SIC1012

Laboratory Skills

Name:

Department of Chemistry, Faculty of Science, Universiti Malaya, 50603 Kuala Lumpur, Malaysia

Preface

Laboratory Skills (SIC1012) is the subject catering for practical skills needed in all sections of chemistry. The experiments are embedded into specific contexts and conducted at different laboratories, which are operated by three organisational sections in the Chemistry Department, *i.e.,* Inorganic Chemistry, Organic Chemistry and Physical Chemistry. This separation, however, is solely based on organisational reason and differing infrastructure for laboratories, it does not reflect varying skill requirements for different directions of chemical laboratory work.

This course emphasises on the practical skills for laboratory operations and not the theory behind the experiments. Students will be exposed and trained on skills and techniques needed for volumetric titration in stoichiometric analysis; qualitative organic analysis in elemental analysis and functional group tests; investigation on chemical reaction kinetics and measurement of reaction enthalpy. The assessment is reflected in a series of experiments hands-on and the practical examination by the end of semester, where students will demonstrate the effective use of laboratory techniques learned. Only selected laboratory operations will be examined by individual basis. The experimental output will be evaluated based on objectives criteria which cover the quality and amount for sample preparations (e.g., purification method such as crystallisation or distillation) or the accuracy of analytical determinations (e.g., titration endpoint). In addition, observations during the operation of the exam task, experimental setup, and conduction, may be considered as well.

Besides the indicated motoric lab skills, lab safety is another focus in this course. While the theory is addressed in lectures (Pre-requisite SIC1011) and briefing, its practical execution will be evaluated during the experiments. At the end of the course, students will be able to

1. Measure chemical properties based on quantitative analysis.
2. Execute test reactions for qualitative analysis of organic compounds.
3. Perform mathematical data-analysis based on experimental measurements.

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SAFETY IN THE LABORATORY

Detailed information on the safety and health practice in Universiti Malaya (UM) can be found online at: UMPortal>PTj Info> OSHE>UM Laboratory Safety Guidelines (LSG) or download via QR code.

LSG

The University has a statutory obligation to comply with the safety requirements and you, as a student, have a duty to abide by the regulations. The following notes are to guide you in good laboratory practice and to familiarise yourself with the safety aspects of your laboratory work.

Emergency Telephone Numbers:

National Emergency Number	999 (Mobile phone, dial 112)
University Security Office	03 7967 7070 / 3582
University Malaya Medical Centre (UMMC)	03 7949 2898 / 2190
Students' Health Clinic	03 7949 2837 / 3737
Office of Safety and Health (OSH)	03 7967 7925
Department of Chemistry office	03 7967 4024 / 2128
Pantai Fire Station (Jalan Pantai Baru)	03 2282 4444
Pantai Police Station (Jalan Pantai Baru)	03 2282 4222 / 2207

Responsible staffs

Lecturer in charge

Inorganic Chemistry Laboratory

Ms. Zailawati Mohamad Zakaria	
Ms. Nurul Hafizah Hamid	**(Inorganic Chemistry I)**
Mr. Muhamad Hafizie Muhamad Sofi	(Inorganic Chemistry II)
Mr. Sugakumar A/L Varuthan	(Inorganic Chemistry III)
Ms. Maemawati Mohamad	(Inorganic Chemistry III)

Physical Chemistry Laboratory

Mr. Mohd Shukri A. Aziz	
Mr. Hashim Mohammad Salleh	**(Physical Chemistry I)**
Ms. Najiyah Ghazali	**(Physical Chemistry I)**
Mr. Md. Hakim Zakaria	(Physical Chemistry II)
Ms. Noor Azlin Che Din	(Physical Chemistry III)

Organic Chemistry Laboratory

Ms. Dara Fiona Mohamad	
Ms. Nurul Ain Hassani	**(Organic Chemistry I)**
Ms. Siti Nur Faridatul Asyikin Said	(Organic Chemistry II)
Ms. Juria Seko	(Organic Chemistry III)
Mr. Zulkiflee Hussin	(Organic Chemistry III)

Safety is the primary concern in any chemical laboratory. Chemicals are almost all potentially hazardous. Fortunately, with sensible and correct precautions, the risks can be minimised if basic safety practices are followed. The responsibility for laboratory safety lies with everyone working in the laboratory. Sensible laboratory conduct does not mean memorising a list of rules! The true test is the actual conduct in the laboratory and safety rules apply to all laboratory activities. Individual safety is affected by the action of fellow workers in the laboratory. Therefore, it is in everyone's best interest to follow safety work practices.

General Safety Rules for the Undergraduate Laboratories

The guidelines below are recommended for working safely in the laboratory.

- No work is to be carried out unless a member of staff is present.
- Plan your work. Follow instructions. If you do not know how to do the experiment safely, ask the lecturer or demonstrator.
- Know the location of all exits for the laboratory and the building. There are two exits in every teaching lab.
- Know the location of the alarm and fire extinguishers and how to operate them. There are two fire extinguishers located at the two sides in the lab.
- Know the location and use of safety showers, eye-washers, and safety aid boxes. The safety shower and eye washer are located right next to the exit the lab.

Fire extinguisher, eye wash and safety shower in First Year Laboratories.

- Know the location of the nearest telephone that can be used during an emergency.
- All persons in laboratories (whether they are doing practical work) **must wear safety glasses** or goggles and laboratory coats. Be aware, that spectacles are NO REPLACEMENT for safety glasses, as they lack side protection. If you need to ware spectacles, ensure that your safety glass can cover the glasses properly. You might find safety glasses a nuisance to wear, but your eyes are very sensitive and chemical spills inside the eye bear high chance for permanent damage. You are not allowed to wear contact lenses in the laboratory.
- Hair should be secured so that it does not hang below the neck. Other clothing that may become entangled should also be secured. It is important to wear suitable clothing. In view of fire hazards, natural fibres, like cotton, are encouraged. Your footwear must incorporate flat heels, slip-resistant soles and the uppers must fully enclose the foot.

- No food, drink (including drinking water!), cigarettes and cosmetics are allowed to be taken into the laboratory or storage place for chemicals.
- Do not smell or taste chemicals.
- Know the potential hazards of the materials and equipment with which you will work. The preparation for an experiment involves the study of the respective material safety data sheets for all chemicals used in that experiment. Refer to the chemicals' Material Safety Data Sheet (MSDS) before usage.
- Do not make skin contact with any substances. Use gloves where necessary, always remembering that they are semi-permeable. Gloves typically only provide a short time protection; when you notice the glove to get wet, remove it asap and replace with a new one. This particularly applies for the common single-use protective gloves.
- Experiments must be conducted on clean working surfaces; any spillage should be cleaned immediately. A high standard of tidiness should be always maintained. Contaminated surfaces and equipment must be cleaned as soon as it is practicable after use. The equipment should then be put away. Do not clutter bench space with unused equipment and bottles of chemicals.
- Waste should be disposed of in appropriate containers. Special waste includes:
    - Broken glassware and other sharps
    - Contaminated solid waste (e.g., used silica gel)
    - Mercury waste (e.g., broken thermometer)
    - Aqueous waste containing heavy metals (e.g., nickel or manganese solutions)
    - Organic waste: Organic waste is segregated into two (2) groups and stored separately, *i.e.,* halogenated waste (examples are chloroform, dichloromethane) and non-halogenated waste (examples are acetone, alcohol, toluene, xylene).
- Bags and other personal items should be placed in the lockers provided outside the laboratory and not left along corridors or on benches.
- All accidents and dangerous occurrence must be reported immediately to the lecturer in charge or the demonstrator or the laboratory assistant. The first aid box is located inside the preparation room of the laboratory. The accident book is also kept in the preparation room; the laboratory assistant must file out a report for all incidents.
- It is important to ensure that hands are washed, and all protective clothing removed before leaving the laboratory.
- Do not wear laboratory coats, gloves, or other personal protective clothing outside of the laboratory and in non-laboratory areas. These clothing may have become contaminated.

Additional Guidelines

Remember that in a laboratory you have fellow students around you. They do not know what you are doing, but they hope and expect that what you are doing is sensible and safe. Always think carefully about what you are about to do.

- Know the lecturer in charge, the demonstrator, and the laboratory assistants of the laboratory.
- Undergraduates are not allowed to work or even be in any of the teaching laboratories at any time outside of the specified laboratory hours unless they have explicit permission from the lecturer in charge. This includes times before and after class, and the lunch break.
- Students should come to the laboratory on time and be prepared by studying the experiment. Therefore, plan your activities before you come to the laboratory.

- Write everything you do, and observations in your notebook so that you can trace your action and make corrections if necessary. Please designate one notebook for this purpose and use it for the whole session / cycle.
- Do not use cracked or broken glassware. Check glassware before using it.
- Never use open flames, unless instructed by the lecturer in charge. If flames are permitted, plan your experiments so that you never leave your flame unattended. There are other sources of heat such as steam baths and hot plates.
- Handle all chemicals with care and read labels before attempting to get them.
- Use a spatula to get solid chemicals. Never using your fingers.
- Be careful not to contaminate reagents with your spatulas or droppers. Do not take more than needed. If you take too much of a chemical or reagent, give it to a fellow student – but do not return it to the bottle.
- Do not wander off with the only bottle of reagent that everyone needs; keep it in its assigned location.
- Do not pipette by mouth. Use only mechanical pipetting devices.
- Never look directly into the mouth of a flask containing a reaction mixture.
- Never point a test tube or reaction flask towards yourself or your neighbour.
- When using a separating funnel, vent frequently and remove the stopper immediately upon setting it upright for separation.
- Never use a thermometer as a stirrer! If a mercury thermometer breaks, immediately contact the lecturer in charge, the demonstrator or laboratory assistant.
- Turn off water, burners, or electrical equipment when not in use.
- Wash your glassware at the end of the laboratory session. You will have clean and dry glassware ready to be used for the next laboratory class.
- Make sure glassware or equipment is put away in the correct locker – your personal locker or the common locker.
- Clean your work area and equipment used before leaving the laboratory.

Experiments' Planning

The laboratory component is an essential part of SIC1012. Attendance at all laboratory classes is compulsory. Students are expected to be prepared. Students may be prohibited from doing an experiment if we believe that they are unprepared.

SAFETY INFORMATION ACKNOWLEDGEMENT
INFORMED CONSENT

(Sign and keep for your record)

I acknowledge receipt and that I have read and understand the lab safety regulations and that I received a briefing on these regulations from my laboratory Instructor/Lecturer. I also acknowledge that I was given the opportunity to ask any relevant questions during the safety briefing. I understand that there may be inherent risks and possible hazardous exposure with laboratory experiments depending on one's medical condition. If pregnant, or you suspect, should become, or plan to become pregnant during the semester, or have a medical condition that may be affected by my participation in this laboratory session, I understand that it is my responsibility to discuss any and all issues with my medical care provider.

Further, I accept any and all risk associated with the use of the Chemistry laboratory(s) and the equipment contained therein. I also understand that I am responsible for my personal property at all times. By signing this agreement, I fully understand and consider it my responsibility to comply with the safety regulations outlined above. I hereby agree for myself, my family, successors, and assigns to hold harmless the Universiti Malaya (UM), Department of Chemistry of the Universiti Malaya, Faculty of Science of the Universiti Malaya, Lecturers, Laboratory Staff and assigns from any and all claims, causes of action, suits, liabilities, damages, losses, demands, costs, expenses or judgments for damages or injuries to myself or others arising from my participation in the lab, whether or not I consulted a medical provider as delineated above.

Signature of the student: _____ Course: _____

Name: _____ Lecturer: _____

Matric number: _____ Session: _____

IC number: _____ Semester: _____

Date: _____

Provide the name and telephone number of two "Emergency Contacts" that can be reached during lab class times. Please note that your medical or physical condition may be released to the contact person at the time of the emergency call.
Indicate the relationship to the person and the telephone location (office, home or cellular). Please print clearly.

_____	_____	_____
Emergency Contact (Name)	Relationship	Phone
_____	_____	_____
Emergency Contact (Name)	Relationship	Phone

Student's copy

SAFETY INFORMATION ACKNOWLEDGEMENT
INFORMED CONSENT

(Return this signed page to your lecturer)

I acknowledge receipt and that I have read and understand the lab safety regulations and that I received a briefing on these regulations from my laboratory Instructor/Lecturer. I also acknowledge that I was given the opportunity to ask any relevant questions during the safety briefing. I understand that there may be inherent risks and possible hazardous exposure with laboratory experiments depending on one's medical condition. If pregnant, or you suspect, should become, or plan to become pregnant during the semester, or have a medical condition that may be affected by my participation in this laboratory session, I understand that it is my responsibility to discuss any and all issues with my medical care provider.

