



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://kimia.um.edu.my/LabManual/fizikal/general-laboratory-instruction-2007.pdf>) 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	:

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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.

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**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!**

## EXPERIMENT 1

### BOMB CALORIMETER

#### Objectives :

1. Calibration of the bomb calorimeter with benzoic acid to obtain the heat capacity of the calorimeter,  $C_{\text{cal}}$ .
2. To determine the heat of combustion,  $\Delta H_c$ , for anthracene.
3. To calculate the standard formation enthalpy of anthracene,  $\Delta H_f$ .

#### 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 pressurized 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.

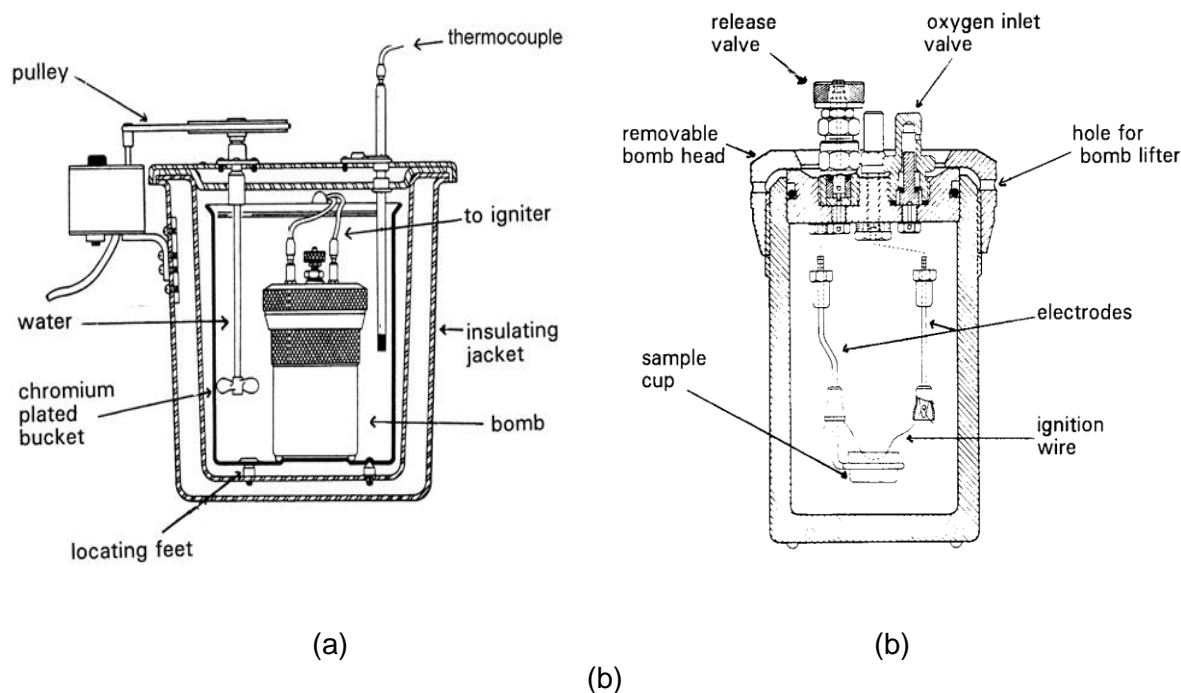


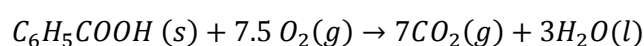
Figure 1. (a) Assembled bomb calorimeter, (b) Parr oxygen bomb.

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  $\Delta U$  rather than  $\Delta H$ . In order to convert to  $\Delta H$ , the heat of combustion at constant pressure, the following expression is used:

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

in which  $\Delta n$  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  $\Delta n$  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 center 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.

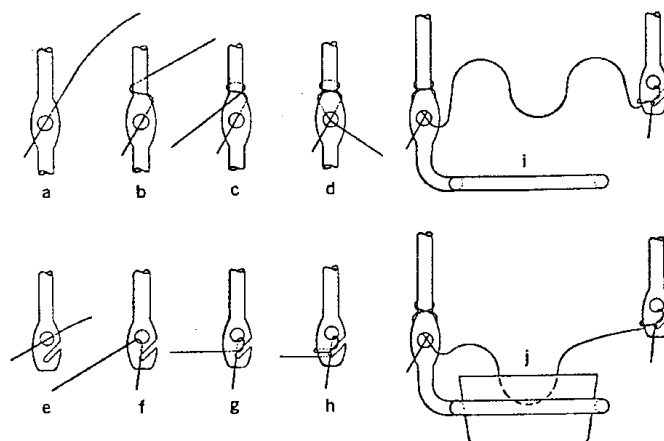


Figure 2. The proper threading of the electrodes and sample placement.

### Liquids in the Bom.

Pipet 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 pressurized 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 minimize 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 pressurize the bomb.
3. Should you accidentally introduced too much of oxygen into the bomb, don't 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 stabilize, 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  $\pm 0.003$  °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 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 other sample.

### **NITROGEN CORRECTION**

When the material is burnt, some the nitrogen in it (and the air) is oxidized and combined with water vapour to form  $\text{HNO}_3$ . 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  $\text{Na}_2\text{CO}_3$  to get the actual amount of  $\text{HNO}_3$  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 standardizing 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 each 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  $T$ ) =  $\Delta T$ ;  $0.6 \times \Delta T = \Delta T$  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 (*temp/min*) at which temperature was rising during the 5 minutes period before firing

$r_2$  = rate (*temp/min*) 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 ( $\text{HNO}_3$ )

= milliliters of standard alkali solution used in the acid titration

$e_3$  = correction in calories for heat of combustion of fuse wires

= centimeters of fuse wire consumed in firing  $\times 2.3$

(when using Parr 45C10 nickel chromium fuse wire, or)

