



UNIVERSITI
MALAYA

Laboratory Manual

PHYSICAL CHEMISTRY

Level III



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INTRODUCTORY NOTE

An experiment in physical chemistry is designed with the aim to illustrate the basic principles in chemistry. Typically, every experiment will be accompanied by its background and underlying theory, detailed experimental procedure and suggestions on methods to analyze the results followed by a brief discussion.

Before the laboratory session, please READ the General Laboratory Instruction (<https://t.ly/72kRt>) which provides the basic principles in physical methods. In the General Laboratory Instruction, you will first be introduced to the basic idea of measurements, standards and associated quantitative aspects such as units, dimensionalities, symbols, and uncertainty. This is followed by accuracy, precision, data analysis, error estimation, general equipment and tools, and scientific writing. It intends to give the necessary background discussion which you MUST read before entering the laboratory. It is also important that you continue to practice the advice given here not only during your study but throughout your lifetime as a scientist. Of course, the brief manual is by no means complete. You may refer to a more elaborate introduction on similar subject in most general chemistry textbooks. There are also many sources on the Internet which you can browse through.

The physical chemistry experiments designed here are to accompany the physical chemistry lecture courses. Through these experiments you will experience measuring some of the physical properties of interest with known precision. Moreover, they will allow you to understand the concept behind the measurements and how to relate experimental results to the basic concepts in the lecture courses.

The quantitative measurements you have made produces numerical values which are subject to error due to many reasons such as the nature of the instrument and how the experiment is designed. Thus, it is equally important to repeat the experimental procedure a few times until the result is consistent. Sometimes the experimental procedure may be varied to check for convergence of the values by different methods. In addition to these, a physical chemist must estimate the value of error in his measurement to get improved accuracy of the measured value compared to a standard value.

A good laboratory practice is to process the raw data immediately to get a rough idea of the results of the experiment immediately. By doing so, anything which deviates from expectation may be checked immediately before dismantling the experimental set up. For example, graph should be plotted roughly during the laboratory. Should a linear behavior be expected and some points are found to deviate, then the experiments related to these odd data points may be repeated immediately.

Laboratory report should be processed immediately for two obvious reasons. First, if the processed result is unsatisfactory, the experiment may be repeated immediately. Secondly, since the detail information about the experiment is fresh in memory a better report will be produced.



CHEMICAL LABORATORY SAFETY AGREEMENT

*****This agreement is applicable for all PHYSICAL AND POLYMER CHEMISTRY Laboratory Classes*****

In the interest of safety and accident-prevention, there are regulations to be followed by all students in designated Chemistry Laboratories at the Department of Chemistry, Faculty of Science, Universiti Malaya (UM). Faculty and staff members are authorised to deny the use of any laboratory to students who do not adhere to the regulations mentioned below or in instances when the safety of any of the student, staff or faculty member in the laboratory might be jeopardised.

Regulations for all Chemistry Laboratories are as follows:

1. Common safety practice and guidelines **MUST** be obeyed at all times when you are in the laboratory. Please refer to the UM or Chemistry Department Safety Handbook regularly. This handbook is available in every laboratory. When unsure on any matter related to safety, seek help from the lecturer-in-charge.
2. Proper attire must always be worn in all chemical laboratories, including shoes that completely cover the foot (no high-heeled shoes), and a shirt that covers the entire upper torso, including the stomach and the back. Lab coats must be worn in the laboratory at all times. Long hair must be tied back. No loose or baggy clothes and dangling jewellery is allowed.
3. Safety eyewear must always be worn during laboratory sessions.
4. **CONTACT LENSES** should not be worn in the lab as chemicals can get between the eye and the lens
5. Prior to handling any chemical, please make sure you have read its Safety Data Sheet (SDS).
6. Do not dispose mercury into the sink. Mercury is expensive, toxic and poisonous. Used and contaminated mercury must be transferred into the residue bottle which is provided. Any spillage of mercury **MUST** be reported to the lab assistant.
7. **DO NOT** dispose of organic solvent into the sink. Any used organic solvent must be transferred into the appropriately labelled waste bottles. Please consult the lab assistant if you are uncertain.
8. When dealing with compressed gases, high pressure or high voltage equipment, please read and understand the instruction thoroughly before proceeding with the experiment.
9. Be organised. Maintain a clean, open work area free of anything except materials directly required for the exercise. Keep laboratory material/equipment away from edges of work surfaces and electrical cords from hanging below the surface of tables.
10. Equipment and/or chemicals should never be taken out of the lab unless authorised by the instructor or laboratory staff.
11. Be familiar with the location and the use of the following in your laboratory: e.g. broken glass receptacle, first-aid kit, emergency gas shut-off valves, closest fire alarm, fire extinguisher, eye wash, safety shower, and emergency exit and routes.
12. Be prepared. Study the assigned experiment before you come to lab. Be familiar with the lab exercise to prevent confusion and accidents. No unauthorised experiments are to be performed. Students must follow the procedural instructions in the lab handout/manual unless modifications to the procedures have been announced by the

laboratory supervisor, in which case the student must follow the supervisor's procedural instructions.

13. NEVER TOUCH ANY FORM OF BROKEN GLASS. Broken glass should be disposed of only by laboratory staff.
14. Lab experiments have been designed to minimize unnecessary exposure to any hazardous substances; however, it is not advisable for pregnant women or those with certain medical conditions to be exposed to any chemicals. We cannot ensure that a pregnant student will not be exposed to chemicals that might be unhealthy for her or her foetus. In addition, we cannot know the level of exposure, the length of exposure or the number of encounters that might occur with any chemical during a semester. By maintaining the safety rules, we expect that all students, including a pregnant student, should be able to carry out lab procedures safely. However, it is the Department's professional advice that pregnant students should be advised NOT to take a lab course unless she is willing to understand and assume the risks. She should certainly be seeking and following proper medical advice from her physician.
15. If you are pregnant, or you suspect, should become, or plan to become pregnant during the semester, or have any medical condition or concern, including but not limited to the following, immunocompromised system, seizures, epilepsy, severe allergies, it is your, the student's, responsibility to consult with your medical care provider regarding any medical issue associated with taking this lab. Students are encouraged to provide their physician with a list of the chemicals that they might be exposed to while in lab. They should also check the SDS sheets to be aware of the hazards of the chemicals.



SAFETY INFORMATION ACKNOWLEDGEMENT INFORMED CONSENT

This copy is to be signed and kept by student

I acknowledge receipt and that I have read and understand the lab safety regulations stated in the Chemical Laboratory Safety Agreement and in UM or Chemistry Department Safety Handbook, 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 I am pregnant, or suspect to be pregnant, 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, 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.

Name	:	Course	:
Matric Number	:	Sem / Session	:
IC Number	:	Lecturer	:
Signature	:	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).

Emergency contact 1

Name: Relationship: Contact number:

Emergency contact 2

Name: Relationship: Contact number:



SAFETY INFORMATION ACKNOWLEDGEMENT INFORMED CONSENT

This copy is to be signed by student and returned to lecturer/PPS

I acknowledge receipt and that I have read and understand the lab safety regulations stated in the Chemical Laboratory Safety Agreement and in UM or Chemistry Department Safety Handbook, 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 I am pregnant, or suspect to be pregnant, 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, 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.

Name : Course :

Matric Number : Sem / Session :

IC Number : Lecturer :

Signature : 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).

Emergency contact 1

Name: Relationship: Contact number:

Emergency contact 2

Name: Relationship: Contact number:

SCIENTIFIC WRITING

Log Book

A scientist keeps all information on his/her experiment neatly and orderly. Thus, as part of your training to become a good scientist, you **MUST** have a log book or sometimes it is called a jotter book. Everything you do and measure in the day must be reported in the jotter book. **DO NOT** use loose papers to record your results. You may lose them. Moreover this log book or jotter book must be numbered and dated accordingly. It is also useful to have a carbonized jotter book which allows you to hand a carbonized copy of the result to the lab supervisor which in this case, the lecturer-in-charge. The log book should be readable to you after many years and certainly readable to other people.

Formal Report

Apart from keeping the laboratory log book, you are required to write a short formal report on every experiment assigned to you. Some lecturers may wish to assign you to write an extended report for one of these experiments. You can also use an Electronic Lab Notebook (ELN). Please discuss with your lecture-in-charge for the detailed format.

Two types of report styles which we recommend are: a short scientific report and an extended scientific report.

- 1) A Short Formal Report will have the following format:
 - i. Title Page
 - ii. Results and Discussion (separate section is highly recommended)
 - iii. Conclusion
 - iv. References

- 2) An Extended Formal Report will have the following format
 - i. Title Page
 - ii. Background and Theory
 - iii. Procedure
 - iv. Results and Discussion (separate section is highly recommended)
 - v. Conclusion
 - vi. Future Work (optional)
 - vii. Appendices (optional)
 - viii. References

Title Page

It contains the title of the experiment, when the experiment was conducted (date), your name and your partner's name (if any), your group and lecturer's name.

Background and Theory

In the short formal report, it is unimportant to write the "Background and Theory" unless you are using a different theory than that suggested in the experimental manual. You may simply refer to the manual or obtain from references.

