Preface

This document covers the necessary basic information you will need in order to complete the laboratory course CHM423. You will be expected to read all of the relevant background material prior to your laboratory.

Madhav Ranganathan
28 July 2012
Laboratory Introduction

Meeting place and times

Place: Physical chemistry Laboratory, New Core Building
Time: Tuesday and Thursday 2:00 pm - 4:50 pm: LATE ARRIVAL WILL BE PENALIZED. NO ONE WILL BE ALLOWED IN THE LABORATORY AFTER 2:15 pm

Instructors:

Instructor-in-charge: Dr. Madhav Ranganathan (madhavr@iitk.ac.in)
Office: SL 302
Phone: 6037
Office hours: by appointment

Lab-in-charge: Buddha Prakash
Gautam Karmankar
Dr. Anjali Pandey

Student Tutors: Dipankar Mondal
Krishnandu Makhal

Course goals:

To convey the challenges and excitement of Physical Chemistry. In addition to learning various experimental methods, you will be exposed to data collection methods, error analysis and report writing. It reinforces the knowledge you have learned in classes and will give you a chance to apply your knowledge. It will make you familiar how to deal with complexity in experimentation, which is an important component of any scientist’s expertise.

Text books

There is no text book for this course. However, there are many excellent reference books. In addition, you can also read about experiments in popular chemistry journals like Journal of Chemical Education.

1. Experimental physical chemistry by Frederick A. Bettelheim
2. Experimental physical chemistry by G. Peter Matthews
3. Experimental physical chemistry by Farrington Daniels
4. Experimental physical chemistry by Halpern and McBane
5. Experiments in Physical Chemistry by Shoemaker, Garland and Nibler

Grading:

The relative weighting of each contribution to your grade is as follows:
Laboratory reports and performance 60%; Quizzes 20%; Final exam 20%
Laboratory Experiments and Laboratory Reports

The course is built around several experiments in various topics in Physical Chemistry. Laboratory reports will be required for all experiments. Reports should be submitted on Thursday, the day you finish one experiment. Even if you have not completed all parts of the laboratory report for the experiment, you will be required to submit the report the day the experiment is over. When you submit the report, you should clearly write the remaining work that needs to be done to complete the report and complete it the following time you submit the report.

Students will work in the laboratory in pairs, but each student will be required to keep their own laboratory report book, which will be graded every week.

The Laboratory Report is very important document. It is simultaneously a laboratory log book and a scientific report. It should contain the significant procedural details that were followed during the experiment. All data should be recorded directly in the laboratory report with a signature of one of the laboratory assistants. However, it should also contain the analysis in the form of graphs/calculations, discussions and literature review of a typical scientific report. Each laboratory report should be independently written. Any matter taken from other sources should be duly referenced. Copying of matter from other students will be taken very seriously and will result in zero marks for the experiment; and a warning against repeating the same.

What should a typical Laboratory Report Contain:

1. Name of the experiment and date of performing the experiment.

2. Aim of the experiment: Please be specific while writing this. For example, “To determine the rate of reaction of A and B using method of D”.

3. Main Concepts/Principles used in the design of the experiment: Again, you have to be specific to the experiment. This can only be written if you take the trouble to thoroughly understand the experiment. You can also write this part by logically going backward from the aim of the experiment.

4. Procedural details: It is NOT necessary to rewrite the entire procedure as given in the manual. You do need to write the following:
   (a) A procedure (not detailed) that is based on the principles in part 3.
   (b) Any actual detail in the procedure that was followed during the experiment, that differs from the manual. In case of interesting apparatus, you may also make a sketch of the same.

Note that items 1, 2, 3 and 4(a) of the laboratory report can be written before starting the experiment so that you can finish the report in time. The remaining parts have to be written during and after the experiment.

5. Recording of data, observations: This should be very clearly written out. It is recommended that the white pages of your report be used for all material written during the experiment, whereas the ruled pages can be used for details.
written before and after the experiment. If your result is in the form of a graph(s), then you should stick the graph(s) to the blank pages of your notebook.

When recording and analyzing data, use the appropriate number of digits (significant figures) for each reading. Remember, the number of digit used in the data gives information about the precision of the measurement. It is very valuable information and should not be taken casually. Be careful with significant figures while doing mathematical and statistical operations. For example, you cannot report an average of 1.0 and 1.1 as 1.05 and use it in further calculations, but you can report the average of 1.00 and 1.10 as 1.05. Similarly, be careful while dividing numbers.

6. Analysis of data: Calculations, graphs and graphical analysis. All graphical analysis have to be done using a computer software like Excel, or any other (Mathematica, Matlab, Maple, gnuplot, Tecplot, xmgrace, open office...). Graph paper can be used to see the graphs during the experiment, but any analysis should be performed through a proper mathematical procedure. You have to attach a print out of the graph with your report. If you have time, you can go to the Computer Center labs in the top floor of the Core labs to make your plots and take printouts during the laboratory hours.

Curve/Line fitting of a graph should not be done by hand. Use a regression scheme. Similarly, slopes and intercepts are to be obtained from least square fit of data. In flection points are more complicated but they can also be calculated using splines and other fits to data. Most plotting software have inbuilt routines for fitting data to various functions.

Proper plotting and analysis of graphs is actually part of a branch of mathematics called regression. Even if you are not fully familiar with regression, you should at least know what is least square fit of data.

7. Results, Questions and Discussions: The result is related to the aim of the experiment. There are questions asked in some of the experiments and you can answer them here. It is very important to discuss the experiment as a whole and the results in particular. The discussion can also contain information about possible sources of error and suggestions to improve the experiment. In addition, it may contain comparison of results to literature values. Reporting results without any useful discussion makes the results completely meaningless.
The Theory/Principles part is brief, but clearly indicates the main guiding principles behind the experiment. This can only be done if you read the experiment carefully before you come to laboratory.
At 610 nm, absorbance $A$ is proportional to $[\text{Mg}]$. Hence we can write

$$A(t) = A(0) e^{-\frac{t}{\tau}} + A(\infty)$$

where $A(0)$ is the base absorbance.

