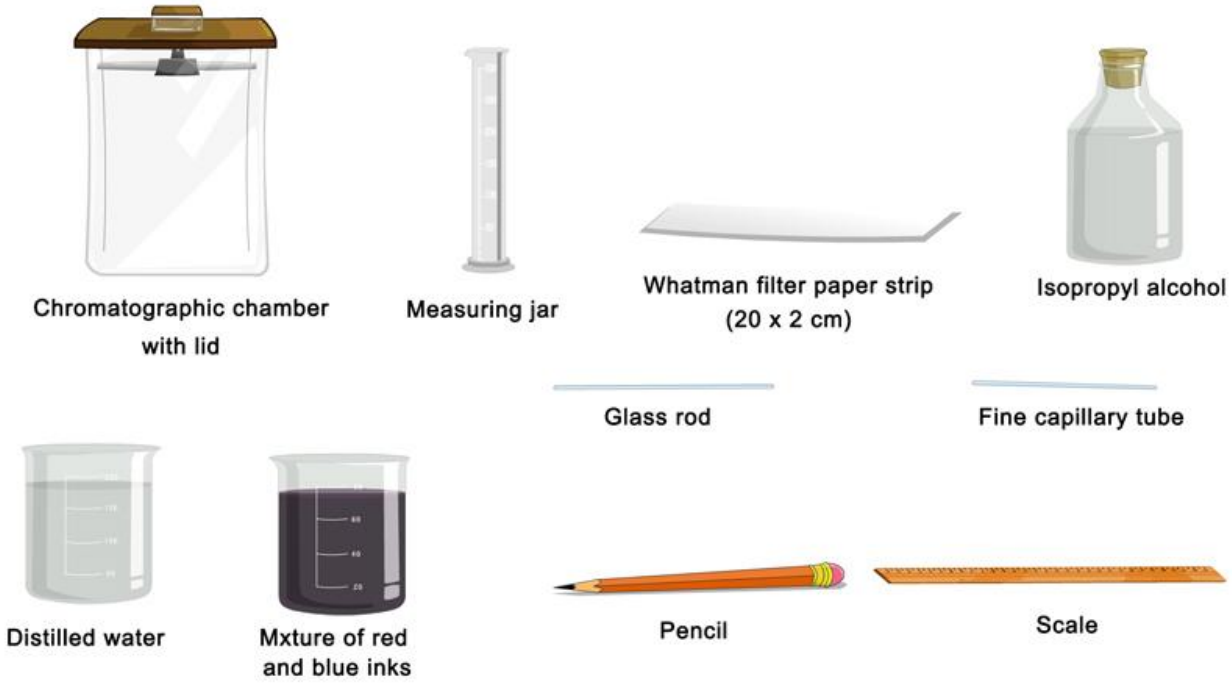
By the end of this, you should be able to:

- understand what is chromatography and paper chromatography
- applied paper chromatography to separate components of ink and paint
- know how to calculate R_f value and its significant

3.0 MAIN CONTENT

3.1 Separation of components from a mixture of red and blue Inks

3.1.1 Materials Required



3.1.2 Experimental procedures

1. Take a Whatman filter paper strip and using a pencil draw a horizontal line 4 cm from one end of the paper. Then draw another line lengthwise (vertically) from the center of the paper. Name the point at which the two lines intersect as P.
2. Using a fine capillary tube, put a drop of the mixture of red and blue inks at the point P. Let it dry in air.

3. Put another drop on the same spot and dry again, so that the spot is rich in the mixture.
4. Pour equal amounts of isopropyl alcohol and distilled water into a chromatographic chamber and mix it well using a glass rod. This is used as the solvent.
5. Suspend the filter paper vertically in the chromatographic chamber containing the solvent in such a way that the pencil line remains about 2cm above the solvent level.
6. Close the jar with its lid and keep it undisturbed.
7. Notice the rising solvent along with the red and blue inks. After the solvent has risen about 15 cm you will notice two different spots of blue and red colors on the filter paper.
8. Take the filter paper out of the jar and using a pencil mark the distance that the solvent has risen on the paper. This is called the solvent front.
9. Dry the filter paper and put pencil marks at the center of the red and blue ink spots.
10. Measure the distance of the two spots from the original line and the distance of the solvent from the original line.
11. Calculate the Rf values of the red and blue inks using the formula,

$$R_f = \frac{\text{Distance travelled by the component from the original line}}{\text{Distance travelled by the solvent from the original line}}$$

1. Observation

Observations can be recorded as shown.

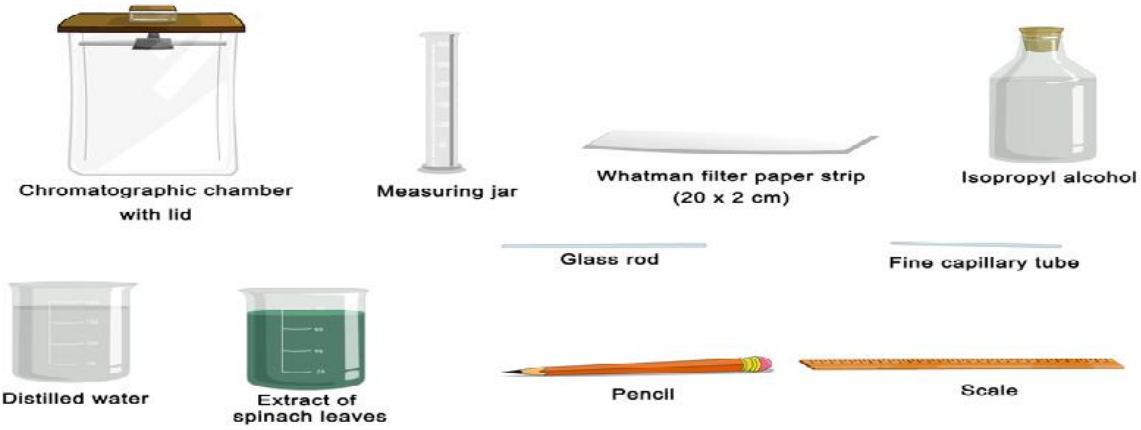
SI No.	Components	Distance travelled by the component from the original line (cm)	Distance travelled by the solvent from the original line (cm)	R_f value
1.	Red			
2.	Blue			

2. Inference

- R_f value of red ink = ……
- R_f value of blue ink =3.2. Separation of pigments from the extract of spinach leaves

3.2 Separation of component of plant

3.2.1 Materials Required



3.2.2 Experimental procedures

1. Take a Whatman filter paper strip and using a pencil draw a horizontal line 4cm from one end of the paper. Then draw another line lengthwise (vertically) from the center of the paper. Name the point at which the two lines intersect as P.
2. Using a fine capillary tube, put a drop of the extract of spinach leaves at the point P. Let it dry in air.
3. Put another drop on the same spot and dry again, so that the spot is rich in the leaf extract.
4. Pour equal amounts of isopropyl alcohol and distilled water into a chromatographic chamber and mix it well using a glass rod. This is used as the solvent.
5. Suspend the filter paper vertically in the chromatographic chamber containing the solvent in such a way that the pencil line remains about 2cm above the solvent level.
6. Close the jar with its lid and keep it undisturbed.
7. Notice the rising solvent along with the colored components of the leaf extract.
8. After the solvent has risen to about 15 cm you will notice two different spots of colored components on the filter paper.
9. Take the filter paper out of the jar and using a pencil mark the distance that the solvent has risen on the paper. This is called the solvent front.
10. Dry the filter paper and put pencil marks at the center of each spot.
11. Measure the distance of each spot from the original line and the distance of the solvent front from the original line.
12. Calculate the Rf values of different components of leaf extract by using the formula,

$$R_f = \frac{\text{Distance travelled by the component from the original line}}{\text{Distance travelled by the solvent from the original line}}$$

Observations can be recorded as shown.

S/N	**Component**	**Distance travelled by the component from the original line (cm)**	Distance travelled by the solvent from the original line (cm)	R_f value
1.	Orange (Carotene)			
2.	Yellow (Xanthophyll)			
3.	Light green (Chlorophyll a)			
4.	Dark green (Xanthophyll)			

3. Inference

- R_f value of orange (Carotene) = ……
- R_f value of Yellow (Xanthophyll) = …….
- R_f value of Light green (Chlorophyll a) = …….

R_f value of Dark green (Chlorophyll b) = …….

SELF ASSESSMENT EXERCISE

i. What are the suitable solvents for the separation of plant pigments with thin layer chromatography

ii. Why do we have two spots (two R_f values) for methionine during paper chromatography

4.0 CONCLUSION

The component of ink, pigments and other coloured components can be identified and separated by paper chromatography technique.

5.0 SUMMARY

In this unit, attempts have been made to:

- explain the theory of thin layer chromatography
- describe the basic technique method of paper chromatography

- describe an experimental procedure of paper chromatography.

Paper chromatography is the simplest and cheapest chromatography technique. It is significant because it can be use to gather baseline information about a mixture prior to further experimental investigation.

7.0TUTOR-MARKED ASSIGNMENT

1. What is the main advantage of thin layer chromatography over paper chromatography?
2. Explain how your observations of the paper chromatogram led to the identification of the components of the unknown amino acid

7.0 REFERENCES/FURTHER READING

Corey, E. J. and Cheng, X. (1998). The logic of chemistry synthesis. Wiley, New York

Leonard, J. Lygo, B. and Procter, G. (2013). Advanced practical organic chemistry. 3rd edition. CRC press, UK.

Li, J. J., Pflum, D. A. and Limberakis, C. (2007). Modern synthesis in the Laboratory. CRC press, UK

Richard, O. C., Norman, C. and Coxon, J. M. (2010). Principles of organic synthesis. CRC press, UK

Vogel, A. I. (2011). Tectbook of practical organic chemistry. 3rd edition. Lonoman, UK.

Vogel, A. I., Tatchell, A. R and Furnis, B. S. (1996). Vogel's textbook of practical organic chemistry. 5th Edition. Pearson Edition, UK

MODULE 2

UNIT 1 DEHYDRATION OF ALCOHOL (CYCLOHEXANOL)

CONTENTS

1.0 INTRODUCTION

There are four basic types of chemical reactions in organic chemistry: **combination**, **elimination**, **substitution**, and **rearrangement**.

The dehydration of alcohols to give alkenes is an important transformation and is an example of elimination reaction. Strong mineral acids such as sulphuric and phosphoric acid catalyze the reaction.

Dehydration of an alcohol can follow either the E2 or the E1 mechanism. However, in each case, acid is required as a catalyst, because OH- is a strong base, it is a poor leaving group, but HOH is a weaker base, and a better leaving group. Adding a strong acid, such as H_2SO_4, to the mixture allows protonation of the -OH group to give water as a leaving group. Once this protonation occurs, the mechanism that is followed depends on the nature of the R group. 1-pentanol (a 1° alcohol), dissociation of water would produce the very unstable 1° carbocation, so we would project that elimination via the E1 mechanism (with carbocation intermediate) will not occur. As a result, reaction would be expected to proceed via the E2 elimination mechanism. However, for 2-pentanol, dissociation of water produces the more stable 2° carbocation. Because water is not a very strong base, the competing E2 mechanism will be slow, which will allow the E1 mechanism to proceed faster for 2-pentanol.

The mechanism below depicts reaction by E2 mechanism to product, in a single, concerted step, elimination, producing an alkene.

The only product, via an E2 reaction mechanism, would be 1-pentene.

E1 mechanism for 2- propanol

Step 1: An acid/base reaction. Protonation of the alcoholic oxygen to make a better leaving group. This step is very fast and reversible. The lone pairs on the oxygen make it a Lewis base.

Step 2: Cleavage of the C-O bond allows the loss of the good leaving group, a neutral water molecule, to give a carbocation intermediate. This is the rate determining step (bond breaking is endothermic)

Step 3: An acid/base reaction. Deprotonation by a base (a water molecule) from a C atom adjacent to the carbocation center leads to the creation of the C=C.

The dehydration reaction will be illustrated by the conversion of cyclohexanol to cyclohexene. The choice of cyclohexanol as starting material is based on the following considerations:

(a) Because of its structure, cyclohexene can give only one alkene upon dehydration, normally cyclohexene.

(b) The rate of dehydration of cyclohexanol using 85% phosphoric acid is conveniently fast.

(c) The product is easily purified by distillation at a readily accessible temperature, (83^{o}C).

(d) When heated with strong acids catalysts (most commonly H_2SO_4, H_3PO_4), alcohols typically undergo 1,2-elimination reactions to generate an alkene and water. Also known as dehydration since it involves the removal of a molecule of water. Alcohol relative reactivity order: $3^{o} > 2^{o} > 1^{o}$

(e) Regioselectivity: major product is usually the more highly substituted alkene (alkene stability) **Zaitsev's Rule.**

(f) Stereoselectivity: trans Æ cis- again controlled by stability

(g) Reaction usually proceeds via an E1 mechanism which proceeds via a carbocation intermediate, which can often undergo rearrangement.

(h) Primary alcohols will proceed via an E2 mechanism since the primary carbocation is highly unfavorable.

(i) Other common strong acids such as HCl, HBr or HI are less suitable catalysts as nucleophilic substitution reactions will probably interfere.

2.0 OBJECTIVES

By the end of this, you should be able to:

- understand how alcohol can be dehydrated
- prepare cyclohexene through acid catalyzed elimination of water from cyclohexanol (dehydration)

3.0 MAIN CONTENT

3.1 Preparation of cyclohexene

3.1.1 Apparatus and reagents required

Reagents	Apparatus
cyclohexanol 85% phosphoric acid, H_3PO_4 (or conc. H_2SO_4) 10% $NaHSO_3$ cold 0.50 % $KMnO_4$ Br_2/CCl_4 (25 mL, 50 mL) $CaCl_2$ (drying agent) Saturated NaCl solution Grease	simple distillation set up beakers (150mL, 250mL) round bottom flask condenser ice thermometer separatory funnel Glass adaptor thermometer adaptor heating mantle Erlenmeyer flask (50 mL) 10-mL graduated cylinder

3.1.2 Experimental procedures

Safety note

Caution: Cyclohexanol is a volatile and flammable liquid and is an irritant. No flames will be allowed in the lab. Wear gloves while handling these chemicals. Concentrated phosphoric acid (or sulphuric acid) is strongly corrosive and toxic -- wear gloves while handling it, and be sure to wash your gloves and your hands immediately after handling it. Sodium sulfate is an irritant -- gloves are recommended.

Procedure - Set up a simple distillation as shown below. Add 8.00 ml (D = 0.96 g/ml) of cyclohexanol and 2 ml of concentrated sulphuric acid (or 5 ml of concentrated phosphoric acid) to a 50 -ml round-bottomed flask. Mix the content thoroughly by swirling before connecting the flask to the distillation setup as shown in Fig.