Procedure

Likewise, in the short formal report, it is unimportant to write the "Procedure" since this is already clearly stated in the manual. If however, a different procedure is adopted for some reason (and this may happen), you must report this clearly.

Results and Discussion

All raw and processed results must be recorded neatly and clearly. Repeated values may be tabulated with clear headers. If there is more than one table, please give a clear and legible title to each one of them.

Discussion section aims to analyze the results you obtain. This is done by describing them, explaining the results with respect to the theoretical expectation either by proving the theory or otherwise. When results are in agreement with the theory, (you may feel happy) the discussion may be written in support of the theory which may now be used to predict other possible conditions. However, if result differ from the expected, the discussion may be more interesting. Here is the case when the theory may be weak or wrong or the experimental result is wrong. Discussion may be centered in scrutiny of the theory and all its assumptions or on the other hand, on possible sources of errors in the experimental procedure.

Conclusion

This summarizes the experimental findings and relates them to the objectives of the experiment.

References

These days, no scientist works in isolation. Thus, as a good scientific practice, the reference section must be included to make students aware that the experiment they conducted is related to many other previous works which have been reported in the literature.

Plagiarism Warning!

Some of these experiments are carried out in groups of usually a pair of students. Therefore expectedly, each member of a group followed an identical procedure in the laboratory and has the same set of raw data. Members of a group are allowed to discuss the analysis of data with one another. However, preparation of the report including data analysis, interpretation and discussion must be prepared by the individual student submitting the report.

The Department does not tolerate plagiarized reports!

GUIDELINES AND MARKING SCHEME FOR PRACTICAL REPORT

Section A: Attendance (Total 5%)

1. Attendance (5%)

Score	Criteria
0	Student did not attend without any valid reasons.
5	Student is present.

Notes:

1. The student **MUST** attend the laboratory session to be eligible for obtaining marks. **NO** marks will be given at all if the student did not attend any laboratory sessions without valid reasons.

2. If the student did not attend any of the laboratory session, there **MUST** be an official explanation (i.e., Sick: MC from doctor; representing UM in activities: Official Letter from the Department/Faculty/University, etc.; Family reasons: Death of family member, etc.).

Section B: Lab Performance – Skills and Technique (Total 20%)

Score	Criteria
0-5	No skill is demonstrated; requires constant reminder about experimental procedures (can lead to poor experimental results); haphazard work area.
6-10	Candidate lacked procedural knowledge (e.g. selection of inappropriate glassware/equipment/software, improper handling of glassware or chemicals); requires some reminder about experimental procedures; messy work area.
11-15	Candidate showed appropriate procedural knowledge (e.g. correct selection of glassware, equipment or software) but made a few mistakes (e.g. wrong meniscus reading); work area cleanliness and safety could still be improved.
16-20	Candidate showed appropriate procedural knowledge with minimal mistakes (high probability to obtain excellent experimental results); work area neat, tidy and safe

Section C: Lab Jotter/Notebook (Total 25%)

1. Pre-entering lab (5%)

Score	Criteria
0	No preparation of experimental procedure.
1-3	Summary of procedures too brief, lack of details and confusing.
4-5	Presents easy to follow steps in lab experimental, logical and adequately detailed.

2. Laboratory Notebook/Jotter (20%)

Score	Criteria
0	No jotter.

1-5	Little effort to record observations/information/data.
6-10	Poor ability to record findings parallel to the lab action/observation; some important features are unavailable.
11-15	Able to record findings parallel to the lab action/observation but could still be improved; all important features are available, but some observations, information and raw data are incomplete.
16-20	Candidate is competent to record findings parallel to the lab action/observation; all important features are available (Date of experiment, complete information, observations and raw data).

Section D: Lab Report (Total 40%)

(I) Short Report

Section	Score	Criteria
Title (5 marks)	0	No title.
	1	Too brief (e.g. "Lab Report", "Mercury in Fish", "Synthesis of Cinnamic Acid" or "Boiling Point of Water").
	2-3	Too long or does not identify the complete subject of study (e.g. "Determination of iron", "Determination of lead", etc.).
	4-5	Identify the complete subject of study and encapsulates the purpose of the report/study (e.g. "Kinetics of the hydrolysis of <i>t</i> -butyl chloride at 30 °C", "Synthesis of triphenylcarbinol via Grignard reaction" or "Determination of iron in red meat via spectrophotometry").
Objectives (5 marks)	0	Section missing completely.
	1-3	Too vague, ambitious or broad in scope; contradict with methods; does not identify subject of study.
	4-5	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.
Results (Data, figures, graphs, tables, observations, % yield, etc.) (30 marks)	0	Section missing completely.
	1-7	No flow of results. Figures, graphs, tables contain errors or are poorly constructed, have missing titles, captions or numbers, units missing or incorrect, numerical data did not have correct significant figures, no error analysis, etc.
	8-15	Most figures, graphs, tables OK, some still missing some important or required features.
	16-23	All figures, graphs, tables are correctly drawn, but some have minor problems (e.g. incorrect significant figures, incomplete observation) or could still be improved.
	24-30	All figures, graphs, tables are correctly drawn, are numbered and contain titles/captions. Observations clearly stated. Numerical data contains correct significant figures and units.
Discussion	0	Section missing completely.

(30 marks)	1-7	Lack of attempt to relate experimental findings and data with contemporary theories. Very incomplete or incorrect interpretation of trends and comparison of data indicating a lack of understanding of results.
	8-15	Some attempt to relate experimental findings and data but using inaccurate theories. Some of the results have been correctly interpreted and discussed; partial but incomplete understanding of results is still evident.
	16-23	Almost all of the results have been correctly interpreted and discussed, only minor improvements are needed.
	24-30	All of the important trends and data comparisons have been interpreted correctly and discussed; good relationship between experimental data and theory; good understanding of results is conveyed.
Safety Precautions (5 marks)	0	Section missing completely.
	1	Sentences are incomplete, focusing on minor points or lack important steps.
	2-3	State only 1-2 major and most important safety precautions.
	4-5	State at least 3 major and most important safety precautions.
Conclusions (10 marks)	0	Section missing completely.
	1-3	Conclusion missing the important points or is not supported by the experimental results.
	4-6	Conclusions regarding major points are drawn, but many are misstated, indicating a lack of understanding.
	7-8	All important conclusions have been drawn, could be better stated.
	9-10	All important conclusions have been clearly made, student shows good understanding.
References (5 marks)	0	Section missing completely.
	1-3	Incomplete references to the books or any other sources used in report.
	4-5	Correct in-text citations and the references in the reference list conform to all respects of 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).
Appearance and Formatting (10 marks)	1-3	Sections out of order, too much handwritten copy, sloppy formatting.
	4-6	Sections in order, contains the minimum allowable amount of handwritten copy, formatting is rough but readable.
	7-8	All sections in order, formatting generally good but could still be improved.
	9-10	All sections in order, well-formatted, very readable.

Total section D marks = $(x/100) \times 40\%$

** Late Report Submission: -1 mark / day

(II) Full Report

Section	Score	Criteria
Title (5 marks)	0	No title.
	1	Too brief (e.g. "Lab Report", "Mercury in Fish", "Synthesis of Cinnamic Acid" or "Boiling Point of Water").
	2-3	Too long or does not identify the complete subject of study (e.g. "Determination of iron", "Determination of lead", etc.).
	4-5	Identify the complete subject of study and encapsulates the purpose of the report/study (e.g. "Kinetics of the hydrolysis of <i>t</i> -butyl chloride at 30 °C", "Synthesis of triphenylcarbinol via Grignard reaction" or "Determination of iron in red meat via spectrophotometry").
Introduction (10 marks)	0	Section missing completely.
	1-3	Very little background information provided, or information is incorrect.
	4-5	Some introductory information, but still missing some major points.
	6-8	Introduction is nearly complete, missing some minor points.
	9-10	Introduction complete and well-written; provides all necessary background principles for the experiment with evidence of extra reading.
Objectives (5 marks)	0	Section missing completely.
	1-3	Too vague, ambitious or broad in scope; contradict with methods; does not identify subject of study.
	4-5	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.
Experimental Procedure (10 marks)	0	Section missing completely.
	1-3	No sub-sections, missing several important experimental details or not written in paragraph format. Parts have been included under the wrong sub-section.
	4-5	Written in paragraph format, still missing some important experimental details.
	6-8	Written in paragraph format, important experimental details are covered, some minor details missing.
	9-10	Well-written in paragraph format, all experimental details are covered.
Results (Data, figures, graphs, tables, observations, % yield, etc.) (20 marks)	0	Section missing completely.
	1-5	No flow of results. Figures, graphs, tables contain errors or are poorly constructed, have missing titles, captions or numbers, units missing or incorrect, numerical data did not have correct significant figures, no error analysis, etc.
	6-10	Most figures, graphs, tables OK, some still missing some important or required features.