If $t_0$ represents the starting time for recording spectrum, we set $t_0 = 0$ to get

$$A(t) = A(0) e^{-\frac{t}{\tau}} + A(\infty)$$

From a plot of $A(t)$ vs time, we can calculate $\tau$ and the rate constant.

**Experimental Details:** (a) The reactants MgI (aq) and a pH 13 buffer solution are introduced in a stopped-flow cell via syringes. The entry of reactants into a mixing chamber produces a stopping syringe which triggers spectrophotometric detection. The wavelength of detection is chosen to be the peak absorbance wavelength of MgI.

**Analysis:** The extremely low value of $R^2$ (close to 1) indicates that the experimental data fits an exponential curve very well. From the graphical output, we have $\tau = 7.75$ s and $\ln(\frac{1}{2}) \approx 0.129$ s$^{-1}$.

**Results and Discussions:** The rate constant for the reaction of MgI with pH 13 buffer under pseudo-first order conditions containing excess of buffer is found to be 0.129 s$^{-1}$.

Under conditions of excess buffer, the absorbance at 610 nm accurately fits an exponential curve indicating the validity.
Experimental Details (b):
Reagents prepared as described in manual.

Recorded absorption spectrum of Mg.
Absorbance peak observed at $\lambda = 619.8$ nm.

The spectrophotometer used is Omicon - SW 417 instrument
with a precision of 0.1 nm.

Procedure followed as described in manual.

Observations: Absorbance at 619.8 nm as a function of
time was directly obtained in the form of a graph.
This graph was fitted to an exponential function
and is attached below.
The experimental graph obtained. Ignore the poor printing. The main graph with the fitting parameters is to be noted. Note that you have to interpret the fitting parameters to the appropriate number of significant figures.
Notice the rather long discussion of the results. This is an important part of the results. Notice that I have not simply written “Sources of error” and included everything under the sun. You have to analyze the errors carefully each time.
Laboratory conduct requirements

The following requirements are essential in order to conduct a safe and productive teaching laboratory:

1. Use apron, covered foot wear and eye protector in the laboratory. This is must.
2. It is your responsibility to bring scale, pencil, calculator, etc. everyday in the laboratory. You may need those sometime.
3. Always work honestly and confidently in the laboratory and do not consult your neighbors.
4. Always keep the apparatus and the working table clean.
5. Read the experimental procedure and be aware of any dangers with any of the materials. Unscheduled experiments should not be performed unless specific permission is given by Instructor/In-charge.
6. Do not evaporate acids or ammonium salts or inflammable solvents or handle poisonous and obnoxious chemicals in the open laboratory. Use the nearest available fume cupboard.
7. When heating substances in test tubes make sure that the open end is not pointed at you or anyone else.
8. Do not touch any chemicals, smell gases. It is possible that different people might react differently on exposure to the same chemical. Therefore, it is best to handle them with appropriate protection.
9. Do not pipette strong acids or bases or organic solvents by mouth (e.g. Chloroform, Benzene and toluene etc.). Use a rubber bulb.
10. Do not drink with beakers.
11. Whenever an accident occurs in the laboratory notify your Instructor/In-charge.
12. Touch things with care. They may be hot.
13. When diluting an acid with water always pour the acid slowly into the water. Do not pour the water into the acid.
14. Read reagent bottle labels carefully before using the contents and do not change glass stoppers of reagent bottles.
15. Never use a larger amount of chemical substances than the maximum suggested.
16. When anything is spilled in the laboratory clean it up immediately by an appropriate method. Consult with your Instructor/In-charge.
17. In case of any accident or anything getting into ones eyes, immediately go outside the laboratory to the safety showers in the courtyard. Stand under the shower for 15 minutes.
18. Use only match box /gas lighter /spirit lamp (not strips of paper) to light your burner and never throw a burning match stick into the sink or waste basket.
19. When you have to use any chemicals or apparatus from the common store do not hurry or push others. Wait for your turn.

20. Do not use filter paper for weighing or wiping or drying.

21. Before you leave check the following:
   (a) Water taps closed?
   (b) Electric switches off?
   (c) Lab table/apparatus cleaned?
   (d) Chemicals/solvents bottle closed?

22. All students must respect the equipment which they use. This means understanding how to use it safely and correctly before starting to use it. This also means that every precaution should be taken to prevent damage to laboratory equipment. Quality equipment used to make accurate and precise measurements is very expensive. You are required to immediately inform the instructor of any equipment malfunction or damage.

23. The computer laboratory should only be used for work related to the laboratory.

24. All students are expected to maintain a professional attitude in the laboratory. All students must treat others in the laboratory with civility and respect. They must conduct themselves in a way that does not interfere with the opportunity of others to learn. This includes keeping unnecessary noise to a minimum. Also, no one is allowed to leave the laboratory without permission of the instructor/lab-in-charge.

Your conduct and safety practices in the laboratory will be graded continuously during the course of each experiment, and the overall grades will be included in the final marks in the laboratory to be used for grading. In addition, poor behavior in the laboratory may lead expulsion from the laboratory.