6.1. Add two boiling stones and heat the flask gently so that the temperature of the distilling vapor does not exceed 100 0C.

Continue the distillation until only a few milliliters (< 2 ml) of high-boiling residue remain in the flask. If white fumes appear near the end of the distillation, stop heating a once by lowering the heating mantle. (NOTE - these fumes are oxides of sulfur, SO_2 , if sulphuric acid is being used).

Note that the distillate in the receiver consists of two layers. Transfer the distillate to a small separatory funnel and add 2 ml of saturated sodium chloride solution (to decrease the solubility of cyclohexene in the water layer), then add drop-by-drop 2 ml of 10% sodium bicarbonate solution (to neutralise the traces of any remaining unreacted acid). Swirl or shake the mixture gently. Allow the layers to separate, and then draw off and discard the lower layer (aqueous layer). Pour the upper layer (organic layer - crude cyclohexene) out the top of the separatory funnel into a small, dry 50- ml Erlenmeyer flask. Add half a teaspoon of anhydrous calcium chloride (used to dry, remove, traces of water) to the cyclohexene and allow it to stand for 10-15 min, swirling it occasionally. The product should be clear, not cloudy

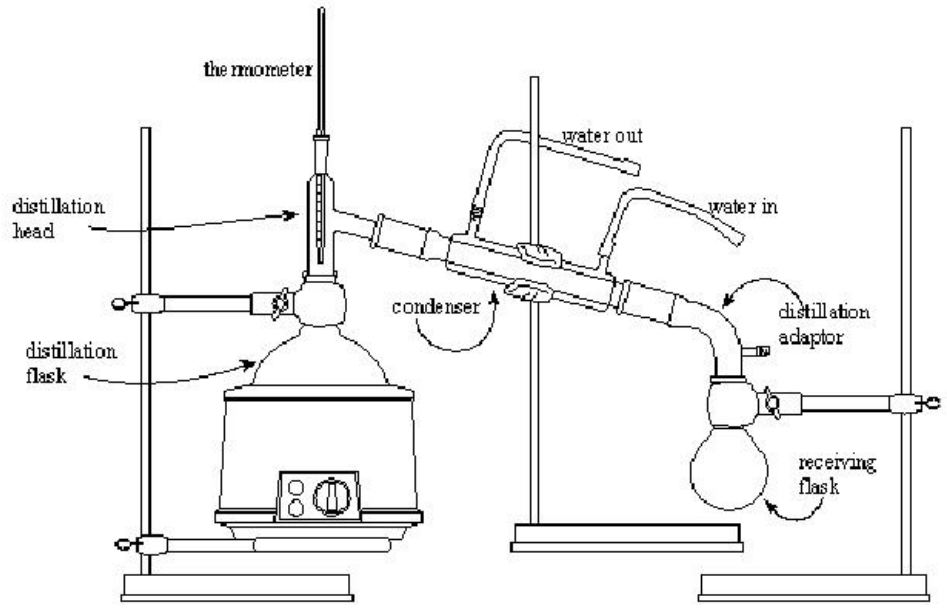


Fig. 1: A Simple Distillation Set Up

3.1.3 The product analysis

(I) Baeyer (cold $KMnO_4$) test - To make sure the product is alkene, test your product with potassium permanganate solution, which is a test for the presence of double bond in

compound Potassium permanganate, a purple solution loses colour with alkenes and forms manganese dioxide, a brown precipitate.

Place 5-6 drops of your alkene product in a small test tube and add 1-2 drops of KMnO4 solution. Swirl the tube to mix the reagents and leave it for observations. Record your observations.

(II) Brominating test - Place 5-10 drops of your alkene product in a small test tube and test with drop- wise bromine (deculturation) for observations. Record your observations and explain your observations

SELF ASSESSMENT EXERCISE

Explain the side reactions when cyclohexanol is used to prepare cyclohexene

4.0 CONCLUSION

Cyclohexene can be prepared through acid catalyzed elimination of water from cyclohexanol (dehydration)

5.0 SUMMARY

Dehydration of an alcohol is a common method of introducing unsaturation into an organic compound. This type of reaction belongs to the important class of organic reactions called elimination reactions. In the elimination of water from an alcohol, the more highly substituted alkene product is formed.

In this study section you have carried out an experiment in which an alkene was formed through the dehydration of alcohol.

6.0 TUTOR-MARKED ASSIGNMENT

1. If 0.138g of cyclohexene (C6H10) was obtained from 0.240g of cyclohexanol ($C_6H_{12}0$), what is the percentage yield of cyclohexene?
2. If in dehydration experiment of 20.0 mL Cyclohexanol, 12.0 g cyclohexene obtained, calculate the theoretical and percentage of cyclohexene.

7.0 REFERENCES/FURTHER READING

Corey, E. J. and Cheng, X. (1998). The logic of chemistry synthesis. Wiley, New York

Leonard, J. Lygo, B. and Procter, G. (2013). Advanced practical organic chemistry. 3rd edition. CRC press, UK.

Li, J. J., Pflum, D. A. and Limberakis, C. (2007). Modern synthesis in the Laboratory. CRC press, UK

Richard, O. C., Norman, C. and Coxon, J. M. (2010). Principles of organic synthesis. CRC press, UK

Vogel, A. I. (2011). Tectbook of practical organic chemistry. 3rd edition. Lonoman, UK.

Vogel, A. I., Tatchell, A. R and Furnis, B. S. (1996). Vogel's textbook of practical organic chemistry. 5th Edition. Pearson Edition, UK

UNIT 2 QUANTITATIVE ANALYSIS OF COMMON FUNCTIONAL GROUPS

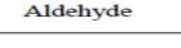
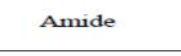
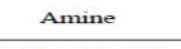
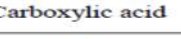
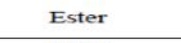
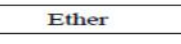
CONTENTS

1.0 INTRODUCTION

Qualitative organic analysis, the identification of organic compounds based on their physical and chemical properties, is analogous in some ways to the identification of plants and animals according to their taxonomy - their structural features and presumed natural relationships. To classify an organic compound into a given family requires first detecting a specific functional group (characteristic set of atoms) in the molecules of organic compounds.

Because functional groups influence the physical, chemical, and spectral properties of an organic compound, a chemist can identify a compound's functional groups by measuring certain physical properties, observing its chemical behavior with different classification reagents, and studying other spectral data. In your experiment, you will subject a series of organic compounds to specific chemical reactions in order to identify which class of functional group the substance belongs to.

Table 1: Some Common Organic Functional Groups

Functional group name	General formula*
Alkene	R–C=C–R'
Alkyl halide	R–Cl or R–Br
Alcohol	R–O–H
Aldehyde	 (R–CHO)
Amide	
Amine	
Carboxylic acid	
Ester	
Ether	R–O–R'
Ketone	

*R, R', and R" are general hydrocarbon groups.

2.0 OBJECTIVES

By the end of unit, you should be able to:

- know and identify functional groups
- give examples of members of functional group families
- predict the results of solubility tests of known compounds
- use solubility test data to classify unknown compounds
  perform simple chemical tests to identify some common functional groups.

3.0 MAIN CONTENT

3.1 Functional group identification

Before outlining the general scheme, you should note one or two points of practical importance.

(a) Quantities of substance for tests. For most tests about 0.1 g solid or 0.1 - 0.2 mL (2 - 3 drops) of liquid material (**NOT MORE**) should be used.

(b) Reagents likely to be met within organic analysis are on the reagent shelves. You are advised to develop a general knowledge of the physical characteristics of common organic compounds. If in doubt about the expected result of a test between a certain compound and a reagent, carry out a trial test with a known compound and compare with the unknown:

(c) Quantities of substance derivatives. Students have wasted much time and material in the past by taking too large a quantity of substance for preparation of a derivative. In general, 0.5 - 1 g (or 0.5 - 1 mL) of substance gives the most satisfactory results. If a practical book instructs one to use larger quantities (3- 4 g or more), the quantities should be scaled down to 1 g or 1mL of the unknown substance and corresponding quantities of reagents should be used.

3.1.1 General Scheme of Analysis

A. Preliminary tests

(a) **Note physical characteristics** - solid, liquid, colour and odour.

(b) Perform an ignition test (heat small amount on metal spatula) to determine whether the compound is aliphatic or

aromatic (i.e., luminous flame - aliphatic; sooty flame - aromatic).

B. Physical constants

Determine the boiling point or melting point. Distillation is recommended in the case of liquids. It serves the dual purpose of determining the b.p., as well as purification of the liquid for subsequent tests.

C. Analysis for elements present

The elements present will be told to you, but read up the method.

D. Solubility tests

Solubility classification

The solubility of an organic compound in various solvents can give valuable information about the unknown. The general rule of "like dissolves like" or "polar compounds dissolve more readily in polar solvents" is useful. Also, organic acids (such as carboxylic acids and phenols) react with bases to form water soluble salts and organic bases (such as amines) react with acids to form water soluble salts. It should be noted that the polarity of an organic compound is increased by the kind and number of polar functional groups in the molecule and that the polarity decreases as the size of the non polar aliphatic group (define aliphatic group in a hyperlink) in the molecule increases.

With this background, one begins the solubility classification by adding 3 drops or 3 mg of the unknown to 3 ml of water and shaking the mixture. If the unknown dissolves, it is a polar compound and in placed in solubility group S1. An unknown in class S1 is then tested as above using ether as the solvent. If it dissolved in both water and ether it is then placed in class S2. For unknowns that do not fall into either class S1 or S2, the unknown's solubility in 5% sodium bicarbonate is determined. If it is soluble, the unknown is placed in class A1. If it is not soluble, the solubility in 5% sodium hydroxide is studied. If it is soluble at this point, the unknown belongs in class A2. If an unknown is insoluble to this point it is next tested for solubility in 5 % hydrochloric acid.

Compounds soluble in 5% hydrochloric acid are placed in solubility class B1. For compounds insoluble to this point the next solvent to try is concentrated sulphuric acid. Unknowns soluble in only this acid are placed in solubility class N1. A further distinction can be made for compounds soluble in concentrated sulphuric acid by testing their solubility in 85% phosphoric acid. Such compounds that are soluble in 85% phosphoric acid are placed in class N2. Finally, for compounds insoluble to this point are placed in class IN.

These solubility classes and their consequences are summarized thus:

S1 These are very polar compounds which consist of salts of carboxylic acids or amines. It is also possible the compound is of low molecular weight and has many polar functional groups such as a carbohydrate.

S2 These compounds are low molecular weight (generally less than 5 carbons) with a polar functional group such as carboxylic acid, amine alcohol, aldehyde or ketone. **A1** Higher molecular weight carboxylic acids fall into this class. **A2** Phenols show this kind of solubility.,

B1 Primary, secondary and tertiary amines fall into this class. However, if there are two or more phenyl groups on the nitrogen, the amine will probably not be basic enough to form the salt and will, thus, be insoluble.

N1 These are higher molecular weight compounds (generally more than 9 carbons) containing an oxygen atom.

N2 These are medium size molecules (generally containing from 5 to 9 carbons) containing an oxygen atom.

IN These are neutral compounds. Alkyl halides and alkanes fall into this class.

The results of a solubility classification should not be strictly interpreted as there are many overlaps. Use the results of this classification only as a focus into which classification tests should be done first.

The solubility of the unknown in the following reagents provides very useful information. In general, about 3 mL of the solvent is used with 0.1 g or 0.2 mL (2 - 3 drops) of the substance. The class of compound may be indicated from Table 7.2:

Table 2: Solubility Table

Reagent and Test	**Class**	**Group of Compounds**
Soluble in cold or hot water. (If the unknown is soluble, do not perform solubility tests below)	Neutral, acidic or basic. (Test with litmus or universal indicator paper)	Lower members of series. Neutral, e.g. alcohols; Acidic, e.g. acids, phenols; Basic, e.g. amines Most amines (except III amines with only aromatic groups

Soluble in dil. NaOH	Acidic	Most acids, most phenols.
Soluble in $NaHCO_3$	Strongly acidic	Most carboxylic acids.
Insoluble in water, acid and alkali	Neutral	Hydrocarbons, nitrohydro-carbons, alkyl or aryl halides, esters and ethers. Higher molecular weight alcohols, aldehydes and ketones

E. Group classification tests

From the previous tests, it is often possible to deduce the functional groups present in the unknown compound.

Individual tests are then performed to identify and confirm the functional groups present.

Note:

1. You are strongly advised against carrying out unnecessary tests, since not only are they a waste of time but also increase the possibility of error. Thus, it is pointless to first test for alcohol or ketone in a basic compound containing nitrogen! Instead tests for amines, etc. should be done on such a compound.

2. A systematic approach cannot be over-emphasized in group classification tests to avoid confusion and error.

F. Consultation of literature

Once the functional group has been identified, you are to make reference to tables in a book on organic analysis, for assessing possibilities and for the preparation of suitable solid derivatives.

It should be noted that whilst two substances with the same functional group may sometimes have very similar boiling points (b.p.) or melting points (m.p.), solid derivatives can usually be chosen from the literature, with melting point differences of about 10 (or more), which distinguish between the two possibilities.

Example:

Compound	**B.P.**	**Derivatives**	
(M.P.)	**2,4-DNPH**	**Semicarbazo ne**	
Diethyl ketone	102	156	139
Methyl n-propyl	102	144	112

G. Preparation of derivatives

The final characterization of the unknown is made by the preparation of suitable solid derivatives. Select the derivative carefully and its melting point should preferably be between 90 - 150 for ease of crystallization and melting point determination.

Attempt the preparation of one derivative. Purify the derivative by recrystallisation, dry and determine the melting point. Submit the derivatives correctly labeled for assessment together with the record.

Recording of results

Record the results in a systematic manner. Record results in the practical book at the time (not written up afterwards).

Make a record of every test carried out, no matter whether a **negative result has been obtained**.

Test, observation and inference should be given. At the conclusion of the analysis, include a brief summary of results giving the name, b.p. or m.p., and formula of the analyzed compound.

Qualitative analysis for elements (for reference only)

In organic compounds the elements commonly occurring along with carbon and hydrogen, are oxygen, nitrogen, Sulphur, chlorine, bromine and iodine. The detection of these elements depends upon converting them to water-soluble ionic compounds and the application of specific tests.

Lasagna's sodium fusion test

C, H, O, N, S, X Next NaCN

-> Na

$NaCN_2S$

Procedure

Place a piece of clean sodium metal, about the size of a pea into a fusion tube. Add a little of the compound (50 mg or 2 - 3 drops). Heat the tube gently at first, allowing any distillate formed to drop back onto the molten sodium. When charring begins, heat the bottom of the tube to dull redness for about three minutes and finally plunge the tube,

while still hot, into a clean dish containing cold distilled water (6 mL) and cover immediately with clean wire gauze.

For liquids it is better to first melt the sodium add the liquid drop by drop.