	11-15	All figures, graphs, tables are correctly drawn, but some have minor problems (e.g. incorrect significant figures, incomplete observation) or could still be improved.
	16-20	All figures, graphs, tables are correctly drawn, are numbered and contain titles/captions. Observations clearly stated. Numerical data contains correct significant figures and units.
Discussion (20 marks)	0	Section missing completely.
	1-5	Lack of attempt to relate experimental findings and data with contemporary theories. Very incomplete or incorrect interpretation of trends and comparison of data indicating a lack of understanding of results.
	6-10	Some attempt to relate experimental findings and data but using inaccurate theories. Some of the results have been correctly interpreted and discussed; partial but incomplete understanding of results is still evident.
	11-15	Almost all of the results have been correctly interpreted and discussed, only minor improvements are needed.
	16-20	All of the important trends and data comparisons have been interpreted correctly and discussed; good understanding of results is conveyed.
Safety Precautions (5 marks)	0	Section missing completely.
	1	Sentences are incomplete, focusing on minor points or lack important steps.
	2-3	State only 1-2 major and most important safety precautions.
	4-5	State at least 3 major and most important safety precautions.
Conclusions (10 marks)	0	Section missing completely.
	1-3	Conclusion missing the important points or is not supported by the experimental results.
	4-6	Conclusions regarding major points are drawn, but many are misstated, indicating a lack of understanding.
	7-8	All important conclusions have been drawn, could be better stated.
	9-10	All important conclusions have been clearly made, student shows good understanding.
References (5 marks)	0	Section missing completely.
	1-3	Incomplete references to the books or any other sources used in report.
	4-5	Correct in-text citations and the references in the reference list conform to all respects of 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).
Appearance and Formatting (10 marks)	1-3	Sections out of order, too much handwritten copy, sloppy formatting.
	4-6	Sections in order, contains the minimum allowable amount of handwritten copy, formatting is rough but readable.

	7-8	All sections in order, formatting generally good but could still be improved.
	9-10	All sections in order, well-formatted, very readable.

Total section D marks = $(x/100) \times 40\%$

** Late Report Submission: -1 mark / day

Section E: Assessment of Understanding/Revision on Conducted Experiments (10%)

Score	Criteria
x	Test/Quiz/Lab Presentation, etc.

* For Section E: Assessment - it is up to the lecturer-in-charge to decide whether he/she wants to carry out the method of assessment (simple test, presentation, etc).

EXPERIMENT 1

BOMB CALORIMETER

Objectives:

1. Calibration of the bomb calorimeter with benzoic acid to obtain the heat capacity of the calorimeter, C_{cal} .
2. To determine the heat of combustion, ΔH_c , for anthracene.
3. To calculate the standard formation enthalpy of anthracene, ΔH_f .

1 Theory

Enthalpies of combustion can be measured by burning a known amount of material in a bomb calorimeter and determining the temperature change. The bomb is pressurised with oxygen to ensure complete combustion. Then the bomb is immersed in bucket filled with fixed amount of water. Heat loss to the surroundings can be prevented by use of a jacket around the calorimeter; the reaction is then adiabatic. The jacket lid is fitted with a calorimeter thermometer and stirrer both of which extend into the water. The sample is ignited by passing a current through a fuse wire within the bomb. As the experiment is to determine the temperature increase of a system under adiabatic conditions, the change of temperature can be adjusted to that of the water surrounding the bomb. **Figure 1** shows the bomb calorimeter.

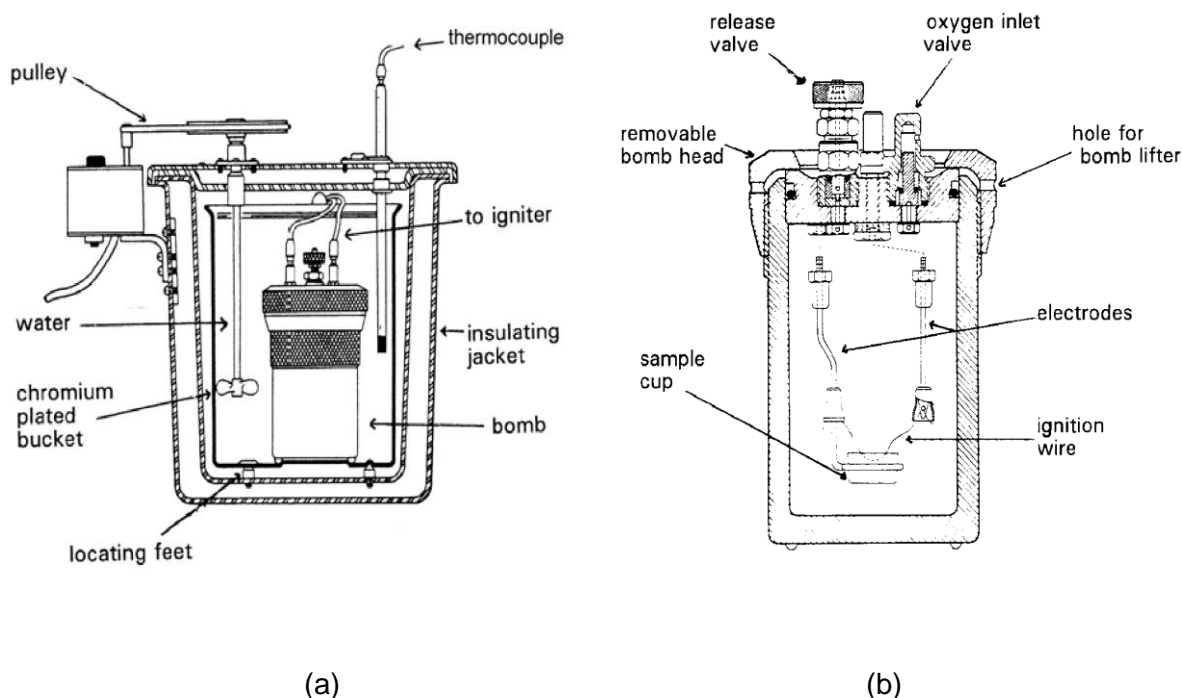


Figure 1. (a) Assembled bomb calorimeter, (b) Parr oxygen bomb.

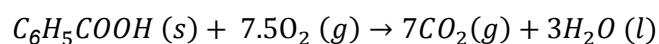
Determination of heat capacity of the calorimeter system is made by igniting a known quantity of a substance of known heat of combustion as a standard. Heat capacity is the amount of

calories necessary to raise the temperature of the entire calorimeter system by one degree Celsius. Benzoic acid of high purity is usually employed. Bomb calorimetry was once widely used in chemistry, since it provides thermodynamic data in a very direct way; it is still used in the fuel and food industries.

In the determination of the heat of combustion with the bomb calorimeter, it must be remembered that the measurement is made at constant volume and not at constant pressure. Therefore, the heat of combustion calculated is ΔU rather than ΔH . In order to convert to ΔH , the heat of combustion at constant pressure, the following expression is used:

$$\Delta H = \Delta U + \Delta nRT$$

in which Δn is the difference between the number of moles of gaseous products formed at 25 °C (at which temperature the standard state of water is the liquid) and the number of moles of gaseous reactants. For the combustion of benzoic acid the chemical equation is



and Δn is equal to -0.5. Hence for the combustion of one mole of benzoic acid at 25 °C

$$\Delta H = \Delta U - (0.5 \times 8.31 \times 298J) = \Delta U - 2480J$$

2 Materials

Apparatus: Parr calorimeter system, fuse wire, oxygen cylinder, conical flask, burette, pipette, thermometer, stopwatch.

Chemicals: benzoic acid, anthracene.

3 Experimental Procedure

3.1 Calibration of the bomb calorimeter with benzoic acid

Use a pellet of benzoic acid weighing between 0.9 to 1.1 g. Determine the corrected temperature rise, also titrate the bomb washings to determine the nitric acid correction and measure the length of unburned fuse wire.

3.2 Heat of combustion for anthracene

Procedure for the anthracene test is exactly the same as for testing of benzoic acid. Use a pellet of anthracene weighing between 0.9 to 1.1 g. Determine the corrected temperature rise, also titrate the bomb washings to determine the nitric acid correction and measure the length of unburned fuse wire.

Pellet Formation

Care must be taken to avoid overcharging the bomb. It must be realized that the peak pressure developed during combustion is proportional to the size of the sample and to the initial oxygen pressure. Pellet size should be limited to **not more than 1.1 grams**. Weigh out approximately 1.0 g of sample. Use the pellet press to make a pellet. **Weigh the pellet** and carefully place it in the stainless steel combustion cup.

Ignition Wire

Measure out approximately 10 cm of fuse wire. It will be necessary to measure the length of unburned wire after combustion since this is an important factor in the calculations. Set the bomb head in the support stand and attach the length of fuse wire as illustrated in **Figure 2**. Insert the wire through each eyelet then slide each cap downward to complete the connection. Place the sample cup (with sample sitting in the centre of the cup) in the cup holder and bend the wire in a 'v' shape. The wire must be bent down as far as possible so that it **touches the surface of the pellet** and stays there.