Unlike what you may think, it is actually a lot of fun to practice safety and think about the possible dangers lurking in each experiment. You may even come up with suggestions for doing the experiments in more safe ways. Once this becomes a habit, it will not leave you for the rest of your life.
The greatest joy of life is that of finding things out. In order to really "find out" things, we perform carefully designed experiments and calculations. A scientist finds beauty not just in the results, but in the procedure of scientific enquiry itself. This laboratory is an opportunity to discover the beauty of science. Treat it as a process of discovery and it will be thoroughly enjoyable experience.
List of experiments

1. Kinetics of Reaction between Ferrous Nitrate and Potassium Iodide using initial reaction rates.
2. Determination of partial molal volume.
3. Determination of the isotherm for a three component system.
4. (a) Spectrophotometric determination of acid dissociation constant
   (b) Formula and stability constant using spectrophotometry.
5. The measurement of electrical conductance for the determination of the equivalent conductance at infinite dilution.
6. (a) Fluorescence quantum yield of an unknown molecule.
   (b) Fluorescence quenching and Stern-Volmer coefficient.
7. (a) Rate of the hydrolysis of sucrose using polarimeter.
   (b) Polarizability from refractive index measurements.
8. (a) Determination of pKa of poly-basic acid with the pH meter.
   (b) Determination of transport number by moving boundary method.
9. IR and Raman spectroscopy of solvent mixtures.
### Academic Calendar and Day Numbers

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### Group Day-wise Experiment Schedule

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Experiment No. 1

Kinetics of the reaction between ferric and iodide ions – use of initial rates

Theory:
Ferric and iodide ions in aqueous solution react according to the stoichiometry at a measurable rate at room temperature.

\[
2\text{Fe}^{3+} + 2\text{I}^- = 2\text{Fe}^{2+} + \text{I}_2
\]

The object of the experiment is to determine the order of the reaction with respect to \(\text{Fe}^{3+}\) and \(\text{I}^-\) ions.

The rate of the reaction may be measured by adding a small known concentration of thiosulphate ions. The iodine produced from the reaction is then very rapidly reduced back to iodine by thiosulphate ions.

\[
2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}
\]

This continues until all the thiosulphate has been converted to tetrathionate, whereupon free iodine is formed in the solution. The color of the iodine is enhanced by the addition of starch solution. Neither of which have any appreciable effect on the rate of the reaction, and noting the times for a blue color just to appear in the solution.

The time interval between the start of the reaction and the change in color of the solution is a measure of the initial rate of the reaction.

At constant temperature and ionic strength, the rate equation for the reaction may be written as

\[
\text{Reaction rate} = -\frac{d[\text{Fe}^{3+}]}{dt} = k[\text{Fe}^{3+}]^m[\text{I}^-]^n
\]  

(1)

where \(m\) is the order of reaction with respect to \(\text{Fe}^{3+}\) and \(n\) is the order of reaction with respect to \(\text{I}^-\). In this experiment we use initial rate method to find \(m\) and \(n\). The basis of the method is to measure the rate of the reaction over a period which is short enough for the reaction not to have proceeded significantly, but long enough to be unaffected by the time which the solutions take to mix at the beginning of the reaction.

The total amount of thiosulphate added (x) divided by the time (t) is a measure of the average rate over that fraction of reaction. Extrapolation of a plot of \(\frac{\text{x}}{\text{t}}\) versus t to zero time gives a measure of the initial rate, \(\frac{\text{x}}{\text{t}}\). Now,

\[
\frac{\text{x}}{\text{t}}\bigg|_0 = k[\text{Fe}^{3+}]^m[\text{I}^-]^n
\]  

(2)

Or

\[
\log\frac{\text{x}}{\text{t}}\bigg|_0 = \log k + m \log[\text{Fe}^{3+}] + n \log[\text{I}^-]
\]  

(3)
Thus a plot of $\log\left(\frac{x}{t} \right)_0$ vs $\log[Fe^{3+}]$ at constant $[I^-]$ will yield a straight line of slope $m$, and a plot of $\log\left(\frac{x}{t} \right)_0$ vs $\log[I^-]$ at constant $[Fe^{3+}]$ will yield a straight line of slope $n$.

The rate constant actually depends on the ionic strength (which is given by $I=\sum C_i Z_i^2$, where $C_i$ is the concentration and $Z_i$ is the charge of the $i^{th}$ ion).

Apparatus and Materials

Apparatus:
Three 500 ml, two 250 ml, and one 100 ml measuring flasks; 5 ml pipette; two 50 ml burettes and standards; 10 ml microburette and stand; 250 ml conical flask, 25 ml pipette, graduated 50 ml pipette, 250 ml beaker; funnel; weighing bottle, thermometer to read room temperature; glass stirring rod; stop clock.

Materials: Ferric nitrate; Potassium nitrate; Potassium iodide; Sodium thiosulphate; 2N Nitric acid solution; Starch indicator.

Procedure:
Preparation of solutions:
Prepare the following solutions, the concentrations being within 5% of these specified:
1) 500 ml 0.017 M Ferric nitrate in 0.01 M Nitric acid
2) 500 ml 0.1 M Potassium nitrate
3) 500 ml 0.025 M Potassium iodide
4) 250 ml 0.1 M Nitric acid
5) 250 ml 0.01 M Sodium thiosulphate.

Set up 50 ml burettes containing the Potassium iodide solution and a microburette containing Sodium thiosulphate solution.

Practice run:
To accustom yourself to the technique, practice a run as described below.

To a mixture of 10 ml of Fe(NO$_3$)$_3$ solution, 10 ml of HNO$_3$ solution, 35 ml of KNO$_3$ solution, 20 ml of water and about 1 ml of starch indicator in the conical flask, add rapidly 25 ml of KI solution and mix; Simultaneously start the stopclock.
After no longer than 20-30 sec, add thiosulphate solution from the burette until the blue colour is just discharged, and then slight excess. Note the volume of thiosulphate added and the time to the nearest second when the blue colour just reappears. Then again add thiosulphate and repeat the same procedure about 10 times until 800 sec.

Order with respect to ferric:
Repeat the above run and perform similar runs keeping the volumes of KI solution, HNO₃ solution, and water constant, but with 10 ml, 20 ml, 30 ml, and 40 ml of Fe(NO₃)₃ solution. Make the total volume 100 ml in each case by addition of the appropriate KNO₃ solution.

Order with respect to iodide:

Repeat the above run and perform similar runs keeping the volumes of Fe(NO₃)₃ solution, HNO₃ solution, and water constant, but with 10 ml and 50 ml of KI solution. Make the total volume 100 ml in each case by addition of the ¼th diluted KNO₃ solution.