= centimeters of fuse wire consumed in firing  $\times 2.7$

when using No. 34B. & S. gage iron fuse wire

Net corrected temperature rise

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

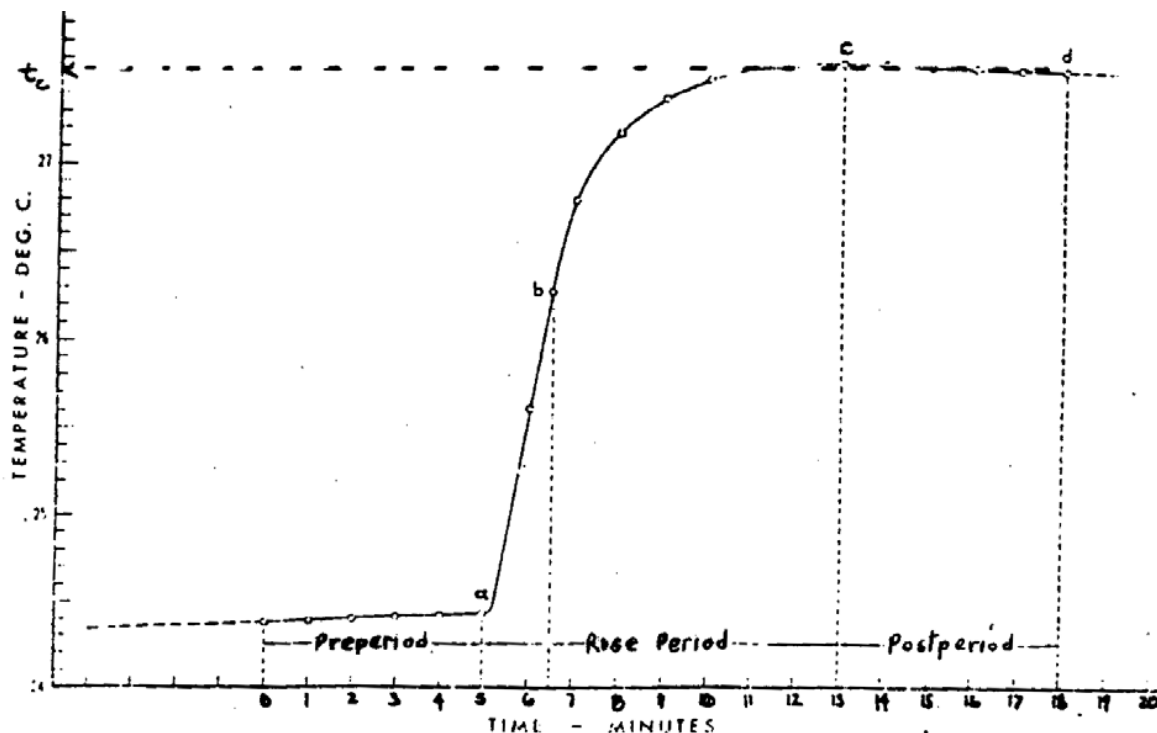


Figure 3. Typical temperature rise curve

## 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 *calories/°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.

$\Delta T$  = net corrected temperature rise in °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:

Standardization with a 1.1651 g benzoic acid sample (6318 cal/g) produces a net corrected temperature rise of 3.077 °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 standardization equation:

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

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

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

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

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

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

## 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 $\Delta H$ :

By definition, a change in enthalpy  $\Delta H$  is related to the corresponding change in internal energy  $\Delta U$  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  $\Delta n_{gas}$  is the increase (or decrease) in the number of moles of gas during combustion.

Thus we obtain our working definition:

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

$\Delta U$  = 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 References

1. Finlay, Practical physical chemistry, 8<sup>th</sup> Ed.
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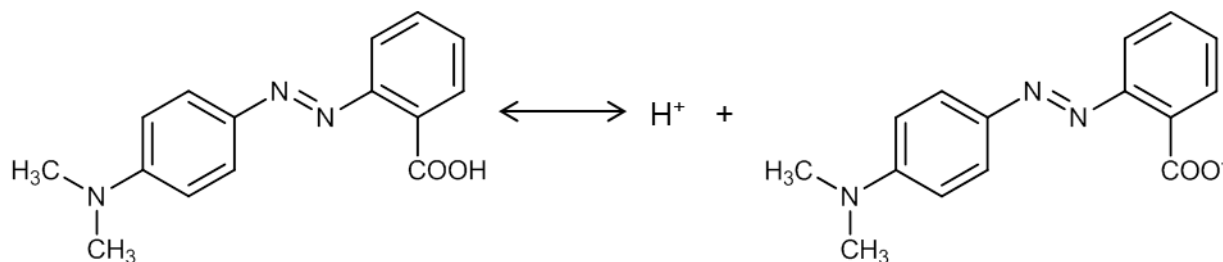
## EXPERIMENT 2

## 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: acid o-(p-dimethylamino-phenylazo) benzoic ( $C_{15}H_{15}N_3O_2$ , Molecular weight 269.31)

Methyl red is a weak acid in which its color in aqueous solution depends on the pH. The  $H^+$  (or  $H_3O^+$ ) in solution determines the ration 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 color changes when the ratio of the two colors 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  $\epsilon$  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  $\epsilon_a$  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

$$c_i L / (A_{obs} - A_{obs}^A) = ([H^+] / K) [1 / (\epsilon_B - \epsilon_A)] + [1 / (\epsilon_B - \epsilon_A)] \quad (7)$$

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

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

With the same procedures, we will obtain the following expression

$$c_i L / (A_{obs} - A_{obs}^B) = (K / [H^+]) [1 / (\epsilon_A - \epsilon_B)] + [1 / (\epsilon_A - \epsilon_B)] \quad (9)$$

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<sup>-3</sup>), sodium acetate solution (concentration 0.04 mol dm<sup>3</sup>) and acetic acid (concentration 0.1 mol dm<sup>3</sup>).

## 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<sup>-3</sup> 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 dm<sup>3</sup>) 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 dm<sup>3</sup> sodium acetate and acetic acid concentrations varying from 0.001 mol dm<sup>-3</sup> to 0.05 mol dm<sup>-3</sup>. 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  $\lambda_A$  and  $\lambda_B$  which give maximum absorption for the acidic solution and basic solution. Record  $A_{\text{obs}}^A$  and  $A_{\text{obs}}^B$  which are seen at  $\lambda_A$  and  $\lambda_B$ .
2. For the methyl red solutions with various concentration of acetic acid, record all pH and  $A_{\text{obs}}$  which is determined at  $\lambda_A$  and  $\lambda_B$ .
3. For  $A_{\text{obs}}$  which was obtained at  $\lambda_A$  calculate  $\frac{1}{(A_{\text{obs}} - A_{\text{obs}}^A)}$  and  $[H^+]$  for each solutions. Record your readings.
4. For  $A_{\text{obs}}$  which was obtained at  $\lambda_B$  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  $\frac{1}{(A_{\text{obs}} - A_{\text{obs}}^B)}$  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  $\lambda_A$  and  $\lambda_B$ .