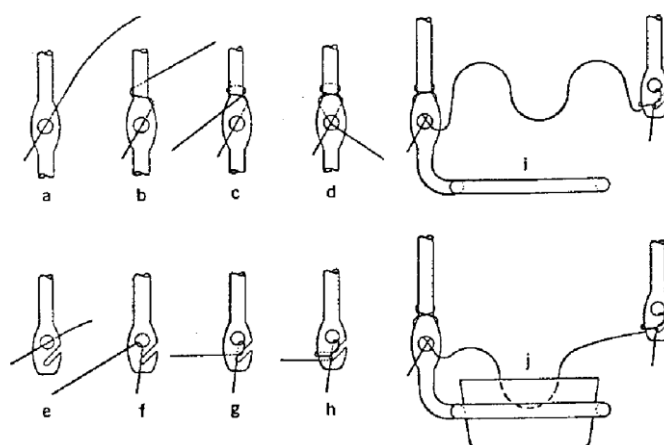


Figure 2. The proper threading of the electrodes and sample placement.

Liquids in the Bomb

Pipette 1.0 ml of distilled water into the bomb to absorb the oxides of nitrogen formed from nitrogen present in the oxygen mixture.

Closing the Bomb

Care must be taken not to disturb the sample when sealing and charging the bomb. Slide the head assembly into the bomb cylinder, screw open the vent cap on the head assembly to allow air to be expelled, and push the head down as far into the cylinder as it will go. Close the vent cap tightly. A tight seal is needed to prevent pressurised oxygen from leaking.

Installing the Oxygen Connection

Mount the bomb in the bench clamp. Slip on the oxygen tank connection hose to the pin on the head assembly.

Filling the Bomb with oxygen

Open the oxygen tank valve. Open the regulator valve **SLOWLY** for gradual flow of oxygen. Watch the gauge as the bomb pressure rises to the desired filling pressure (25-30 atm.). Once the desired pressure is reached, close the control valve followed by the tank valve. If oxygen is introduced too rapidly, the sample could be blown away from its initial position inside the

bomb. Use the quick-release valve to QUICKLY remove oxygen tank connection to minimise oxygen escape. Slight leakage is normal but continual leakage is a problem.

Precautions:

1. If there is a continual escape of gas from the bomb head connections once the oxygen tank valve is unscrewed the bomb is defective and should not be used.
2. If the bomb does not hold pressure and you can hear oxygen escaping around the vent cap, then the cap is not sealed tightly enough. Tighten the screw cap by hand again and try to pressurise the bomb.
3. Should you accidentally introduced too much of oxygen into the bomb, do not proceed with the combustion. Unscrew the oxygen tank connection and exhaust the bomb in the hood. This can be done by opening the vent cap. Reweigh the sample before repeating the filling procedure.

Operating the Calorimeter

Place the chromium plated elliptical bucket into the fiberglass jacket such that the three indentations in the bucket register with the locating feet in the jacket. Fit the wire bomb lifter into the holes in the knurled bomb screw cap, loosen the bench clamp, then raise the bomb by a finger inserted through the hole in the lifter. Do not hold the outside of the lifter, this would cause it to open thus releasing the bomb. Place the bomb onto the indentation in the bottom of the bucket then remove the lifter. Connect the ignition wire to the terminal socket on the bomb head.

Fill to the mark a 2000 mL volumetric flask with water. Transfer this quantitatively to the bucket. Lift the jacket lid from the large stand onto the jacket. Turn the stirrer by hand to be sure that it runs freely, then slip the drive belt onto the pulley. Start the stirrer and wait 5 or 10 minutes to allow the apparatus to thermally stabilise, then start a timer and take temperature readings every 20 seconds. Although the thermometer is calibrated in 0.02 °C divisions, you should be able to estimate temperatures to about ± 0.003 °C with the help of the thermometer magnifier. Record the temperature until it has changed at a uniform rate (probably about 0.01 – 0.02 °C in every 100 seconds) for 5 or 6 readings.

The Parr instruction manual gives the following warning:

"CAUTION: DO NOT HAVE THE HEAD, HANDS OR ANY PART OF THE BODY DIRECTLY OVER THE BOMB DURING THE FIRING PERIOD, AND DO NOT GO NEAR THE BOMB FOR AT LEAST 20 SECONDS AFTER FIRING."

Plug in the power supply then, noting the time, stand back and push the firing button for 5 seconds. The red light should normally flash on for about $\frac{1}{4}$ second. At approximately 20 seconds after ignition the temperature will begin to rise. The rate of rise will be large at first and then decrease as the bomb, water and bucket approach a new equilibrium temperature. The nature of temperature rise is indicated by the typical temperature rise curve shown in **Figure 3**. It is not necessary to plot a similar curve for each test, but accurate time and temperature observations must be recorded to identify the critical points needed to calculate the caloric value of the sample or the energy equivalent for the calorimeter.

The time required to reach the 60 % point can be found by linear interpolation from readings taken during the rise period. This requires temperature observations at **45, 60, 75, 90, and 105 seconds after firing.**

After rapid rise period (about 4 or 5 minutes after ignition), record temperature at one-minute intervals until the differences between successive readings has been constant for five minutes. After the last temperature observation has been made, stop the motor, remove the belt and lift the cover and the stirrer from the calorimeter. Lift the bomb out of the bucket; remove the remove the ignition leads and wipe the bomb with a clean towel. Use the lifter to put the bomb into the bench clamp. Carefully unscrew the release valve to release the residual gas pressure before attempting to remove the cap. After all pressure has been released, unscrew the cap, lift the head out of the cylinder and place it on the support stand. Check the interior of the bomb for soot or other evidence of incomplete combustion. If such evidence is found, the test will have to be discarded. Wash all the interior surfaces of the bomb with a jet of distilled water and collect the washings in conical flask. Titrate the bomb washing with a standard sodium carbonate solution using methyl orange or methyl red indicator. A 0.0725 N sodium carbonate solution is recommended for this titration to simplify the calculation. Remove all unburned pieces of fuse wire from the bomb electrodes, straighten and measure the length of the remaining ends of the fuse wire.

Dry the inside of the bomb then **repeat** the above procedure with the other sample.

NITROGEN CORRECTION

When the material is burnt, some the nitrogen in it (and the air) is oxidised and combined with water vapour to form HNO_3 . This reaction result in acid formation within the bomb, and require a correction to account for the heat liberated in the formation. You can rinse this acid out of the bomb and titrate with Na_2CO_3 to get the actual amount of HNO_3 produced.

Fuse Wire Correction

The wire used as a fuse for igniting the sample is partly consumed in the combustion. Thus the fuse generates heat both by the resistance it offers to the electrical current and by the heat of combustion of that portion of the wire which is burned. It can be assumed that the heat input from the electric firing current will be the same when standardising the calorimeter as when testing an unknown sample, and this small amount of energy therefore can be neglected. However, the amount of wire consumed will vary from test to test and therefore a correction must be made to account for the heat of combustion of the metal.

The amount of wire taking part in the combustion is determined by subtracting the length of the recovered unburned portion from the original length of 10 cm. The correction is then computed for the burned portion by assuming a heat of combustion of 2.3 calories per cm for Parr 45A10 (No. 34 B & S gage "Chrome C") wire.

4 Calculations

For reach run, plot the corrected temperature vs. time. Determine an approximate temperature change and the time at which the temperature was at 60% of the net change. The following data should be collected for each run:

a = time of firing

b = time (to nearest 0.1 min.) when the temperature reaches 60% of the total rise (maximum T - minimum T) = ΔT ; $0.6 \times \Delta T = \Delta T$ at 60% of total rise. The time at this temperature can be determined from the plot.

T_a = temperature at beginning of period (after initial temp. rise and before firing) in which the rate of temperature change became constant.

T_c = temperature at time c

r_1 = rate $\left(\frac{\text{temp}}{\text{min}}\right)$ at which temperature was rising during the 5 minutes period before firing

r_2 = rate $\left(\frac{\text{temp}}{\text{min}}\right)$ at which the temperature was rising during the 5 minutes period after time c . If the temperature was falling instead of rising after time c , r_2 is negative and the quantity $-r_2(c - b)$ becomes positive and must be added when computing the corrected temperature rise.

e_1 = correction (in calories) for heat of formation of nitric acid (HNO_3)
= millilitres (mL) of standard alkali solution used in the acid titration

e_3 = correction (in calories) for the heat of combustion of fuse wires
= centimetres (cm) of fuse wire consumed in firing $\times 2.3$
(when using Parr 45C10 nickel chromium fuse wire) OR
= centimetres (cm) of fuse wire consumed in firing $\times 2.7$
(when using No. 34B. & S. gage iron fuse wire)