Determine the order of the reaction with respect to Fe³⁺ and I⁻ ions.
**Experiment No. 2**

**Determination of partial molal volume**

Theory

The quantitative study of solution has been greatly advanced by the introduction of the concept of partial molal quantities. A property of a solution, e.g. the volume of a mixture of alcohol and water, changes continuously as the composition is changed. A partial molal property of a component of a solution is defined as follows. Let \( Y \) represent any extensive property of a binary solution; at constant temperature and pressure. Then, \( Y \) will be a function of the two independent variables \( n_1 \) and \( n_2 \), which represent the numbers of moles of the two components present. The partial molal property of component 1 is then defined by the relation

\[
Y_1 = \left( \frac{\partial Y}{\partial n_1} \right)_{n_2,T,P}
\]

(1)

Similarly for component 2,

\[
Y_2 = \left( \frac{\partial Y}{\partial n_2} \right)_{n_1,T,P}
\]

(2)

The usefulness of the partial molal quantities lies in the fact that it may be shown mathematically that

\[
Y(n_1, n_2) = n_1 Y_1 + n_2 Y_2 \quad T,P \text{ constant}
\]

(3)

Any extensive property of the solution may be expressed in this manner in terms of partial molal properties, which themselves are function of the concentration of the solution, temperature and pressure.

In the case of the volume of the solution,

\[
V = n_1 \bar{V}_1 + n_2 \bar{V}_2 \quad T,P \text{ constant}
\]

(4)

The partial molal volumes \( \bar{V}_1 \) and \( \bar{V}_2 \) may be evaluated from density measurement. Lewis and Randall have given a procedure for finding the partial molal volume by defining another quantity, the apparent molal volume with symbol \( \varphi_V \).

The apparent molal volume is defined by the relation

\[
\varphi_V = \frac{V - n_1 \bar{V}_1^0}{n_2} \quad T,P \text{ constant}
\]

(5)

Where, \( V \) = volume of solution containing \( n_1 \) moles of component 1 and \( n_2 \) moles of component 2. \( \bar{V}_1^0 \) = molar volume of component 1 at given \( T, P \).

Since \( V = n_2 \varphi_V + n_1 \bar{V}_1^0 \)

\[
\bar{V}_2 = \left( \frac{\partial V}{\partial n_2} \right)_{n_1,T,P} = \varphi_V + n_2 \left( \frac{\partial \varphi_V}{\partial n_2} \right)_{n_1,T,P}
\]

(6)

and

\[
\bar{V}_1 = \frac{V - n_2 \bar{V}_2}{n_1} = \frac{1}{n_1} \left[ n_1 \bar{V}_1^0 - n_2 \left( \frac{\partial \varphi_V}{\partial n_2} \right)_{n_1,T,P} \right]
\]

(7)

Now the above equations can be converted in terms of the quantities which can be easily measured in the laboratory, i.e., densities. Further if we consider 1000 g of
component 1, \( m_1 = 1000/M_1 \) and \( n_2 = m_2 = W_2/M_2 \) (where \( m_1 \) and \( m_2 \) are the molalities, \( M_1 \) and \( M_2 \) are the molecular weights, of solvent and solute respectively), then

\[
V = \frac{1000 + m_2 M_2}{\rho} \quad \text{and} \quad n_1 \overline{V_1} = \frac{1000}{\rho_1} \quad \text{and} \quad \phi_V = \frac{1}{\rho} \left[ \frac{1000[\rho_1 - \rho]}{m_2 \rho_1} + M_2 \right] \tag{8}
\]

where, \( \rho_1 \) = density of pure component 1; \( \rho \) = density of solution of molality \( m_2 \) of component 2 having molecular weight \( M_2 \).

when component 1 is water the equation 6 and 7 can be rewritten as

\[
\overline{V_2} = \phi_V + m_2 \left( \frac{\partial \phi_V}{\partial m_2} \right) \quad \text{and} \quad \overline{V_1} = \overline{V_1^0} - \frac{m_2}{55.55} \left( \frac{\partial \phi_V}{\partial m_2} \right) \tag{9}
\]

\( \phi_V \) can be calculated at each concentration from equation 8 by measuring the density of the respective solution. Plot \( \phi_V \) vs. \( m_2 \) and draw a smooth curve. \( \frac{\partial \phi_V}{\partial m_2} \) can be calculated by drawing a tangent at any concentration. Calculate \( \overline{V_2} \) and \( \overline{V_1} \) from equations 9 and 10.

Experimental

2. Clean two Pycnometers of capacity either 10 ml or 20 ml by washing them with cleaning solution and rinsing them 5 to 6 times with distilled water. Dry them in a 120°C oven and cool them in a room temperature.

3. During the time of drying and cooling, prepare mixtures (at least six) of 50 ml each, containing methanol and water in concentration varying from 0.1 to 0.9 mole fraction of methanol. Keep these solutions in a thermostat.

4. Find the weight of the empty Pycnometer (\( W_0 \)).

5. Fill it with distilled water and ensure that water is filled up to the top of the capillary. Weigh the Pycnometer and calculate the volume of the Pycnometer using the relation \( V_p = (W_W - W_0) / \rho_W \); where \( W_W \) is the weight of the Pycnometer filled with water and \( \rho_W \) is the density of water at room temperature.

6. Similarly weigh the Pycnometers filled with each solution and calculate the density of each mixture using the volume of the Pycnometer obtained in step 4.

Calculations:

1. Calculate the molality (\( m_2 \)) of each solution and value of \( \phi_V \) using the equation 8.
2. Plot $\phi_V$ vs. $m_2$, obtain smooth curve and find $\left[ \frac{\partial \phi_V}{\partial m_2} \right]$ at several concentrations.

3. Calculate $V_2$ and $V_1$ at the above concentration using equations 9 and 10. Plot them against $m_2$ and draw a smooth curve for each of two quantities.
Experiment No. 3

Isotherm for a three-component system: chloroform / acetic acid / water

Theory:
The simplest representation of a three-component system is one in which a liquid system separates into two phases. Such a system has two domains: a domain of perfect miscibility and another domain in which two immiscible liquid phases are in equilibrium.