#### 6 Reference

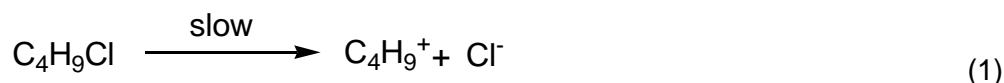
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**EXPERIMENT 3****THE HYDROLYSIS OF *tert*-BUTYL CHLORIDE, C<sub>4</sub>H<sub>9</sub>Cl****Objectives :**

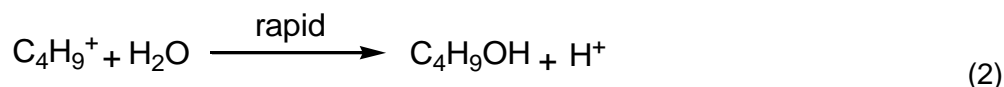
1. To determine the order of reaction and the rate constant,  $k$ , for the hydrolysis of *t*-butyl chloride (*t*-BuCl), C<sub>4</sub>H<sub>9</sub>Cl, at 30 °C, 35 °C and 40 °C.
2. To investigate the effect of concentration to the rate constant at constant temperature.
3. To calculate the activation energy,  $E_a$ , for the hydrolysis of *t*-butyl chloride.

**1 Theory**

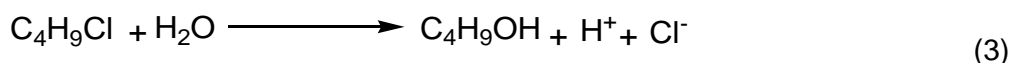
The rate of reaction for the hydrolysis of C<sub>4</sub>H<sub>9</sub>Cl can be monitored *via* the measurement of the electrical conductivity. This hydrolysis can neither be catalyzed by the hydrogen ion nor by the hydroxyl ion. Instead, the rate determining step is the slow ionization, given as



followed by the rapid step which involves the reaction of C<sub>4</sub>H<sub>9</sub> 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<sup>-1</sup>).
- 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  $\lambda_t$ .
- 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 °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 °C. Record this conductivity as  $\lambda_\infty$ .
- 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 Discussions

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  $\lambda_0$  is the conductivity at  $t = 0$ ,

$\lambda_t$  is the conductivity at time  $t$ , and

$\lambda_\infty$  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,  $E_a$

- **Other group can be assign to perform the experiment in 35°C and 40°C.**

The Arrhenius equation given as

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

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 Reference**

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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 chain length,  $n$ , concentration,  $C$  and branching effects on the alcohol to the surface tension,  $\gamma$ .
2. To find surface excess concentration,  $\Gamma$  maximum surface excess concentration,  $\Gamma_{\max}$  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). The chemicals that display such kind of property are called surfactants. Usually, the surfactant molecule has one part of unpolarized chain namely paraffin chain and the other part is a polarized or an ionized moiety. A molecule that has such potential of two different properties will influence the properties of its solution. The polarized chain will contact with aqueous phase but for the hydrocarbon chain, it does not have any affinity with water. Therefore, the surfactant molecule adsorbs on the surface with its orientation obeying that condition. Adsorption 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,  $\Gamma$ , can be obtained from the surface tension,  $\gamma$ , and the internal concentration,  $C$ , through the absorption Gibbs equation:

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

#### Units

$\Gamma$  in mol m<sup>-2</sup>;

$\gamma$  in mol N m<sup>-1</sup>

$R$  is 8.314 J K<sup>-1</sup> mol<sup>-1</sup>;

$T$  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<sup>-3</sup> 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<sup>-3</sup> 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 Discussions

Plot a graph of  $\gamma$  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  $\gamma$  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  $\Gamma$  for the concentrations using the adsorption Gibbs equation. Finally, plot  $\Gamma$  versus concentration and determine the limiting value for the highest concentration. Describe the shape of the graph. 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  $0.195 \text{ cm}^2$ .

Repeat the calculation for the *t*-butyl alcohol and comment it.

#### 5 Reference

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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.

## EXPERIMENT 5

### DETERMINATION OF VAPOUR VISCOSITY

**Objective :** To measure the vapour viscosity,  $\eta$  of n-pentane, diethylether, and methylene dichloride at 35 °C.

#### 1 Theory

When a gas passes through a tube in a laminar flow, the separating distance between the layers of flow is called mean free path. This distance will not be influenced by the intermolecular force between the molecules because the friction flow in the gas phase as a consequence of momentum transfer from fast moving layer to the slower moving layer. This explains why the viscosity of gas is so much smaller than the viscosity of a liquid. The gas viscosity is also depends on surrounding temperature and in the case of real gas, the viscosity depends on the square-root of the temperature in Kelvin. This change in viscosity is more prominent in the case of an ideal gas. In contrary, the liquid viscosity decreases when the temperature is increased. For hard sphere molecules, according to molecular kinetic theory, the viscosity is given by the following equation:

$$\eta = \frac{5\pi}{32} (\rho c l) = \frac{(RTM)^{\frac{1}{2}}}{\pi^{\frac{3}{2}} N \sigma^2} \quad (1)$$

where,

$\rho$ = density of gas	$T$ = temperature
$c$ = mean speed	$M$ = molecular mass
$l$ = mean free path	$\sigma$ = collision cross-sectional area
$R$ = gas constant	$N$ = Avogadro number

Equation (1) shows that the viscosity of an ideal gas is indirectly proportional to the pressure. Nevertheless, this is not true for a real gas due to the fact that there intermolecular interaction exists between the molecules.

There are two common methods to determine gas viscosity, there are; (a) viscous reactance method and (b) transpiration method. In the viscous reactance method, two objects in the form of either cylindrical, disc or spherical shapes are placed side-by-side to one another in the gas medium of interest. When one of the objects are swung towards the other in order to move

the gas and subsequently would swing the other object. The gas viscosity is then determined from the rate of oscillation of the second object.

In the second transpiration method, the gas viscosity can be determined in two ways:

- (a) Time-volume measurement whereby the gas of interest is let to flow through a capillary upon certain pressure
- (b) Time-pressure measurement during the vacuuming process through the capillary. However, the size and dimension of the capillary must be precisely known in order to determine the absolute gas viscosity value. This can be done by using a standard gas of known viscosity.

## 2 Materials

**Chemicals:** n-pentane, diethylether, and methylene dichloride.

## 3 Experimental Procedure

Set the temperature of water bath to be about 35°C. Check for leaks by closing all valves and vacuum the manifold. Leakage can be detected by observing the manometer pressure gauge for every 10 minutes.

Then introduce dry air, through the silica gel into the system. While the capillary is being vacuum, record the manometer heights at certain time intervals for 20-30 minute. Record readings such as pressure in inside the manifold,  $P_m$  and the atmospheric pressure,  $P_a$ . The reading of  $P_a$  can be obtained from the barometer provided. The different in pressure  $P$ , is given by  $P = P_a - P_m$ .