The net corrected temperature rise

$$\Delta T = T_c - T_a - r_1(b - a) - r_2(c - b)$$

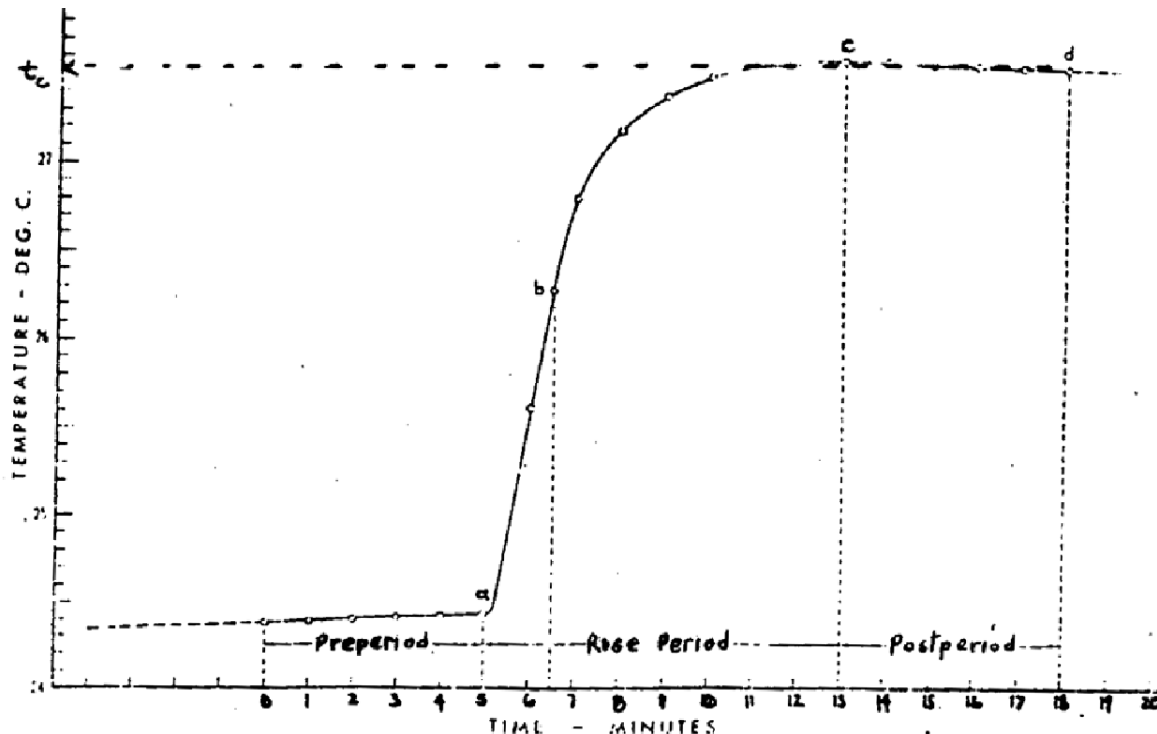


Figure 3. Typical temperature rise curve

1. Calibration of the calorimeter with benzoic acid

ENERGY EQUIVALENT FACTOR (W) OF THE CALORIMETER:

The energy equivalent, W , of the calorimeter is the energy required to raise the temperature one degree Celsius, expressed as calories per degree Celsius. The data obtained from the trials with benzoic acid will be used for the determination.

$$W = \frac{Hm + e_1 + e_3}{\Delta T}$$

W = energy equivalent (heat capacity) of the calorimeter in $\frac{\text{calories}}{^\circ\text{C}}$

H = heat of combustion of the standard benzoic acid sample in calories per gram

m = mass of the standard benzoic acid pellet in grams.

ΔT = net corrected temperature rise in $^\circ\text{C}$

e_1 = correction for heat of formation of nitric acid in calories

e_3 = correction for heat of combustion of the firing wire in calories

Example:

Standardisation with a 1.1651 g benzoic acid sample (6318 cal/g) produces a net corrected temperature rise of 3.077 $^\circ\text{C}$. The acid titration required 11.9 ml of standard alkali and 8 cm of fuse wire were consumed in the firing. Substituting in the standardisation equation:

$$W = \frac{(6318)(1.1651) + 11.9 + 18.4}{3.077} = 2402.1 \text{ cal}/^\circ\text{C}$$

where:

$$H = 6318 \text{ cal/g}$$

$$m = 1.1651 \text{ g}$$

$$e_1 = (11.9 \text{ ml})(1 \text{ cal/ml}) = 11.9 \text{ cal}$$

$$e_3 = (8 \text{ cm})(2.3 \text{ cal/cm}) = 18.4 \text{ cal}$$

$$\Delta T = 3.077 \text{ }^\circ\text{C}$$

2. Gross heat of combustion for anthracene, H_g

$$H_g = \frac{\Delta TW - e_1 - e_3}{m}$$

Molar Heat of Combustion of anthracene at Constant Pressure ΔH :

By definition, a change in enthalpy ΔH is related to the corresponding change in internal energy ΔU by the equation:

$$\Delta H = \Delta U + \Delta(PV)$$

When heat is given off in the combustion, the convention is negative. Also assuming that the gaseous products obey the perfect gas law and that the $\Delta(PV)$ terms of solids and liquids are negligible:

$$\Delta(PV) = \Delta n_{gas}RT$$

Where Δn_{gas} is the increase (or decrease) in the number of moles of gas during combustion. Thus we obtain our working definition:

$$\Delta H = \Delta U + \Delta n(RT)$$

ΔU = gross heat of combustion

R = ideal gas constant

T = temperature of the products if they were returned to the initial temperature of the experiment at the time of firing.

5 Experiment

- (a) Determine the water equivalent of the bomb calorimeter with benzoic acid.
- (b) Determine the heats of combustion of anthracene. Repeat the experiment if necessary. Hence calculate the standard enthalpy of formation and compare with the literature values.

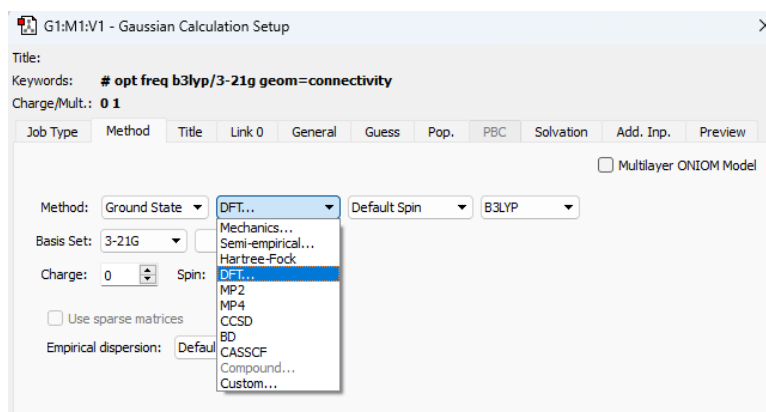
6 Quantum Chemical Calculation for Standard Enthalpy of Combustion of Anthracene

Objective

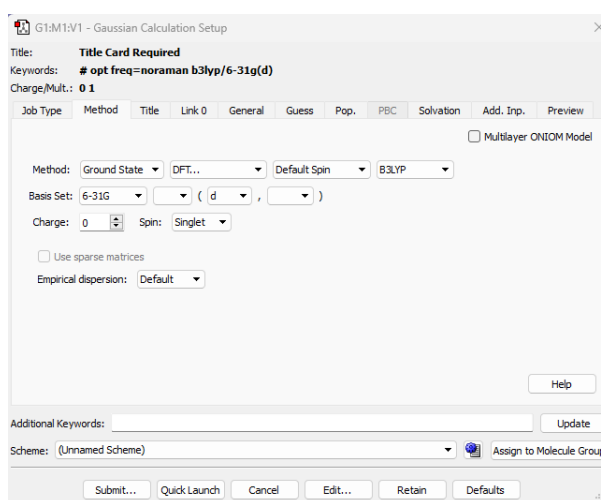
To calculate the standard enthalpy of combustion of anthracene using quantum chemical methods and compare it with experimental values.

Computational Methodology

1. **Software and Computational Resources:**
 - Use Gaussian software to calculate the electronic energy by approximating the Schrodinger Equation.
2. **Molecular Geometry Optimization:**
 - **Calculation Setup:**
 - Use GaussView to prepare the molecular geometry draft of anthracene, O₂, CO₂ and H₂O.
 - Submit each draft geometry separately to Gaussian in Window for calculation as shown below instruction
 1. Select **Calculate**
 2. Select **Gaussian Calculation Setup**
 3. Select **Opt+Freq** in Job Type
 4. Select **DFT** in Method section and choose **B3LYP**