CAUTION: The tube shatters, and any residual sodium metal reacts with water. Stir the mixture, boil for 1 - 2 minutes, on a tripod and filter hot through a fluted paper.

The 'fusion' filtrate which should be clear and colorless, is used for the **specific tests described below**:

1. To a portion (2 mL) of the 'fusion' filtrate add 0.2 g of powdered ferrous sulphate crystals. Boil the mixture for a half a minute, cool and acidify by adding dilute sulphuric acid drop wise. Formation of a bluish-green precipitate (Prussian blue) or a blue solution indicates that the original substance contains nitrogen. If no precipitate appears, allow to stand for 15 minutes, filter and inspect filter paper.

2. Sulphur

To the cold 'fusion' filtrate (1 mL) add a few drops of cold, freshly prepared, dilute solution of sodium nitroprusside. The latter may be prepared by adding a small crystal of the solid to 2 mL of water. Production of a rich purple colour indicates that the original substance contains Sulphur. This test is very sensitive. Only strong positive results are significant.

3. Halogens (halides)

Acidify a portion (1 mL) of the 'fusion' filtrate with 2N nitric acid, and if nitrogen and/or Sulphur are present, boil for 1 - 2 minutes. * Cool and add aqueous silver nitrate (1 mL), compare with a blank. Formation of a heavy, white or yellow precipitate of silver halide indicates halogen. If a positive result is obtained: acidify the remaining portion of the 'fusion' filtrate with dilute sulphuric acid, boil and cool. Add carbon tetrachloride (1 mL) and a few drops of freshly prepared chlorine water. Shake the mixture.

(a) If the carbon tetrachloride layer remains colorless - indicates chlorine.

(b) If the carbon tetrachloride layer is brown - indicates bromine.

(c) If the carbon tetrachloride layer is violet - indicates iodine.

If nitrogen and/or Sulphur are also present, the addition of silver nitrate to the acidified 'fusion' solution will precipitate silver cyanide and/or silver sulphide in addition to the silver halides. The removal of hydrogen cyanide and/or hydrogen sulphide is affected by boiling the 'fusion' solution.

3.2 Group classification tests

Tests for unsaturation

1. Cold dilute potassium permanganate solution.
2. Solution of bromine in carbon tetrachloride.

Tests for compounds containing nitrogen

1. Amines
   (a) Nitrous acid
   (b) Confirmatory tests.
2. Compounds which give amines or ammonia on acid or alkaline hydrolysis: amides, substituted amides, anilides, nitriles.
3. Compounds which give amines on reduction: nitro, nitroso, azo, hydrazo, nitriles.

Tests for compounds containing C, H and possibly oxygen

1. Carboxylic acids: Na_2CO_3 or $NaHCO_3$ solution liberate carbon dioxide.
2. Phenols
   (a) Sodium hydroxide solution (soluble). Insoluble in and no CO_2 from $NaHCO_3$ (except when electron attracting groups present, e.g. 2,4-dinitrophenol).
   (b) Ferric chloride solution. (c) Bromine water.
3. Aldehydes and Ketones
   (a) 2,4-dinitrophenylhydrazine (as Brady's reagent) for C=O.
   (b) Iodoform test for CH_3CO-.
4. Aldehydes only (reducing properties)
   (a) Fehling's solution.
   (b) Tollen's reagent (ammoniacal $AgNO_3$ solution).
   (c) Jones reagent.
5. Alcohols
   (a) Lucas' reagent to distinguish I, II and III alcohols.
   (b) Jones reagent.
   (c) Metallic sodium (use dry liquid and dry tube).
6. Sugars
   (a) Molisch's test.
7. Esters
   (a) Hydroxamic acid test. (b) Hydrolysis.

3.3 Functional Group Classification Tests

Introduction to qualitative tests - The first test that should be done is a solubility test to determine the class or classes to which the unknown belongs. From the results of the solubility tests, some idea of the type of organic compound should be evident. If the solubility test results put the unknown substance in the 'Neutral' section, it is

recommended that the classification tests be done in this order: aldehydes, ketones, alcohols, esters, amides, nitriles, ethers, alkenes and alkynes. Select a test from the list of tests that would help confirm the presence or absence of the suspected functional group class. Do as many tests that may be necessary to absolutely confirm the functional group to which the unknown belongs. Be careful to interpret correctly the test results for those unknowns that may contain two or more functional groups. At that point, proceed to the preparation of derivatives to identity the exact identity of the unknown.

2,4-Dinitrophenylhydrazine test (for aldehydes and ketones) - This test will be positive for an aldehyde or ketone as indicated by the formation of a yellow, orange or red precipitate which is called a 2,4-dinitrophenylhydrazone. This precipitate can also be used as a derivative for the unknown if its melting point is determined (see below for derivative use). The colour of the precipitate can help further identify the extent of conjugation for the carbonyl group. Highly conjugated aromatic aldehydes or ketones generally give red solids whereas non conjugated carbonyl compounds give yellow products.

Acetyl chloride (for acidic hydrogen compounds) - This test will help identify carboxylic acids, phenols and alcohols. A positive test will be noted by the evolution of heat which may be hard to detect. So, this test may give false positive or negative tests depending on the expertise of the person doing the test. In some cases, a solid (usually white) may form. If this happens, the solid, if isolated and its melting point is determined, could be used as a derivative for the unknown. If water is present in the unknown, the test will probably give a false positive test as acetyl chloride reacts vigorously with water.

Basic hydrolysis (for amides, esters and nitriles) - Amides and esters can be hydrolyzed by heating in a sodium hydroxide solution. This reaction pH gives the acid as a water-soluble carboxylate salt. Acidifying this solution with concentrated hydrochloric acid would result in a precipitate if the carboxylic acid is water insoluble. If this precipitate is formed, it should be filtered and used as a derivative for the unknown.

Beilstein test (for halogenated compounds) - Placing a small amount of an organic compound on the end of a copper wire and heating it in the open flame of a Bunsen burner results in a transient green colour in the flame if the compound contains a halogen atom. If the unknown is volatile, it may evaporate before it burns resulting in a negative test.

Benedict test (for aldehydes and sugars) - When easily oxidized organic compound (such as aldehydes and reducing sugars) is heated with Benedict's solution (which is a blue solution containing a complex copper (II) ion) a brick red precipitate of cuprous oxide forms. If the unknown is not soluble in the reagent a negative test may be observed due to the lack of a reaction.

Bromine in carbon tetrachloride (for alkenes and alkynes) - When a solution bromine in carbon tetrachloride is added drop wise to an unknown compound, the brownish colour of elemental bromine disappears as the bromine adds to the unsaturated organic compound.

Ceric nitrate (for alcohols and phenols) - Alcohol with 10 carbons or less will give a red colour with ceric nitrate solution whereas phenols will give a green-brown to brown precipitate. Easily oxidized compounds may destroy the ceric nitrate solution before the test may be observed.

Chromic acid (for aldehydes, primary and secondary alcohols) - Easily oxidized compounds convert the red chromium (VI) ion to a green chromium (III) precipitate.

Combustion (for flammable or combustible organic compounds) - When a few milligrams of an organic liquid or solid are placed directly into a Bunsen burner flame they often burn. Note that highly halogenated organic compounds may not burn. Very volatile compounds may evaporate before burning or burn very rapidly. The manner in which a compound burns can give some information about its nature. Highly oxygenated compounds burn with a blue flame, aliphatic compounds give a yellow flame and aromatic compounds give a sooty flame.

Ferric chloride (for phenols) - Some (but not all) phenols give a colour when ferric chloride solution is added. This test is not a definitive one and the results should be carefully evaluated.

Ferric hydroxamate (for esters, acid chloride and anhydrides) - Esters of carboxylic acids give a magenta colour with this reagent. Acid chloride and anhydrides give a magenta or burgundy colour with the test reagent.

Ferrous hydroxide (for nitro compounds) - Most compounds that contain a nitro group will give a brown to red-brown precipitate of ferric hydroxide by oxidation of ferrous hydroxide.
Heinsberg test (to distinguish primary, secondary and tertiary amines) - Benzene sulfonyl chloride can be used to

distinguish primary, secondary and tertiary amines. The amine functional group must be confirmed before this test can be performed as the test will give very confusing results with any other functional group. Primary amines give a solid benzene sulfonamide product that is soluble in 5% sodium hydroxide. Secondary amines give a solid benzene sulfonamide product that is insoluble in 5% sodium hydroxide. Tertiary amines do not react with benzene sulfonyl chloride.

Hydroxylamine hydrochloride (for aldehydes and ketones) - Aldehydes and most ketones give a red colour when added to a solution of hydroxylamine hydrochloride in ethanol-water that has a universal indicator added.

Iodoform test (for methyl carbonyl compounds) - This test is mainly used to identify methyl ketones. The iodoform regent iodinates the methyl group which they cleave in the basic solution One should confirm the presence of a carbonyl group in the unknown before this test is done as misleading results could occur with other compounds. For example, acetaldehyde and alcohols that have a methyl group bonded to the C-OH group can also give a positive test since such an alcohol can be oxidized to a methyl ketone by the iodoform reagent.

Lucas test (to distinguish primary, secondary and tertiary alcohols of six carbons or less) - A solution of zinc chloride in aqueous hydrochloric acid can be used to distinguish primary, secondary and tertiary alcohols. The unknown compound must be soluble in the reagent in order for the test to be valid. When a tertiary alcohol is added dropwise to the reagent, an immediate second layer or a liquid alkyl chloride is formed. Secondary alcohols form a second layer of the insoluble alkyl chloride in three to 5 minutes. Primary alcohols are unreactive with the Lucas reagent.

Nitrous acid (to distinguish primary, secondary and tertiary amines) - Primary aromatic amines give nitrogen gas evolution with the nitrous acid reagent. Other aromatic amines can undergo coupling reactions to form colored products.

pH in ethanol (to distinguish low molecular weight acidic or basic compounds) - The pH of compounds that are soluble in water or aqueous alcohol can be measured. If the pH is in the acid range the compound can be a carboxylic acid, acid chloride or anhydride. If the pH is in the basic range, the compound may be an amine. Organic salts may hydrolyze in water which can lead to acidic or basic solutions

Potassium permanganate (for compounds that can be oxidized) - Organic compounds that can be readily oxidized will convert the purple of the permanganate ion to a brown precipitate of manganese dioxide. Such organic compounds include: aldehydes, reducing sugars, primary or secondary alcohols and some alkenes and alkynes.

Silver nitrate in ethanol (for alkyl halides that can undergo SN1 reactions) - Tertiary alkyl halides will give a white to yellow silver halide precipitate with this reagent. Some secondary halides will react more slowly. Aryl and vinyl halides do not react.

Sodium fusion (for compounds that contain halogen, nitrogen or sulfur) - When an organic compound is placed in molten elemental sodium the molecules are violently destroyed. Any halogen, nitrogen or Sulphur in the original molecule is converted to ionic materials which are then identified. The halide is identified by precipitation with silver ions. The sulfide ion is identified by precipitation with lead ions. The cyanide ion formed the nitrogen in the molecule is converted into Prussian blue by ferrous sulfate.

Sodium iodide in acetone (for alkyl halides that can undergo Sn2 reactions) - Primary and some secondary alkyl chlorides or bromides will give a precipitate of sodium iodide in the reagent. Alkyl iodides will not give the precipitate. Aryl or vinyl halides do not react.
Solubility (for general classification of organic compounds). See **solubility classification** section above.

Tollen's test (for aldehydes and reducing sugars) - Water soluble aldehydes and reducing sugars give a silver mirror or black precipitate of elemental silver with the Tollen's reagent.

General notes: Terms and techniques used in qualitative analysis

1. **Mixing solutions**

   After addition of any reagent to a solution, one must ensure proper mixing. To mix the reagent and the solution in a centrifuge tube, tap the bottom of the centrifuge tube against the table or snap it with your fingers while holding the upper part in the other hand.

2. **Centrifuging**

   Precipitates are separated from the supernatant solution by **centrifuging**. This is the process of separating more dense solid particles from less dense liquid (solution) by spinning (separation by means of centrifugal force). The apparatus used here is called a centrifuge. It must be balanced to properly function. Balancing is done by putting the centrifuge tube containing the reaction mixture (tightly capped) in a sleeved

centrifuge slot, then placing a centrifuge tube with an equal volume of tap water in a slot across from the first tube. Make sure that the tubes are tightly capped before they are place d in the centrifuge.

3. **Decanting**
   The supernatant solution is transferred from above the precipitate to another tube by **decanting.** When a two-phase system (solid-liquid) is considered: after the solid settled to the bottom upon centrifuging, decanting is pouring the supernatant liquid out of the tube, leaving the solid behind.
4. **Rinsing precipitates**
   All precipitates, after they have been separated from the supernatant solution, must be rinsed with distilled water before proceeding to the identification of the cation present. This process must be done to remove any cations present in the supernatant solution adhering to the solid. The presence of these ions may cause confusing results in the process of further identification or separation. The solid remaining after the supernatant solution has been removed is mixed with 10 drops of distilled water and the tube is tapped to thoroughly mix the contents. The tube is centrifuged, rinse water decanted, and the process repeated one to two more times.

The qualitative analysis is a general name for the methods used in the determination of the identity rather than the amount of chemical species (quantitative analysis). The qualitative process usually utilizes the reaction(s) characteristic for the given chemical species and interprets the obtained results using a deductive thought process.

SELF ASSESSMENT EXERCISE

What are the functional group for alcohol, carboxylic acid, ethanal, ethenone and ethyl acetate.

4.0 CONCLUSION

All organic molecules have functional groups and properties that are unique for identification through proper qualitative and quantitative tests.

5.0 SUMMARY

This study section must have exposed you to identification of some functional groups and give examples of members of functional group families. The student is also made to learn how to predict the results of

solubility tests of known compounds, and to use solubility test data to classify unknown compounds.

6.0 TUTOR-MARKED ASSIGNMENT

1. Define the term qualitative analysis.
2. How do you differentiate between an aromatic and an aliphatic hydrocarbon in the lab?
3. Which of the following alcohols will react most rapidly with the Lucas reagent (HCl, $ZnCl_2$)?

   a) $(CH_3)_3COH$ b) $CH_3CH_2CH_2CH_2$
   c) $(CH_3)_2CHCH_2OH$ d) $CH_3CHOHCH_2CH$

7.0 REFERENCES/FURTHER READING

Corey, E. J. and Cheng, X. (1998). The logic of chemistry synthesis. Wiley, New York

Leonard, J. Lygo, B. and Procter, G. (2013). Advanced practical organic chemistry. 3rd edition. CRC press, UK.

Li, J. J., Pflum, D. A. and Limberakis, C. (2007). Modern synthesis in the Laboratory. CRC press, UK

Richard, O. C., Norman, C. and Coxon, J. M. (2010). Principles of organic synthesis. CRC press, UK

Vogel, A. I. (2011). Tectbook of practical organic chemistry. 3rd edition. Lonoman, UK.