The Gibbs phase rule governs the equilibrium conditions

\[ F = C - P + 2 \]  

where \( F \) is the degree of freedom, \( P \) is the number of phases and \( C \) is the number of components. Therefore, if the two external variables (temperature and pressure) are fixed, one degree of freedom exists when two phases are present, whereas two degrees of freedom exist when there is perfect miscibility.

The behavior of a ternary system at constant temperature and pressure can be presented in a diagram with three co-ordinates.

The composition of a ternary system may be described by one point in a triple co-ordinate diagram.

The object of the experiment is to determine the phase diagram at room temperature for the chloroform/acetic acid/water system. Mixtures of these three liquids may be homogeneous or separate into two layers. The boundary, on a triangular diagram, between the area within which the system is homogenous and the area
within which two phases coexist, is termed as the isotherm. If a mixture separates into two layers, the composition of the conjugate solution is given by points on the isotherm. A line joining them passes through the point representing the overall composition of the system.

Procedure

Determination of the isotherm:

Set up burettes containing acetic acid, chloroform, and water. CAUTION: Glacial acetic acid is corrosive. Make up accurately, in the clean, dry, glass-stoppered bottles, mixtures of chloroform and acetic acid containing 1.5, 2.0, 2.5, 3.5, 6.5, 9.5, 13.0 and 16.0, 18.0 ml of chloroform, the total volume of each mixture being 20 ml.

Run water into each mixture, shaking well after each addition, until the homogeneous solution becomes permanently turbid; note the volumes of water added. Note room temperature.

Determination of tie-lines:

Using the burettes as before, make up accurately in clean, dry, bottles two mixtures having the compositions (X) 10 ml of water, 3.5 ml of acetic acid, 6.5 ml of chloroform, and (Y) 7 ml of water, 7.5 ml of acetic acid, 5.5 ml of chloroform, shake each bottle for about 30 min. and allow at least 20 min. for layers to separate.

Meanwhile, prepare 250 ml of approximately 1.0 N sodium hydroxide solution, and standardize with weighed amounts of oxalic acid, using phenolphthalein indicator.

Then weigh accurately the four clean, dry, conical flasks and their corks. Remove about 5 ml of each of the four layers using the pipette (use separating funnel if necessary), which should be clean and dry each time, run each sample into a conical flask and reweigh. In sampling the lower layer, gently blow through the pipette as it passes through the upper layer so that none of this enters the pipette. Titrate the acid in each sample with the sodium hydroxide solution, using phenolphthalein indicator.

From the titters, calculate the weight per cent of acetic acid in each layer. This fixes the positions on the isotherm of the ends of the tie-lines, since it is known which layers are chloroform-rich and which water-rich. Indicate the ends (X', X" and Y', Y"), and join them by straight lines.

Density of water: 0.9947 g/cc at 30°C
Density of acetic acid: 1.1491 g/cc at 30°C
Density of chloroform: 1.4892 g/cc at 30°C

Repeat the complete experiment and plot two curves in one graph paper to show the reproducibility.
Experiment No. 4 (a)

Spectrophotometric determination of the acid dissociation constant of methyl red

Theory:
In aqueous solution methyl red is a zwitterion and has a resonance structure between the two extreme forms shown in the following figure:

![Resonance structure of methyl red](image)

The protonated red form (HMR) of methyl red exists in acid solutions. When base is added, a proton is lost and the yellow anion (MR\(^-\)) is formed. The basic deprotonated form is yellow and it absorbs blue and violet light. The acid dissociation constant, \(K_a\), for methyl red is:

\[
K_a = \frac{[H^+] [MR^-]}{[HMR]} \quad (1)
\]

or,

\[
pK_a = pH - \log \frac{[MR^-]}{[HMR]} \quad (2)
\]

The acid dissociation constant may be calculated from measurements of the ratio \([MR^-]/[HMR]\) at known pH values. Since both these species absorb strongly in the visible region, \([MR^-]/[HMR]\) ratio may be determined spectrophotometrically. The wavelengths where the two species have maximum absorbances, \(\lambda_1\) and \(\lambda_2\), are determined. The absorbance of a series of concentrations of HMR and MR\(^-\) are measured at these wavelengths to determine if Beer-Lambert law is obeyed.

Beer-Lambert law states that at the given \(\lambda\),

\[
A = \varepsilon c l \quad (3)
\]

where \(\varepsilon\) = molar extinction coefficient of absorbing solute (\(\varepsilon\) depends on \(\lambda\)), \(l\) = length of light path in cell = 1 cm, \(c\) = concentration of absorbing solute.

If Beer’s law holds, absorbances of a mixture of HMR and MR\(^-\) is represented by:

\[
A_{\lambda_1} = \varepsilon_{a1} l [HMR] + \varepsilon_{b1} l [MR^-] \quad (4)
\]

\[
A_{\lambda_2} = \varepsilon_{a2} l [HMR] + \varepsilon_{b2} l [MR^-] \quad (5)
\]
Thus from absorbancy measurements at two different wavelengths, the concentrations of both HMR and MR$^-$ can be calculated.

Equipment and solutions
1. Spectrophotometer
2. pH meter
3. Stock solutions of 0.01 g methyl red in 100 ml 95% C$_2$H$_5$OH.
4. 95% C$_2$H$_5$OH(ethanol), 0.1 M HCl, 0.1 M NaAc, 0.01 M and 0.1 M HAc.
5. 5, 10 ml, 25 ml pipettes.
7. 100 ml volumetric flasks.

Experimental procedure

1. Preparation of acid solution:
   
   10 ml of the methyl red solution is taken, then 10 ml of 0.1 M HCl is added and the solution is diluted down to 100 ml with distilled water in a volumetric flask.