5. Select **6-31G(d)** in Basis Set



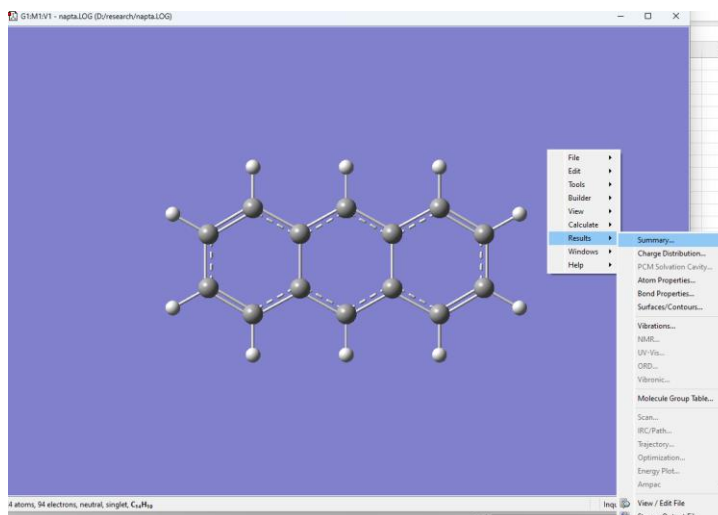
6. Select **Submit**

7. Save the input file in your directory and the calculation will begin.

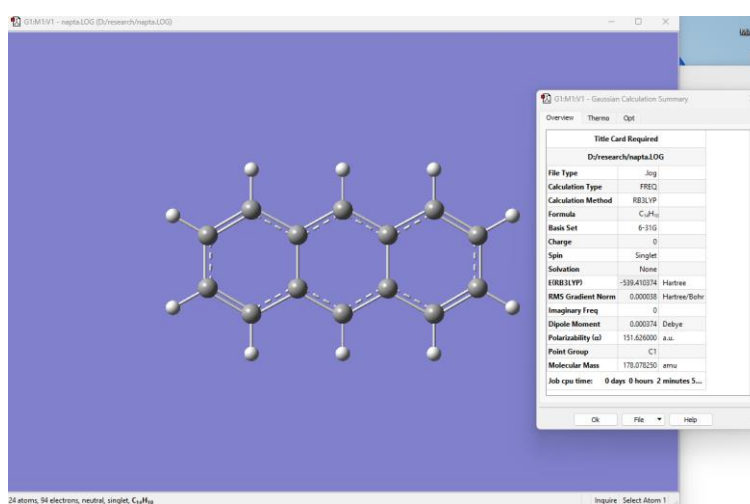
○ **Optimisation and Data Compilation:**

- Perform geometry optimization at B3LYP level using the 6-31G(d) basis set.
- Geometry optimisation performed to relax the geometry at minima on potential energy surface.
- Only minima structure can be used for calculating the enthalpy of reaction such as combustion.
- Once computation done (Normal Termination in Gaussian Calculation), there are FOUR Gaussian calculation output log files.
- Open each of the log file and extra the electronic energies as shown below.

1. Select **Results** -> **Summary**



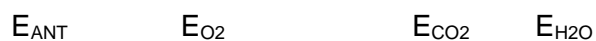
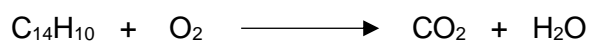
2. Copy and Paste the electronic energy into Excel



3. Repeat for the other log files.

3. Calculation of Standard Enthalpy of Combustion:

- Use the following thermodynamic equation to calculate the standard enthalpy of combustion based on the electronic energies obtained.



Chemical System	Electronic Energies / Hartree
E _{ANT}	-539.53049
E _{O₂}	-150.32004
E _{CO₂}	-188.58094
E _{H₂O}	-76.408954

- $\Delta H_{\text{combustion}} = (E_{\text{CO}_2} \times 14 + E_{\text{H}_2\text{O}} \times 5) - (E_{\text{ANT}} + E_{\text{O}_2} \times 16.5)$

- $\Delta H_{\text{combustion}} = (-188.58094 \times 14 + -76.408954 \times 5) - (-539.53049 + -150.32004 \times 16.5)$
 $= -2.36678 \text{ hartree} \times 2600 \text{ (conversion factor to kJ mol}^{-1}\text{)}$
 $= -6214 \text{ kJ mol}^{-1}$

4. **Comparison with Experimental Values:**

- Compare the calculated standard enthalpy of combustion with the experimental value obtained from bomb calorimetry and literature review.

7 **References**

1. Finlay, Practical Physical Chemistry, 8th Ed.
2. "Mahler-Cook" Bomb Calorimeter manual
3. Shoemaker and Garland, Experiments in Physical Chemistry, 2nd Edition, McGraw-Hill, 1962.

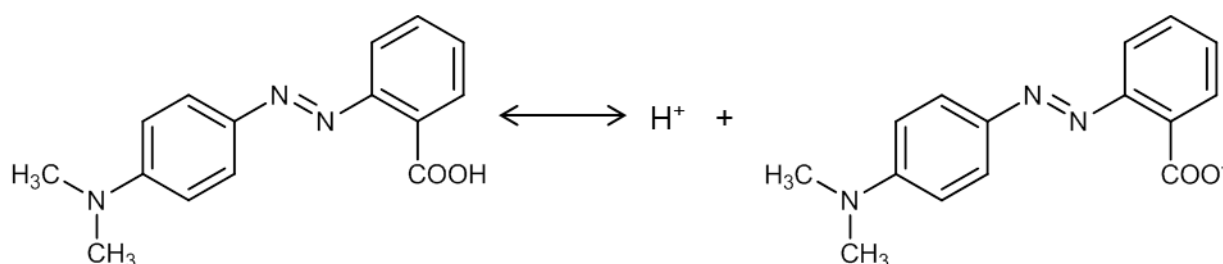
EXPERIMENT 2

DETERMINATION OF ACID DISSOCIATION CONSTANT FOR METHYL RED

Objective: Determine the acid dissociation constant for methyl red (a type of dye) using visible spectrophotometry.

1 Theory

The constant K , for this equilibrium:



Methyl red (acidic form), HMR

Methyl red (basic form), MR^-

Is given as $K = \frac{[H^+][MR^-]}{[HMR]}$

Methyl red is a type of dye: *o*-(*p*-dimethylaminophenylazo)benzoic acid ($C_{15}H_{15}N_3O_2$, Molecular weight 269.31).

Methyl red is a weak acid in which its colour in aqueous solution depends on the pH. The H^+ (or H_3O^+) in solution determines the ratio of MR^- to HMR as the following equation:

$$\frac{[MR^-]}{[HMR]} = \frac{K_a}{[H_3O^+]}$$

At $pH \leq 4.2$ the solution is red and $pH \geq 6.2$ the solution is yellow. The human eye is sensitive towards colour changes when the ratio of the two colours is between 0.1 and 10. For methyl red in solution:

$$\frac{[MR^-]}{[HMR]} = 0.1 \quad \text{red solution}$$

$$\frac{[MR^-]}{[HMR]} = 10 \quad \text{yellow solution}$$

The ratios are equal to $10K_a$ and $0.1K_a$ respectively. If we write HMR and MR^- respectively as A and B, so

$$K = \frac{[H^+][B]}{[A]} \quad (1)$$

For any material which absorbs light, according to Beer-Lambert law, absorption A_{obs} is given as

$$A_{obs} = \epsilon Lc$$

where c is concentration, L is path length and ϵ is coefficient of absorption which depends on the type of material which absorbs and to the wavelength of absorption.

For system which is being investigated in this experiment, at one particular wavelength, the absorbing coefficient A_{obs} is given as

$$A_{obs} = \epsilon_A[A]L + \epsilon_B[B]L \quad (2)$$

Equation (2) can be written as

$$A_{obs} = \epsilon_a([A] + [B])L \quad (3)$$

where ϵ_a is the effective absorption coefficient.

From equation (2) and (3), we get,

$$\frac{[A]}{[B]} = \frac{[\epsilon_B - \epsilon_a]}{[\epsilon_a - \epsilon_A]}$$

Insert this equation into (1) will obtain

$$\frac{[H^+]}{K} = \frac{[\epsilon_B - \epsilon_a]}{[\epsilon_a - \epsilon_A]} = \frac{[(\epsilon_B - \epsilon_A) - (\epsilon_a - \epsilon_A)]}{(\epsilon_a - \epsilon_A)}$$

Or

$$\frac{1}{(\epsilon_a - \epsilon_A)} = \frac{[H^+]}{K} \left(\frac{1}{\epsilon_B - \epsilon_A} \right) + \left(\frac{1}{\epsilon_B - \epsilon_A} \right) \quad (4)$$

If the initial concentration of methyl red (c_i) is constant for all solutions, so $[A] + [B] = c_i$ and equation (3) can be written as

$$A_{obs} = \epsilon_a c_i L \quad (5)$$

For solutions which has methyl red in acidic form, the absorption, A_{obs}^A will be given as

$$A_{obs}^A = \epsilon_A c_i L \quad (6)$$

Combining equation (5) and (6) will produce

$$\frac{1}{(\epsilon_a - \epsilon_A)} = \frac{c_i L}{(A_{obs} - A_{obs}^A)}$$

And by combining the above equation with equation (4) will have

$$\frac{c_i L}{A_{obs} - A_{obs}^A} = \left(\frac{[H^+]}{K} \right) \left[\frac{1}{(\varepsilon_B - \varepsilon_A)} \right] + \left[\frac{1}{(\varepsilon_B - \varepsilon_A)} \right] \quad (7)$$

since c_i and L for all solutions are constant, the plot of $\frac{1}{A_{obs} - A_{obs}^A}$ versus $[H^+]$ will give a straight line where,

$$K = \frac{\text{Intercept}}{\text{Slope}}$$

For methyl red which exists in basic solution, the absorption will be given as

$$A_{obs}^B = \varepsilon_B c_i L \quad (8)$$

With the same procedures, we will obtain the following expression

$$\frac{c_i L}{A_{obs} - A_{obs}^B} = \left(\frac{K}{[H^+]} \right) \left[\frac{1}{(\varepsilon_A - \varepsilon_B)} \right] + \left[\frac{1}{(\varepsilon_A - \varepsilon_B)} \right] \quad (9)$$

And the plot of $\frac{1}{A_{obs} - A_{obs}^B}$ versus $\frac{1}{[H^+]}$ will give a straight line where K can be determined by

$$K = \frac{\text{Slope}}{\text{Intercept}}$$

2 Materials

Apparatus: UV-Vis spectrophotometer, pH meter, cuvettes, volumetric flask, pipette, thermometer.