Introduce 5-10 ml of pentane into the manifold by using round bottom quick fit reservoir flask. Secure and seal with silicon grease. Vacuum until almost all the pentane evaporated. Immediately close the valve and let the temperature equilibrate with the room temperature. Make sure that all the pentane completely evaporated. Then vacuum through the capillary and record your manometer readings at certain time intervals. Repeat the experiment with diethyl ether and dichloromethane respectively.

## 4 Results and Calculation

The following equation can be used for your calculation:

$$\frac{1}{P} = \frac{\pi r^4 t}{16VL\eta} + \left(\frac{1}{P_0}\right) = \frac{kt}{\eta} + \left(\frac{1}{P_0}\right) \quad (2)$$

where,

$P$  = pressure at time  $t$

$L$  = capillary length

$P_0$  = initial pressure at time  $t = 0$

$k$  = manifold constant

$r$  = capillary radius

$t$  = time

$V$  = volume of the system

Plot  $1/P$  against  $t$  for the dry air and all the three gases investigated. Given that the viscosity of dry air at  $35^\circ\text{C}$  is 188.6 microPoise, determine the viscosities for all gases. Assuming that the volume of the system and the length of the capillary are  $700\text{ cm}^3$  and  $81\text{ mm}$  respectively. Determine the radius of the capillary using the data obtain from the dry air.

Discuss your results with respect to the boiling point temperature of pentane, diethyl ether and dichloromethane respectively.

## 5 Questions

1. Derive equation (2) from the Poiseuille equation and the ideal gas equation.

Poiseuille equation is given by:

$$Q = \frac{r^4(P_1 - P_2)}{8L}$$

where,

$Q$  = the volume flow rate in the laminar flow

$(P_1 - P_2)$  = differential pressure at the both ends of capillary

2. At what pressure will the mean free path be equals to the length of the capillary?
3. Is equation (2) valid when the mean free path is greater than the length of the capillary tube?

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3. R. A. Alberty & R. J. Silbey, "Physical Chemistry", ed. 2, John Wiley, 1996.

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**EXPERIMENT 6****ROTATIONAL – VIBRATIONAL SPECTRA OF HCl AND DCl**

**Objective :** To obtain the vibrational spectra of HCl and DCl gas, determine the spectroscopic parameters, and relate these to structural information.

**1 Theory****1.1 Introduction**

Spectroscopy is the study of interaction between electromagnetic waves (EMW) and matter. IR radiation can be used to probe vibrational and rotational transitions. In this experiment we shall study the vibration-rotation spectra of HCl and DCl.

The first step that we do when we obtain a spectrum is to assign the spectrum. By 'assign' we usually mean identifying the types/characteristics of transitions between energy levels that are represented by the peaks in the spectrum. Or in other words we are specifying the quantum number changes in the transition. There may be more than one quantum number needed to specify a particular energy level, depending on the complexity of the problem. The way we go about assigning and interpreting a spectrum is as follows:

- a) Specify a model for the energy levels. Typically, we use the energy levels available from solving the Schrodinger equation for a simple system, such as the rigid rotor or the harmonic oscillator in the case of radiation in the IR region.
- b) We then determine the selection rules which apply to these levels and thus predict the form of the spectrum, taking into account that the intensities will be affected by the populations of the energy levels as predicted by the Boltzmann distribution. The Boltzmann distribution is given by:

$$\frac{n_i}{n_j} = \frac{g_i}{g_j} \exp\left(\frac{-\Delta E}{kT}\right) \quad (1)$$

- c) We then compare the predicted spectrum with the real spectrum, and see if they can be made to match up. Typically there will be parameters to adjust, such as rotational constants and vibrational frequencies. The process of matching up the experimental and predicted spectra is often aided by looking for patterns, such as repeated spacing of lines.
- d) If there is reasonable agreement between the two spectra, then the assignment process is complete.



e) It should be noted that the match between the experimental and predicted spectra is rarely perfect. Usually we need to refine our model for the energy levels in order to obtain a better fit – for example in this experiment, by introducing the effects of anharmonicity or centrifugal distortion.

The process of assigning and understanding a spectrum is thus one of refining the model in order to obtain the best agreement. The whole process of assigning and understanding the spectrum allows one to obtain several spectroscopic constants which can then be used to calculate properties of the molecule such as the bond length. Please refer to references for further reading.

## 1.2 Rotational States

The simplest model that considers rotational states is the rigid rotor (RR). This model considers two atoms at a fixed distance that rotate as a unit.

The quantized energy levels of the rigid rotor are given in Eq. 2;

$$E_j = \frac{\hbar^2}{2I} J(J + 1) \quad (2)$$

where  $I$  is the moment of inertia shown in Eq. 3;

$$I = \mu r^2 \quad (3)$$

where  $\mu$  is the reduced mass, given by:

$$\mu = \frac{m_A m_B}{m_A + m_B} \quad (4)$$

and  $r$  is the distance between the two atoms in the rigid rotor.

$J$  is the rotational quantum number and spans integers from 0 to  $\infty$ . The degeneracy of the  $J^{\text{th}}$  quantum level is  $2J+1$ .

## 1.3 Vibrational States

The simplest model for vibrations is the simple harmonic oscillator (SHO). The vibrational levels for the harmonic oscillator are given by Eq. 5, where  $v$  spans integers from 0 to  $\infty$ ;

$$E_v = \left(v + \frac{1}{2}\right) h\nu \quad (5)$$

and  $\nu$  is the frequency of vibration. This frequency is in turn given by;

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = \frac{1}{2\pi} \sqrt{\frac{V''(x)}{\mu}} \quad (6)$$

where the harmonic oscillator potential is  $V(x) = \frac{1}{2}kx^2$ , hence, the spring constant is directly related to the curvature, or the second derivative, of the harmonic oscillator potential,  $V''(x)$ .