2. Preparation of basic solution:
   
   10 ml of the methyl red solution is taken, 10 ml of 0.1 M NaAc is added and the solution is diluted down to 100 ml with distilled water in a volumetric flask.

   Absorbance of each of these solutions (2) and (3) is measured between 350 nm – 650 nm. Then, plots of absorbance versus wavelength are prepared for the acid and base solutions. Two maximum absorbance wavelengths $\lambda_1$, $\lambda_2$ are chosen. At one of these the acidic form HMR has the largest absorbance and at the other, basic form MR$^-$ has the largest absorbance compared with the rest.

3. Application of Beer-Lamber law:

   Take absorbance at the chosen $\lambda_1$ and $\lambda_2$ for the acidic and basic solutions by running dilutions of 1/2, 1/4, and 1/8 for both the acid and basic solutions. Serial dilutions are strongly encouraged. Absorbance versus concentration values should then be plotted for both of the acid and basic forms of methyl red. Whether Beer’s law is applicable or not should be stated.

Note: Do not use water for dilutions. 0.01 M HCl solution should be used to dilute the acid solutions and 0.01 M NaAc solution should be used to dilute the base solutions.

4. Determination of the pKa:

Prepare the following solutions by mixing NaAc and HAc solutions.

1. 4.5 ml 0.1 M NaAc + 11 ml 0.1 M HAc + 10 ml stock MR $\rightarrow$ total 100 ml with water
2. 4.5 ml 0.1 M NaAc + 6.7 ml 0.1 M HAc + 10 ml stock MR $\rightarrow$ total 100 ml with water
3. 4.5 ml 0.1 M NaAc + 31.5 ml 0.01 M HAc + 10 ml stock MR $\rightarrow$ total 100 ml with water
4. 4.5 ml 0.1 M NaAc + 13.5 ml 0.01 M HAc + 10 ml stock MR $\rightarrow$ total 100 ml with water
5. 4.5 ml 0.1 M NaAc + 4.5 ml 0.01 M HAc + 10 ml stock MR $\rightarrow$ total 100 ml with water
Measure the absorbances of each of these solutions at $\lambda_1$, $\lambda_2$ and the pH values also, by using a pH-meter.

Calculations

By using Beer-Lambert Law ($A = \varepsilon cl$), determine the values of $\varepsilon l$ as a constant at the selected $\lambda_1$ and $\lambda_2$ for the acidic and basic forms of methyl red. Then apply the equations

$$A_{\lambda_1} = \varepsilon_{a1} l [HMR] + \varepsilon_{b1} l [MR^{-}]$$
$$A_{\lambda_2} = \varepsilon_{a2} l [HMR] + \varepsilon_{b2} l [MR^{-}]$$

in order to calculate $[HMR]$ and $[MR^{-}]$ values for each of the buffer solutions.

Finally calculate $pK_a = pH - \log \left( \frac{[MR^{-}]}{[HMR]} \right)$ for methyl red and take the average of the five calculated pKa values to report the acid dissociation constant of Methyl Red.
Experiment No. 4(b)

Formula and stability constant of a complex by spectrophotometry:
Ferric salicylate

Theory:
When a solution containing ferric ions is mixed with a solution of salicylic acid, a violet-coloured complex is formed. Since it is the anion of salicylic acid which complexes with the ferric ion, the apparent value of the stability constant of the complex varies with pH. This experiment will be carried out at a pH of 2.5. Under this condition, the phenolic –OH group is undissociated. Evidence for the existence of only one complex species in solution is gained from the presence of an isobestic point.

The equilibrium for the formation of a ferric salicylate complex, in the absence of any other species, may be written as

$$Fe^{3+} + n[Sal^-] \leftrightarrow Fe^{3+}(Sal^-)^n$$  \hspace{1cm} (1)

The stability constant $K$ is defined as

$$K = \frac{[Complex]}{[Fe^{3+}][Sal^-]^n}$$  \hspace{1cm} (2)

Where, $[Fe^{3+}]$ and $[Sal^-]$ refer to the concentration of the free species.

The optical absorbance of the complex “A” is given by the Beer-Lambert Law

$$A = \log \frac{I_0}{I} = \varepsilon [Complex] l$$  \hspace{1cm} (3)

Where, $\varepsilon$ is the extinction coefficient of the complex, and $l$ is the path length.

The empirical formula of the complex may be found by Job’s method, which applies to two reactants that combine to form a complex. Equimolar solutions are made up, and then mixed in volume ratios 1:9, 2:8, ..., 8:2, 9:1. The total reagent concentration is therefore the same in each case. The maximum amount of equilibrium product will be formed when the proportions of reactants employed correspond to the empirical formula of the product. In practice the maximum absorbance of each solution due to the complex is plotted against the mole fraction of one component to give a Job plot. The maximum of this curve then indicates the empirical formula of the complex. In present case we expect the maximum to occur for the 5:5 mixture, confirming the 1:1 formula Fe$^{3+}$(Sal$^-$).

To determine the stability constant, one needs to find the concentration of the complex by means of equation 2. Since $A$ and $l$ can be measured, one have to find out $\varepsilon$.

Let $x$ be the concentration of Fe$^{3+}$ added to the solution, and let $y$ be the concentration of salicylic acid added. Then for any mixture
K = \frac{|\text{Complex}|}{[\text{Fe}^{3+}][\text{Sal}^-]} = \frac{|\text{Complex}|}{|x-|\text{Complex}||y-|\text{Complex}||} = \frac{A\epsilon l}{|x-A\epsilon l||y-A\epsilon l|} \quad (4)

Rearranging,

\frac{xy}{A} = \frac{1}{\epsilon l} \left[ \frac{1}{K^{+}(|x+y|)} - \frac{A}{(\epsilon l)^2} \right] \quad (5)

The total concentration (x+y) is constant. It follows that a graph of \( \frac{xy}{A} \) vs A should be linear and the slope will yield \( \epsilon \). The intercept the value of K can be determined.