Vogel, A. I., Tatchell, A. R and Furnis, B. S. (1996). Vogel's textbook of practical organic chemistry. 5th Edition. Pearson Edition, UK.

MODULE 3

UNIT 1 VERIFICATION OF ARRHENIUS AND TRANSITION STATE EQUATIONS

CONTENTS

1.0 INTRODUCTION

The rate of the reaction between sodium thiosulphate and hydrochloric acid can be monitored by the time it takes the formation of Sulphur precipitate to be formed. There are several theories of reaction rates including collision theory, Arrhenius theory and the Transition state theory. However, the Arrhenius and the Transition state theories are the most quantitative theories. The Arrhenius theory uses activation energy (E_a) to predict the rate of reaction (k) and can be expressed as

$$k = Aexp\left(\frac{-E_a}{RT}\right)$$

From the logarithm of both sides of the above equation, we have,

$$logk = logA - \frac{E_a}{2.303RT}$$

This implies that a plot of logk versus 1/T should give a linear plot with slope equal to $E_a/2.303R$ and intercept equal to logA.

Similarly, the Transition state equation can be written as,

$$logk = log\left(\frac{R}{Nh}\right) + \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT}$$

This also implies that a plot of logk versus 1/T should give a straight line with slope equal to $\frac{\Delta H^0}{2.303R}$ and intercept equal to $log\left(\frac{R}{Nh}\right) + \frac{\Delta S^0}{2.303R}$. The rate constant can be approximated by monitoring the rate of reaction between sodium sulphate and hydrochloric acid as shown in the following equation

$Na_2S_2O_3 + 2HCl = 2NaCl + SO_2 + S + H_2O$

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- know the effect of temperature on the rate of a chemical reaction
- be able to apply the Arrhenius equation to find the activation energy of a chemical reaction
- to be able to apply the Transition state equation in calculating thermodynamic parameters

3.0 MAIN CONTENT

3.1 Verification of Arrhenius equation

3.1.1 Apparatus and reagents

Conical flask, Thermometer, stop clock, Measuring cylinder, White ceramic tiles, Sodium thiosulphate, Hydrochloric acid.

3.1.2 Experimental procedure

Measure 25 ml of the given sodium thiosulphate solution into a conical flask and place water bath at a temperature of 298 K. Leave the conical flask in the water bath for about five minutes until the solution temperature is the same as that of the water bath. Mark letter 'X' on the white tile you place the conical flask. The 'X' mark is important because the time it takes the mark to disappear signifies the end of the reaction. 25 ml of 3M hydrochloric acid solution is added to the solution and the stop watch is turned on. The flask should be gently swirled in a circular motion and the time it takes the X mark to disappear is recorded. Repeat the experiment using the same reaction conditions but at various temperatures, i.e. 208, 218 and 228 K respectively.

The rate of the chemical reaction can be calculated using the following equation,

$$Rate\ (s^{-1}) = \frac{1}{Tine\ taken}$$

SELF-ASSESSMENT EXERCISE

i. Apart from temperature, what are the other factors that affect the r ate of chemical reaction
ii. What is the relationship between Arrhenius and thermodynamic parameters (Hint: Compare the Arrhenius equation with the Transition state equation)

4.0 CONCLUSION

The Arrhenius equation can be used to estimate the activation energy while the Transition state equation can be used to estimate enthalpy and entropy changes.

5.0 SUMMARY

The rate of a chemical reaction can be measured with respect to time of completion of the reaction. The rate provides quantitative information that can be useful in estimating the activation energy, the enthalpy change, entropy change and free energy change, etc.

The rate of chemical reaction generally increases with increase in temperature. The activation energy gives information on the minimum energy needed for a given chemical reaction to proceeds. This implies that below the activation energy, an energy barrier exist bit above the activation energy, the barrier is overcome.

6.0 TUTOR-MARKED ASSIGNMENT

1. Present your results in the following format,

Temperature (K)	**Rate (/s)**	**1/T (/K)**	**Log(rate)**	**Log(Rate/T)**
298				
208				
218				
228				

2. Plot a graph of reaction rate versus temperature and explain the significant of the trend obtained for the plot
2. Use Arrhenius theory to plot a graph of log (Rate) versus 1/T. From the graph, calculate the activation energy and the Arrhenius constant.
3. Plot the Transition state plot (i.e. a plot of log(Rate/T) versus 1/T) and from the slope and intercept of the plot, calculate the enthalpy and entropy changes of the reaction.
4. From the results obtained from 3, calculate the standard free energy change for the reaction and state if the reaction is spontaneous or not. Give reason for your results.

7.0 REFERENCES/FURTHER READING

Atkins, P. and de Paula, J. (2018). *Atkins 'Physical chemistry*. 11th Edition. Oxford University Press. UK.

Engel T. and Reid, P. (2005). *Physical chemistry*. Pearson Cummings. San Francisco. New York.

Jack, R. and Scholz, F. (2017). *Wilhelm Ostwald. The Autobiography*. Springer, Germany, ISBN: 978-319-46955-3 and 978-3-319-46953 (print)

Hammerich, O. and Speiser, B. (2015) *Organic electrochemistry* 5th edition, revised and expanded. Taylor & Francis Publication, UK. ISBN: 978-1-4200-8401-6 (hardback), 978-1-4200- 8402-3

Kulikovsky, A. (2018). *Analytical models for PEM fuel cell impedance*. Andrei Kulikovsky, USA. 2018, ISBN: 9781521470749

Levine, N. I. (2009). *Physical chemistry*.5th Edition. Higher Education. Boston.

Molina, A. and Gonzalez, J. (2016). *Pulse voltammetry in physical electrochemistry and electroanalysis. Theory and applications*. Springer, UK, ISBN: 978-3-319-21250-0

Monk, P. (2004). *Physical chemistry: Understanding the Chemical World*. John Wiley and Sons Ltd. England.

UNIT 2 REFRACTIVE INDEX MEASUREMENTS

CONTENTS

1.0 INTRODUCTION

This section consists of four experiments on refractive index measurements and their applications. These include:

- Experiment on the verification of the relationship between refractive index and concentration
- Experiment on the verification of the relationship between molar refraction and mole fraction of two components mixtures
- Experiment on the verification of agreement between two methods often used for measuring molar refraction
- Experiment on the verification of effect of temperature on refractive index

Refractometry is an analytical method associated with the measuring the refractive index for quantitative or qualitative analysis. Refractive index is a measure of the extent light is refracted (i.e. bend) when it passes from one medium to another. It is the ratio of the velocity of light in a vacuum to the velocity of light in a medium. This can be expressed as

$$n = \frac{v_{vac}}{v_{med}} \quad (1)$$

where n is the refractive index, v_{vac} and v_{med} are the velocities of light in the vacuum and the second medium respectively. From the Figure below, it is evident that refractive index can also be expressed as the ratio of the sine of angle of incidence (i) to the sine of the angle of refraction (r). That is,

$$n = \frac{Sin\, i}{Sin r} \quad (2)$$

Refractive index is a dimensionless quantity and ranges from about 1.3 to 1.5 for most organic mixture and is temperature and wavelength dependent. The instrument for measuring refractive index is called refractometer. The most useful refractometer is called Abbe refractometer, which uses a 258.3 nm sodium D line monochromatic light to measure refractive index of a medium. However, there are some hand held refractometer, which can be used for in situ measurement of

refractive index. In this work, we shall measure the refractive index of different organic compound and that of their mixtures. The relationship between the refractive indices of the various components of the mixture shall also be varied.

The term, specific refraction can be defined as,

$$r = \frac{n^2-1}{n^2+1}.\frac{1}{\rho} \quad (3)$$

On the other hand, molar refraction is expressed as

$$R = \frac{n^2-1}{n^2+2}.\frac{M}{\rho} \quad (4)$$

where n is the refractive index, M is the molar mass and ρ is the density of the liquid.

The molar refraction for homogenous mixture of two components (I and 2 respectively) can be written as,

$$R_{12} = \frac{n_{12}^2-1}{n_{12}^2+2}.\frac{X_1M_1+X_2M_2}{\rho_{12}} \quad (5)$$

It is also possible to estimate the molar refraction of a two-component system from the values of their specific refraction and mole fractions, according to the following equation,

$$R_{12} = R_1M_1 + R_2M_2 \quad (6)$$

This X_1 and X_2 are the mole fractions of pure components, 1 and 2 respectively. M_1 and M_2 are the molar weights of components 1 and 2 respectively.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- verify of the relationship between refractive index and concentration
- verify of the relationship between molar refraction and mole fraction of two components mixtures
- verify of agreement between two methods often used for measuring molar refraction
- verify of effect of temperature on refractive index

3.0 MAIN CONTENT

3.1 Experimental procedures

Methodology 1: **Relationship between refractive index and mole fraction of pure component of ethanol**

You are provided with different concentrations of ethanol. Measure the refractive indices of the respective concentration and record your results in the format provided in the Table 1 below,

C (M)	Refractive index (n)
0.1	
0.2	
0.3	
0.4	
0.5	
0.6	

Plot a graph of refractive index against concentration and comment on the relationship between refractive index and concentration.

Methodology 2: Refractive index of mixture of ethanol and water

(i) Prepare six different solutions of ethanol in water in the following ratio, 0:100, 10:90. 20:80, 30:70, 40:60, 50:60, 60:40, 70:30, 80:20 90: 10 and 100:0.
(ii) Calculate the mole fractions of the respective components.
(iii) Measure the relative density of the mixture
(iv) Measure the refractive index of the respective mixture
(v) Record your results in the format given in Table 2 below,
(vi) Calculate the molar refraction of the various components using equations 5 and 6 respectively

Table 2

Ratio	$\bar{X}^{ethanol}$	$\bar{X}^{water}$	M_1	M_2	Density	$\bar{R}^{12}_{(Eq.5)}$	$\bar{R}^{12}_{(Eq6)}$
0:100							
10:90							
20:80							
30:70							
40:60							
50:70							
60:40							
70:30							
80:20							
90:10							
100:0							

From your results,

(i) plot a graph of mole fraction of the water (and ethanol in the same graph) against refractive index. What is the relationship between mole fraction and refractive index?

(ii) Compare the results obtained according to equations 5 and 6 by plotting a graph of one set of data against the data. Is there a significant difference between the two set of results?

Methodology 3: Effect of temperature on refractive index of ethanol

(i) Prepare the solutions of ethanol in water (using a ratio of 50:50) in four different text tube.

(ii) Use water bath to gradually increase the temperature of the solutions to 30, 40, 50 and 60 °C respectively.

(iii) Measure the refractive index of the respective solution at a given temperature and record your result in Table 3 below

Table 3

Temperature (îC)	**Refractive index**
30	
40	
50	
60	

From your results, plot a graph of refractive index against temperature and comment on the nature of relationship between refractive index and temperature.

SELF ASSESSMENT EXERCISE

i. What is the highest speed of light that is possible?

ii. What is index of refraction?

i. What is the relationship between refractive index and optical density?

4.0 CONCLUSION

Refractive index can be used to explore several analytical parameters and quantify them for useful purposes.

5.0 SUMMARY

Measurement of refractive index can provide significant information for several parameters in physical chemistry. The science of refractometry can link refractive index with concentration and mole fraction. There is a relationship between refractive index and density or viscosity of a system. Hence refractometry is a significant area of physical chemistry.

6.0 TUTOR-MARKED ASSIGNMENT

1. State the factors that quantitatively affects the refractive index of a medium.
2. What are the analytical benefits of refractive index measurement :

7.0 REFERENCES/FURTHER READING

Atkins, P. and de Paula, J. (2018). *Atkins 'Physical chemistry*. 11th Edition. Oxford University Press. UK.

Engel T. and Reid, P. (2005). *Physical chemistry*. Pearson Cummings. San Francisco. New York.

Jack, R. and Scholz, F. (2017). *Wilhelm Ostwald. The Autobiography*. Springer, Germany, ISBN: 978-319-46955-3 and 978-3-319-46953 (print)

Hammerich, O. and Speiser, B. (2015) *Organic electrochemistry* 5th edition, revised and expanded. Taylor & Francis Publication, UK. ISBN: 978-1-4200-8401-6 (hardback), 978-1-4200- 8402-3

Kulikovsky, A. (2018). *Analytical models for PEM fuel cell impedance*. Andrei Kulikovsky, USA. 2018, ISBN: 9781521470749

Levine, N. I. (2009). *Physical chemistry*.5th Edition. Higher Education. Boston.

Molina, A. and Gonzalez, J. (2016). *Pulse voltammetry in physical electrochemistry and electroanalysis. Theory and applications*. Springer, UK, ISBN: 978-3-319-21250-0

Monk, P. (2004). *Physical chemistry: Understanding the Chemical World*. John Wiley and Sons Ltd. England.

UNIT 3 KINETIC AND THERMODYNAMIC STUDY OF THE CORROSION OF IRON IN H_2SO_4

CONTENTS

1.0 INTRODUCTION

Corrosion is an electrochemical process that leads to the degradation of metals and subsequent returns to its natural state. Most metals are not found free in nature but are found in combine state called ore. Extraction of metal from their ores forms the basis of chemical metallurgy. It is the extracted metals that are useful for numerous mechanical or other applications and not the ore. However, when metals come in contact with aggressive medium (such as acid, bases and salts), it undergoes an electrochemical reaction and corrodes. At the anode, oxidation takes place and at the cathode, reduction takes place.