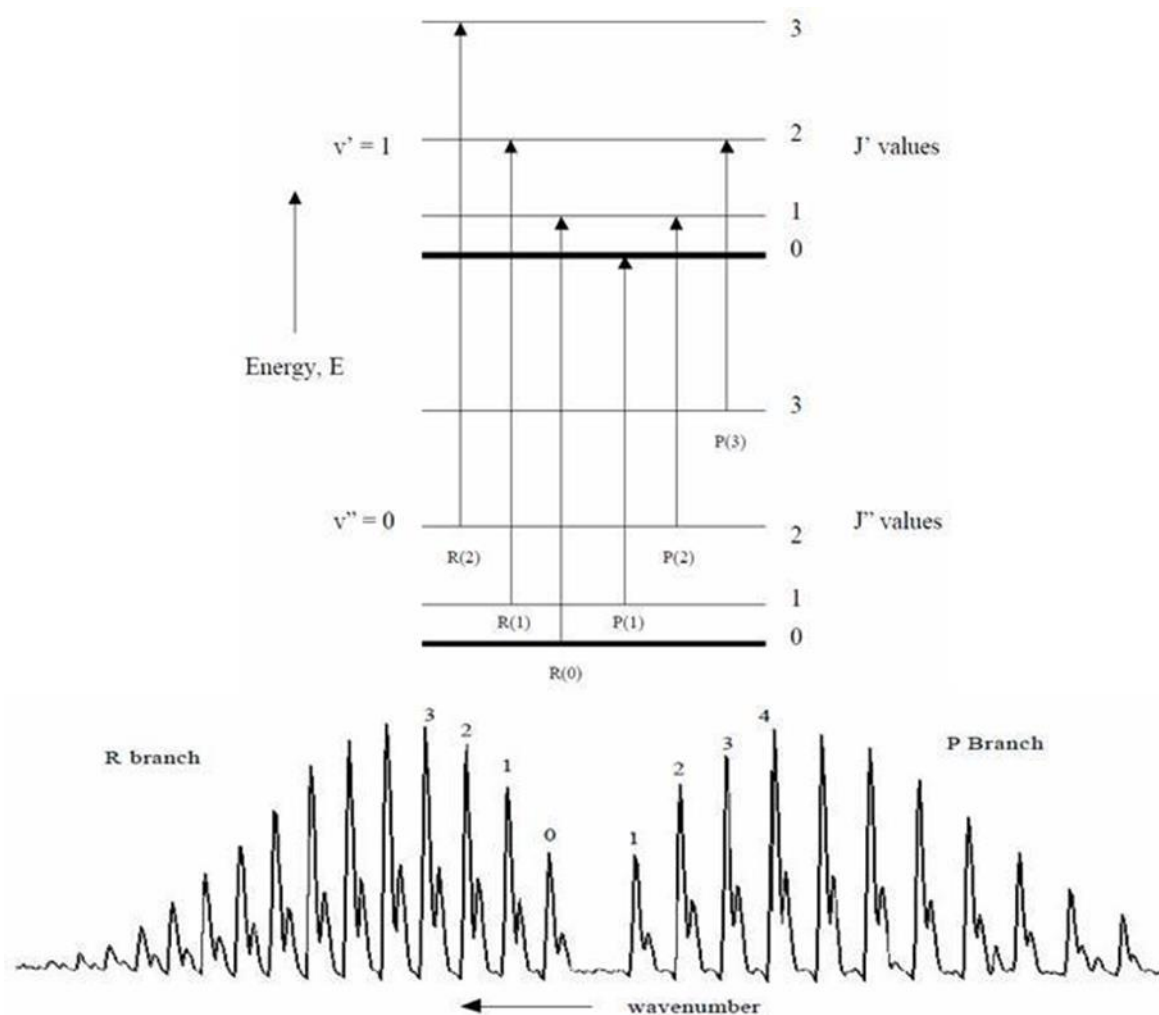
#### 1.4 Interaction between Rotational and Vibrational States (rotational-vibrational spectra)

When a gas-phase molecule undergoes a vibrational transition, the energy of the absorbed photon may be slightly lower than or slightly higher than the exact energy needed to change the state of the molecule from  $u = 0$  to  $u = 1$ . This excess (or slight deficiency) of energy can lead to a simultaneous rotational transition provided  $\Delta J (J' - J'') = 0, \pm 1$ . These selection rules were derived using the rigid rotor and harmonic oscillator assumptions. The resulting rotational-vibrational (ro-vib) spectra can be divided into three branches. Transitions where  $\Delta u = +1$  and  $\Delta J = +1$  are called the "R branch", those where  $\Delta u = +1$  and  $\Delta J = -1$  are called the "P branch", and those where  $\Delta u = +1$  and  $\Delta J = 0$  are the "Q branch".

For diatomic molecules the Q branch is a forbidden transition (rotation about the bond axis has no effect on the dipole moment) and is not observed in a diatomic molecule ro-vib spectrum.

**Figure 1** illustrates the energy levels for the two lowest vibrational states of a diatomic molecule and shows some of the transitions that are allowed between the sublevels. Also shown is an IR spectrum of HCl. Notice that the spectrum is separated into two branches, with a gap between them. The gap is where the infrared transitions would be if no change in the  $J$  value occurred, *i.e.*,  $\Delta J = 0$ . This region is known as the Q branch and only involves a change in the vibrational quantum number. The low frequency branch (P branch) consists of  $\Delta J = -1$  transitions and the high frequency branch (R branch) consists of  $\Delta J = +1$  transitions. Note that the quantum numbers for the lower state in the transition are traditionally labelled as  $u''$  and  $J''$  while those for the upper state are labelled  $u'$  and  $J'$ .

**Notice that as you count away from the center of the spectrum the intensity of individual lines increases, goes through a maximum and then falls off in the wings. How do you account for this behaviour?**



**Figure 1:** Spectral lines and allowed transitions of a ro-vib spectrum. The splitting arises from the  $H^{35}Cl$  and  $H^{37}Cl$  (isotope effect) with  $H^{35}Cl$  peaks being the dominant.

To begin the assignment work, we have to decide on consistent units for the parameters in this experiment. The following Table provides values that may be helpful.

Table 1: Useful constants and conversion factors.

$h$	$6.626 \times 10^{-27}$ erg s	$6.6261 \times 10^{-34}$ Js
$k$	$1.381 \times 10^{-16}$ erg/K	$1.38066 \times 10^{-23}$ J/K
$1 \text{ cm}^{-1}$	$1.986 \times 10^{-16}$ erg	$1.98630 \times 10^{-34}$ J
$m^1H$	1.007825 amu	$1.672623 \times 10^{-27}$ kg
$m^2D$	2.0140 amu	$3.3425 \times 10^{-27}$ kg
$m^{35}Cl$	34.968852 amu	$5.803558 \times 10^{-27}$ kg

		26
$m^{37}\text{Cl}$	36.965903 amu	$6.135000 \times 10^{-26}$ kg

If we assume that the vibrational and rotational energies can be treated independently, the total energy of a diatomic molecule is simply the sum of its rotational (rigid rotator) and vibrational energies (SHO), as shown in Eq. 7, which combines Eq. 1 and Eq. 4.