Chemicals: methyl red standard solution, hydrochloric acid (concentration 0.1 mol dm^{-3}), sodium acetate solution (concentration 0.04 mol dm^{-3}) and acetic acid (concentration 0.1 mol dm^{-3}).

3 Experimental Procedure

PART A

100 mL methyl red standard solution is prepared by adding 40 mL stock solution to 30 mL alcohol and diluted with distilled water.

Two solutions will have to be prepared in order to choose a suitable wavelength to measure the absorption of several methyl red solutions which will be needed. One solution consists of methyl red in acidic form (which will be named acidic solution), while another solution consists of the basic form (which will be named basic solution). The acidic solution can be prepared by adding 5 mL methyl red standard solution with 10 mL hydrochloric acid (with 0.1 mol dm^{-3}

concentration) and diluting this mixture to 100 mL. The base solution requires the dilution of 5 mL methyl red standard solution and 25 mL sodium acetate solution (concentration 0.04 mol dm³) to become 100 mL.

Record the spectrum from 400 nm to 700 nm for both solutions. You will have to draw a rough plot while performing more measurements to obtain the wavelength region of maximum absorption. With those results, choose the two most suitable wavelengths based on the absorption maximum A_{obs} with the change of pH.

PART B

You will also have to prepare several methyl red solutions which contain 0.01 mol dm³ sodium acetate and acetic acid concentrations varying from 0.001 mol dm⁻³ to 0.05 mol dm⁻³. Make sure that the total methyl red used for each solution are the same as for those prepared for the acidic and basic solution. Determine the pH value and absorption A_{obs} for the two wavelengths which you have selected earlier for each solution. At least two readings must be taken for each determination.

The pH meter must be calibrated with two standard buffer solutions for pH 4 and pH 7.

4 Results and Calculation

1. Plot the spectrum for acidic solution and basic solution. Determine the wavelengths λ_A and λ_B which give maximum absorption for the acidic solution and basic solution (See **Appendix 1** for Gaussian Peak Fitting). Record A_{obs}^A and A_{obs}^B which are seen at λ_A and λ_B .
2. For the methyl red solutions with various concentrations of acetic acid, record all pH and A_{obs} which are determined at λ_A and λ_B .
3. For A_{obs} which was obtained at λ_A calculate $\frac{1}{A_{\text{obs}} - A_{\text{obs}}^A}$ and $[H^+]$ for each solution. Record your readings.
4. For A_{obs} which was obtained at λ_B record $\frac{1}{A_{\text{obs}} - A_{\text{obs}}^B}$ and $\frac{1}{[H^+]}$ in a table.
5. Plot $\frac{1}{A_{\text{obs}} - A_{\text{obs}}^A}$ versus $[H^+]$ and determine the slope and intercept by using the least square method. Determine the K value and its uncertainty.
6. Repeat (5) but plot $\frac{1}{A_{\text{obs}} - A_{\text{obs}}^A}$ versus $\frac{1}{[H^+]}$.

5 Questions

1. Derive equation (9) starting from equation (8).
2. Compare K values obtained from (5) and (6). Which of these values are accurate.
3. Discuss whether the experiment can be performed using wavelengths other than λ_A and λ_B .

6 Reference

R. Chang, Physical Chemistry, 2nd edition, Macmillan, 1981, Chapter 12.

APPENDIX 1: Fit Gaussian Peak on UV/Vis Spectrum of Methyl Red in Acidic and Basic Solutions

Objective: To determine the wavelength of maximum absorbance for methyl red in acidic and basic solutions

Statistical Software & Resource

1. Download the JMP Software
 - Login to the staff or student portal
 - Navigate to **Download Software > Main Software > SAS Academic Suite & SAS JMP**
 - Select the version supported by your operating system
 - Click **Download**
2. Download the JMP License File
 - Login to the staff or student portal
 - Navigate to **Download Software > Main Software > SAS Academic Suite & SAS JMP**
 - Select the license based on the version of your JMP
 - Right-click to download the linked SID file (*.txt) to your desired location
3. Installation instruction:
 - Navigate to the **/JMP/JMP/<version>/<OS>** directory
 - Double-click the JMP installer **setup.exe** file

Fitting Gaussian Peak with JMP

1. Launch JMP:
 - Open JMP after installation
 - Click **Open License** when prompted
 - Navigate to select the downloaded SID file (*.txt) and then click **Open**
 - Enter your name and department, if you wish, and then click **OK**
 - Navigate to a permanent location and click **Save** to save the license file
 - Click **OK** to finish the licence installation and launch JMP
2. Import the Spectrum Data:
 - Select **File > Open**
 - Navigate to the data file (*.csv or *.xlsx) containing your spectrum data

- Click **Open**
 - Save the imported data by selecting **File > Save as**
3. Fit Gaussian Peak:
- Launch the Fit Curve platform
 - Select **Analyze > Specialized Modeling > Fit Curve**
 - Specify Column Roles
 - Assign *Absorbance* to the **Y, Response** role
 - Assign *Wavelength* to the **X, Response** role
 - Click **OK**
 - Specify the Peak Model
 - Click the Fit Curve red triangle and select **Peak Model > Fit Gaussian Peak**
4. Examine Model Fit Report:
- **Prediction Model** - the algebraic form of the prediction formula and the parameters are given by:

$$f(x) = a \cdot \exp\left(-\frac{1}{2} \cdot \left(\frac{x - b}{c}\right)^2\right)$$

where

 - a is the peak height
 - b is the peak position
 - c represents the peak width
 - **Summary Fit** - the fit statistics for the Gaussian peak model
 - **Parameter Estimates** - the estimates of values of the parameters a , b , and c , which define the shape of Gaussian curve

Estimating the Key Characteristics of the Peak

1. Compute the 95% Confidence interval for Lambda-max:
The wavelength of maximum absorbance is given by:

$$\lambda_{max} = b \pm U_b$$

where

U_b is the uncertainty in b , calculated as:

$$\frac{b_{upper\ 95\%} - b_{lower\ 95\%}}{2}$$

2. Compute the Peak Bandwidth:

$$FWHM = 2 \cdot \sqrt{2 \ln 2} \cdot c \pm U_{FWHM}$$

where

U_{FWHM} is the uncertainty in the FWHM, calculated as:

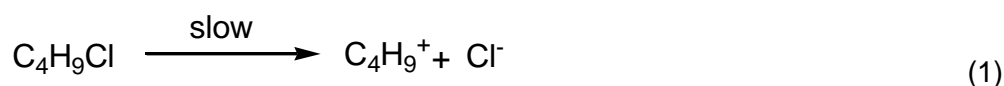
$$2 \cdot \sqrt{2 \ln 2} \cdot \left(\frac{c_{upper\ 95\%} - c_{lower\ 95\%}}{2} \right)$$

EXPERIMENT 3**THE HYDROLYSIS OF *TERT*-BUTYL CHLORIDE, C₄H₉Cl****Objectives:**

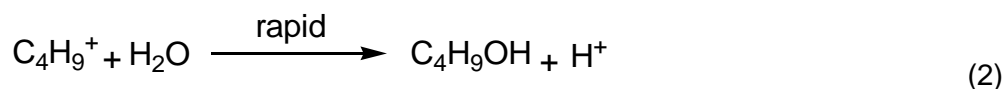
1. To determine the order of reaction and the rate constant, k , for the hydrolysis of *t*-butyl chloride (*t*-BuCl), C₄H₉Cl, at 30 °C, 35 °C and 40 °C.
2. To investigate the effect of concentration to the rate constant at constant temperature.
3. To calculate the activation energy, E_a , for the hydrolysis of *t*-butyl chloride.

1 Theory

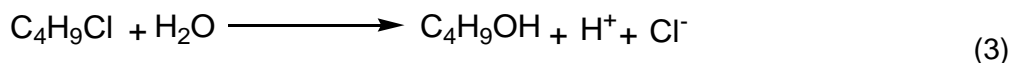
The rate of reaction for the hydrolysis of C₄H₉Cl can be monitored *via* the measurement of the electrical conductivity. This hydrolysis can neither be catalysed by the hydrogen ion nor by the hydroxyl ion. Instead, the rate determining step is the slow ionisation, given as



followed by the rapid step which involves the reaction of C₄H₉ with water,



Hence, the overall reaction can be written as



Here, the electrical conductivity of the solution increases as the reaction proceeds due to the formation of the strong electrolyte, HCl.

2 Materials

Apparatus: Water bath with temperature controller, conductivity meter, boiling tubes, pipette, conical flask with stopper, thermometer, stopwatch.

Chemicals: Ethyl Alcohol, 80% (v/v), *tert*-butyl chloride.