Although there are different types of corrosion, the commonest type of corrosion is uniform corrosion, which involves the uniform wearing away of the surface of the metal. In corrosion study, several monitoring processes are known, including weight loss, potentiodynamic, electrochemical impedance, hydrogen gas evolution, polarization and other methods. In this experiment, we shall adopt the weight loss method which correlates weight loss with the rate of corrosion. According to the weight loss protocol, corrosion rate may be expressed as follows,

$$Corrosion\ rate\ (mm/y) = \frac{87.6\Delta W}{\rho A t}$$

where ΔW is the weight loss (i.e the difference between the initial weight of metal (before corrosion) and final weight of the metal (after corrosion).A is the area of the metal (in cm^2), t is the period of contact of the metal with the acid (i.e. time in hours) and ρ is the density of the metal in g/cm^3. Most corrosion reactions are first order and the general equation can be written as,

$$-\log(weight\ loss) = k_1 t$$

Therefore, a plot of -log (weight loss) against time should give a slope equal to the rate constant, k_1. Also, thermodynamic consideration reveals that the Transition state equation can be used to estimate the enthalpy and entropy change as follows,

$$log\left(\frac{CR}{T}\right) = \frac{R}{Nh} + \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

Where R is the gas constant, N is the Avogadro's number, h is the Planck constant while ΔS and ΔH are entropy and enthalpy changes. It follows that a plot of log (CR/T) against 1/T gives a slope numerically equal to $\frac{\Delta H}{R}$ and intercept equal to $\frac{R}{Nh} + \frac{\Delta S}{R}$

Finally, the activation energy can be estimated using the Arrhenius equation, i.e.

$$\log(CR) = \frac{-E_a}{2.303RT} + logA$$

where E_a is the activation energy and A is the Arrhenius constant. That means the slope of the plot of log (CR) versus 1/T is $-E_a/2.303R$ while the intercept is logA

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- determine the rate of corrosion of iron in 5 M H_2SO_4 at different temperature
- determine the kinetic order associated with the corrosion of mild steel in H_2SO_4
- estimate the activation energy associated with the corrosion of iron in solution of H_2SO_4 using the Arrhenius equation
- estimate the enthalpy and entropy changes associated with the corrosion of iron metal using the Transition state equation

3.0 MAIN CONTENT

3.1 Experimental procedure

3.1.1 Kinetic study of the corrosion of mid steel in tetraoxosulphate (VI) acid

Apparatus and reagents
Mild steel coupon (5 x 4 x 0.1 cm)
5 M H_2SO_4 solution
Acetone
Analytical balance
Beakers

Aluminum foil
Zinc dust
Distilled water
Soft washing brush

Experimental methodology

i. Set up five beakers and to each of them add 150 ml of 5M H_2SO_4
ii. Weigh five different samples of mild steel coupon respectively
iii. Immersed different mild steel coupons (of known weight) to each of the beaker such that the mild steel is completely covered by the acid solution
iv. Cover each of the beaker with aluminum foil
v. The first, second, third, fourth and fifth beakers should be allowed to stand for 20, 30, 40, 50 and 60 minutes respectively.
vi. At the completion of each period of immersion, withdraw the mild steel coupon from the acid solution, wash it (with the aid of soft brush) in distilled water containing 50 % zinc dust and rinse it in a solution of acetone after washing. Allow the coupon to dry in the air and measure the new weight of the coupon. Weight loss is given as the difference between the initial weight (w_1) and that of the final weight (w_2). Record your result
vii. Repeat vi for the remaining samples and for each sample record the new weight and weight loss.

Treatment of data

Period of immersion (minute)	Initial weight of mild steel coupon (w_1)	Final weight of mild steel coupon (w_2)	Weight loss (w_1-w_2)	Corrosion rate (mm/y)	log (weight loss)
20					
30					
40					
50					
60					

From your data, plot the following graphs

(a) -log (weight loss) versus time. Calculate the slope of your graph
(b) Weight loss against time and calculate the slope of your plot
(c) Corrosion rate against time and calculate the slope of your graph. Answer the Answer the following questions

(a) What is the order of the corrosion reaction of mild steel: Give reason for your answer?

(b) What is the average corrosion rate of the mild steel?
(c) Calculate the half-life of the corrosion reaction

3.1.2 Thermodynamic study of the corrosion of mild steel

Repeat, the experiment as in the former but vary the temperature instead of time. That is maintain the temperature of the first, second, third, fourth and fifth beaker at 30, 40, 50 and 60 °C respectively (use thermostatic oven to maintain the temperature). Record your results as shown in the Table below

Treatment of data

Temperature	Initial weight of mild steel coupon (w_1)	Final weight of mild steel coupon (w_2)	Weight loss (w_1-w_2)	1/T	Corrosion rate (CR)	Log (CR)	Log (CR/T)
30							
40							
50							
60							

SELF-ASSESSMENT EXERCISE

i. How does the electrical double layer structure affect corrosion?
ii. Why is corrosion said to be an electrochemical; process?
iii. Name four methods you can use to control corrosion

4.0 CONCLUSION

Corrosion is an electrochemical process that can adequately be modelled using kinetic and thermodynamic functions.

5.0 SUMMARY

Corrosion is an electrochemical process that operates to return metals to their natural state (i.e. the ore form). The chemistry of corrosion can adequately be modelled by studying the kinetics, thermodynamic and adsorption processes. This study section has successfully exposed the student to the kinetic and thermodynamic of corrosion of iron, been the commonest and widely applied metal.

6.0 TUTOR-MARKED ASSIGNMENT

From your data, plot the following graphs:

1. Log (corrosion rate) against 1/T (ice Arrhenius plot)
2. Log (corrosion rate/temperature) against 1/T (i.e. the Transition state plot)
3. Calculate the following,
4. Activation energy for the corrosion reaction
5. Entropy change of the reaction
6. Enthalpy changes of the reaction
7. Free energy change of the reaction

7.0 REFERENCES/FURTHER READING

Atkins, P. and de Paula, J. (2018). *Atkins 'Physical chemistry*. 11th Edition. Oxford University Press. UK.

Engel T. and Reid, P. (2005). *Physical chemistry*. Pearson Cummings. San Francisco. New York.

Jack, R. and Scholz, F. (2017). *Wilhelm Ostwald. The Autobiography*. Springer, Germany, ISBN: 978-319-46955-3 and 978-3-319-46953 (print)

Hammerich, O. and Speiser, B. (2015) *Organic electrochemistry* 5th edition, revised and expanded. Taylor & Francis Publication, UK. ISBN: 978-1-4200-8401-6 (hardback), 978-1-4200- 8402-3

Kulikovsky, A. (2018). *Analytical models for PEM fuel cell impedance*. Andrei Kulikovsky, USA. 2018, ISBN: 9781521470749

Levine, N. I. (2009). *Physical chemistry*.5th Edition. Higher Education. Boston.

Molina, A. and Gonzalez, J. (2016). *Pulse voltammetry in physical electrochemistry and electroanalysis. Theory and applications*. Springer, UK, ISBN: 978-3-319-21250-0

Monk, P. (2004). *Physical chemistry: Understanding the Chemical World*. John Wiley and Sons Ltd. England.

UNIT 4 DETERMINATION OF HEAT OF NEUTRALIZATION

CONTENTS

1.0 INTRODUCTION

In chemical reactions, energy change is observed. This energy change is usually in the form of heat and at constant pressure it is defined as **heat of reaction** or **enthalpy change (ΔH).** To form 1 mole of compound from its constituent elements, necessary amount of enthalpy change occurs and this change is defined as **enthalpy of formation**. If heat is released during the reaction, ΔH is shown with negative sign and the reaction is called **exothermic reaction.** If heat is absorbed during the reaction, ΔH is shown with positive sign and the reaction is called **endothermic reaction.**

Direct measurement of enthalpies of formation is difficult experimentally, so indirect methods involving enthalpies of reaction are used. Hess's Law states that the change in a thermodynamic property such as enthalpy depends on the initial and final states and is independent of path followed. An example for Hess's Law is given below.

$\frac{1}{2}N_2(g) + \frac{3}{2}H_2 \rightarrow NH_3(g)$ $\Delta H_{formation}(NH_3(g)) = \Delta H_1$

$NH_3(g) \rightarrow NH_3(aq)$ $\Delta H_{dissolving} = \Delta H_2$

Assume that ΔH_1 and ΔH_2 are known. If first and second reactions are added, net reaction becomes;

$\frac{1}{2}N_2(g) + \frac{3}{2}H_2 \rightarrow NH_3(g)$ $\Delta H_{formation}(NH_3(aq)) = \Delta H_1 + \Delta H_2$

which is also formation reaction of $NH_3(aq)$.

Given that ΔH_1 = - 45.8 kJ/mol and ΔH_2 = - 35.4 kJ/mol, we can calculate the ΔH formation of $NH_3(aq)$ as -81.2 kJ/mol.

The heat is measured experimentally by allowing the reaction to take place in a thermally insulated vessel called as **calorimeter**. If the calorimeter is perfectly insulated, no heat change occurs between system and surrounding and the system is defined as adiabatic (Q=0).

Consequently, at constant pressure, ΔH_{system} is also equal to zero. The formulation of enthalpy changes of the system, ΔH_{system}, is shown as in Equation (1).

ΔH_{system} = ΔT (heat capacity of calorimeter + heat capacity of contents) (1) For endothermic reaction in adiabatic system, Equation (1) can be written as below.

$\Delta H_{system} = n\Delta H_{reaction} + C_p\Delta T$

$0 = n\Delta H_{reaction} + C_p\Delta T$ $n\Delta Hreaction = - C_p\Delta T$

In a similar manner, for exothermic reaction in an adiabatic system, Equation (1) can be simplified as:

$\Delta H_{system} = -n\Delta H_{reaction} + C_p\Delta T$

$0 = -n\Delta H_{reaction} + C_p\Delta T$ $n\Delta H_{reaction} = C_p\Delta T$

In this experiment, you will determine the heat of formation of various ammonium salts $NH_4X(s)$ where X is Cl, NO_3 or SO_4 by combining measurements of the heat for the neutralization reaction;

$NH_3(aq) + HX(s) \rightarrow NH_4X(aq)$ ΔH_{neut}

And the heat of the dissolution reaction;

$NH_4X(s) + H_2O \rightarrow NH_4X(aq)$ ΔH_{diss}

with known heats of formation of $NH_3(aq)$ and HX (aq).

2.0 OBJECTIVES

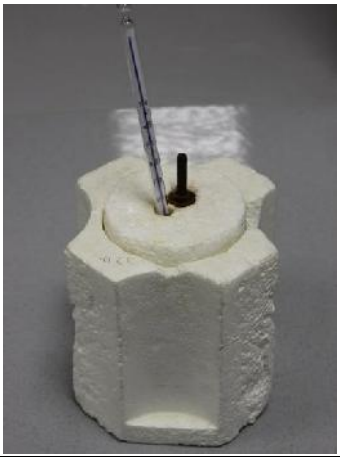
- calculate enthalpy change of a reaction by using calorimeter
- understand the difference between endothermic and exothermic reaction

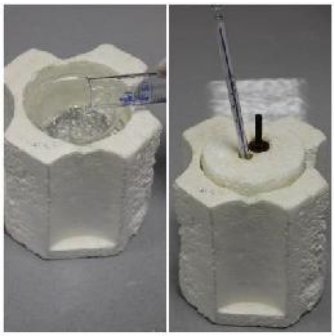
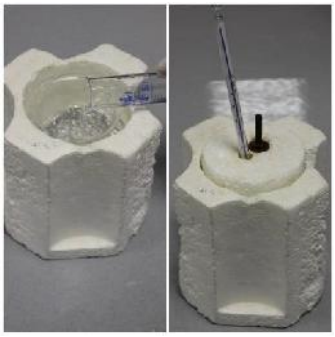
3.0 MAIN CONTENT

3.1 Experimental determination of heat of neutralization

3.1 Apparatus and reagent

Nitric acid (HNO_3)	250 mL beaker	Graduated cylinder
Ammonia (NH_3)	Thermometers	
Ammonium nitrate (NH_4NO_3)	Styrofoam cups	

PART A: Heat of Neutralization	
1. Obtain a sytrofoam cup. In the first cup, place 50 mL of 1.5 M NH_3.	
2. Place a thermometer in the cup containing the NH_3 and record temperature at 30 seconds intervals.	

3. Add the acid solution to the NH_3 and swirl to mix. Continue taking temperature data at 30 seconds intervals while swirling the solution occasionally.	
PART B: Dissolving	
1. Place a volume of distilled water equal to the final volume of solution from part (A) in a Styrofoam cup and record temperature data at 30 seconds intervals.	
2. Weigh out that mass of NH_4NO_3 salt into a clean, dry beaker.	
3. Immediately, add the weighed amount of salt, swirl to dissolve (use stirring rod if necessary), and continue taking temperature data at 30 seconds intervals.	

Time (s)	Temperature of NH_3 solution in ˚C before adding 1.5 M HNO_3	Temperature of distilled water in ˚C before NH_4NO_3
0		
30		

60		
90		
120		
150		
180		
Time (s)	Temperature of NH_3 + 1.5 M HNO_3 solution in ˚C	Temperature of NH_4NO_3 solution in ˚C
0		
30		
60		
90		
120		
150		
180		

SELF ASSESSMENT EXERCISE

i. Why is the molar heat of neutralization of strong acid by strong base always constant ?
ii. Hence what do you expect for a weak acid/strong base (b) a strong acid/weak base and (c) a weak acid/weak base
iii. What is neutralization and why is neutralization an exothermic process?
iv. What is molar heat of neutralization?

4.0 CONCLUSION

Colorimetry provide an avenue for the determination of heat of neutralization and associated paramters

5.0 SUMMARY

The heat of neutralization for different acids and different bases may differ from each other but the heat of neutralization of strong acid by strong base is always constant because strong acid and bases undergoes complete neutralization

6.0 TUTOR-MARKED ASSIGNMENT

Plot temperature versus time graph using your data and determine ΔH_{neut} for (a) and ΔH_{diss} for (b).

Take ΔH_f of 1.5 M NH_3 as -81.2 kJ/mol and ΔH_f of 1.5 M HCl as -165.1 kJ/mol, calculate the ΔH_f of $NH_4Cl(s)$.
Do the same calculations for $NH_4NO_3(s)$ using -206.0 kJ/mol for the ΔH_f of 1.5 M HNO_3.
Calculate ΔH_f of $(NH_4)_2SO_4$ using -884.2 kJ/mol for the ΔH_f of 1.5 M H_2SO_4. [Note that all ΔH_f are per mol (not per 1.5 mol)]

7.0 REFERENCES/FURTHER READING

Atkins, P. and de Paula, J. (2018). *Atkins 'Physical chemistry*. 11th Edition. Oxford University Press. UK.

Engel T. and Reid, P. (2005). *Physical chemistry*. Pearson Cummings. San Francisco. New York.

Jack, R. and Scholz, F. (2017). *Wilhelm Ostwald. The Autobiography*. Springer, Germany, ISBN: 978-319-46955-3 and 978-3-319-46953 (print)

Hammerich, O. and Speiser, B. (2015) *Organic electrochemistry* 5th edition, revised and expanded. Taylor & Francis Publication, UK. ISBN: 978-1-4200-8401-6 (hardback), 978-1-4200- 8402-3

Kulikovsky, A. (2018). *Analytical models for PEM fuel cell impedance*. Andrei Kulikovsky, USA. 2018, ISBN: 9781521470749

Levine, N. I. (2009). *Physical chemistry*.5th Edition. Higher Education. Boston.

Molina, A. and Gonzalez, J. (2016). *Pulse voltammetry in physical electrochemistry and electroanalysis. Theory and applications*. Springer, UK, ISBN: 978-3-319-21250-0

Monk, P. (2004). *Physical chemistry: Understanding the Chemical World*. John Wiley and Sons Ltd. England.