$$E_{v,J} = \frac{\hbar^2}{2I}J(J+1) + \left(v + \frac{1}{2}\right)h\nu \quad (7)$$

Although for low energy vibrational transitions (and low energy rotational transitions), this assumption may work, it is still a very simplified view of the problem. In actuality, diatomic molecules are not perfectly rigid rotors. Two corrections need to be considered. Firstly, the rotations distort the molecule and change  $r$ . The higher the rotational quantum number,  $J$ , the longer the molecule becomes. This centrifugal distortion effect is usually very small and important only for very large  $J$  values. Secondly, the harmonic oscillator model also has limitations. The fact that diatomic molecules dissociate makes it clear that they are not perfect harmonic oscillators. A potential that takes into account the fact that diatomic molecules can dissociate is the Morse oscillator potential, Eq. 8, where  $D_e$  is the dissociation energy and  $\beta$  is a number that determines the width of the potential.

$$V(x) = D_e(1 - e^{-\beta x})^2 \quad (8)$$

The energy levels for a Morse oscillator are similar to the harmonic oscillator energy levels but include an anharmonic term. As the vibrational quantum number  $u$  increases, the levels get closer together.

Combining these two corrections, the energies of the rotational-vibrational levels are given, in units of  $\text{cm}^{-1}$ , by Eq. 9;

$$E_{v,J} = \nu_e \left(v + \frac{1}{2}\right) - \nu_e x_e \left(v + \frac{1}{2}\right)^2 + B_v J(J+1) - D_v J^2(J+1)^2 \quad (9)$$

The first and second terms account for the vibrational energy, and the third and fourth terms account for the rotational energy. The fundamental vibrational frequency of the molecule is  $\nu_e$ . The first anharmonic correction to the vibrational frequency is  $\nu_e x_e$ .  $B_v$  is the rotational constant for a given vibrational level, and  $D_v$  is the centrifugal distortion constant.  $B_v$  may be obtained from the equilibrium geometry of the molecule using the following relationships (Eq. 10 & 11), where  $B_e$  is the equilibrium rotation constant,  $\alpha$  is the anharmonicity correction factor to the

rotational energy and  $I_e$  is the equilibrium moment of inertia.

$$B_v = B_e - \alpha \left( v + \frac{1}{2} \right) \quad (10)$$

$$B_e (cm^{-1}) = \frac{h}{8\pi^2 c I_e} \quad (11)$$

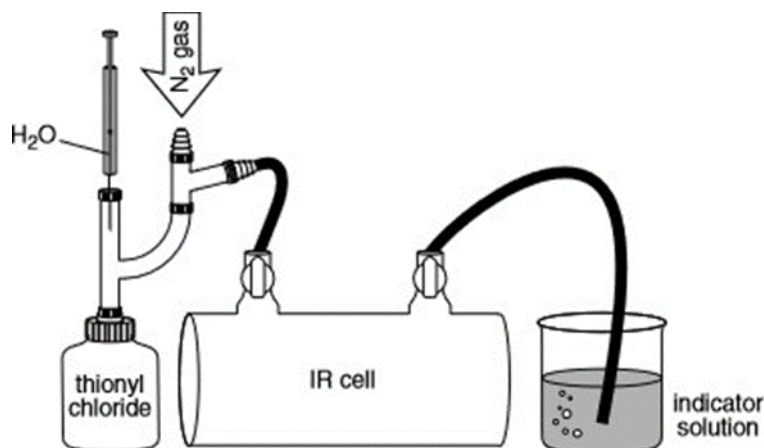
## 2 Materials

**Chemicals:** Thionyl chloride and deuterium oxide.

## 3 Experimental Procedure

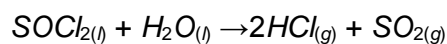
This part of the experiment will be carried out by the PPS in charge of the lab. You will be explained how this is carried out. Students will then proceed to the IR lab in the 1<sup>st</sup> floor and run the spectrum using the prepared IR cell.

**CAUTION!** Thionyl chloride is a lachrymator. HCl gas is corrosive and care must be taken to contain it within the optical cell and bubble the excess through water.



**Figure 2:** The apparatus used to produce and transfer HCl/DCl gas to an IR gas cell.

A reaction that involves thionyl chloride and a mixture of water and deuterium oxide to produce HCl/DCl gas and SO<sub>2</sub> gas proceeds according to the following reaction:



The microscale apparatus is constructed in a fume hood similar to the block diagram shown in **Figure 2**. The PPS in charge will carry out the procedure. Please inform the PPS when you are going to the IR room. The IR cell is already prepared and ready to be used in the IR room.

The PPS in the IR spectrum will assist you in taking the spectrum.

## 4 Data Analysis

### Assigning the Spectrum

The first step in obtaining **spectroscopic constants** is to assign the spectrum. Several methods may be used but the most obvious way for a diatomic molecule is to count outward from the gap between the R and P branches. Remember that there the Q branch line ( $J'' = 0 \rightarrow J' = 0$ ), which forms the middle of this gap, is a forbidden transition, so you will not see a peak for it. Next you need to tabulate the transition frequencies of each isotope ( $\text{H}^{35}\text{Cl}$ ,  $\text{H}^{37}\text{Cl}$ ,  $\text{D}^{35}\text{Cl}$ , and  $\text{D}^{37}\text{Cl}$ ) for later manipulation. If you did not obtain the peaks of  $\text{H}^{37}\text{Cl}$  and  $\text{D}^{37}\text{Cl}$  isotopes, just continue with the  $\text{H}^{35}\text{Cl}$  and  $\text{D}^{35}\text{Cl}$  peaks.

### Finding Rotational Constants, $B_v$

Note that the rotational constant B is different for each vibrational level. In order to obtain B for each vibrational level, first, consider the  $u = 1$  level. Note that if you subtract the frequency of the P( $J''$ ) line from that of the R( $J''$ ) line, the difference is given by Eq. 12, where ( $J''$ ) is written as (J) for simplicity.