3 Experimental Procedure

- Add 50 mL of aqueous alcohol (80% alcohol v/v) into a large boiling tube, cover the tube, and immerse it into a water bath whose temperature is kept constant at 30 °C.
- While waiting for the temperature of the alcohol to equilibrate, prepare a tube with a conductivity probe.
- When the thermal equilibrium of the alcohol is achieved, pipette 0.3 mL of *tert*-butyl chloride into the alcohol. Stir the mixture to ensure homogeneity.

- Insert the conductivity probe into the mixture and start the stopwatch immediately.
- The conductivity can be measured with a conductivity meter. However, prior to using the conductivity meter, it has to be calibrated with the standard KCl (0.745 g/L solution, producing 1.41 mS cm^{-1}).
- The conductivity readings can now be obtained. Initially, the conductivity readings for this experiment are recorded every 30 s for a period of 5 min, after which the readings are taken every 2 min for a period of 1 h. Record the conductivity as λ_t .
- After taking the readings, transfer the conductivity probe into an empty boiling tube. The boiling tube which contains the reaction mixture is then stoppered and placed in a beaker of water with a temperature of $60 \text{ }^\circ\text{C}$ for a period of 15 min in order to complete the hydrolysis.
- When the hydrolysis is complete, cool the boiling tube by immersing it again in the water bath. The final conductivity reading is taken when the reaction mixture in the boiling tube is at $30 \text{ }^\circ\text{C}$. Record this conductivity as λ_∞ .
- REPEAT THE ABOVE PROCEDURE using 0.2 mL and 0.4 mL of *tert*-butyl chloride in order to investigate the effect of concentration to the rate constant at constant temperature.
- ASSIGN TWO OTHER GROUPS TO REPEAT THE ABOVE PROCEDURE using 0.2 mL of *tert*-butyl chloride at 35°C and 40°C to calculate the activation energy, E_a .

4 Calculations and Discussion

The conductivity of the solution is proportionate with the amount of hydrogen chloride formed. (Alternatively, plot a calibration curve from the successive dilutions of the final reaction mixture with the solvation of 80% alcohol-water, and measure the conductivity for each dilution.)

The rate constant for a first-order reaction can be written as:

$$k = \frac{1}{t} \ln \frac{(\lambda_\infty - \lambda_0)}{(\lambda_\infty - \lambda_t)} \quad (4)$$

in which λ_0 is the conductivity at $t = 0$,

λ_t is the conductivity at time t , and

λ_∞ is the conductivity when the reaction is complete.

The plot of $\ln \frac{(\lambda_\infty - \lambda_0)}{(\lambda_\infty - \lambda_t)}$ against time, t , is a straight line with slope, k . The half-life for this reaction is independent of the initial concentration of *tert*-butyl chloride, and the value of k is independent of the conductivity units used. Hence, the cell constant for the conductivity probe is negligible. In addition, the results are also not influenced by the existence of a trace foreign electrolyte since the calculation for k depends only on the difference between the two rates.

ATTENTION:

If the value of k obtained for the different volume of *tert*-butyl chloride differs more than 5%, you are required to repeat the experiment.

Show that the rate law is suitable with the mechanism suggested in the reaction.

THE ARRHENIUS PLOT

Relates the rate constant, k , to the activation energy, E_a

- **You will also need to perform the experiment in 35°C and/or 40°C in the following week/session**

The Arrhenius equation given as

$$k = Ae^{-\frac{E_a}{RT}}, \text{ can be linearised as } \ln k = \ln A - \frac{E_a}{RT},$$

where:

k = reaction rate constant,

A = pre-exponential factor,

E_a = activation energy [J/mol],

R = gas constant = 8.314 [J/(K.mol)], and

T = absolute temperature [K].

Plotting $\ln(k)$ versus $1/T$ will give a straight line with a slope of $-E_a/R$, from which the activation energy E_a is calculated.

5 References

1. Hughes, E. A. Robertson R. E. Sugamori S. (1965). The Hydrolysis of *t*-Butyl Chloride in Water: Temperature-dependence of the Energy of Activation, Journal of the Chemical Society (Resumed).
2. Euranto, Erkki & Kanerva, Liisa. (1983). Interpretation of the temperature dependence of the Arrhenius activation energy in solvolytic reactions. J. Chem. Soc., Faraday Trans. 1. 79. 10.1039/f19837901483.

EXPERIMENT 4

INFLUENCE OF CHAIN ELONGATION ON SURFACE ACTIVITY FOR NORMAL ALIPHATIC ALCOHOL

Objectives:

1. To determine the effects of chain length (n), concentration (C), and branching of alcohols on surface tension (γ).
2. To find the surface excess concentration (Γ), maximum surface excess concentration (Γ_{\max}) and minimum area occupied per alcohol molecule, A_{\min} for n -amyl and t -butyl alcohols.

1 Theory

Surface activity is defined by the tendency of a particular chemical to adsorb on surface. As a result, the concentration of the chemical on the surface is higher than that of in the solution (bulk concentration). Chemicals that exhibit these properties are called surfactants. Typically, a surfactant molecule consists of one part that is a nonpolar chain, such as a hydrocarbon chain, and another part that is polar or ionized. A molecule with these two distinct properties can significantly influence the characteristics of its solution. The polarised chain will interact with aqueous phase, while the hydrocarbon chain, has no affinity with water. Therefore, the surfactant molecule adsorbs at the surface in a manner that follows this orientation. Adsorption of surfactant molecules on the surface will cause a decrease in surface tension which the phenomena can be considered as a way to describe the surface activity.

Quantitatively, the surface excess concentration (Γ) can be obtained from the surface tension (γ) and the internal concentration (C), through the Gibbs adsorption equation:

$$\Gamma = \frac{1}{RT} \frac{d\gamma}{d \ln C}$$

Units

Γ in mol m⁻²;

γ in mol N m⁻¹

R is 8.314 J K⁻¹ mol⁻¹;

T in K

2 Materials

Apparatus: Torsion balance, du Noüy ring, volumetric flasks, sample holder and thermometer.

Chemicals: Alcohol solutions of methyl, ethyl, n -propyl, n -butyl, n -amyl and t -butyl alcohol.

3 Experimental Procedure

For the present procedure, all glasses must be washed carefully at first using chromic acid. The surface tension for distilled water must be determined as well.

SOLUTION A: Various chain length

0.1 mol dm⁻³ alcohol solutions of methyl, ethyl, *n*-propyl, *n*-butyl and *n*-amyl can be prepared in 100 mL volumetric flask from the alcohol solutions of 0.40, 0.58, 0.75, 0.95 and 1.08 mL, respectively. Dilute the alcohol to the marked level with distilled water.

The surface tension of each solution can be determined at room temperature using a torsion balance (Procedure for the operation of this equipment can be found from the laboratory assistant).

SOLUTION B: Various concentrations of amyl alcohol

Prepare solutions of amyl alcohol with concentrations of

$$0.01, 0.02, 0.04, 0.06, 0.08, 0.10 \text{ mol dm}^{-3}$$

whereas solutions of 0.15, 0.18 and 0.2 mol dm⁻³ have readily been prepared. Shake the solutions to ensure all the alcohols have been diluted and determine the surface tension of each solution as described above.

SOLUTION C: Various concentrations of *t*-butyl alcohol

Repeat the procedures using *t*-butyl alcohol. Prepare a stock solution containing 6 g *t*-butyl alcohol in 100 mL solution in a 100 mL volumetric flask. Dilute solutions of

$$0.5, 1, 3, 5, 7, 10 \text{ and } 13 \text{ mL}$$

to 100 mL with distilled water in volumetric flasks. Determine the surface tensions for the solutions.

4 Calculations and Discussion

Plot a graph of surface tension (γ) versus the number of carbon atoms in alcohol. Explain the result obtained. The decreasing of surface tension can be assumed as a measurement of the alcohol surface activity.

Plot surface tension (γ) versus $\ln C$ as well for the amyl alcohol and draw a tangent on the line curve at

$$C = 0.02, 0.04, 0.06, 0.08, 0.12 \text{ and } 0.18 \text{ mol dm}^{-3}.$$

Calculate surface excess concentration (Γ) for the various concentrations using the Gibbs adsorption equation. Finally, plot surface excess concentration (Γ) versus concentration.

- i. Describe the shape of the graph.
- ii. Determine the limiting value of surface excess concentration.
- iii. Use the limiting value in calculating the average surface area per amyl alcohol molecule. Compare the area with the cross-sectional area of paraffin chain, namely 0.195 cm².
- iv. Discuss the significance of determining the limiting value of surface excess concentration (Γ) in the study of surfactants.
- v. Repeat the calculation for the *t*-butyl alcohol and comment on it.

5 References

1. Gonzalo Vazquez, Estrella Alvarez, and Jose M. Navaza. (1995). Surface Tension of Alcohol Water + Water from 20 to 50 degree C. *J. Chem. Eng. Data*, 40, 3, 611-614.
2. Chodzińska, A., Zdziennicka, A. & Jańczuk, B. (2012). Volumetric and Surface Properties of Short Chain Alcohols in Aqueous Solution–Air Systems at 293 K. *J Solution Chem* 41, 2226-2245.