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Signature of the student: _____ Course: _____

Name: _____ Lecturer: _____

Matric number: _____ Session: _____

IC number: _____ Semester: _____

Date: _____

Provide the name and telephone number of two "Emergency Contacts" that can be reached during lab class times. Please note that your medical or physical condition may be released to the contact person at the time of the emergency call.
Indicate the relationship to the person and the telephone location (office, home or cellular). Please print clearly.

Emergency Contact (Name)	Relationship	Phone
Emergency Contact (Name)	Relationship	Phone

Department's copy

LAB SCHEDULE

In view of the organization of this course in sections, which are operated at different laboratories, it is important to have your own individual lab schedule. Please prepare the following personal schedule. Although lab-classes are typically scheduled from week 1 to 7 or 8 to 14, public holidays may require an adjustment of the schedule.

No.	Sem.-Week	Date	Laboratory	Experiment
1	*E.g., 1-W1*	*E.g., 10 Oct. 2021*	*E.g., Inorg. 1*	*E.g., Experiment 1*

PREPARATION FOR THE LAB

A proper preparation for a laboratory class involves:

- Studying of the lab-manual for the respective experiment
- Reviewing of the hazards for the experiment
  This particularly covers the study of safety data sheet for **all chemicals used** in the experiment.

Comprehension of the Experiment

A proper understanding of an experiment is essential for its safe and successful execution. All actions described in the experimental procedure shall be critically read and questioned on their importance for a successful operation of the experiment. If the relevance of a certain step cannot be determined, the respective section shall be discussed with the lecturer in charge during the briefing section of the lab. In general, every step in an experimental procedure should have a rational, otherwise the respective step shall be omitted.

The study of the laboratory manual might not be enough to grasp the scope of an experiment. In this case, additional references (textbooks, internet resources etc) shall be reviewed. This time-consuming preparation is reflected in the learning time assignment for laboratory classes, which includes a significant time allocation for the preparation before the actual class.

Based on the study of the laboratory manual you shall be able to:

- Identify the objectives for the experiment
- Relate the conduction of the experiment with the learning objectives
- Construct a roadmap for the experiment, to guide you during the actual lab class

Hazard Analysis

Safety data sheet for most chemicals can be easily found on the internet. Although the information is specific for every product, the safety data sheets for different manufacturers rarely differ much. For a chemical hazard analysis of an experiment, it is, therefore, not important to know the specific brand and product code of the chemical.

The study of safety data sheet for chemicals exceeds a simple reading of the document. Safety data sheets are prepared to summarise all known hazards associated with the chemical. However, the relevance of the hazards depends on the conditions, at which the chemicals are operated. A simple example might help to illustrate this.

> "A solid chemical with severe risk for lung damage upon inhalation requires considerable measures, if fine powders are operated in possibly open machinery places, e.g., milling of the chemical into dust. On the other hand, the lung hazard for the same chemical can be considered irrelevant, if the chemical is operated in large chunks to be dissolved in a solvent, since the inhalation risk of either a solution or large particles is near to zero."

The analysis of hazards for a chemical, therefore, requires a cross-check of potential hazard scenarios within a safety data sheet with the experimental conditions and the specific specification of the compound (e.g., fine powder, granules, or blocks). This affects not only the identification of hazards but also has impact on personal protective equipment needed for the operation. While dust or even respirator mask are highly recommended for the milling operation, no protection is required for the other application above.

If significant hazards of a chemical for an experiment are detected during the preparation of an experiment, the matter shall be discussed with the lecturer in charge of the experiment during the briefing session of the experiment.

Experiment Roadmap

Experimental procedures are rarely written to follow gradually word-by-word. Typically, a procedure shall provide all information required for the successful operation of the experiment. However, a proper following of the procedure frequently requires the reading of **the entire process** prior to operation at the lab. Again, a simple example can help to illustrate this:

Add solution B to solution A **at a rate to maintain moderate reflux of the reaction mixture**. In case of a word-by-word instruction, the constraining statement for the experiment will be read at a time, when the addition of solution B to solution A is already complete, hence too late for any for any adjustments. The second part of the sentence in the procedure cautions on the operation of the previous instruction – in this case to slowly add solution B to solution A to avoid overheating the reaction mixture due to a strong exothermic reaction. To simplify the execution of the experiment, it is recommended to transform the experimental procedure into a diagram, scheme or tabular instruction that can be followed stage by stage. This experimental roadmap can subsequently be used as detailed instruction for the execution of the experiment.

Creation of experiment roadmaps

1. Separate the experimental procedure into a set of simple operation instructions
2. Combine the individual instructions in a hierarchical order, or road map
3. Specify important conditions that must be met prior to any step. Place a caution reminder note **BEFORE** the respective step and highlight it to avoid overreading.
4. Include a statement for waste treatments and cleaning-up instructions, if relevant for the experiment.

Images can be faster captured than text. Therefore, an experimental roadmap in form of a diagram or scheme or flow chart (with limitations of words) is usually more effective than text-based instructions.

LABORATORY NOTEBOOK

A lab notebook is used to record all the work carried out in the laboratory and the experimental data. In industry or in academic research, it is an important legal document that can be used to provide evidence regarding the discoverer and date of discovery of new chemicals or processes.

In the undergraduate laboratory course, it is important to develop the skill of recording a good lab notebook. The records will be needed to generate lab reports at some point in the course, and the keeping of the lab notebook will be assessed regularly by your lecturer.

Marks will be awarded for continued good use and practices of the notebook throughout the laboratory classes.

All relevant aspects of an experiment should be recorded, together with the order in which steps were carried out. All observations should be noted, in principle even those that at first sight appear unimportant.

General Guidelines

1. Use ballpoint pen and press hard if you are using duplicate pages.
2. Write on one side only.
3. Do not erase or use whiteout. If you make a mistake, draw a single line through the error (strikethrough) and write the correct entry on the top or side of it.
4. Do not remove an original page. If the entire page is incorrect, draw a single diagonal line through the page and state the reason for this line.
5. Record all data and results (with units) directly into your notebook.
   DO NOT record data on scrap paper, your hand etc. **to be transferred later**. A laboratory notebook does not need to look nice but must be logically ordered and reasonable readable.
6. Start a new page for each new experiment.
7. Write the title of the experiment, date, and your name at the top of each page.
8. NEVER skip a space for later additions.
9. Be neat and thorough! Someone should be able to pick up your notebook twenty years from now and be able to repeat your experiments.
10. NEVER mix-up instructions for the lab with records of experimental procedures. A lab notebook should only **reflect solely the procedure you HAVE followed**, not the one you intended to follow. Instruction notes of schemes for the operation of an experiment – typically prepared before the lab starts – are useful and encouraged. However, this should NOT be placed into the laboratory notebook.

At the beginning of each experiment, record:

- The date
- Structural formula (abbreviated, if necessary) and all reagents in order of addition
- Molecular formula (preferably structural formula) and molecular weights
- Literature references for the procedure (or for analogous preparations)
- List of apparatus (with sketches in unusual cases)
- Simplified procedures from your reading of lab manual; it can be a flow chart or schematic diagram, to your preference, which transforms the lengthy and wordy procedures into simple yet informative procedures briefly. If this scheme is placed inside the laboratory notes, it is essential that the section is clearly labelled as

'instructions or 'procedure' and **NOT MIXED UP WITH ANY EXPERIMENTAL RECORDS** during the experiment. Also, instruction notes DO NOT REPLACE any MISSING INFORMATION within the experiment records. The lab notes recorded during the experiment must be complete on its own.

Good Lab Notebook Organization

The first page of the lab notebook should be used as a cover page and should include name, course, and email address (in case of loss). The second page should be left blank to be used as a content's page. This page should be completed as the lab course progresses. Begin to write experimental data into the lab notebook from the third page onwards. A ball point pen is better than a fountain pen as it is less likely to smudge if water is splashed on it.
Lab notebooks need to be looked after carefully. Do not soil them with chemicals as they may transfer hazardous substances out of the laboratory. Do NOT place TLCs into your lab notebook. The chemicals can contaminate your lab notes and even damage your lab notes over time. If you want to keep record of TLC, sketch it instead.

Practical Lab-Note Design

Date

Title/ Chemical reaction for synthesis
(add molecular weights below formula)

Include information on **team members**, if applicable

References (authors may be omitted and may use the abbreviation)

Simple version of **Experimental/ Methodology**

Time	Action	Observation
E.g.,		
9:25 am	1.2 g compound A (optional calc. amount in mol)	
9:30 am	30 mL solvent B	
	dissolve A in B	yellow solution of A in B, exotherm
9:32 am	cool with water bath	
9:45 am		temperature T
9:45 am	record spectrum 1 (conditions)	
9:50 am	2 mL reagent C	measurement 1
9:55 am	1 mL reagent C	measurement 2
	…	

If experiment record continues, reference to page number

page #

The tabular format for lab notes above is typically suitable for almost any kind of chemical experiment, including syntheses, analyses, and instrumental measurements. The time record is not always required but enables later a detailed analysis of the experiment. Calculated secondary data, like amounts in mol, are not important inside the lab notes, because they, unlike any primary data or observation, can be determined later. All operations and observations shall be recorded instantly, since otherwise there is a chance for either wrong or missing records. This practically disfavours the inclusion of secondary data, unless the experiment provides a lot of time between actions/ observations. Important physical data for chemicals applied, like concentration or density, shall be recorded to avoid time consuming data search after the experiment.

WRITING A REPORT

Kindly refer to SIC1011 Practical Manual for the detailed explanation and instruction on writing a Laboratory Report.

LAB REPORT GUIDELINE & MARKING SCHEME

Section 1 Lab Performance (Total 45%)

1. Pre-entering lab (15%)

Score	Criteria
0	No preparation of experimental procedure, no proper attire-shoes; goggle; lab coat.
1-8	Summary of procedures too brief, lack of details and confusing; incomplete safety attire.
9-15	Presents easy to follow steps in lab experimental, logical, and adequately detailed; safety attire checked.

2. Skill & Techniques (30%)

Score	Criteria
0	No skill is demonstrated.
1-10	Wrong glassware used, wrong technique, spillage and wasting of chemicals.
11-20	Right glassware used, incorrect or lack of lab technique.
21-30	Presents correct lab skill, clean and tidy.

Section 2: Lab report (Total 40%)

Section	Score	Distribution	Criteria
Title	5	0-1	No title, or too brief
		2-3	Too long, or does not identify the complete subject of study
		4-5	Identify the complete subject of study and encapsulates the purpose of the report/study.
Objective	15	0	Section missing completely.
		1-7	Be too vague, ambitious, or broad in scope.
			Just repeat each other in different terms.
			Just be a list of things related to the topic.
			Contradict with methods.
			Does not identify subject of study.
		8-15	Concise and brief.
			Be interrelated and describes how to achieve that
			objective.
			Clearly identify the subject of study.
			Related to the experiment that has been done.
Introduction	10	0	Section missing completely.
		1-5	Background info only from lab manual
		6-10	Clearly written, well structured, with evidence of extra reading.
			Clear outline of study's hypotheses.
			Does show something novel in it as compared to the supplied handout/laboratory manual.
			Does include the rationale for performing the experiment.
Experimental		0	Section missing completely.

	10	1-5	One or more subsections (e.g., chemicals or instrumentation) are missing. Confusing statement. Parts have been included under the wrong sub-section.
		6-10	Contains all the relevant information about the method used; clearly and systematically described in such a way that a reader could replicate the study from the description.
Results	20	0	No discussion section.
		1-6	Very lack attempt to relate experiment findings and collected data.
		6-12	Showing attempt to discuss the findings and collected data but using inaccurate theories and justifications.
		13-20	Able to demonstrate analysis skill in discussing the results, including the inaccuracies of data, using logic and appropriate statements to justify the experiment outcome.
Discussion	20	0	No discussion section.
		1-6	Very lack attempt to relate experiment findings and collected data.
		6-12	Showing attempt to discuss the findings and collected data, but using inaccurate theories and justifications.
		13-20	Able to demonstrate analysis skill in discussing the results, including the inaccuracies of data, using logic and appropriate statements to justify the experiment outcome.
Safety caution	5	0	Section is not present.
		1-3	Sentences are not in complete, focusing on minor or lack important steps.
		4-5	Tabulate at least 3 major and most important safety caution.
Conclusions	10	0	Section missing completely
		1-5	Conclusion is drawn but not supported by experimental evidence. No sensible conclusion is drawn.
		6-10	Conclusion is reflecting to the objectives tabulated. Conclusion is drawn and supported by experimental evidence. Able to present the outcome of the work and relating the findings to the objectives.
References	5	0	Reference not included in the report
		1-3	Incomplete references to the books or any other sources used in report.
		4-5	References in the text and in the reference, list conformin all respects to the formatting convention (e.g., APA format). Complete references to the books or any other sources used in report. References in text are matched with references in reference list (e.g., no missing references).
Total	**100**		

Late submission of report: -1 mark/ day

Section 3: Assessment of understanding/ Revision on conducted experiments (15%)

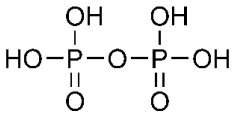
Score	Criteria
0	Unable to answer any questions.
1-3	Very little attempt to answer the question.
4-7	Most answers are incorrect, and some are irrelevant to the question type.
8-11	Some answers maybe very short or incomplete.
12-15	Questions are answered accurately to the best abilities.