#### DERIVE EQUATION 12

$$R(J) - P(J) = B_1 [(J+2)(J+1) - J(J-1)] - D_1 [(J+2)^2(J+1)^2 - J^2(J-1)^2] \quad (12)$$

This equation can be simplified to Eq. 13 and then rearranged into a more useful slope-intercept form (Eq. 14) so that a plot of  $[R(J) - P(J)]/(2J + 1)$  versus  $(J^2 + J + 1)$  can be used to obtain  $B_1$  and  $D_1$ .

$$R(J) - P(J) = 2B_1(2J+1) - 4D_1(2J+1)(J^2 + J + 1) \quad (13)$$

$$\frac{R(J) - P(J)}{2J+1} = 2B_1 - 4D_1(J^2 + J + 1) \quad (14)$$

To obtain the rotational constants for the  $u=0$  level, perform the same type of manipulation for  $R(J-1) - P(J+1)$ , whose difference is given by Eq. 15, which simplifies to Eq. 16. These equations apply to both the HCl and DCl species.

$$R(J-1) - P(J+1) = B_0[(J+1)(J+2) - J(J-1)] - D_0[(J+1)^2(J+2)^2 - J^2(J-1)^2] \quad (15)$$

$$R(J-1) - P(J+1) = 2B_0(2J+1) - 4D_0(2J+1)(J^2 + J + 1) \quad (16)$$

### Finding Molecular Parameters

Using the  $B_v$  values and Eq. 10, you can obtain  $B_e$  for each isotope. Subsequently, you can calculate the equilibrium bond length (combining Eqs. 11 and 3) and the average bond length for each isotope and vibrational level. If the assumptions we have made are all correct,  $r_e$  and  $\alpha$  should be independent of the isotope. Is this true within the precision of the data?

## 5 Discussion

Include a table of  $B_0$ ,  $B_1$ ,  $D_0$ ,  $D_1$ ,  $B_e$ ,  $\alpha$ , and  $r_e$  for each isotopomer ( $H^{35}Cl$ ,  $H^{37}Cl$ ,  $D^{35}Cl$  and  $D^{37}Cl$ ) and all graphs used for obtaining these values.

Compare your values with those given in the literature (based on the given references). You should include percent error calculations assuming the literature value to be correct.

1. Do the values of the spectroscopic constants  $B_e$ ,  $B_v$  and  $D_v$  vary with isotope and/or with vibrational level in a way that you would expect?
2. Does  $r_e$  change for each isotope? Explain your answers.
3. In general, what accounts for the uneven spacing on the lines in the P and R branches of a vibration-rotation spectrum?
4. Using the appropriate Boltzmann distribution equation, model the intensities of the absorption peaks of your experimental data. Does your data match this theory? How would the distribution change at higher temperatures?
5. What additional spectroscopic information could be obtained from your data?

Include the data that you obtained experimentally and the spectra with the line positions labeled. Be sure to also include all your calculations.

## 6 References

1. P.W. Atkins and J. de Paula, *Physical Chemistry*, Oxford University Press.
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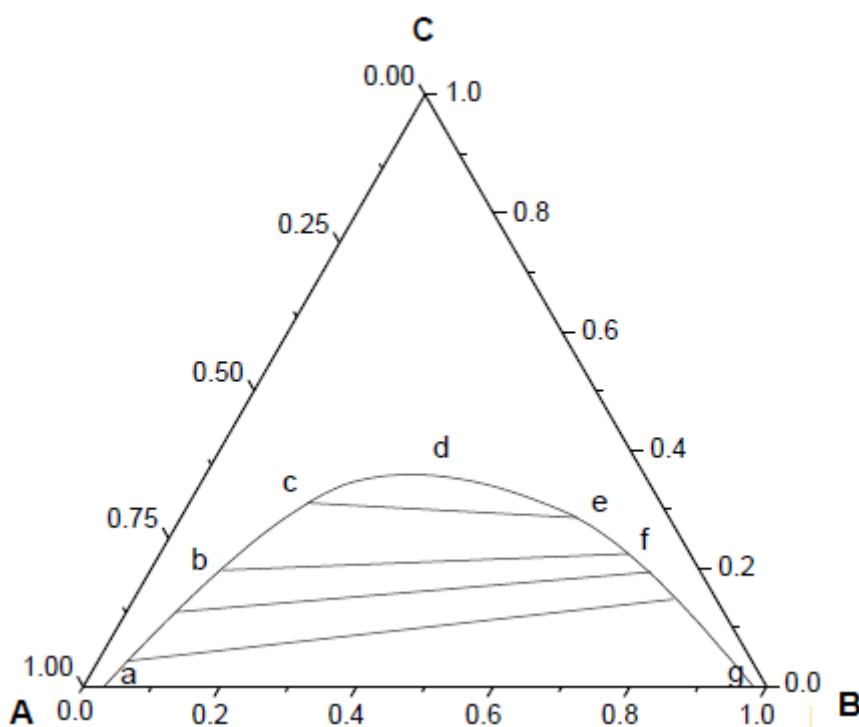
## EXPERIMENT 7

**PHASE DIAGRAM OF A THREE-COMPONENT PARTIALLY IMMISCIBLE LIQUID SYSTEM**

**Objective :** To develop a ternary phase diagram for a liquid system of water-toluene-DMSO at 25 °C.

### 1 Theory

The composition of a ternary system may be described by one point in a triple coordinate diagram. The phase diagram of a ternary liquid system separating into two phases is given in Figure 1. The points on the dome (curve abcdefg), represent the compositions at which the two phases separate.



**Figure 1:** Phase diagram of a ternary system with two immiscible liquids, A and B.

Above this dome only a single phase, hence complete miscibility exists. At a composition described by a point under this dome, the system will separate into two phases. The **a** and **g** positions in Figure 1 indicate that there is slight miscibility between components A and B. If no miscibility existed between components A and B, the **a** position would coincide with corner A and the **g** position with corner B. The diagram also indicates that it is the third component, C,



that is really miscible with either A or B in all proportions. In such a phase diagram the tie lines have a very important aspect: they connect the concentration of the two phases experimentally found to be in equilibrium with each other. For instance, when a mixture with composition **h** (Fig. 1) is prepared, it separates into two phases. Phase one (rich in A and C, and poor in B) has the composition designated on the diagram by **b**. Phase two (rich in B and C, but poor in A) has a composition designated by point **f**. The quantitative ratio of the two phases is given by:

$$\frac{\text{Phase one}}{\text{Phase two}} = \frac{fh}{bh}$$

and, therefore, once a phase diagram is available it can be used to determine the compositions and proportions of the phases that would result when a mixture of specified overall composition is prepared.

You may notice that the dome in Figure 1 is not symmetrical and the tie lines are not parallel to each other. This is simply because the solubility of C in the two phases (A and B) is not the same. In whatever direction the tie lines are slanted, they connect points of equilibrium compositions. These equilibrium compositions, **b** vs. **f** and **c** vs. **e**, become increasingly similar with each subsequent tie line, starting from the base of the dome and proceeding upward. Similarly, the tie lines become shorter and finally converge to a composition. This is called isothermal critical point or the plait point.