MODULE 4

UNIT 1 EXPERIMENTS ON PH

CONTENTS

1.0 INTRODUCTION

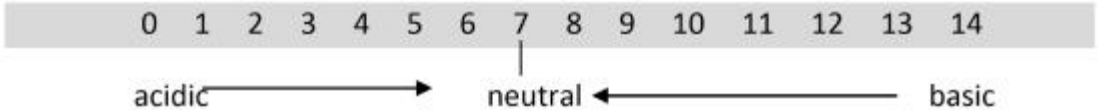
A pH value is a number, usually between 0 and 14, that represents the acidity or basicity of a solution. The "pH" is always written with a lowercase "p" and an uppercase "H", which stands for "power of hydrogen." pH values are related to hydrogen ion (H^+) concentrations.
The mathematical relationship between pH and H^+ is described by the equation

$$p^H = -log[H^+]$$

There is an *inverse* relationship between pH and H^+ concentration (in brackets, expressed in units of *molarity*, M). As the H^+ concentration decreases, the pH value increases, and vice versa. When the pH value is a whole number (e.g. pH 7), the number is equal to the negative exponent of the H^+ion concentration.

$$p^H\ value = X \rightarrow [H^+] \rightarrow 10^{o-X}M$$

So for pH 7, the H^+concentration is 10^{-7} M. The pH values of everyday chemicals typically range from pH 0 to pH 14. Values between 0 and 7 indicate an acidic solution. Values between 7 and 14 indicate a basic solution. A pH of exactly 7 indicates that a solution is neutral, neither acidic or basic. Pure water is usually pH 7.
The *pH scale* is shown below.



The lower the pH value, the more *acidic* the solution; the higher the pH value, the more *basic* the solution. Basic solutions are also called *alkaline* solutions. It should be noted that the pH scale does extend beyond 0 and 14. Strong laboratory acids typically have pH values less than 0 (negative pH values) and strong laboratory bases typically have pH values greater than 14. Thus, they are considerably more dangerous.

The concept of pH is widely used in all areas of science including agriculture, biology, engineering and medicine. Many commercial products use pH as an advertisement tool, such as shampoo and water; more recently, food and drink of certain pH has been touted as more healthful.

A *pH indicator* is a substance that, when a small amount of it is added to a solution of unknown pH, will change its color. This is a way to determine pH of a solution visually. The indicator used in this lab will be obtained from a natural source, red cabbage. Cabbage indicator yields a particular color depending on the pH of the solution. pH indicators are a good way to easily and quickly show the approximate pH by color when compared to a standard. An everyday example where a pH indicator is used is for testing a water sample from a swimming pool.

While pH indicators are useful for qualitative purposes, when an exact quantitative value is needed, a *pH meter* is used. A laboratory pH meter typically has a special probe capped with a membrane that is sensitive to H^+ion concentrations. The meter reading shows an exact pH value of the solution probed.

pH meters are used to measure pH values of water samples, such as determining acidity of rainwater samples. Rain water is contains dissolved carbon dioxide that produces a weakly acidic solution. Rain naturally has a pH between 5 and 6. The pH of rain in parts of the U.S. is less than pH 5, which is harmful to aquatic life and human health. This is acid rain.

Living organisms are very sensitive to the effects of acids and bases in their environment. An excess of H^+or OH^-can interfere with the functioning of biological molecules, especially proteins. Thus, in order to maintain homeostasis and survive, organisms must maintain a stable internal pH.

A *buffer* is a solution whose pH resists change on addition of small amounts of either an acid or a base. To be a good buffer, a solution should have a component that acts as a base (H^+ out of solution) and a component that acts as an acid (puts more H^+) into solution when there is an excess of OH^-).

The buffering capacity of a solution is tested by adding small amounts of acid (for example, HCl) and base (for example, NaOH) and checking the pH after each addition. If the pH changes only slightly, the solution is a good buffer. Eventually its buffering capacity will be exhausted, however, and the pH will change dramatically.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- to set up and show how to use a pH indicator
- to determine the pH of common solutions
- to understand pH differences of acids and bases
- to learn to use a laboratory pH meter
- to understand relationship between pH and H+ ion concentration

3.0 MAIN CONTENT

3.1 Experimental Procedure

3.1.1 Materials and Equipment

400-mL beaker, ring stand, wire gauze, Bunsen burner, large test tubes, dropper pipet, stirring rod, wash bottle with distilled water, laboratory pH meter, 0.1 M acetic acid, 0.1 M $NaC_2H_3O_2$, 0.1 M acetic acid ($HC_2H_3O_2$), 0.1 M hydrochloric acid (HCl), 0.1 M sodium hydroxide (NaOH), pH paper
Safety

Exercise appropriate caution when using the Bunsen burner.
Personal Protective Equipment (PPE) required: safety goggles, lab coat, closed-toe shoes Materials and Equipment

3.1.2 Experimental Procedure

Part A: Preparing pH indicator and pH standards

1. Tear a few leaves of red cabbage into small pieces and place the leaves into a 500-mL beaker. Add about 500-mL of distilled water to this beaker. Make sure that all of the leaf pieces are completely submerged.

2. Gently boil the mixture on heating plate until it appears dark purple in color (5-10 min). Turn off the heat and allow to cool (5 min).
3. Add cabbage indicator solution to pH standard solutions, labeled 1-13. Students will record the colors of the pH standards.
4. Each group will bring a small beaker to the front and take ~50 mL of the cabbage indicator back to their bench.

Part B: Qualitative Analysis for pH Values of Everyday Chemicals

1. Obtain 10 large test tubes (clean, but may be wet). Label each test tube with the solutions to be tested.
2. Pour about 3-mL of each solution into the appropriately labeled test tube.
3. Using a dropper pipet, add an equal volume of cabbage indicator solution. If necessary, stir to mix with a clean stirring rod (rinse with distilled water between uses).
4. Record the resulting color of the sample after mixed with the cabbage indicator. Compare this color with pH standards at the front of the laboratory to determine the pH of the sample. The color may be between the pH standard colors (e.g. green-blue instead of green or blue alone). For these, record the pH to 0.5 values (e.g. pH = 9.5 instead of 9 or 10).

Note
Do not discard the contents in these test tubes as they will be used in the next section.

Part C: Quantitative Analysis for pH Values of Everyday Chemicals

1. Plug the probe into one port on the side of the pH meter. Plug the AC adapter into the other side of the pH meter; plug the adapter into an electrical outlet. You should see a pH value reading.
2. Prepare the probe to make pH measurements: remove from the storage bottle and thoroughly rinse the lower section of the probe with distilled water/wash bottle.
   Note: Do not completely submerge the probe. The handle is not waterproof.
3. Use the same ten test tubes containing samples from Part B. Or, complete steps 1 and 2 of Part B to obtain ten samples for analysis. Insert the pH probe directly into each test tube. **SPECIAL CARE IS NEEDED WHEN INSERTING THE PROBES INTO THE TEST TUBES. The probes must NOT touch the glass rim of the test tubes or the pH blub can easily be broken and the probe destroyed.**
4. Record the pH value (to 0.01 pH) shown on the pH meter screen.
5. After each pH measurement, the probe must be thoroughly rinsed with distilled water.

6. When you are finished making measurements, rinse the probe with distilled water. Slide the cap onto the probe, and then screw the cap onto the storage bottle so the tip of the probe is immersed in the storage solution.

Part D: Effect of Buffers on pH

1. Obtain 4 large test tubes. Label the test tubes A, B, C, and D.
2. Add 10-mL of distilled water to tubes A and C.
3. Add a 5-mL quantity of both 0.1 M H $C_2H_3O_2$ (acetic acid) and 0.1 M $NaC_2H_3O_2$ (sodium acetate) to tubes B and D. This mixture of acetic acid and sodium acetate is a buffer solution. Stir to mix completely.
4. Using pH paper, determine the pH of the contents of each test tube (A-D). Use the stirring rod to dab a small drop of the solution to be tested onto a piece of pH paper. Then compare the color obtained to the pH scale on the instructor's desk to determine the pH value. Record these pH values to 0.1
5. Add 5 drops of 0.1 M (ice{HCl}\) (hydrochloric acid) to test tubes A and B. Record the pH using pH paper.
6. Add 5 drops of 0.1 M NaOH (sodium hydroxide) to test tubes C and D. Record the pH using pH paper.

12.3 Lab Report: Acids, Bases and pH

Part A: Color of Red Cabbage Indicator with pH standards

pH standard	Colour with cabbage indicator
1	
2	
3	
4	
5	
6	
7	
8	
9	
10	
11	
12	

Parts B and C: pH of Everyday Chemicals

Chemical	**Colour with indictor**	**Qualitative pH (to 0.5)**	**Acid, base or neutral**	**Qualitative pH to 0.01)**
Soda				
Shampoo				
Ammonia cleansert				
Breach				
Laundry detergent				
Lemon juice				
Vinegar				
Bottled water				
0.1 M HCl				
0.1 M NaOH				

Part D: Effect of Buffers on pH

Tube	**Contents**	**Initial pH**	**Chemical added**	**New pH**	**pH change**
A	Water		HCl		
B	Buffer solution (acetic acid and sodium acetate)		HCl		
C	water		NaOH		
D	Buffer solution (acetic acid and sodium acetate)		NaOH		

SELF-ASSESSMENT EXERCISE

i. Sodium hydroxide is a strong base. What is the pH of a 0.02M sodium hydroxide solution?
   A. 2
   B. 1.3
   C. 12.4
   D. 12.0

2. You are presented with a solution that has a pOH of 2.13. What is the pH of this solution?
   A $10^{-2.3}$
   B. 2.13
   C. 6.57
   D. 11.87

3. What is the pH for a 0.05M solution of hydrochloric acid?
   A. 6.95
   B. 1.3
   C. -0.3
   D. 0.05

4.0 CONCLUSION

Knowledge of pH is essential in our daily life including the food we eat, domestic chemicals and other components of the ecosystem. pH governs the reactivity or effect of chemicals on the target materials.

5.0 SUMMARY

The results and findings of the experiments reveals that knowledge of pH is needed in everyday life, considering the wide varieties of chemicals that used at home, industries, school, etc. Different applications may require different pH. In some cases, the pH needs to be stabilized by using buffer solutions.

6.0 TUTOR-MARKED ASSIGNMENT

1. What is an acidic solution? What is a basic solution?
2. What is an alkaline solution?
3. What is a pH indicator? What are common uses of pH indicators?
4. Write the mathematical equation that relates pH value and H^+ concentration:

- Circle correct choice:

Acids have (high OR low) pH, and (high OR low) H^+ concentration.
Bases have (high OR low) pH, and (high OR low) H^+ concentration.

5. When the H^+ concentration is expressed in brackets H^+ what are the units of the for H^+ concentration?
6. Does a solution with pH 10 have equal, less or more H^+ than of a solution with a pH 6? Calculate the H^+ for both solutions, include units in your answer:

- For pH 10, $[H^+]$ = _____
- For pH 6, $[H^+]$ = _____

7. The two methods of determining pH values (pH indicator versus pH meter) should show similar pH values for those solutions. What was different?
8. Explain why rain is naturally acidic, but not all rain is classified as “acid rain.
9. Here are examples of what an individual might do to reduce acid rain. For each, explain the connection to production of acid rain.

- avoid running a washing machine with a small load
- add additional insulation on a home hot water heater

- walking instead of driving to work

7.0 REFERENCES/FURTHER READING

Atkins, P. and de Paula, J. (2018). *Atkins 'Physical chemistry*. 11th Edition. Oxford University Press. UK.

Engel T. and Reid, P. (2005). *Physical chemistry*. Pearson Cummings. San Francisco. New York.

Jack, R. and Scholz, F. (2017). *Wilhelm Ostwald. The Autobiography*. Springer, Germany, ISBN: 978-319-46955-3 and 978-3-319-46953 (print)

Hammerich, O. and Speiser, B. (2015) *Organic electrochemistry* 5th edition, revised and expanded. Taylor & Francis Publication, UK. ISBN: 978-1-4200-8401-6 (hardback), 978-1-4200- 8402-3

Kulikovsky, A. (2018). *Analytical models for PEM fuel cell impedance*. Andrei Kulikovsky, USA. 2018, ISBN: 9781521470749

Levine, N. I. (2009). *Physical chemistry*.5th Edition. Higher Education. Boston.

Molina, A. and Gonzalez, J. (2016). *Pulse voltammetry in physical electrochemistry and electroanalysis. Theory and applications*. Springer, UK, ISBN: 978-3-319-21250-0

Monk, P. (2004). *Physical chemistry: Understanding the Chemical World*. John Wiley and Sons Ltd. England.

https://www.varsitytutors.com/high_school_chemistry-help/calculating-ph-and-poh

https://chem.libretexts.org/Bookshelves/Ancillary_Materials/Laboratory_Experiments/Wet_Lab_Experiments/General_Chemistry_Labs/Online_Chemistry_Lab_Manual/Chem_9_Experiments/08%3A_Acid%2C_Bases_and_pH_(Experiment)

UNIT 2 DETERMINATION OF RELATIVE MOLECULAR MASS FROM COLLIGATIVE PROPERTIES

CONTENTS

1.0 INTRODUCTION

The vapour pressure of a pure liquid at a given temperature is a characteristic property of that liquid. However, when a nonvolatile solute is dissolved in the liquid, the vapour pressure of the liquid is reduced. This lowering of the vapour pressure causes a change in the melting point, boiling point, and osmotic pressure of the liquid. The magnitude of the change in these properties depends upon the number of solute particles dissolved in a given amount of the solvent, but not upon the nature of the particles (their identity). Such properties are called colligative properties. The addition of ethylene glycol to the water in a car radiator in order to raise its boiling point, or the use of salt to lower the melting point of ice on a sidewalk is some everyday applications of colligative properties.

Most substances can exist as solid, liquid, or gas, depending upon the temperature and pressure. Whether a particular substance exists as a solid, liquid, or gas under conditions of standard temperature and pressure is dependent upon the nature of the substance and includes such properties as the molecular weight of the substance or the intermolecular forces of attraction between molecules.

If a substance that exists as a solid is heated, it will eventually melt to form a liquid. Suppose a substance that is a solid at room temperature is slowly heated. As energy is added to the solid, the temperature of the solid will begin to rise. Once the melting point of the solid is reached, however, the temperature of the solid-liquid mixture will remain constant until all the solid has been converted into a liquid. Only then will the temperature rise again. Does this make sense? If we are continuing to add heat to the sample, how can the temperature remain constant? The answer to this question is that the energy being added is used to bring about the phase change rather than to heat the sample. The process of melting involves a

breakdown of the attractive forces between molecules and requires energy.

A similar process occurs as a liquid sample is cooled. As heat is removed from the liquid, the temperature of the liquid will drop until the freezing point of the liquid is reached. Once the liquid begins to solidify, the temperature of the liquid-solid mixture remains constant until all of the liquid has solidified, and only then will the temperature begin to drop again. This is the reason oranges are sprayed with water if a freeze is expected; the temperature of a water-ice mixture cannot drop below the freezing point of water until all of the water has frozen. It is important to note that freezing and melting are really the same thing and occur at the same temperature for a particular substance.