Experiment 1 **Inorganic Chemistry**

SODIUM ACID SALT OF HEPTAOXODIPHOSPHORIC ACID

1. INTRODUCTION

Heptaoxodiphosphoric acid (common name: pyrophosphoric acid) is a tetrabasic binuclear oxoacid.Its chemical formula is $H_4P_2O_7$ and its structural formula is shown below.



Heptaoxodiphosphoric acid forms acid salts with metal ions. The general formula of the acidsalts of Group 1 metal ions is $M_xH_{4-x}P_2O_7$ (the value of *x* is 1, 2 or 3). In this experiment, you will first prepare a sodium acid salt of heptaoxodiphosphoric acid ($Na_xH_{4-x}P_2O_7$) from tetrasodium heptaoxodiphosphate (common name: tetrasodium pyrophosphate;chemical formula: $Na_4P_2O_7$). You will then determine its chemical formula as follows:

In the first step of the determination, an aqueous solution of silver nitrate ($AgNO_3$) is added to the acid salt to completely precipitate the normal salt, tetrasilver heptaoxodiphosphate, $Ag_4P_2O_7$. The equation is:

$$Na_xH_{4-x}P_2O_7(s) + 4\ Ag^+(aq) \longrightarrow Ag_4P_2O_7(s) + (4-x)H^+(aq) + xNa^+(aq)$$

The number of moles of hydrogen ion (nH^+) present in the solution containing the precipitated $Ag_4P_2O_7$ is determined by neutralisation titration with a standard solution of sodium hydroxide.

$$H^+(aq) + NaOH(aq) \longrightarrow Na^+(aq) + H_2O(l)$$

In the second step of the determination, the precipitated $Ag_4P_2O_7$ is dissolved in nitric acid. The number of moles of Ag^+ ion (nAg^+) present in the solution is determined by titration with a standard solution of thiocyanate (SCN^-).

$$Ag^+(aq) + SCN^-(aq) \longrightarrow AgSCN(s)$$

The value of *x* in the chemical formula $Na_xH_{4-x}P_2O_7$ is then calculated from the following relationship:

$$\frac{nAg^+}{nH^+} = \frac{4}{(4-x)}$$

2. LEARNING OUTCOME

I. Able to calculate the ion moles in chemical compound.
II. Able to determine chemical formula from ion moles quantification.

3. METHODOLOGY

A. Preparation of $Na_xH_{(4-x)}P_2O_7$

1. Weigh 5.0 g of tetrasodium heptaoxodiphosphate monohydrate ($Na_4P_2O_7.H_2O$) in a 250 mL conical flask. Add about 20 mL of distilled water and heat the mixture on a hot plate at 80 °C until

a clear solution is obtained.

2. Add an equal volume of glacial ethanoic acid to the hot solution. Maintain the temperature of the mixture at 80 °C for several minutes until a white crystalline solid separate out.

3. Add 25 mL of ethanol to the hot mixture, filter the white crystalline solid under suction, and wash with ethanol and finally with acetone. Allow the solid to dry in air and record its yield.

B. Number of moles of H^+ ions (Analysis is to be done in duplicate)

1. Accurately weigh 0.15 - 0.20 g of the white solid prepared in (A) into a small conical flask and dissolve it in 50 mL of distilled water.

2. Add 1 g of sodium ethanoate crystals, stir to dissolve the crystals, and then add with continuousstirring, 18 mL (excess) of silver nitrate solution (5%). Continue stirring vigorously until the whiteprecipitate formed coagulated (do not heat the solution).

3. Filter the precipitate on a sintered glass funnel attached to a Buchner flask and wash the precipitate thoroughly with cold distilled water. Combine the washed water with the filtrate in the Buchner flask.

4. Detach the sintered glass funnel containing the precipitate from the Buchner flask and **keep it for the analysis of Ag^+ ion in C.**

5. Add sodium chloride aqueous solution (5%) to the filtrate in the Buchner flask until all silver ions are precipitated as silver chloride. Add a few drops of phenolphthalein to the mixture and titrateit with a standard solution of sodium hydroxide (the molarity of sodium hydroxide solution is about 0.1 M) until the colour changes from white colour to pale pink.

6. Calculate the number of moles of H^+ ions.

C. Number of moles of Ag^+ ions (Analysis is to be done in duplicate)

1. Discard the content of the Buchner flask from **B** and wash it three times with distilled water. Attach the sintered glass funnel containing the dry precipitate (from **B**) to the clean Buchner flask.

2. Dissolve the precipitate using several 10 mL portions of hot nitric acid (3M). Finally, wash the sintered glass funnel three times with cold distilled water. Combine the washed water with the filtrate in the Buchner flask.

3. Add 2 mL concentrated iron(III) alum solution and then titrate it with a standard solution of ammonium (or potassium) thiocyanate (the molarity of the standard solution is about 0.1 M) untila permanent reddish colour is formed even after the flask is shaken vigorously.

4. Calculate the number of moles of Ag^+ ions.

4. QUESTIONS

1. Calculate the value of x.

2. Write the chemical formula and IUPAC name of the sodium acid salt of heptaoxodiphosphoricacid.

3. Calculate the percentage yield of the sodium acid salt of heptaoxodiphosphoric acid.

Experiment 2 **Inorganic Chemistry**

SYNTHESIS AND STOICHIOMETRIC ANALYSIS OF HEXAAMMINENICKEL(II)CHLORIDE

1. INTRODUCTION

Hexaamminenickel(II) chloride, $[Ni(NH_3)_6]Cl_2$, is a coordination compound whose nickel atom and six ammonia molecules constitute the cation; the anion is the chloride ion.

The amount of ammonia in the compound is determined by adding a known excess quantity of an acid to neutralize the ammonia; the excess acid is determined by back-titration using a standard solution of sodium hydroxide, with bromocresol green as the indicator. This indicator is yellow in acidic solution and blue in basic solution.

The chloride ion in the compound is titrated against mercury(II) nitrate, with diphenylcarbazone as the indicator. The colour of the indicator at the end point is pale purple.

$$Hg^{2+} + 2Cl^- \longrightarrow HgCl_2$$

2. LEARNING OUTCOME

I. Able to synthesis a complex via crystallization and purification methods.
II. Able to quantify chemical component in a chemical complex via back titration method.

3. METHODOLOGY

A. Procedure for the synthesis of hexaamminenickel(II) chloride

1. Dissolve 4.0 g hydrated nickel(II) chloride in 6 mL distilled water in a 50-mL flask.
2. In the fume cupboard, add 12 mL concentrated ammonia to the above solution and warm themixture for about 10 minutes on a hot plate.
3. Cool the solution in an ice-bath, and while stirring it with a glass rod, add 6 mL ethanol. Notethe formation of a solid.
4. When all the solid has formed, filter it under suction and wash it with a few mL of cold concentrated ammonia solution, followed with ethanol, and finally with acetone.
5. Record the weight of the solid.

B. Procedure for the analysis of ammonia (This analysis is to be done in duplicate.)

1. Weigh about 0.2 g of hexaamminenickel(II) chloride and place it in a 250-mL conical flask.
2. Dissolve the compound by adding 25 mL standard hydrochloric acid from a burette. (Note themolarity of the standard acid)
3. Add 3-5 drops of bromocresol green to the solution in the conical flask.
4. Titrate with standard sodium hydroxide solution until the colour of the indicator changes to pale blue.

C. Procedure for the analysis for chloride ion (This analysis is to be done in duplicate.)

1. Weigh about 0.2 g of hexaamminenickel(II) chloride and dissolved it in 10 mL of distilled water.
2. Add 2 drops of bromophenol blue indicator to the solution, and using a dropper, add nitric acid (1M) until the colour of the solution changes to green. Add 5 drops of diphenycarbazone and

25 mL of 2-propanol to the mixture.

3. Titrate the mixture with standard mercury(II) nitrate solution until the colour of the indicatorchanges to pale purple. (Standard hydrochloric acid 0.270 M)

Calculations

Weight of hexaamminenickel(II) chloride

	Weight / (g)
$[Ni(NH_3)_6]Cl_2$ + watch glass	
Watch glass	
$[Ni(NH_3)_6]Cl_2$	

Analysis for NH_3

Weight of $[Ni(NH_3)_6]Cl_2$/g		
Molarity of HCl		
Initial volume of HCl, $V_{initial}$/mL	25.00	25.00
Molarity of NaOH		
Final burette reading/mL	a1	b1
Initial burette reading/mL	a_2	b_2
Volume of NaOH/mL	a_1-a_2	b_1-b_2
Volume of excess HCl, V_{excess}* /mL	X_1	X_2
Volume of reacted HCl, $V_{reacted}$/ mL	25.00 – X_1	25.00 – X_1
Moles of NH_3#		
Weight of NH_3		
% NH_3 in $[Ni(NH_3)_6]Cl_2$		

*$V_{(HCl,\ excess)} = M_{(NaOH)}\ V_{(NaOH)} / M_{(HCl)}$

moles of ammonia = moles of HCl = $M_{(HCl)}\ V_{(HCl)reacted}$ /1000

Analysis for Cl^- ion

Weight of $[Ni(NH_3)_6]Cl_2$/g		
Molarity of Hg^{2+}		
Final buret reading/mL	a_1	B_1
Initial buret reading/mL	a_2	B_2
Volume of Hg^{2+}/mL	a_1-a_2	B_1-b_2
Moles of Cl^-*		
Weight of Cl^-		
% Cl^- in $[Ni(NH_3)_6]Cl_2$		

*moles of Cl^- = 2 moles of Hg^{2+} = 2 $M_{(Hg2+)}\ V_{(Hg2+)}$ / 1000

4. QUESTIONS

1. Write an equation for the formation of $[Ni(NH_3)_6]Cl_2$ and calculate its percentage yield in your experiment.

2. Assuming that the complex consists of Ni^{2+}, NH_3 and Cl^- only, verify that its empirical formula is $[Ni(NH_3)_6]Cl_2$ from your analytical results. What is the other information needed for you to derive its molecular formula?

Experiment 3 **Organic Chemistry**

QUALITATIVE ELEMENTAL ANALYSIS

1. INTRODUCTION

The analysis and identification of the structures of unknown substances constitutes a very important part of experimental organic chemistry. Often, a common first step in the identification of an unknown substance is to determine the elements present in the sample. Organic chemists often use spectroscopic techniques to establish the structure of a compound. However, it is often useful to supplement the spectral data with other information such as the existence of elements other than carbon, hydrogen and oxygen. Elements such as nitrogen, sulphur, iodine, chlorine, and bromine in organic compounds can easily be detected by means of straightforward chemical tests.

A French chemist, J.L. Lassaigne has developed a method used for the qualitative determination of elemental nitrogen, sulphur and the halogens in an organic compound known as the Lassaigne' test or more commonly as the sodium fusion test. In this method, the organic substance is heated with sodium metal under condition that ensure the conversion of nitrogen, sulphur, and halides into ionizable inorganic substances as shown below:

$$\text{Organic compound (containing C, H, O, N, S, X, where X = Cl, Br or I)} + Na^0 \xrightarrow{\text{heat}} NaCN + Na_2S + NaX + NaOH$$

PRE-LAB READING/DISCUSSION

- Elemental analysis
- Lassaigne's test
- Test for different elements

APPARATUS

Pyrex test tube (4.5 x 45 mm)
Test tube
Evaporating dish

CHEMICAL

Sodium metal
Unknown compound (X, Y or Z)
Reagents
Distilled water

2. PROCEDURE

LASSAIGNE'S TEST

Place about 10 mg or one (1) (small) droplet of the unknown (A, B or C) and about 50 mg of freshly cut sodium metal into a glass tube (Note 1). Heat the tube as strongly as possible until the bottom of the tube is glowing red, holding the tube at this heat for about 5 min. For liquid unknown, start with moderate heating to avoid fast evaporation. Quickly plunge the hot tube in an evaporating dish containing distilled water (~ 10 mL) (Note 2) and cover the dish. Boil the solution on a hot plate for a few minutes while gently crushing the residue with a glass rod. Filter and a colourless filtrate should be obtained. If the volume of filtrate is too little, add distilled water to the filtrate. Use the filtrate for the tests below. A coloured filtrate indicates incomplete decomposition, and the entire fusion procedure will have to be repeated.