## 2 Experimental

The phase diagram of a dimethyl sulfoxide-water-toluene system will be obtained. In order to obtain the points on the miscibility curve dome, one has to titrate different mixtures of DMSO-toluene with water to the point at which cloudiness appears. This can be accomplished in the following manner: Stopper and number 10 to 15 Erlenmeyer flasks of 100 mL capacity. From two burettes (one containing DMSO and another, toluene) prepare mixtures of DMSO and toluene in different proportions. For example, in the first bottle, add 15 mL of DMSO and 0.2 mL of toluene, in the second bottle add 14 mL of DMSO and 1 mL of toluene, and so forth; in the last bottle, combine 1 mL of DMSO and 14 mL of toluene.

Titrate each bottle with water, **slowly** from a third burette to the point of slight turbidity. **Be very careful because any over-titration will result in separation of phases.**

Measure the refractive index of each titrated mixture. Prepare a table to show your results.

Since the phase diagram to be drawn will represent an isothermal equilibrium, the following precautions must be observed. After the original mixtures of DMSO and toluene are prepared, they should be thermostated at 25 °C. The titration must be done slowly as the mixing of DMSO with water is exothermic. Therefore, the water should be added **very slowly**, with constant swirling of the Erlenmeyer flask in the thermostat so that thermal equilibrium is achieved before the endpoint is reached.

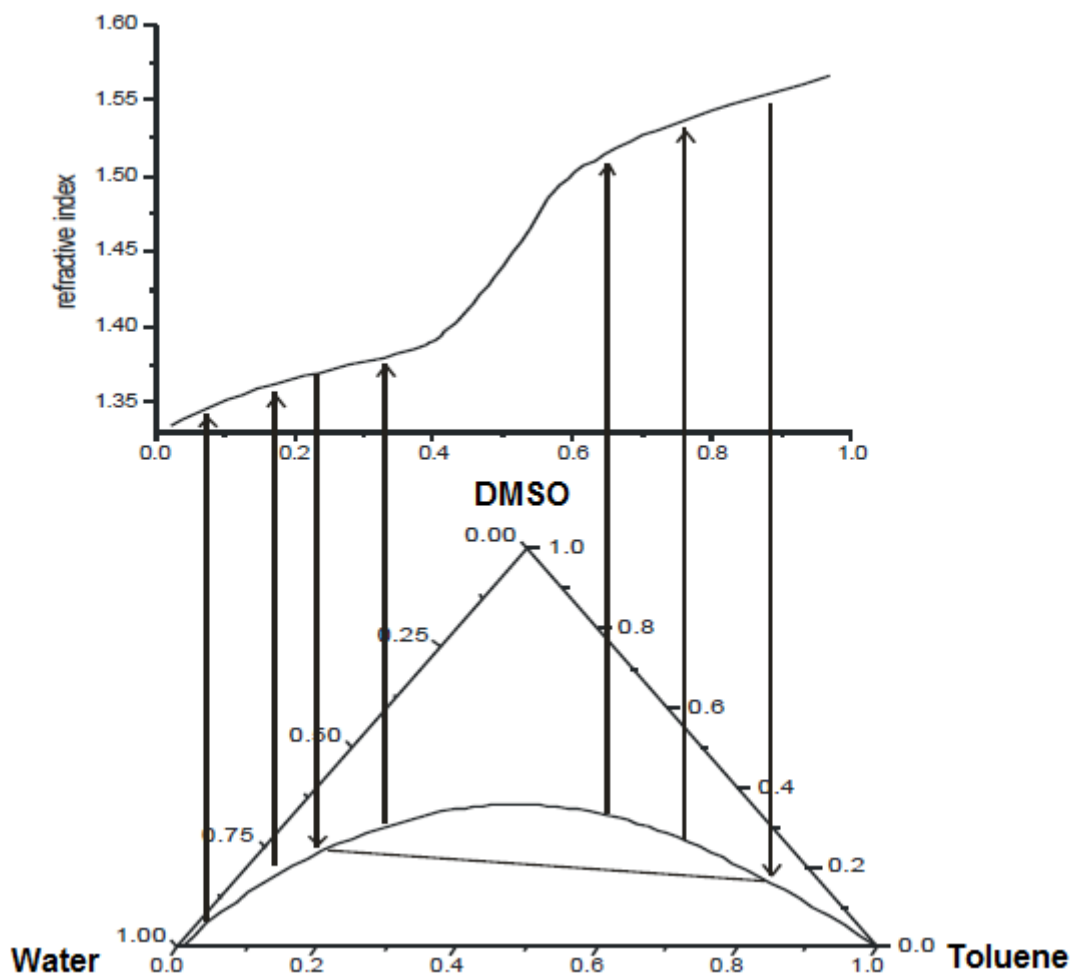
After the endpoint of the titration has been reached and the refractive index of each mixture has been measured, add a slight excess of water to each bottle. Allow sufficient time in the thermostat for the two phases to separate.

After the phases have separated, take a small aliquot from each phase and measure the refractive indices. Again, present your data with a table. Knowing the densities of the pure liquids as well as the amount of the components, convert the data collected in Table 1 into mole fraction composition. Plot your composition data thus obtained on a ternary phase diagram using Microsoft Excel. Refer to the following webpage for a guided walkthrough: <https://chemostratigraphy.com/how-to-plot-a-ternary-diagram-in-excel/>. Connect the points to form the miscibility curve.

**Table 1:** Mole fraction of components

$V_{\text{H}_2\text{O}}$ / mL	$m_{\text{Toluene}}$ / g	$m_{\text{DMSO}}$ / g	$m_{\text{H}_2\text{O}}$ / g	$n_{\text{Toluene}}$ / mol	$n_{\text{DMSO}}$ / mol	$n_{\text{H}_2\text{O}}$ / mol	$X_{\text{Toluene}}$	$X_{\text{DMSO}}$	$X_{\text{H}_2\text{O}}$
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Plot the refractive index diagram above the three co-ordinate diagram in a manner similar to that given in Figure 2 by drawing vertical lines from the points representing the titration end point compositions. Selecting a proper refractive indices scale as the y-axis, plot the refractive indices obtained at each titration end point composition. Once a diagram such as in Figure 2 is obtained, use the refractive index calibration curve to obtain the tie lines.



**Figure 2:** Three-component phase diagram with the representative refractive indices of the different compositions.

### 3 Discussion Questions

1. What is the composition at which a plait point (isothermal critical point) may exist in your ternary system?
2. If you start with a complex mixture of 40% toluene, 20% DMSO (or acetone and so forth), and 40% water, what is the estimated composition of the two-phase? In what proportion would you obtain these phases?