Procedure:

Prepare 2.5 mM Fe\(^{3+}\) (by Ferric Ammonium Sulphate) and 2.5 mM salicylic acid in M/500 hydrochloric acid. Make up 9 different solution with the volume ratio of 1ml : 9 ml , 2ml :8ml, ...., 8ml:2ml, 9ml:1ml. Make up the volume to 50 ml using M/500 hydrochloric acid. Obtain the spectra of pure ferric, salicylic acid and the mixtures.

Calculation:

Verify the empirical formula of the complex by Job’s method.
Find the extinction coefficient of the complex and its stability constant.
Experiment No. 5

The measurement of electrical conductance for the determination of the equivalent conductance at infinite dilution and the dissociation constant of acetic acid

Theory:

Materials are usually classified as conductors, semiconductors or insulators in terms of their behavior toward the flow of current. Conductors have very little resistance to the passage of current. Ohm’s law states that,

\[ V = i R \]

(1)

where \( V \) is the potential in volts, \( i \) is the current in amperes and \( R \) is the resistance in ohms.

The resistance depends upon the nature and geometry of the conductor.

\[ R = \rho \frac{l}{A} \]

(2)

where \( l \) is the distance, \( A \) is the are and \( \rho \) is the specific resistance.

It is more convenient to focus attention on the conductance, \( L \), rater than on the resistance, \( R \). The relationship is

\[ R = \frac{1}{L} \]

(3)

where \( L \) is conductance and is expressed in mhos or ohms\(^{-1}\). In terms of conductance equation 2 is written as

\[ L = \kappa \frac{A}{l} \]

(4)

where \( \kappa \) is the specific conductance, i.e. the conductance of a tube of material 1 cm long having a cross section of 1 cm\(^2\). The unit of \( \kappa \) is mho cm\(^{-1}\).

The equivalent conductance (\( \Lambda \): cm\(^2\) Ohm\(^{-1}\) mole\(^{-1}\)) is defined as the conductance of a solution containing 1 gm-equivalent of electrolyte such that the entire solution is placed between two electrodes 1 cm apart. The specific conductance of an electrolyte solution depends upon the equivalent and is related to the specific conductivity as

\[ \Lambda = \frac{\kappa}{c} \]

(5)

where \( c \) is the electrolyte concentration (moles cm\(^{-3}\))

The equivalent conductance of an electrolyte can be measured by using a conductivity cell. For any particular conductivity cell the ratio \( l/A \) is a constant known as the cell constant, \( X \).

From equation (4)

\[ \kappa = L \frac{l}{A} = L X \]

(6)

Generally it is very difficult to make one conductivity cell having exactly the electrode surface area of 1 cm\(^2\) and 1 cm apart. The cell which is to be used is filled
with a standard solution, whose specific conductance is known, and by measuring the conductance cell constant is determined.

The equation 5 can be re-written as

\[ \Lambda = \frac{L}{X} c \]  

(7)

Strong electrolytes such as potassium chloride dissociate fully into ions when dissolved in water. At low concentration, the molar conductivity obey an expression of the type

\[ \Lambda = \Lambda_0 - A' \sqrt{c} \]  

(8)

where \( \Lambda_0 \) is the equivalent conductance at infinite dilution and \( A' \) is a constant for the system. By using equation 8 one can determine \( \Lambda_0 \) for a strong electrolyte from measurement of \( \Lambda \) at a series of concentrations.

Kholrausch proposed that when complete dissociation exists in infinite dilution, each ionic species migrates independently. The \( \Lambda_0 \) value can be then considered to be the sum of equivalent ionic conductances at infinite dilution

\[ \Lambda_0 = \lambda_0^+ + \lambda_0^- \]  

(9)

Kholrausch additivity law can be used to obtain \( \Lambda_0 \) for a weak electrolyte as

\[ \Lambda_0^{CH_3COOH} = \lambda_0^+ + \lambda_0^- = \Lambda_0^{HCl} + \Lambda_0^{CH_3COONa} - \Lambda_0^{NaCl} \]  

(10)

For weak electrolyte the degree of dissociation (\( \alpha \)) can be written as

\[ \alpha = \frac{\Lambda}{\Lambda_0} \]  

(11)

and dissociation constant can be written as

\[ K_d = \frac{ca^2}{1-\alpha} \]  

(12)

Apparatus and materials:

Dip type conductance cell, conductivity bridge, thermostat at 25.0 ± 0.1°C; two 250-ml and three 100-ml measuring flasks; 50-ml pipette; 250-ml beaker; 3-in. filter funnel; weighing bottle; glass stirring rod; connecting wire and connectors.

Specific to part A: two 100 ml measuring flasks, 25 ml pipette.

Specific to Part B: 250 ml measuring flask, 20 ml pipette, 50 ml burette and stand, three 250 ml conical flasks.

Procedure:

Preparation of Solutions:

Weigh accurately 0.2 or 0.3 g of potassium chloride, dissolve in water and make up to 250 ml. This solution will be referred to as the calibrating solution. (Make the solution of concentration whose specific conductance is known to you.)

Specific to Part A. By weighing sodium chloride, prepare standard solutions (250 ml) having concentrations of about 0.06M and 0.0077M. By means of the 50 ml and 25 ml pipettes, and 100 ml measuring flasks, accurately dilute each of these solutions by factors of two- and four-fold. Similarly, dilute the least concentrated of the resulting...
solutions two-fold. Retain a sample of the water used in the preparation of these solutions for subsequent conductance measurements. Do similar for sodium acetate and HCl.

Specific to Part B. Prepare 250 ml of approximately 0.1 M Acetic acid solution by dilution of the 2M acid. By means of 20-ml and 50-ml pipettes, and 100-ml measuring flasks, accurately dilute the solution two-and five-fold. Further, accurately dilute the least concentrated of the resulting solutions two-fold to give 100 ml of approximately 0.01 M Acetic acid solution.

Prepare 250 ml of approximately 0.1 M sodium hydroxide solution and standardize with weighed portions of oxalic acid, using Phenolphthalein indicator. Standardize the 0.1M acetic acid solution with the sodium hydroxide solution.