Notes:
1. Precautions must be taken when handling sodium. Contact with sodium metal might cause burn on the human skin. When handling sodium metal, avoid all contact with water.
2. Generally the glass tube will shatter, and any residual sodium will react with water. Cover the dish immediately with wire gauze once the tube is immersed in water to avoid any splatter.

First aid measures to treat sodium induced injuries:
1. If splashed unto eyes, immediately flush water at the eye wash station for at least 15 minutes. Eye washing requires assistance to force the eye open, while reflexes try to shut the eye; attempts to do without help will almost certainly lead to loss of eyesight. Immediate action is required; the first five minutes will decide about saving or loosing eyesight.
2. Upon skin contact, washed the part with lots of water for as long as possible. In all cases, one must seek for medical aid as soon as possible. All accidents and dangerous occurrence must be reported immediately to the lecturer in charge or the demonstrator or the laboratory assistant. Apart from medical emergencies, sodium might also cause fire!

TESTS FOR NITROGEN

Add about 0.5 mL of the filtrate to a tube containing about 0.1-0.2 g of powdered iron(II) sulphate crystals. Heat the mixture gently while shaking until it boils. Without cooling, add just sufficient dilute sulphuric acid to dissolve the gelatinous hydroxides of iron. A Prussian blue precipitate of iron(III) ferrocyanide, $Fe_4[Fe(CN)_6]_3$ indicates the presence of nitrogen. If a blue precipitate is not immediately apparent, allow the mixture to stand for 15 minutes and then filter through a filter paper and wash the paper with water to remove all other coloured solution. Any Prussian blue present (if there is any) should be visible on the paper. If there is still doubt as to whether the Prussian blue precipitate was formed, another sodium fusion should be carried out and the test repeated. In the absence of nitrogen, the solution should be pale yellow due to iron salts.
If sulphide ion is present, black precipitate of iron(II) sulphide appears. Add dilute sulphuric acid and boil the mixture for about 30 seconds. The iron(II) sulphide dissolves and a precipitate of Prussian blue appears if nitrogen is present.

TESTS FOR SULPHUR

Acidify ~ 0.5 mL of the filtrate with dilute acetic acid. Add a few drops of 1% lead acetate solution. A black precipitate of lead sulphide indicates the presence of sulphur.

TESTS FOR HALOGENS

i. IF NITROGEN AND/OR SULPHUR PRESENT

If either nitrogen or sulphur is present, the cyanide and sulphide ions must first be removed. Acidify ~ 0.5 mL of the filtrate with dilute nitric acid and concentrate to half of its original volume to expel any hydrogen cyanide or hydrogen sulphide that might be present in the mixture (**CAUTION: carry out the reactions in a fume cupboard**). Dilute the mixture with an equal volume of distilled water.
Add 1-2 drops 5% of aqueous silver nitrate solution to 2-3 mL of the fusion solution. An immediate heavy precipitation indicates the presence of chlorine, bromine, or iodine.

ii. IF NITROGEN AND SULPHUR ARE ABSENT

Acidify a portion of the filtrate with dilute nitric acid and add an excess of 5% silver nitrate solution. Precipitation indicates the presence of chloride, bromide or iodide. Silver chloride

precipitate is white, silver bromide precipitate is pale yellow and silver iodide precipitate is yellow.
Silver chloride, silver bromide and silver iodide have different solubilities in 5% ammonium hydroxide solution. Decant the solvent and treat the precipitate with dilute aqueous ammonia solution. Add 2 mL 5% ammonium hydroxide to the precipitate. Silver chloride is soluble in ammonium hydroxide, silver bromide is slightly soluble and silver iodide is insoluble in ammonium hydroxide solution.
The presence of iodine and bromine may be further confirmed by the following tests. These tests may also be used if it is suspected that more than one halogen is present in the compound.

iii. TESTS FOR IODINE

Acidify about 3 mL of the filtrate with 10% sulphuric acid solution and heat to boiling for a few minutes. After cooling, add 1 mL of dichloromethane followed by a drop of 5% sodium hypochlorite (bleach). The production of a purple or violet colour in the dichloromethane layer indicates the presence of iodine.

iv. TESTS FOR BROMINE

Acidify about 3 mL of the filtrate with 10% sulphuric acid solution and heat to boiling for a few minutes. After cooling, add 1 mL of dichloromethane followed by a drop by drop of 5% sodium hypochlorite (bleach), while shaking, until a possible purple colour (presence of iodine) disappears. The appearance of a reddish-brown colour indicates the presence of bromine.

v. OTHER TESTS FOR HALOGENS

To test for chlorine in the presence of iodine and/ or bromine, acidify the filtrate with 5% nitric acid and boil the solution for a few minutes. Add enough 0.1 M silver nitrate to precipitate out the halogen completely as silver halides. Filter the precipitate and add about 3 mL of 0.1% NaOH solution. Boil the mixture for about 2 minutes and filter the solution. Acidify the filtrate with 5% nitric acid and add a few drops of 0.1 M silver nitrate. A white precipitate indicates the presence of chlorine.

3. REFERENCES

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3. Mahmood, K.; Rahman, N.A. *Kaedah Kimia Dalam Pengenalpastian Sebatian Organik*, University of Malaya Publisher., 2000.
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4. POST-LAB QUESTIONS

1. Write the chemical equation for the formation of a black precipitate when sulphur is present in the sample.
2. Explain why the mixture is boiled in a fume cupboard when nitrogen and sulphur are present in the sample?
3. How are the sodium wastes from the experiment destroyed?

Experiment 4 **Organic Chemistry**

CHEMICAL PROPERTIES OF HYDROCARBONS, ALCOHOLS, ALDEHYDES, KETONES, CARBOXYLIC ACIDS AND AMINES

1. INTRODUCTION

Before the advancement of spectroscopic techniques, the determination of chemical properties was very important for the identification, characterisation, and determination of the structure of a compound. Many reagents and reaction conditions were found to give characteristic and specific results with compounds containing specific functional groups. These reagents or reaction conditions are used as qualitative tests and serve to indicate the presence or absence of certain functional groups in a substance.

There are hundreds of qualitative tests that can be used to characterize or distinguish the functional groups in the unknown substances. The procedures for some of these tests are described below.

PRE-LAB READING/DISCUSSION

- Functional groups and their properties
- Chemical reactivity

A. HYDROCARBONS

Organic compounds with only hydrogens and carbons are called hydrocarbons. According to the structure, hydrocarbons can be classified into two main groups, which are aliphatic and aromatic hydrocarbons. Generally, aliphatic hydrocarbons are classified as either saturated hydrocarbon such alkanes and cycloalkanes, and unsaturated hydrocarbons, for example alkenes, alkynes and their cyclic analogues.

Alkanes or paraffins are saturated aliphatic hydrocarbons containing only sigma (σ) bond whereas the alkenes and alkynes contain both sigma (σ) and pi (π) bonds.

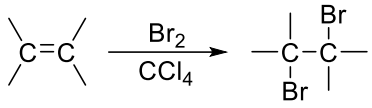
The non-reactivity of alkanes with most chemical reagents such as acids, bases, oxidizing and reducing agents at room temperature explains why its name is paraffin, which means, inert. Alkanes react with chlorine and bromine very slowly at room temperature but, much faster in the presence of light. This is a substitution reaction in which one or more halogen atoms will replace one or more hydrogen atoms in the carbon chain. With bromine as the halogen and in the presence of light, the mono-substitution reaction is represented by the following general equation:

$$CH_3CH_2CH_3 + Br_2 \xrightarrow{h\nu} CH_3CH(Br)CH_3$$

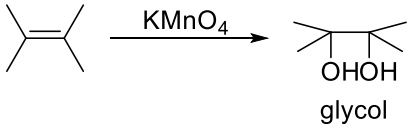
The reaction of hydrocarbons with bromine in carbon tetrachloride is one of the tests used to differentiate between a saturated and an unsaturated aliphatic hydrocarbon. If the substance is an alkane, almost no reaction occurs. However, in the presence of light or sunlight, bromine will decolorise slowly as substitution reaction is taking place and hydrogen bromide is liberated. To test for hydrogen bromide, blow across the mouth of the test tube containing the chemical reactants. If hydrogen bromide is present, it will dissolve in the water vapour and forms streaks of vapour droplets on the inside of the test tube.

Alkenes are reactive at room temperature. The centre of reactivity is the double bond that can become saturated by the addition of other molecules. For example, bromine in carbon

tetrachloride reacts immediately with alkenes at room temperature to produce dibromide. The discolouration of bromine is evidence that the reaction has taken place, even in the dark, without the liberation of hydrogen bromide. This reaction is used to differentiate between unsaturated and saturatedhydrocarbons.



Another good test for unsaturated hydrocarbon is the use of aqueous potassium permanganate solution or known as Baeyer's test. Alkenes react with neutral permanganate solution to form glycol causing the purple permanganate colour to disappear and a brown precipitate of manganese(II) dioxide to form.



glycol

Hydrocarbons may also be differentiated by their solubility in sulphuric acid. Alkanes are not soluble in concentrated sulphuric acid while both alkenes and alkynes are protonated by the sulphuric acid and become soluble. Aromatic hydrocarbons, on the other hand, do not dissolve easily in concentrated sulphuric acid but dissolve readily in fuming sulphuric acid.

PROCEDURE

The following alkanes are provided for the tests below:

Heptane, cyclohexene and toluene

IGNITION TEST

Pour about 0.5 mL heptane into an evaporating dish. With a burning wooden splinter, ignite the alkane. Note the characteristic of the reaction and the colour of its flame. Repeat this test for both cyclohexene and toluene.

SOLUBILITY TEST

Add 1 mL heptane into a tube containing 2 mL of distilled water. Shake the tube and record your observations. Repeat the test for both cyclohexene and toluene. Test the solubility of these hydrocarbons in each other using 1 mL sample in a clean and dry test tube for each test.

BROMINE TEST

Prepare two test tubes containing about 1 mL heptane into each tube, add 4-5 drops of bromine 4% solution in dichloromethane. Place one of the test-tube in a cupboard (dark place) and the second one under sunlight. Observe and record your observations after 15 minutes. Repeat the test for cyclohexene and for toluene.

POTASSIUM PERMANGANATE TEST

Add 1 mL of the 0.01 M potassium permanganate solution into test tube containing 0.5 mL heptane. Shake the tube and record your observation. Repeat this test for cyclohexene and toluene.

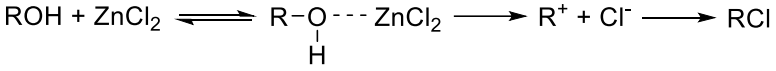
CONCENTRATED SULFURIC CID TEST (SULPHONATION)

In a dry test tube, pour 1 mL concentrated sulphuric acid carefully. Add 0.5 mL of heptane into the tube and shake. Record your observation. Repeat this test for the other two hydrocarbons.

B. ALCOHOLS AND PHENOLS

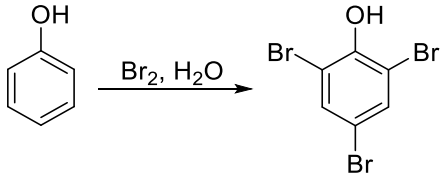
Alcohol is a class of organic compounds containing hydroxyl group, -OH, as the functional group. Alcohol can be classified into three which are primary alcohol (1°), secondary alcohol (2°) and tertiary alcohol (3°).

The three different classes of alcohol can be differentiated through the rate of reaction of the alcohol with hydrogen halide using the Lucas reagent (a mixture of concentrated hydrochloric acid and zinc chloride). Primary alcohols react very slowly while secondary alcohols react within 5 minutes of the addition of the Lucas reagent and form a cloudy mixture due to the formation of alkyl chloride. In the case of tertiary alcohols, two phases will appear almost immediately due to the formation of alkyl chloride upon the addition of the Lucas reagent.



Alcohols can also be oxidized to aldehydes, ketones, and carboxylic acids. The product formed depends upon the class of alcohol used. The three classes of alcohols differ in their oxidation behaviour where primary alcohols yield aldehydes and secondary alcohols yield ketones upon oxidation. Tertiary alcohols yield no carbonyl product under the normal oxidizing conditions. The common reagent used for oxidation of alcohols is potassium dichromate.