The freezing point of a liquid is depressed when it contains a dissolved solid. A solution of salt water, for example, will freeze lower than the normal freezing point of water. The freezing point depression, or the difference between the freezing points of the pure solvent and solution, depends upon the number of particles in solution. The greater the concentration of the solution, the greater will be the freezing point depression. For a given concentration, a solute that dissociates will also bring about a greater freezing point depression. For example, a solution of NaCl will have twice the freezing point depression of a solution of sucrose of the same concentration. The sucrose is a molecular substance that does not dissociate in solution, but the NaCl will dissociate into Na^+ and Cl^- ions in solution, giving twice as many particles in solution.

The freezing point depression of a solution is represented by the following equation:

$\Delta T = K_f m$

Where: ΔT = the freezing point depression K_f = the freezing point depression constant m= the molality of the solution, or the number of moles of solute per kilogram of solvent.

The freezing point depression constant, K_f, is different from solvent to solvent. Therefore, a given quantity of solute will not always bring about the same freezing point depression. Some typical values are listed in the table below. You can see from this table that, of the substances listed, naphthalene has the largest value. What this means is that a 1.0 molar solution of a non-dissociating solute dissolved in naphthalene would freeze 6.8 degrees below the normal freezing point of naphthalene.

Solvent	**K_f (°C/m)**
Water	1.86
Benzene	5.12
Naphthalene	6.8
Chloroform	4.68
Cyclohexane	20.4

The equation listed above can be exploited in several ways. Suppose a known quantity of solute is dissolved in a known quantity of solvent and the freezing point depression is measured. If the molecular weight of the solute is known, the only unknown variable is the freezing point depression constant. If the freezing point depression constant is known, the equation can be solved for the number of moles of solute, from which the molar mass of the solute can be calculated. This is the approach to be taken in lab today. In the first part of the experiment, the freezing point of pure paradichlorobenzene will be determined. In the second part of the experiment, the freezing point depression constant for paradichlorobenzene will be determined by adding a known quantity of naphthalene and measuring the freezing point of the resulting solution. In the last part of the experiment, the molar mass of an unknown solute will be determined based upon the freezing point of a solution.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- investigate the phenomenon of freezing-point depression as a colligative property
- determine the molar mass of an unknown solute using freezing point depression.

3.0 MAIN CONTENT

3.1 Experimental Procedure

3.1.1 Determining the freezing point of pure paradichlorobenzene

Set up a hot water bath using a tripod, burner, and an 800- or 1000-mL beaker. Obtain the mass of an empty large test tube. Fill the test tube approximately one-fourth to one-third full of solid para dichlorobenzene and again determine the mass of the tube. Subtract the two masses to obtain the mass of paradichlorobenzene. Clamp the test tube in place in the hot water bath. Once all the

paradichlorobenzene has melted, remove the tube from the water bath and insert a rubber stopper containing a thermometer and wire stirrer. Stirring the sample constantly, record the temperature of the sample every 30 seconds. Graph your results and record the melting point of pure paradichlorobenzene.

3.1.2 Determination of the freezing point depression constant:

Weight out approximately 0.50 grams of naphthalene, $C_{10}H_8$, on a small piece of weighing paper. Return the test tube to the hot water bath and once the sample has completely melted, add the naphthalene. Remove the test tube from the hot water bath and repeat the above procedure. Calculate the freezing point depression of the solution, the molality of the solution, and from this data the freezing point depression constant for paradichlorobenzene. Return the test tube to the hot water bath and heat until the sample has melted. Pour the melted solution into the "PDB WASTE" container. If any solid remains in the test tube, wash it with a small portion of acetone. Any acetone waste should also go into the waste container. You may wish to repeat this procedure a second time.

3.1.3 Determination of the molar mass of an unknown solute:

Refill the test tube with fresh paradichlorobenzene and determine the mass of the test tube and contents. Weight out approximately 0.50 grams of unknown solute on a small piece of weighing paper. Add this to the test tube. Heat the test tube in the hot water bath until the mixture as completely melted. Remove the test tube from the water bath, insert the stopper containing the thermometer and wire stirrer, and record the temperature of the solution as in the previous trials. Determine the freezing point of the solution, the freezing point depression, and from this data calculate the molar mass of the unknown solute. Reheat the test tube and pour the molten solution into the "PDB WASTE" container. If the tube does not come completely clean, wash with a small portion of acetone. You may wish to repeat this procedure a second time.

SELF ASSESSMENT EXERCISE

1. Which observation(s) reflect(s) colligative properties?
   (I) A 0.5 m NaBr solution has a higher vapor pressure than a 0.5 m $BaCl_2$ solution.
   (II) A 0.5 m NaOH solution freezes at a lower temperature than pure water.
   (III) Pure water freezes at a higher temperature than pure methanol.
   (a) only I
   (b) only II
   (c) only III
   (d) I and II

(e) I and III

2. The vapor pressure of pure water at 85ºC is 434 torr. What is the vapor pressure at 85ºC of a solution prepared from 100 mL of water (density 1.00 g/mL) and 150 g of diglyme, $C_6H_{14}O_3$, a nonvolatile substance?
(a) 361 torr
(b) 390 torr
(c) 425 torr
(d) 388 torr
(e) 317 torr

3. The vapor pressure of a solution containing a nonvolatile solute is directly proportional to the
(a) molality of the solvent.
(b) osmotic pressure of the solute.
(c) molarity of the solvent.
(d) mole fraction of solvent.
(e) mole fraction of solute.

4. If 4.27 grams of sucrose, $C_{12}H_{22}O_{11}$, are dissolved in 15.2 grams of water, what will be the boiling point of the resulting solution? (K_b for water = 0.512 ºC/m) (Note: If the K_f and K_b are not given on the exam, you can find them on the back of the exam envelope.)
(a) 101.64 ºC
(b) 100.42 ºC
(c) 99.626 ºC
(d) 100.73 ºC
(e) 101.42 ºC

5. What are the ideal van't Hoff factors for the following compounds: $Ba(OH)_2$, $C_6H_{12}O_6$, K_3PO_4, HNO_3 ?
(a) 1, 1, 1, 1
(b) 2, 1, 2, 2
(c) 3, 1, 4, 2
(d) 6, 3, 5, 5
(e) none of the above

6. Calculate the approximate initial boiling point (in ºC) of a solution of 285 g of magnesium chloride in 2.0 kg of water. (Assume complete dissociation of the salt.)
(a) 103.1 ºC
(b) 101.6 ºC
(c) 102.3 ºC
(d) 100.8 ºC
(e) 104.8 ºC

7. A solution made by dissolving 9.81 g of a nonvolatile nonelectrolyte in 90.0 g of water boiled at 100.37 ^{o}C at 760 mm Hg. What is the approximate molecular weight of the substance? (For water, K_b = 0.51 ^{o}C/m)
(a) 240 g/mol
(b) 150 g/mol
(c) 79 g/mol
(d) 61 g/mol
(e) 34 g/mol

8. What is the freezing point of an aqueous 1.00 m NaCl solution? (K_f = 1.86 ^{o}C/m) (Assume complete dissociation of the salt.)
(a) -1.86 ^{o}C
(b) +1.86 ^{o}C
(c) -3.72 ^{o}C
(d) -0.93 ^{o}C
(e) 0.0 ^{o}C

9. A 17.3 mg sample of an organic compound (a non-electrolyte) was ground up with 420 mg of camphor to form a homogeneous mixture melting at 170.0 ^{o}C. What is the apparent formula weight of the organic compound? (K_f of camphor = 37.7 ^{o}C/m, m.p. of camphor = 178.4 ^{o}C) (Note: This is a freezing point depression problem - note the K_f of camphor - camphor is the solvent.)
(a) 353 g/mol
(b) 285 g/mol
(c) 231 g/mol
(d) 185 g/mol
(e) 166 g/mol

10. Calculate the osmotic pressure associated with 50.0 g of an enzyme of molecular weight 98,000 g/mol dissolved in water to give 2600 mL of solution at 30.0 ^{o}C.
(a) 0.484 torr
(b) 1.68 torr
(c) 1.96 torr
(d) 2.48 torr
(e) 3.71 torr

11. A 250 mL solution containing 21.4 g of a polymer in toluene had an osmotic pressure of 0.055 atm at 27 ^{o}C. What is the apparent formula weight of the polymer?
(a) 15,000 g/mol
(b) 18,000 g/mol
(c) 26,000 g/mol
(d) 32,000 g/mol
(e) 38,000 g/mol

4.0 CONCLUSION

Study on colligative properties of a substances can provide a link to analysis of mole related parameter and molar mass

5.0 SUMMARY

Most substances can exist as solid, liquid, or gas, depending upon the temperature and pressure. Whether a particular substance exists as a solid, liquid, or gas under conditions of standard temperature and pressure is dependent upon the nature of the substance and includes such properties as the molecular weight of the substance or the intermolecular forces of attraction between molecules.

In this unit, you learnt how to investigate the phenomenon of freezing-point depression as a colligative property and determine the molar mass of an unknown solute using freezing-point depression.

6.0 TUTOR-MARKED ASSIGNMENT

Make three graphs - a cooling curve pure paradichlorobenzene versus time, a cooling curve of for the para dichlorobenzenenapthalene mixture versus time, and a cooling curve of the paradichlorobenzene - unknown solute mixture versus time.

1. Calculate the freezing point depression constant for paradichlorobenzene.
2. Calculate the molar mass of the unknown solute.

7.0 REFERENCES/FURTHER READING

Corey, E. J. and Cheng, X. (1998). The logic of chemistry synthesis. Wiley, New York

Leonard, J. Lygo, B. and Procter, G. (2013). Advanced practical organic chemistry. 3rd edition. CRC press, UK.

Li, J. J., Pflum, D. A. and Limberakis, C. (2007). Modern synthesis in the Laboratory. CRC press, UK

Richard, O. C., Norman, C. and Coxon, J. M. (2010). Principles of organic synthesis. CRC press, UK

Vogel, A. I. (2011). Tectbook of practical organic chemistry. 3rd edition. Lonoman, UK.

Vogel, A. I., Tatchell, A. R and Furnis, B. S. (1996). Vogel's textbook of practical organic chemistry. 5th Edition. Pearson Edition, UK

UNIT 3 DETERMINATION OF PARTITION FUNCTION

CONTENTS

1.0 INTRODUCTION

This series of experiments will familiarize you with the common technique of liquid-liquid extraction. Extraction is an excellent way to separate the components of a mixture based on differential solubility in two immiscible solvents, normally water and an organic solvent. Separating a water-soluble compound from an organic-soluble compound is simply a matter of dissolving them in the solvent mixture and physically separating the two layers.

This is an especially powerful technique for chemists who have a good command of acid-base properties (and pK_as) and understand how solubility depends on polarity. One can often take advantage of acidity and basicity to move a compound from one layer to another as desired and effect a clean separation.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- examine the partitioning of benzoic acid between an organic and an aqueous layer and separate it from a neutral organic compound
- examine the partitioning of an indicator, whose colour depends on the pH
- use what you have learnt to separate a three-component mixture.

3.0 MAIN CONTENT

3.1 Experiment

A: *Determination of the partition coefficient for benzoic acid in CH_2Cl_2 and H_2O*

Equipment and supplies
You need a centrifuge tube fitted with a cap and a couple Pasteur filter pipettes. Syringe pipettes will be provided for each solvent used in this part of the experiment. Your instructor will instruct you on how to use the syringe pipettes. The chemicals needed for this experiment are benzoic acid, methylene chloride, water and anhydrous sodium sulfate.

CAUTION! Methylene chloride is a known carcinogen. When working with it, wear two sets of gloves (a blue pair over a white pair) and avoid breathing the fumes. Keep all containers and apparatus with methylene chloride in the hood at all times.

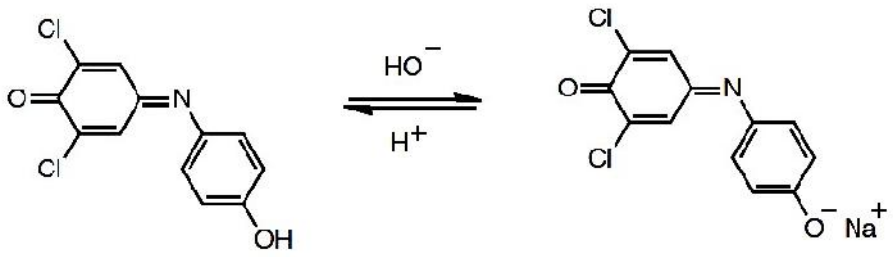
Procedure
Add 50 mg of benzoic acid followed by the addition of 1 ml of water and 1 ml of Methylene Chloride to a centrifuge tube. A syringe is supplied for each transfer (a syringe is attached to each solvent bottle). Cap the centrifuge tube and either carefully shake the contents of the vigorously for 30 seconds by hand or use a Vortex mixer. Remove the cap and allow the two layers to separate. Which solvent is the top layer? Which solvent is the bottom layer? What is a quick and simple technique/way to identify either layer?

Carefully remove the organic phase using a Pasteur pipette, Transfer the methylene chloride layer to a dry conical vial and add about 50 mg of anhydrous sodium sulfate. As sodium sulfate is a drying agent (absorbs water) and removes trace of moist only, you might add some extra anhydrous sodium sulfate in order to dry the organic phase completely. Recap the vial and let the sodium sulfate dry the organic phase for 15 minutes.

Transfer the dried organic phase via a dry Pasteur pipette to a tared and dry conical vial containing a boiling chip. Rinse the sodium sulfate with about 600 $\propto$ l of methylene chloride and combine the organic extracts. Why is a rinse performed? Evaporate the organic solvent in the fume hood using a warm sand bath and reheat the vial to remove the last traces of solvent (and water) until a constant weight of the solid is obtained. Turn in your dried product in a properly labeled plastic bag. Determine the amount of benzoic acid recovered and calculate a value for the distribution coefficient (K_D).

3.2 Experiment B:

Microscale partitioning of a colored indicator
In this experiment, we will use an indicator, 2,6- dichloroindophenol (In-OH), to see how acidity and basicity can be used to move a compound between organic and aqueous layers. Think about what's happening at each step of the procedure.



In-OH pK_a=5.9
Red-organic soluble

In-O Na^+
Blue-water soluble

A solution of 25 mg of In-O^- Na^+ in 50 ml of 0.02 M NaOH will be provided. It should be BLUE; if it's not blue, don't use it, and don't just put it back either — hand it to your TA. Add 0.1 ml (100 ∝l) of the solution to a 2 ml pre- made mixture of 1:1 H_2O-CH_2Cl_2 in a 5-ml conical vial. Note the appearance of the mixture. Shake the vial and note any change that occurs. Next, add 100∝ l of 0.05 M aq HCl and note the appearance of the mixture — what color is present, and where is it? Shake and observe. Finally, add 100∝ l of 0.1 M aq NaOH, then shake. How do you explain the observed changes? Repeat this entire experiment using diethyl ether in place of dichloromethane.