Phenols are compounds in which the hydroxyl group is attached directly onto a benzene ring. Phenols are usually acidic and usually dissolve in 5% aqueous sodium hydroxide solution. Most phenols react with ferric chloride solution to give red, blue, purple, or green complexes. Phenols also react readily with bromine water to give a substituted product in the form of a white precipitate. For example, the reaction between phenol and bromine water gave the 2,4,6-tribromphenol as shown below.



PROCEDURE

The following alcohols are provided for the tests below:

Aliphatic alcohols: ethanol, 2-butanol and 2-methyl-2-propanol (t-butanol)
Aromatic alcohols: phenol, *m*-cresol and catechol

IGNITION TEST

Pour about 0.5 mL ethanol into an evaporating dish. With a burning wooden splinter, ignite the ethanol. Observe the characteristic of the flame. Repeat the test for 2-butanol, 2-metyl-2-propanol (t-butanol) and phenol.

SOLUBILITY TEST

Add 0.5 mL ethanol to a test tube containing 1 mL distilled water. Shake the test tube and record your observation. Repeat the solubility test for 2-butanol, 2-metyl-2-propanol (t-butanol) and phenol. Repeat the test for the solubility of ethanol, 2-butanol, *t*-butanol and phenol in 1 mL ether and in 1 mL toluene. Record your observations.

REACTION WITH SODIUM

Pour about 1 mL absolute ethanol into a dry test tube. Add a small piece of sodium (about half the size of a pea) to the absolute ethanol. Observe and record the reaction. Add some water after the reaction is completed and test the solution with a litmus paper. Repeat the same procedure with both 2-butanol and t-butanol.

OXIDATION REACTION

Push one end of a 20 cm length copper wire into a cork and coil the other end by making two or three turns about a thin glass rod. Heat the coil in Bunsen flame until it ceases to impart any colour to the flame. While still warm, dip the coil into a test tube containing ethanol (1 mL). Repeat this process several times. Cool the test tube in water bath and add one drop of the alcohol into a test tube containing 1 mL of Schiff‟s reagent. Shake the tube slowly and note the formation of a pink or purple colouration. If the compound does not dissolve in the Schiff‟s reagent, cover the test tube with a cork and shake it vigorously until an emulsion form. Record your observation. Repeat the experiment with 2-butanol and t-butanol.
[Important: Before reusing the wire for another compound, ensure that the material from the previous test has been destroyed by heating it and that the flame is not coloured].

LUCAS TEST

The Lucas reagent can be prepared by dissolving 6.4 g of zinc chloride in 4 mL of concentrated hydrochloric acid. Add 3 mL of Lucas reagent to 0.5 mL ethanol in a dry test tube quickly. Cover the tube with a cork, shake it and let the mixture stand for a while. Observe carefully for any changes taking place. Record the time required for the reaction to occur. Repeat the test using 2-butanol and t-butanol.

ESTERIFICATION TEST

Add 1 mL glacial acetic acid and 5 drops of concentrated sulphuric acid to 2 mL absolute ethanol. Ensure that the mixture is homogeneous and warm it in water bath. Cool and pour the mixture into evaporating dish containing 5 mL of 10% sodium carbonate. Note the smell of the vapour released. Repeat the test using 2-butanol, *t*-butanol and phenol.

IRON(III) CHLORIDE TEST

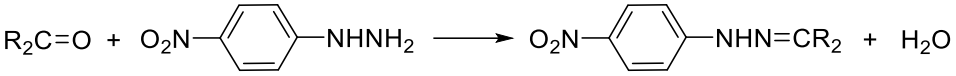
Dissolve about 0.05 g phenol in 2.5 ml of water. (If the compound does not dissolve, prepare a hot saturated aqueous phenol solution, filter, and use 1 mL of the cold filtrate). Place the solution in a test tube and add 1 drop of neutral 1% iron (III) chloride solution. Observe the change in colour of the solution. Add another drop after 2-3 seconds. A positive test is indicated by a transient or permanent coloration (usually purple, blue, or green) of the solution. Repeat the test using *m*-cresol and catechol.

BROMINE WATER

Dissolve 0.05 g phenol in 2.5 mL of water and add bromine water dropwise until the bromine colour is no longer discharged. The discharge of the bromine colour is a positive test for the presence of a phenol. In some cases, a white precipitate of the bromophenol may also form. Repeat the test using *m*-cresol and catechol.

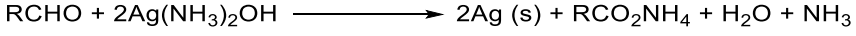
C. CARBONYL COMPOUNDS: ALDEHYDES AND KETONES

Aldehydes and ketones are organic compounds containing the carbonyl functional group, C=O. Aldehyde has the general formula, RCHO while ketone has the general formula RR'CO where R and R' are alkyl or aryl groups. An aldehyde or ketone will undergo a general reaction with Brady reagent, 2,4-dinitrophenylhydrazine (2, 4-DNPH), to produce 2,4-dinitrophenyl- hydrazone which will appear as orange or yellow precipitate. This reaction is commonly used to ascertain the presence of a carbonyl group in a compound.

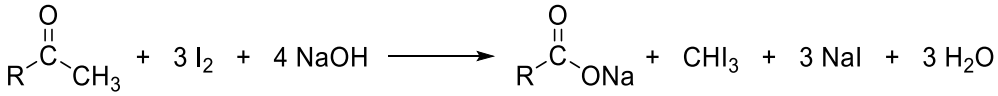


(R = H, alkyl or aryl)

Aldehydes can be distinguished from ketones through several tests. One test involves the use of a Schiff's reagent which will produce a violet-pink solution with aldehydes but not ketones. Some aromatic aldehydes such as vanillin also give a negative result with Schiff's test. Another test that can distinguish aldehydes from ketones is through weak oxidizing agents such as the Tollen's reagent (ammonium nitrate complex in ammonia solution). A positive reaction is indicated by the formation of a silvery mirror on the side of the tube.



Iodoform test is a useful test for the identification of methyl ketones and secondary methyl carbinols. This test involves a reaction in which the methyl group of the ketone is removed from the molecule and produces iodoform (CHI_3) (see equation below). A positive test is indicated by the formation of yellow precipitates or suspension of iodoform.



Secondary alcohols with a methyl group adjacent to the carbon bearing the hydroxyl group such as ethanol can be oxidized to methyl ketones by "iodine bleach" or hypoiodide. Hence, alcohols such as ethanol will also produce yellow iodoform precipitates as methyl ketones in an iodoform test.

PROCEDURE

The following carbonyl compounds are provided for the tests below:

Aldehydes: propanal and benzaldehyde
Ketones: propanone and acetophenone

BRADY TEST

The 2,4-dinitrophenylhydrazine reagent (Bready reagent) can be prepared by dissolving 3 g of 2,4-dinitrophenylhydrazine in 15 mL concentrated sulphuric acid. This solution is added, with stirring to 20 mL water and 70 mL 95% ethanol and filtered.

Dissolve about 0.5 mL or 50 mg of the compound to be tested in 2 mL 95% ethanol. Add 2 to 3 drops of this mixture into the test tube containing 3 mL 2, 4-dinitrophenylhydrazine reagent.

Shake the tube and observe the formation of any precipitate. If no precipitate forms immediately allow the mixture to stand for 5-10 minutes. Record your observations.

SODIUM BISULPHITE SOLUTION TEST

The alcoholic sodium bisulphate reagent can be prepared by adding 1 mL ethanol to 4 mL 40% aqueous solution of sodium bisulphate. The reagent must be filtered before use. Add aldehyde or ketone (about 0.2 mL or 2 mg) into a test tube containing 1 mL alcoholic sodium bisulphite solution. *Plug the test tube with a cork and shake thoroughly. Record any observations.

TOLLENS' TEST

Tollens' reagent can be prepared by adding one drop of NaOH 10% solution to a 2 mL 5% silver nitrate solution in a test tube. Add ammonia 5% solution drop by drop until all the precipitate (silver oxide) dissolves. Avoid using excess ammonia to obtain a sensitive reagent (Note 1). Add 2-3 drops or 0.1 g of the compound that is to be tested to the Tollens' reagent. Shake the tube slowly and note the formation of silver mirror/precipitate for the presence of an aldehyde group. If there is no precipitate after 10 minutes, warm the mixture in a water bath at 30°C for 5-10 minutes. Record your observation.

Note 1: The reagent must be prepared fresh before use and should not be stored.

FEHLING'S TEST

Fehling's solution can be prepared as follows:

Prepare *solutions* #1 and #2.

Solution #1: Dissolve 17.32 g hydrated copper sulphate crystal in 200 mL water and dilute the solution to 250 mL.

Solution #2: Dissolve 86.5 g sodium potassium tartrate and 35 g sodium hydroxide in 100 mL water and dilute the solution to 250 mL.

Mix 2.5 mL of *Solution #1* and 2.5 mL of *Solution #2* immediately before use.

Dissolve 0.2 g or 1 mL of the compound to be tested in 5 mL water and add 5 mL of the Fehling's reagent to the solution. Slowly shake the tube and heat the mixture to boiling. Cool the mixture to room temperature and note the occurrence of any precipitation. Record your observations.

SCHIFF'S TEST

Schiff's reagent is prepared by dissolving 0.005 g 4-rosaline hydrochloride (fuchsin in 50 mL distilled water followed by addition of 2 mL saturated sodium bisulphite solution. After 1 hour, add 1 mL concentrated hydrochloric acid and then leave the solution to stand for 24 hours. This reagent is colourless and very sensitive.

Add 1-2 drops of the compound to be tested to 1 mL Schiff's reagent in a test tube. Shake it slowly and observe the colour develop in 4-5 minutes. If the compound does not dissolve in the Schiff's reagent, cap the test tube with a cork and shake it vigorously until an emulsion form. Record your observations.

BENZALDEHYDE OXIDATION

Place benzaldehyde (2-3 drops) in a watch glass and leave for 1 hour at room temperature. Record your observations.

THE IODOFORM TEST

I_2/KI solution is prepared by adding 20.0 g potassium iodide and 10.0 g iodine in 80 mL distilled water. The mixture is stirred until it forms a deep brown solution.

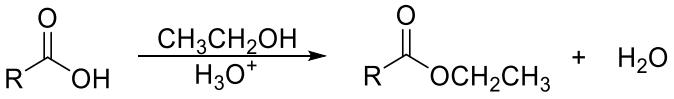
Place about 5 drops of propanone in a test tube and add 2 mL of distilled water (Note 1). Shake the test tube until all the samples have dissolved. Add 1 mL 10% sodium hydroxide solution and then slowly add the iodine-potassium iodide solution (I_2/KI), with shaking, until the dark colour of iodine persists. Continue adding the I_2/KI solution until the iodine colour is not discharged for 2 minutes at 60 °C.

Remove the excess iodine by adding a few drops of 10% sodium hydroxide solution, with shaking. Add equal amount of water and allow the mixture to stand at room temperature for 15 minutes. A positive test is indicated by the appearance iodoform as of yellow precipitate. Filter and dry the precipitate and take the melting point of the iodoform (literature m.p.: 119-121 °C). Repeat the above test with ethanol and acetophenone.
Note 1: Use dioxane if compound is not soluble in water.

D. CARBOXYLIC ACIDS, AMIDES AND ESTERS

Carboxylic acid is an organic acid with the general structure of RCO_2H and the carboxyl group ($-CO_2H$) as the functional group. They are primarily identified by spectroscopic and solubility test. Hence, carboxylic acids can be detected by their solubility in 5% NaOH solution as well as in the weakly basic 5% $NaHCO_3$ solution. However, it is also worth noticing that sulphonic acid and several derivative phenols like 2,4-dinitrophenol and 2,4,6-trinitrophenol are also soluble in 5% $NaHCO_3$ solution.

There are also a few chemical tests that can be used to confirm the presence of a carboxyl group. Carboxylic acids react with sodium bicarbonate solution to produce the carboxylate anion and carbon dioxide gas. Another test for carboxylic acid involves esterification reaction of carboxylic acids which give a sweet-smelling ester as the product shown below.



Esters are carboxylic acid derivative which characteristically have a sweet, fruity smell. The presence of an ester group can be tested by reacting it with hydroxlamine to give an alcohol and hydroxamic acid, which when treated with ferric chloride gives characteristic a burgundy or magenta ferric hydroxamate complex.

Esters can also be cleaved by hydroiodic acid to produce alkyl iodide and carboxylic acid. The alkyl iodide produced can be treated with mercuric nitrate to yield an orange-coloured mercuric iodide.

Another carboxylic acid derivative is amide. Like esters, amides react with hydroxyamine hydrochloride to form hydroxamic acid which react with ferric chloride to form the magenta coloured ferric hydroxamate.

Amides can also be hydrolysed to produce the carboxylate salt and ammonia or amine. The presence of ammonia or low molecular weight amine can be detected using the litmus paper.

PROCEDURE

The following carboxylic acids and carboxylic acid derivatives are provided for the tests below:
Carboxylic acid: ethanoic acid (acetic acid) and benzoic acid
Amides: ethanamide and benzamide.
Esters: ethyl acetate and methyl benzoate

REACTION OF CARBOXYLIC ACID WITH SODIUM BICARBONATE SOLUTION

Place 1 mL 5% $NaHCO_3$ in a watch glass. Add 1- 2 drops carboxylic acid (or 0.1 g, if solid). Record your observations.

ESTERIFICATION OF CARBOXYLIC ACID

Add 1 mL glacial acetic acid and 5 drops of concentrated sulphuric acid to 2 mL ethanol in a test tube. Warm the mixture for 2 minutes. Cool, and pour cautiously into aqueous sodium carbonate solution in an evaporating dish and smell immediately. An acid would yield a sweet, fruity smell of an ester. (However, acids of high molecular weight often give almost odourless esters).

SODIUM HYDROXIDE HYDROLYSIS OF AMIDES

Add 0.2 g ethanamide to 5 mL 10% NaOH solution in a test tube. Shake the mixture and record your observations. Then, heat the solution to boiling and note the smell of the vapour released. Test the vapour with a moist red litmus paper and record your observations.

Cool the test tube and acidified with aqueous HCl solution and note all your observations. Repeat the test with benzamide.

ACID HYDROLYSIS OF AMIDES

Heat the solution of 0.2 g ethanamide with 10% sulphuric acid to boiling. Cool the test tube and note the smell of the vapour released. Test the vapour with a moist red litmus paper. Repeat the test using benzamide.

TEST FOR ESTER

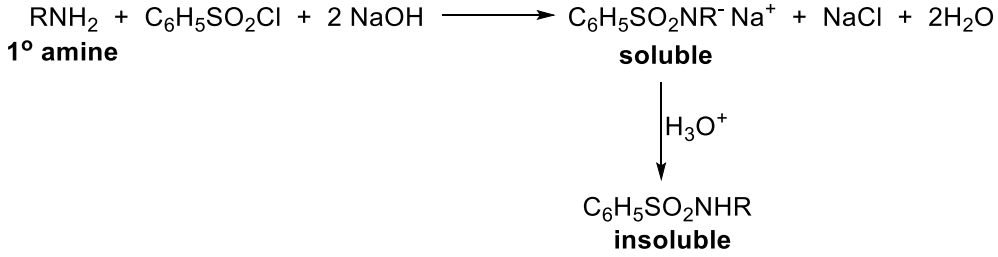
In a test tube, add 1-2 drops ethyl acetate to a saturated alcoholic solution of hydroxylamine hydrochloride (3 drops) and a methanolic solution of 20% potassium hydroxide (3 drops). Heat the mixture to boiling. Cool the mixture and acidified with 0.5 M HCl solution. Add iron(III) chloride solution drop by drop to the mixture and record all observations. Repeat the test with methyl benzoate.

E. AMINES

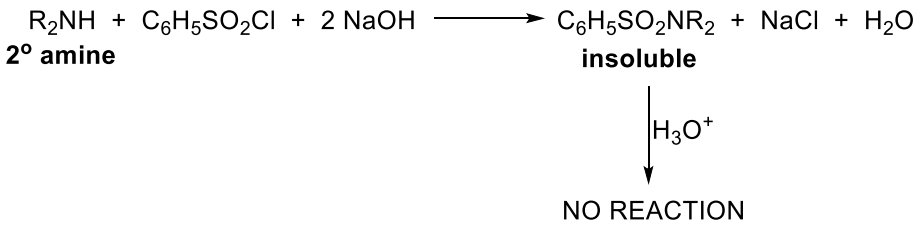
Amines are derivatives of ammonia in which one or more of the hydrogens has been replaced by an alkyl or aryl group. They have the general formula R-NH_2 (primary, 1º), R_2NH (secondary; 2º) or R_3N (tertiary, 3º), in which R is an alkyl or aryl group. The hydrogens on the primary and

secondary amines are active and undergo reaction with sodium metal to form a salt and liberate hydrogen gas. Primary and secondary amines react with acetyl chloride to produce amides which often precipitate out from the solution. Heat is also usually evolved in this reaction. Tertiary amines, however, do not react with acetyl chloride since they lack hydrogen on the nitrogen atom.

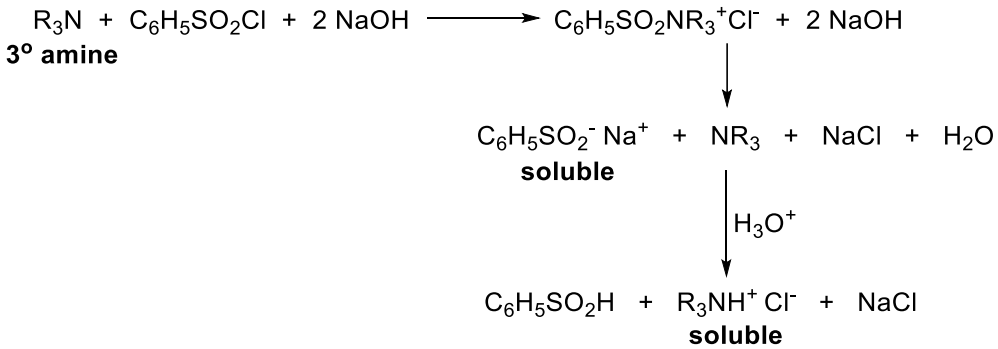
The **Hinsberg test** can also be used to distinguish between 1º, 2º and 3º amines. This test involves the reaction between the amines and the benzenesulfonyl chloride reagent under basic conditions. Primary amines react with benzenesulphonyl chloride under basic conditions to form the sodium salt of sulphonamide which is soluble in the reaction mixture. Precipitation of the sulphonamide will occur when the mixture is acidified.



Similarly, secondary amide will react with benzenesulphonyl chloride under basic condition to form the sodium salt of sulphonamide which is insoluble in the reaction mixture and remains insoluble upon acidification.

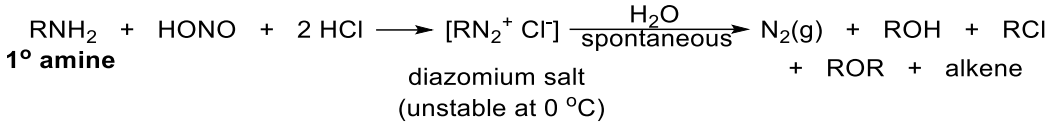


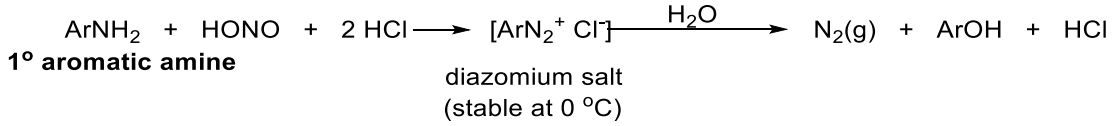
Tertiary amines undergo reactions with benzenesulphonyl chloride under basic condition to form the quartenary ammonium sulphonate salts which gives sodium sulphonate and insoluble tertiary amines in basic solution. Acidification of the reaction mixture gives sulphonic acids and soluble amine salts.



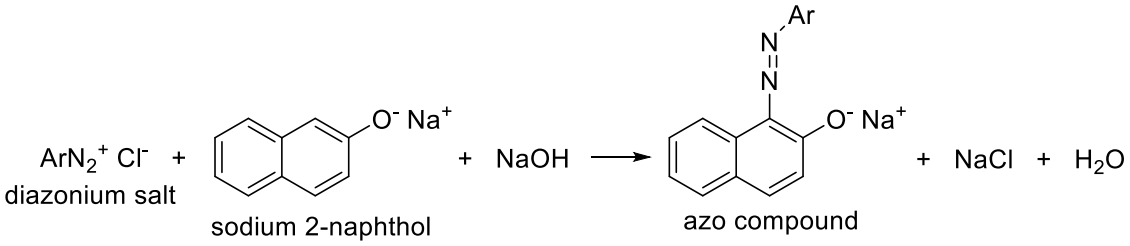
Amines also react with nitrous acid and this reaction is used to distinguish not only 1º, 2º or 3º but also between aliphatic and aromatic amines. Primary aliphatic amines and aromatic amines

react with nitrous acid to form an intermediate diazonium salt with the evolution of nitrogen gas. A primary aliphatic diazonium salt is unstable even at 0 °C and decomposes spontaneously with a rapid loss of nitrogen gas while primary aromatic amine diazonium salt is more stable at 0 °C and decomposes to liberate nitrogen gas only upon heating.

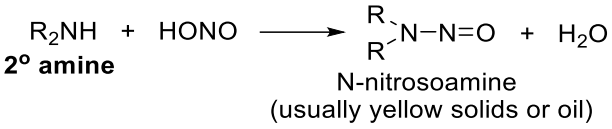




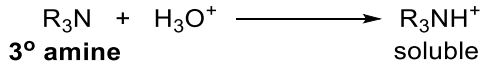
The diazonium salt of the primary aromatic amine reacts with phenolic compounds such as 2-naphthol to form an orange-red azo compound.



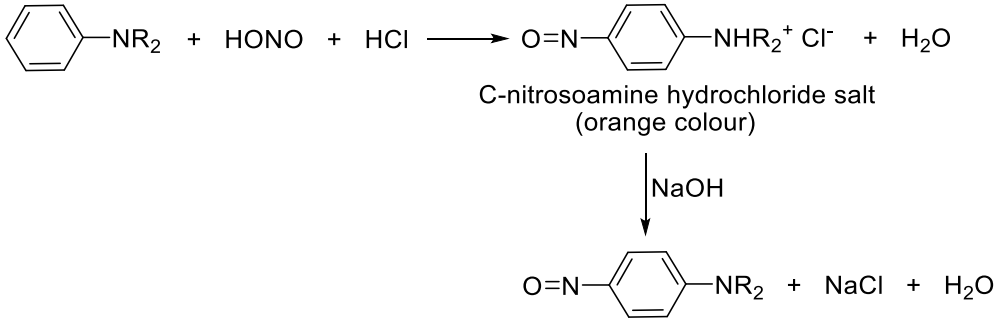
Secondary amines undergo a reaction with nitrous acid to form N-nitrosoamines which are usually yellow low melting solids.



Tertiary aliphatic amines do not react with nitrous acid but form soluble salts as shown below.



However, the orange- c o l o u r e d hydrochloride salt of the C-nitrosoamine is formed when a tertiary aromatic amine is reacted with nitrous acid. Treatment of the C-nitrosoamine salt with base will liberate the C-nitrosoamine as bright green or blue solid.



PROCEDURE

The following amines are provided for the tests below:

Propylamine, diethylamine, triethylamine, aniline, *N*-methylaniline and *N*,*N*-dimethylaniline

HINSBERG TEST

To 0.3 mL propylamine (or 300 mg, if solid) in a test tube, add 5 mL 10% NaOH solution and 0.4 mL benzenesulfonyl chloride. Stopper the test tube and shake the mixture vigorously. Test the solution to make sure that it is still alkaline. After all the benzenesulfonyl chloride has reacted, cool the solution, and separate the residue from the solution, if any. Treat the solution with 10% HCl solution and record your observations. Positive tests are indicated as follows:

1° amines: dissolve in base and precipitate in acid.

2° amines: precipitate in base but no change in acid.

3° amines: precipitate in base and dissolve in acid.

Repeat test using propylamine, diethylamine, triethylamine, aniline, *N*-methylaniline and *N,N*-dimethylaniline.

NITROUS ACID TEST

Add 0.5 mL or 0.5 g of the amine to 1.5 mL concentrated HCl diluted with 2.5 mL water and cool the solution to 0 ^{o}C. Dissolve 0.5 g of sodium nitrite in 2.5 mL water and add this solution dropwise, with shaking, to the cold solution of the amine hydrochloride. Continue the addition until the mixture gives a positive test for nitrous acid. The test is carried out by placing a drop of the solution on starch-iodide paper; a blue color indicates the presence of nitrous acid. If the test is positive, transfer 2 mL of the solution to a clean test tube, warm gently, and examine for evolution of gas.

The presence of a primary aliphatic amine is indicated by a rapid bubbling or frothing as the aqueous sodium nitrate is added at 0 ^{o}C. Primary aromatic amines from diazonium salt with the evolution of gas only upon warming.