3.3 Experiment C:

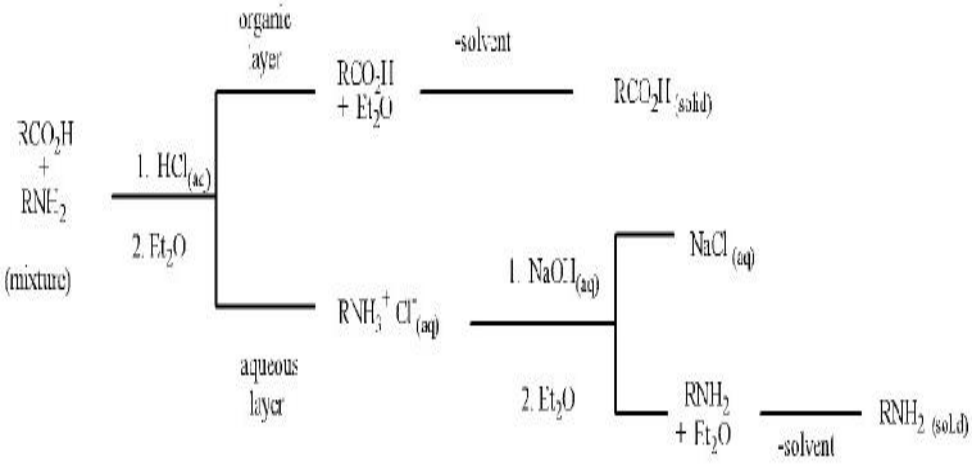
Macroscale separation of an acid, a base, and a neutral compound
In this experiment, you will take advantage of acidity and basicity to separate benzoic acid, benzocaine (ethyl p-aminobenzoate), and fluorenone. This experiment will be done on a larger scale than the previous experiments, so you'll need to use a separator funnel ("sep funnel").

Vent the funnel frequently and carefully by pointing it away from yourself and others.

Diethyl ether is rather volatile, so work in the hood as much as possible to avoid filling the lab with fumes.

A few helpful hints: (1) Some of the ether will evaporate during the procedure, so you may need to add a little more - try to keep the volume from getting too low. (2) You will need to remove one layer or another in each step of the extraction - do not throw anything away until you're done! Even though you may think there's nothing valuable in there, you could be mistaken. Chemists more experienced than you have accidentally tossed valuable - really valuable - compounds in the waste bottle. If you save all the solutions you can backtrack until you find out where you lost the goodies. (3) Keep a beaker under the sep funnel as you fill it in case the stopcock leaks (or if you forget to close it). (4) Be sure that all your flasks are labeled so you can keep track of what's what. (5) Be careful in neutralizing strongly acidic or basic solutions. These are exothermic processes. It's good practice to have an ice bath nearby just in case things get out of hand.

Before coming to lab, you MUST have in your notebook a flow chart showing each step of the separation procedure, including the structures of the compounds and which compounds go where in each step. An example is provided below.



A mixture of the three compounds (in unknown ratio) will be provided. Weigh out 300 mg of this mixture and dissolve it in about 10 ml of diethyl ether in a hood. Transfer the solution to your 30-ml separating funnel.

Carefully add 4 ml of 3 M aqueous HCl, shake (remember to vent the funnel frequently!), allow the layers to separate, and remove the aqueous layer. Repeat this step with another 4-ml portion of 3 M aq HCl and combine this with the other aqueous layer. (Note that these directions can be shortened by saying: "extract the Et_2O solution twice with 4 -ml portions of 3 M aq HCl", or "... with 2 x 4 ml 3 M aq HCl".) Add 6 M aq

NaOH drop wise to the acidic aqueous solution until it is basic (use litmus paper). Cool the solution in ice for 10 - 15 min, isolate the solid by suction filtration, rinse it with two 2- ml portions of cold water, and allow it to air-dry. (What is this solid?)

Extract the ether solution with 2 x 4-ml of 3 M aq NaOH. Set the combined aqueous layers aside. Wash the ether solution with 2 x 2 ml water followed by 2 ml of brine (saturated aq NaCl), and transfer it to a clean, dry Erlenmeyer flask. ("Wash" means basically the same thing as "extract". To "extract" is to obtain good stuff; to "wash" is to remove dirt, i.e. impurities.) Add about 0.5 - 1 g of anhydrous Na_2SO_4, stopper the flask, and set it aside. This drying agent soaks up any residual water. Most of the sodium sulfate should be free flowing; if it's all clumped, add a little more.

Take the basic aqueous solution from above and acidify it by drop wise addition of 6 M aq HCl. Cool the solution in ice, isolate the solid by suction filtration, rinse it with two 2-ml portions of cold water, and allow it to dry. (What is this solid?!)

Filter the drying agent from the ether solution and rinse it with some ms of ether. Evaporate the solvent with a stream of dry air in the hood. After all the solvent is gone, there should be a solid left.

Determine the mass, % recovery, and melting points of the three solids, label them, and turn them in.

SELF ASSESSMENT EXERCISE

i. 5.0 g of an organic compound is shaken in a separating funnel containing 20 ml of water and 80 ml of ether and was allowed to reach equilibrium. Given that the Kpc water to ether is 6, calculate the amount of organic compound that has dissolved in the ether.

ii. Calculate the partition coefficient of caffeine in water/methylene chloride from the following data: 10.3 g/100 mL for methylene chloride and 2.04 g/100 mL for water.

iii. In a very controlled experiment (not ours), a student is sure that 0.500 grams of caffeine is dissolved in 125 mL of water. The student extracts the caffeine using a single extraction of 21 mL of methylene chloride. How much caffeine is in the methylene chloride? How much remains in the water? (use the partition coefficient calculated in 2 above)

4.0 CONCLUSION

Determination of partition function provide a useful parameter for handling solvents and has a wider industrial and laboratory applications

5.0 SUMMARY

If a solute is added to two immiscible solvents, A and B. in contact with each other, the solute distributes itself between the two and equilibrium is set up between the solute molecules in solvent A and the solute molecules in solvent B. The ratio of the concentration of the solute in the two solvents is:

$$k - \frac{Concentration\ of\ solute\ in\ solvent\ A}{Concentration\ of\ solute\ in\ solvent\ B}$$

where K is known as the partition coefficient or distribution coefficient. In this unit, you have come in contact with three different experiments demonstrating partition coefficient:

The partitioning of benzoic acid between methylene chloride and water
Using an indicator to see how acidity and basicity can be used to move a compound between organic and aqueous layers .

Take advantage of acidity and basicity to separate benzoic acid, benzocaine (ethyl p-aminobenzoate), and fluorenone.

7.0 REFERENCES/FURTHER READING

Corey, E. J. and Cheng, X. (1998). The logic of chemistry synthesis. Wiley, New York

Leonard, J. Lygo, B. and Procter, G. (2013). Advanced practical organic chemistry. 3rd edition. CRC press, UK.

Li, J. J., Pflum, D. A. and Limberakis, C. (2007). Modern synthesis in the Laboratory. CRC press, UK

Richard, O. C., Norman, C. and Coxon, J. M. (2010). Principles of organic synthesis. CRC press, UK

Vogel, A. I. (2011). Tectbook of practical organic chemistry. 3rd edition. Lonoman, UK.

Vogel, A. I., Tatchell, A. R and Furnis, B. S. (1996). Vogel's textbook of practical organic chemistry. 5th Edition. Pearson Edition, UK

UNIT 4 TEMPERATURE MEASUREMENT AND HEAT OF DISSOLUTION

CONTENTS

1.0 INTRODUCTION

Temperature is a measure of how hot or cold an object is. Whenever there is a temperature difference, there will be a spontaneous heat flow from the object at higher temperature to the object at lower temperature. Thermometer is the instrument used to determine temperatures.

Celsius and Kelvin scales are used for metric and SI units respectively while Fahrenheit scale is the choice for British units. These three scales are related by the following relationships:

$K = {}^0C + 273$ $^0F = 9/5\ (^0\ C) + 32$ $^0C = 5/9\ (^0F - 32)$

+Every change, physical or chemical, is associated with a change in energy, usually in the form of heat. The energy change of a reaction that occurs under a constant pressure is defined as the heat of the reaction or the enthalpy change. If heat is evolved during the change, the process is exothermic, and if heat is absorbed during the change, the process is considered to be endothermic. By convention, enthalpy change for an exothermic process has a negative value while that of an endothermic process has a positive value.

We are familiar with different forms of energy. Heat energy, light energy, electrical energy, nuclear energy, chemical energy of the bonds in a molecule, are just a few examples of different forms of energy. From the law of conservation of energy, during any physical or chemical change:

Energy lost = Energy gained

In this experiment, you will become familiar with temperature measurements and record the temperature changes that occur when ammonium chloride and calcium chloride are dissolved in water. From this data, you will be able to calculate the heat energy given off or absorbed during this dissolution process (heat of dissolution).

Heat absorbed/ evolved = (mass) (specific heat) (temperature change)
The SI unit for heat is joule (J) while a non-SI unit calorie (cal) is widely used in scientific measurements. The relationship between these two units is: 1 cal = 4.184 J

Specific Heat is the amount of heat required to raise the temperature of one gram of a substance by one degree Celsius. It can be expressed in cal / g.^{0}C or Joules / kg Kelvin. Water has a relatively high specific heat of 1 cal /g.^{0}C while metals usually have low specific heat. To calculate the heat of dissolution in water, specific heat of the aqueous solution will be considered to be that of pure water, 1 cal / g.^{0}C.

Calorimeter is an instrument used to measure heat flow in and out of a system. In this experiment, the calorimeter will consist of two Styrofoam cups, one nesting in the other.

2.0 OBJECTIVES

By the end of this unit, you should be able to:

- measure the enthalpy/heat flow as different solutes are dissolved in aqueous solution
- determine the heat of solution.

3.0 MAIN CONTENT

3.1 Experimental procedure

3.1.1 Materials:

Beaker (100 mL), Thermometer, Hot Plate, Graduated Cylinder (50 mL), Ring Stand, Thermometer Clamp, Stirring Rod, Balance, Spatula, Styrofoam Cups (2), Cardboard Square, Sodium Chloride (NaCl), Calcium Chloride ($CaCl_2$), Ammonium Chloride (NH_4Cl), Ice.

A. Temperature measurement

1. Using thermometer, measure the temperature of 50 mL of water in a 100 mL beaker. Be sure that the bulb is steady during the measurement and not touching the glassware. The bulb needs to be fully immersed in the liquid.
2. Place a 100 mL beaker with 50 mL water on a hot plate. Place a thermometer in the water with the help of a stand and clamp. Bring the water to a boil indicated by steady stream of bubble formation from within the liquid. Once water starts to boil temperature is going to be steady until all of the water boils off. Measure the boiling point of water.

3. Make about 30 mL of an ice-water mixture in a 100 mL beaker. Stir the ice slush and measure the temperature.
4. Add three tea spoons full of table salt, sodium chloride, to the slush and stir. Measure the temperature of the mixture.

B. Heat of dissolution

Work in pairs for this section.

1. Weigh out about 10 grams of $CaCl_2$. Be sure to record the exact mass. Construct a calorimeter by nesting two Styrofoam cups, one inside the other. Add 50 mL of water to the calorimeter. Allow the water to stand for five minutes to reach a stable temperature.
   Place a small piece of card board to cover the cup. Make a small hole at the center of the card board and insert the thermometer through the hole. Make sure the thermometer bulb is under water. Measure the temperature of water. This is the initial temperature (T_i).
2. Holding the calorimeter steady, add all of the CaCl2 to water, place the cover, and stir rapidly with a thermometer. Be careful with the bulb of the thermometer while stirring.
3. After mixing, time - temperature data should be recorded. One partner should record the temperature while bother reads the time and keeps the record.
4. For five minutes, right from the start of mixing, take temperature at intervals of every 30 seconds. The highest temperature reached is the final temperature (T_f) of water.
5. Print the temperature versus time plot using the graph paper provided in the lab book.
6. After recording your data, wash contents of the cup down the sink with lots of water.
7. Repeat steps 1 - 7 using approximately 10 grams of ammonium chloride. The minimum temperature reached in this case is the final temperature (T_f).

SELF ASSESSMENT EXERCISE

- Differentiate between heat of solution and molar heat of solution
- solvent Under what condition can dissolution be exothermic or endothermic?
- How can you measure enthalpy of solution in the laboratory?
- Outline three steps involves in calculation of molar heat of solution

4.0 CONCLUSION

Different solutes have different heat of dissolution in a given solvent. Such measurement is useful in characterizing the behaviour of such solute in a given solvent

5.0 SUMMARY

Temperature and heat of dissolution are quantities that can be measured in the laboratory.

In this unit, you have been able to:

- demonstrate the enthalpy/heat flow as different solutes are dissolved in aqueous solution determine the heat of solution

6.0 TUTOR-MARKED ASSIGNMENT

Report Sheet

Part A - Temperature measurement

Water at room temperature: _____ ^oC

Boiling Water: _____ ^oC

Ice water: _____ ^oC

Ice water with salt: _____ ^oC

Part B - Heat of Dissolution

Heat gained by water during the dissolution of $CaCl_2$:

Mass of $CaCl_2$: _____ g

Mass of Water: _____ g

Total Mass of Solution: _____ g

T_i : _____ ^oC T_f : _____ ^oC

Temperature change: _____ ^oC

Heat of dissolution per gram of solute: _____ cal/g. (show calculation)

Dissolution of $CaCl_2$ is exothermic or endothermic? _____.

$CaCl_2$ can be used in hot packs or cold packs? _____.

Heat lost by water during the dissolution of NH_4Cl:

Mass of NH_4Cl: _____ g

Mass of Water: _____ g

Total Mass of Solution: _____ g

T_i : _____ ^oC T_f : _____ ^oC

Temperature change: _____ ^oC

Heat of dissolution per gram of solute: _____ cal/g. (show calculation)

Dissolution of NH_4Cl is exothermic or endothermic? _____.

NH_4Cl can be used in hot packs or cold packs? _____.

7.0 REFERENCES/FURTHER READING

Corey, E. J. and Cheng, X. (1998). The logic of chemistry synthesis. Wiley, New York

Leonard, J. Lygo, B. and Procter, G. (2013). Advanced practical organic chemistry. 3rd edition. CRC press, UK.

Li, J. J., Pflum, D. A. and Limberakis, C. (2007). Modern synthesis in the Laboratory. CRC press, UK

Richard, O. C., Norman, C. and Coxon, J. M. (2010). Principles of organic synthesis. CRC press, UK

Vogel, A. I. (2011). Tectbook of practical organic chemistry. 3rd edition. Lonoman, UK.

Vogel, A. I., Tatchell, A. R and Furnis, B. S. (1996). Vogel's textbook of practical organic chemistry. 5th Edition. Pearson Edition, UK