The solution from the primary aromatic amine should be subjected further to the coupling reaction as follows:

Add 2 mL of the cold diazonium solution to a solution of 0.1 g 2-naphthol in 2 mL 10% sodium hydroxide solution and 5 mL water. The formation of an orange-red dye with the evolution of gas upon warming indicates the presence of a primary aromatic amine.

A secondary amine will give a pale-yellow oil or low-melting solid without any evolution of gas. An immediate positive test for nitrous acid (as indicated by the blue colour on a starch-iodide paper) with no evolution of gas indicates a tertiary aliphatic amine.

Tertiary aromatic amines will react with nitrous acid to produce a dark-orange solution of the C-nitrosoamine hydrochloric salt. Treating 2 mL of this solution with 10% sodium hydroxide or sodium carbonate solution will give a bright-green or blue nitrosoamine base which can be purified and characterised.

Perform the above test with propylamine, diethylamine, aniline, N-methylaniline and N,N-dimethylaniline.

2. REFERENCES

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2. Mahmood,K; Rahman, N.A. Kaedah Kimia Dalam Pengenalpastian Sebatian Organik, University of Malaya Publisher. 2000.
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5. Pasto, D.J.; Johnson, C.R.; Miller, M.J. Experiments and Techniques in Organic Chemistry, New Jersey: Prentice-Hall International, Inc" 1992.
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Experiment 5 **Physical Chemistry**

CHEMICAL KINETICS

Objective: To determine the rate constant of hydrolysis of methyl acetate

1. INTRODUCTION

Chemical kinetics concerns the quantitative study of chemical rates of reaction as well as explaining the steps or mechanism of reactions. The rate of a chemical reaction generally depends on the concentration of species/reactants, temperature, and catalyst.

Rate of reaction can be measured as the rate of the disappearance of reactants or the rate of formation of products in a chemical reaction. Rate of reaction is generally defined as dc/dt (differentiation of concentration with respect to time).

The overall order of a reaction is defined to be the sum of the individual orders of reaction in each of the species involved. Thus, a reaction whose rate is proportional to the concentration of only one of the reactants or products of the reaction (i.e., the reaction is first order in that species) is termed a first order reaction. In this experiment, you will study a reaction that, under the experimental conditions you will employ, corresponds to such a case. Rates of reaction can be determined experimentally. The differential equation for the rate law of a first order reaction whose rate depends only on the concentration of one reactant can be written (in the case of unit stoichiometry) as:

$$-\left[\frac{dc}{dt}\right] = kc \qquad (1)$$

Where,
c = concentration of the reactant on which the rate depends,
t = time,
k = rate constant or specific rate constant.

	A	⟶	B
time = 0	a		
time = t	(a-x)		x

In an experiment, it is generally more useful to write equation (1) in the form of equation (2)

$$\frac{dx}{dt} = k(a - x) \qquad (2)$$

Where,
a = initial concentration of reactant, and
(a - x) = decrease in concentration of reactant after time t (proportional to the amount that has reacted). Or Integrating equation (2) produces equation (3)

$$\ln \frac{a}{a - x} = kt \qquad (3)$$

Rearranging equation (3) gives equation (4)

$$\ln(a - x) = -kt + \ln a \qquad (4)$$

Therefore, for a first order reaction, a graph of ln (a - x) versus t is a straight line with gradient, -k. Quantities that are proportional to concentration can be used instead as replacement for concentration in the above equations.

In 1889 Arrhenius found that the values of rate constants increase exponentially with temperature. The relationship between rate constant and temperature is given by the Arrhenius equation:

$$K = Ae^{-\left[\frac{Ea}{RT}\right]} \qquad (5)$$

where, A = pre-exponential factor, and
E_a = activation energy of the reaction

For more precise rate data, experiment can be repeated with careful temperature control.

Determination of the rate constant of hydrolysis of methyl acetate with HCl 0.5 M as catalyst

1. Theory

When esters such as methyl acetate react with water, some are converted to alcohol and acid, and the reaction can be explained as:

$$CH_3COOCH_3 + H_2O \rightleftharpoons CH_3COOH + CH_3OH \qquad (6)$$

This is a reversible reaction, but with the presence of excess water, this reaction can be considered as a complete reaction. Hydrolysis occurs slowly in pure water, with acid as catalyst.

If this reaction is conducted in a dilute solution with the presence of a known concentration of strong acid, the rate and order of the reaction depends only on the concentration of methyl acetate. This is thought to be due to the concentration of water which is constant throughout the experiment and the concentration of acid does not change. The rate of reaction, however, is proportional to the concentration of acid.

2. Materials

Apparatus: Conical flasks, burette, pipette, stopwatch, water bath.
Chemicals: Methyl acetate, HCl 0.5 M, NaOH 0.1 M and phenolphthalein indicator. (These solutions are prepared)

3. Experimental Procedure

1. Transfer 100 mL HCl 0.5 M into a conical flask with a stopper and place the flask in the water bath.
2. Place another conical flask or bottle that contains methyl acetate in the same water bath.
3. While the temperature of these chemicals equilibrates, prepare a burette filled with NaOH 0.1 M.
4. Record the temperature of the water bath every 15 minutes.

5. When the temperature of the chemicals is in equilibrium with the temperatures of the water bath (after ≈ 10 minutes), pipette 5 ml of methyl acetate into the conical flask that contains the acid. Record and consider this moment as the initial time for the reaction (t_o) in measuring the reaction time (t). Shake the conical flask well and do not take it out of the water bath.
6. Using a pipette, take 5 mL of the mixture, quickly placing it into a 250 mL conical flask that contains 25 ml of icy water to stop the reaction. Record the time this is done and consider this as the time of reaction, t. In this case, t is equal to 0 minutes.
7. The acid/methyl acetate solution (in which reaction has been stopped) is then quickly titrated with NaOH 0.1 M using phenolphthalein as the indicator. (Make sure the solution is cold during titration).
8. Take titre readings for consecutive 5 mL solution mixtures that have reacted in the following time intervals: 10, 20, 30, 45, 60 and 80 minutes. Follow the same procedures as above (steps 6 and 7).
9. Make sure you record the time the reaction is stopped for every consecutive 5 mL mixture taken from the source mixture.
10. Finally, heat the remaining mixture for about 10 minutes until it boils to complete the reaction. Cool it down and titrate the solution twice.

4. Calculations

The difference ($V_\infty - V_t$) is proportional to the concentration of ester left (unhydrolysed) at time t, where V_t is the volume of NaOH required in titration (for the mixture that had reacted in time t) and V_∞ is the volume of NaOH required for the mixture that completed the reaction (boiled).

A plot of $\ln(V_\infty - V_t)$ versus t will give a straight line with a gradient of – k.

5. References

1. Mahan, B.H. (1987). *University Chemistry*, 4th edn. Addison-Wesley.
2. Finlay, A. (1954). *Practical Physical Chemistry*, 8th edn. Longmans.

Notes: Please quote experimental error estimates for all your data presented.

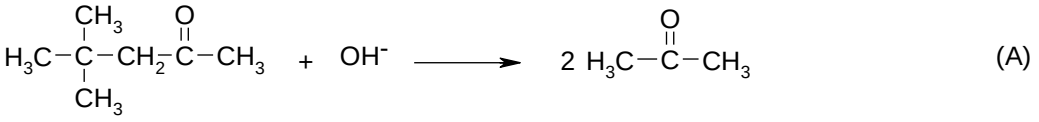
Experiment 6 **Physical Chemistry**

Determination of rate constant of a dissociative reaction

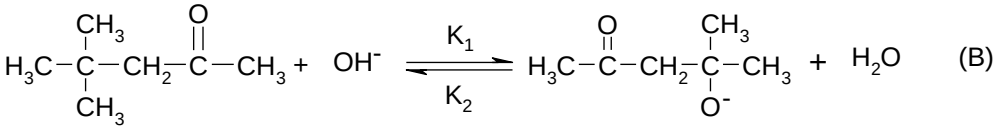
Objective: To determine the rate constant of a dissociative reaction of 4-Methyl-4-hydroxy-2-pentanone, MHP (diacetone alcohol)

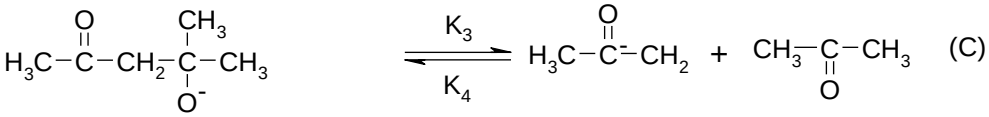
1. INTRODUCTION

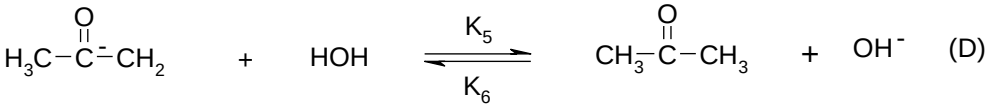
4-Methyl-4-hydroxy-2-pentanone, MHP (diacetone alcohol), undergoes dissociation in the presence of hydroxyl ions to form acetone:



This reaction is reversible, though the equilibrium constant is quite large. It is assumed to occur via the steps shown below:







In step (B), the reactant, MHP, is in fast equilibrium with its ions. The ion then dissociates to form acetone and the carbanion as shown in step (C). Step (D) shows that the carbanion takes one proton from water to give acetone and a hydroxyl ion. Since step (B) is a fast equilibrium, the overall rate of reaction will depend on the step that is rate determining, i.e., step (C) or step (D).

CASE I

If (C) is the rate-determining step, the rate equation is:

$$d[CH_3COCH_2C(CH_3)_2O^-] / dt = K_3 [CH_3COCH_2C(CH_3)_2O^-] \quad (1)$$

Since (B) is the fast step, thus

$$K = K_1 / K_2 = \{[CH_3COCH_2C(CH_3)_2O^-][HOH]\} / \{[MHP][OH^-]\}$$

And $$[CH_3COCH_2C(CH_3)_2O^-] = K [MHP][OH^-] / [HOH] \quad (2)$$

Substituting the above equation in equation (1), the rate equation becomes

$d[CH_3COCH_2C(CH_3)_2O^-] / dt = K_3 K [MHP][OH^-] / [HOH]$ (3)

One molecule of $CH_3COCH_2C(CH_3)_2O^-$ is consumed in step (C) while one molecule of MHP reacts with OH^- to form one molecule of $CH_3COCH_2C(CH_3)_2O^-$ in step (B) so that equilibrium in step (B) is re-established. Thus, rate of change of MHP concentration is the same as rate of change of $[CH_3COCH_2C(CH_3)_2O^-]$

$$d[MHP] / dt = d[CH_3COCH_2C(CH_3)_2O^-] / dt$$

and equation (3) can be written as

$- d[MHP] / dt = K_3 K [MHP][OH^-] / [HOH]$ (4)

If OH^- and HOH are in excess, their concentrations will be the same as their initial concentrations and the reaction will be pseudo first order. Thus, equation (4) will be

$$- d[MHP] / dt = k [MHP] \quad (5)$$

where $k = K_3 K [OH^-] / [HOH]$

CASE II

If the forward reaction in step (D) is the rate-determining (slowest) step, the rate equation is:

$$-d[CH_3COCH_2^-] / dt = K_5 [CH_3COCH_2^-][H_2O] \quad (6)$$

Since steps (B) and (C) are in fast equilibrium,

$$K_1 / K_2 = [CH_3COCH_2C(CH_3)_2O^-][HOH] / [MHP][OH^-] \quad (7)$$

and $K_3 / K_4 = [CH_3COCH_2^-] [CH_3COCH_3] / [CH_3COCH_2C(CH_3)_2O^-]$ (8)

Since the rate equation must be expressed using measurable quantities,

$$[CH_3COCH_2C(CH_3)_2O^-] = (K_1 / K_2) [MHP][OH^-] / [HOH]$$

$$[CH_3COCH_2^-] = K_3 / K_4 [CH_3COCH_2C(CH_3)_2O^-] / [CH_3COCH_3]$$

$$= (K_3K_1 / K_4K_2) [MHP][OH^-] / [HOH][CH_3COCH_3] \quad (9)$$

and $d[CH_3COCH_2^-] / dt = d[MHP] / dt$ (= - rate) (10)

Thus, the rate equation becomes

$$d[MHP] / dt = \{K_5K_3K_1 / K_4K_2\}\{[MHP][OH^-] /[CH_3COCH_3]\} \quad (11)$$

This shows that the decomposition rate of MHP is inversely dependent on the concentration of acetone.

As such, Case I and II can be differentiated because the added acetone will reduce the rate in Case II but will not disturb the rate in Case I.

This reaction is accompanied by a change in volume. Thus, the extent of reaction can be followed from the volume measurement.

For the condition involving excess MHP, the rate is not influenced by the addition of acetone. The kinetics of this reaction will obey the rate law (4) and not (11). By arranging the conditions so that the concentrations of OH^- and H_2O remain constant, the reaction will achieve the pseudo-first order and the rate will only depend on the concentration of MHP.

$$- d[MHP] / dt = k [MHP] \quad (12)$$

where $k = K_3K_1[OH^-] / K_2 [H_2O]$

From here $\ln \{[MHP]_o / [MHP]\} = kt$ (13)

or $\ln \{a / (a – x)\} = kt$ (14)

It can be shown that equation (14) can be re-presented as,

$$(V – V_\infty) / (V_o – V_\infty) = e^{-kt} \quad (15)$$

[Show in your report how equation (15) can be derived from equation (14).]

2. MATERIALS

Apparatus: Dilatometer, conical flask, burette, pipette, thermometer, stopwatch.
Chemicals: NaOH, MHP(diacetone alcohol), acetone.

3. EXPERIMENTAL PROCEDURE

The change in volume during a reaction can be measured with a dilatometer as shown in Figure 1. It involves a bulb connected to a capillary with graduated small diameter; a small change in volume can be measured from the height of the meniscus of the liquid in the capillary. The dilatometer is very brittle and must be handled with care. Before each test is carried out, it must be properly washed and dried.

TEST 1

1. Place the dilatometer in a water bath at 30 ^oC with only its bulb immersed in the water.
2. Add 34 cm^3 of 0.1 mol dm^{-3} NaOH into a conical flask through a burette. The flask is then stoppered and placed in the same water bath.
3. After 15 minutes, 1 cm^3 of acetone is added to the above conical flask step (2) through a pipette, followed by addition of 2 cm^3 of MHP from another pipette. The contents are then poured into the funnel of a dilatometer. The stopcock is opened, and the solution is allowed to fill up the bulb until it is exactly below the capillary.
4. With the stopcock closed, the position of the meniscus is determined every 30 seconds for 600 seconds.
5. After allowing it to remain for another 600 seconds, a similar set of readings is taken (i.e., Δ = 600 seconds).

6. The height of the meniscus can be measured "relative" to any suitable scale attached to the capillary column.

Fig.1 Dilatometer

TEST 2

Repeat the above procedure using 35 cm^3 of NaOH solution and 2 cm^3 of MHP only (without acetone).

4. CALCULATIONS

Guggeneim[1] has suggested a method to determine the rate constant of a first order reaction in which the amount of x_i that had reacted can be determined directly but the initial concentration is not known. This method can be used in this experiment as it involves a first order reaction, using a physical measurement in which the final reading cannot be made, or equilibrium cannot be achieved.

If times t_1, t_2, t_3 and so on, and $(t_1 + \Delta)$, $(t_2 + \Delta)$ and $(t_3 + \Delta)$ and so on, are chosen as a time interval constant, the following equations are true:

$$(V - V_\infty) = (V_o - V_\infty)\, e^{-kt} \qquad (16)$$

$$(V' - V_\infty) = (V_o - V_\infty) = e^{-k(t+\Delta)} \qquad (17)$$

where V and V' are volumes at times t_1 and $(t_1 + \Delta)$.

Equation (17) minus equation (16) gives:

$$(V - V') = (V_o - V_\infty)\, e^{-kt}\,(1 - e^{-k\Delta}) \qquad (18)$$

or

$$kt + \ln(V - V') = \ln[(V_o - V_\infty)(1 - e^{-k\Delta})] \qquad (19)$$

The right-hand side of equation (19) is a constant. Thus,

$$\ln(V - V') = -kt + \text{constant} \quad (20)$$

or

$$\log(V - V') = -(k/2.303)\, t + \text{constant} \quad (21)$$

From here, a graph of ln(V – V') against time, t gives a straight line of slope –k (or alternatively, a graph of log(V – V') against time gives a straight line of slope -k/2.303).

5. DISCUSSION

Compare the two tests carried out at the same temperature. What is the effect of acetone on the rate of reaction? Are the rate constants similar to each other within experimental error? Is this conclusion consistent with the mechanism expressed in equation (4) or in equation (11)? Give your reasons.

6. REFERENCES

1. E. A. Guggenheim, *Phil. Mat.,* 1926, 2, 538.
2. V. K. La Mer and M. L. Miller, J. Am. Chem. Soc., 1935, 57, 2674.
3. Atkins, P. W. (1998), *Physical Chemistry*, 7th ed. Oxford.
4. Levine, I. N.(2002), *Physical Chemistry*, 5th ed. McGraw Hill.

Notes: Please quote experimental error estimates for all your data presented.

APPENDIX

To measure the rate of reaction from changes in a physical property

Consider a general reaction,

$$nA + mB + pC \rightarrow rZ\,, \qquad (A)$$

where Z includes all the products. Let the value of a physical property at any time t,

$$\lambda = \lambda_M + \lambda_A + \lambda_B + \lambda_C + \lambda_Z\,, \qquad (B)$$

where λ_M is the contribution from the first reactant and the all the other λs change with concentration, for example,

$$\lambda_A = \zeta_A\,[A] \qquad (C)$$

where ζ_A is a proportionality constant. Let the initial concentrations of reactants be a, b, c respectively and the change in the extent of reaction x is the no. of moles that have reacted during time t, then

$$\lambda = \lambda_M + \zeta_A(a - nx) + \zeta_B(b - mx) + \zeta_C(c - px) + \zeta_Z\, rz \qquad (D)$$

and

$$\lambda_o = \zeta_M + \zeta_A\, a + \zeta_B\, b + \zeta_C\, c \qquad (D1)$$

$$\lambda_\infty = \lambda_M + \zeta_B(b - ma/n) + \zeta_C(c - pa/n) + \zeta_Z\, ra/n \qquad (D2)$$

where λ_o and λ are initial and final values of λ, and in equation (D2) it is assumed that A is the is the reactant in infinite excess.

Subtraction of (D1) from (D2) gives:

$$\lambda_\infty - \lambda_o = \zeta_Z\,(ra/n) - \zeta_A\, a - \zeta_B\,(ma/n) + \zeta_C(pa/n) \qquad (D3)$$

and subtraction of (D1) from (D) gives:

$$\lambda_\infty - \lambda_o = \zeta_Z\, rx - \zeta_A\, nx - \zeta_B\, mx + \zeta_C\, px \qquad (D4)$$

which may be summarized as

$$\lambda - \lambda_o = x\Delta\zeta\,; \quad \zeta\infty - \lambda_o = (a/n)\Delta\,\zeta \qquad (D5)$$

and $$\lambda_\infty - \lambda = (a/n - x)\Delta\,\zeta \qquad (D6)$$

where $$\Delta\zeta = \zeta_Z\, r - \zeta_A\, n - \zeta_B\, m + \zeta_C\, p \qquad (E)$$

From here, we can derive a useful kinetic expression.

$$nx / a = (\lambda - \lambda_o) / (\lambda_\infty - \lambda) \qquad (F)$$

$$a / (a - nx) = (\lambda - \lambda_o) / (\lambda_\infty - \lambda) \qquad (F1$$

Experiment 7 **Physical Chemistry**

DETERMINATION OF HEAT OF REACTION

Objective: To determine the heat of polymerization of acrylamide

1. INTRODUCTION

The heat of a chemical reaction depends on the conditions under which the process involved occurs. Under constant volume, the heat of reaction is known as the internal energy change, ΔU while, under constant pressure it is known as the enthalpy change, ΔH.

Heat of reaction can be determined by a calorimetric method. The reaction is conducted in an insulated container. The rise in temperature is measured with a sensitive thermometer. The product of the temperature rises, and the heat capacity of water and calorimeter will be equal to the heat evolved.

In this experiment, the heat of reaction is measured under almost adiabatic condition (i.e., no or negligible heat loss) by conducting the reaction in a Dewar flask. The heat evolved is measured from the rise in temperature of the reacted mixture.

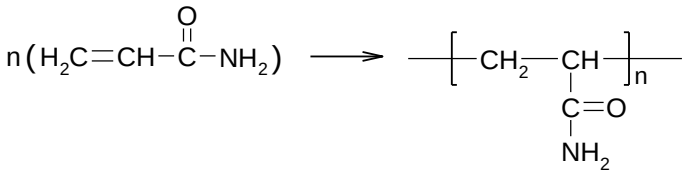
The heat capacity of the Dewar flask can be determined by carrying out a reaction with known enthalpy change. A suitable reaction for this purpose is the strong acid-strong base neutralisation with known heat of reaction (57,300 J mol^{-1}).

If ***x*** mole acid is neutralised, the heat capacity (C) of the Dewar flask can be calculated from the equation,

$$(ms + C)\Delta T = \boldsymbol{x}\ (57{,}300) \qquad (1)$$

where, m = mass of solution, g
s = specific heat of solution, 4.2 J g^{-1} K^{-1}
ΔT = rise in temperature, K

The reaction studied is a free radical polymerisation of acrylamide using a redox system with persulphate as the initiator. (In a polymerisation reaction, monomer molecules react to form a chain of repeating units; these chains are known as polymer molecules). The reaction can be represented as follows:



Acrylamide is a stable solid crystal; however, its monomer solution is unstable above 70 °C particularly in the absence of oxygen. It is best polymerised in an aqueous solution at 50 – 70 °C using persulphate as the initiator, or at room temperature with a reducing agent e.g., bisulphite, added in to expedite the production of free-radicals. The free radical initiators are produced as shown in the following reactions:

$S_2O_8^{2-} \xrightarrow{60\ °C} 2\ SO_4^{\cdot -}$

and with the presence of bisulphite,

$S_2O_8^{2-} + HSO_3^- \xrightarrow{RT} SO_4^{2-} + SO_4^{\cdot -} + HSO_3^{\cdot}$

Production of free radicals can be further enhanced with the addition of ferrous ions as in the reaction below:

$S_2O_8^{2-} + Fe^{2+} \longrightarrow SO_4^{2-} + SO_4^{\cdot -} + Fe^{3+}$ and

$HSO_3^- + Fe^{3+} \longrightarrow HSO_3^{\cdot} + Fe^{2+}$

The reactions involved are known collectively as a **REDOX** system.

2. EXPERIMENTAL

A. Calibration of Dewar Flask

1. Fill the flask with an **accurate** volume of approximately 210 mL 1M NaOH solution. Use a thermometer and record its temperature when stabilised.
2. Fill into a beaker an **accurate** volume of approximately 190 mL 1M HCl solution (≈ 90% the amount of base).
3. Remove the thermometer from the flask. Clean and dry it. Measure the temperature of HCl acid in the beaker. The temperature of HCl should be ± 0.2 °C of that of NaOH solution. Heat or cool it if necessary.
4. Once achieved, immediately pour all the acid into the Dewar flask and stir thoroughly. Observe and record the temperature every 30 seconds for the first 5 minutes, and then every minute until a maximum temperature is reached.

Calculate the **heat capacity** of the Dewar flask using equation (1).
NOTE: ***x*** is the mole of acid with excess base.

B. Measurement of the Heat of Polymerisation

1. Dissolve an **accurate** amount of approximately 10 g acrylamide in about 100 mL distilled water. Add more water to make it to 400 mL. Transfer the solution to the Dewar flask.
2. Place a thermometer (0 – 50 °C) into the Dewar flask and record its reading once stabilised.
3. Remove the thermometer and add the following into the flask:

- 5 mL of 5% w/v potassium persulphate solution
- 5 mL of 5% w/v sodium bisulphite solution
- 2 mL of freshly prepared saturated solution of ferrous sulphate

4. Carefully place the thermometer in the flask and shake it well. Record the temperature every minute until it reaches a maximum.
5. Plot a graph of **temperature** *vs.* **time.** Calculate the heat of polymerisation of acrylamide using the following assumptions:

(i) the change is complete
(ii) the specific heat of the monomer and polymer is 2.1 J g^{-1} K^{-1}
(iii) the specific heat of water is 4.2 J g^{-1} K^{-1}

6. Observe and take note of any changes in the viscosity of the mixture before and after the polymerisation.
7. Add approximately 5 mL of the solution into 50 mL acetone. Record and describe your observations.

3. QUESTION

Describe the shape of **temperature** *vs.* **time** curve of acrylamide. How would the assumption (i) above be verified? Does this reaction involve absorption or release of heat?

4. REFERENCES

1. http://www.lokchem.com/prodc5.htm.
2. CRC Handbook of Chemistry and Physics, 85th Edition, 2004

Notes: Please quote experimental error estimates for all your data presented.