Determination of the cell constant:-

Rinse the clean cell and electrodes twice with the calibrating potassium chloride solution. Then pour sufficient of the potassium chloride solution into the cell to fill the electrode chamber completely.

Treatment of results
The cell constant
From the known concentration of the calibrating potassium chloride solution, calculate the cell constant.

Values of equivalent conductance
Calculate the concentration of each solution for which conductivity measurements were made.

Specific to Part A.
Plot a graph of $\Lambda$ vs the dilution (V, i.e. the volume of solution containing one equivalent). From this graph, estimate the value of the equivalent conductance at infinite dilution estimate the value of the equivalent conductance at infinite dilution ($\Lambda_0$).

Plot a graph of $\Lambda$ vs $\sqrt{c}$ and extrapolate to $c = 0$ to obtain a second value for $\Lambda_0$.

Specific to Part B
For each solution of acetic acid studied, calculate a value of the degree of dissociation ($\alpha$) and of the dissociation constant ($K_d$).
Experiment No. 6(a)

Fluorescence quantum yield determination of an unknown molecule

Theory:

The quantum yield of a given reaction is given as the ratio of the number of molecule decompose to the number of photons absorbed by the sample:

\[ f = \frac{\text{No. of molecule decompose}}{\text{No. of photon absorbed}} = \frac{\text{Rate of decompose}}{\text{Rate of absorption}} \]  

(1)

For fluorescence quantum yield, the rate of decomposition is the that which involves emission of photons.

The quantum yield \( \phi \) can also be described by the relative rates of the radiative and non-radiative pathways, which deactivate the excited state as

\[ f = \frac{k_R}{k_R + k_{NR}} \]  

(2)

where \( k_r \) and \( k_{nr} \) correspond to radiative and non-radiative processes, respectively. In this equation, \( k_{nr} \) describes the sum of the rate constants for the various processes that compete with the emission process. These processes include photochemical, and dissociative processes including other, less well characterized changes that result in a return to the ground state with simultaneous dissipation of the energy of the excited state into heat. These latter processes are collectively called non-radiative transitions and two types have been clearly recognized: intersystem crossing and internal conversion. Intersystem crossing related to the radiationless spin inversion of a singlet state (S1) in the excited state into a triplet state (T1).

It is easier to determine the “relative” quantum yield of a fluorophore by comparing it to a standard with a known quantum yield.

If fluorescence quantum yield of the sample is \( f_f^s \) with fluorescence intensity \( = I_f^s \) and absorption intensity \( = I_a^s \), we can write

\[ f_f^s = \frac{I_f}{I_a} \]  

(3)

similarly, for the reference
\[ f'_f = \frac{I'_f}{I'_0} \quad (4) \]

\[ \frac{f'_s}{f'_f} = \frac{I'_s}{I'_a} \frac{I'_r}{I'_a} \quad (5) \]

\( I_f \) is a directly measurable quantity, however, \( I_a \) is not.

\[ I_a = I_0 - I \quad (6) \]

\[ 1 - \frac{I_a}{I_0} = e^{-2.303 \cdot A} = 1 - 2.303 \cdot A; \text{ when } A \text{ is small} \quad (7) \]

\[ a = 2.303 \cdot A \cdot I_0 \text{ or } I_a \mu A \quad (8) \]

So, we can write

\[ f'_s = f'_f \left( \frac{I'_s}{I'_r} \right) \left( \frac{A'_r}{A'_s} \right) \quad (9) \]

Fluorescence quantum yield standard

- Quinine sulfate in 0.1 M sulphuric acid = 0.577
- Rhodamine 6G in ethanol = 0.940

Procedure

Your task is to record the absorption and emission spectrum of the given unknown compound in specified solvent along with the fluorescence quantum yield reference material and calculate the relative quantum yield of the unknown compound.
Experiment No. 6(b)

**Fluorescence spectrum and stern-volmer quenching constant**

Theory:

Electronically excited molecule dispose their excess energy in various ways: they may lose energy by emitting photon or pass energy to other molecules through collision, may undergo reaction, change oxidation state and so on. When a photon is emitted by an excited singlet state, the process, known as fluorescence, is generally rapid.

The molecular potential energy curve of the singlet ground state $S_0$ and of an excited state $S_1$ of a typical organic molecule in solution are shown in the diagram. Since the excitation of an electron in a large molecule has little effect on the nuclear framework, the potential energy curves of the $S_0$ and $S_1$ states are usually similar, as are the spacings of their vibrational levels.

The energy gaps between vibrational levels are quite large, so at room temperature most molecules are in the vibrational ground state, $v = 0$. The absorption spectrum thus arises from transitions from this state to different vibrational levels $v^e$ of the $S_1$ state. Collisions with solvent rapidly remove excess vibrational energy from the molecules, bringing them down to the lowest vibrational level, $v^e = 0$. Frequently, electronic energy is also lost through radiationless processes, but fluorescent molecules may emit a photon, and in this way return to one of the vibrational levels in the ground state. For most molecules in solution, the fluorescence spectrum is independent of the wavelength of the exciting light.

The excited molecule is denoted by $A^*$ and can now do one of several things.

- It can emit a photon and in the process get converted back to the ground state. This process is a first-order rate process with a rate constant denoted by $k_f$.
  \[ A^* \rightarrow A + \nu \]

- A second possibility is for the excited molecule to lose its energy in the form of heat rather than light. This is known as nonradiative process with a rate constant denoted by $k_{nr}$.
The quantum yield of fluorescence, $\Phi_0$, can be written as

$$\Phi_0 = \frac{k_f}{k_f + k_{nr}}$$  \hspace{1cm} (1)

Now, let add some other molecule, Q, in the system, which interact with the excited molecule. Then there will be a additional decay rate of the excited molecule, with rate constant $k_q$, which also depends on the concentration of the other molecule, Q.

$$A^* + Q \rightarrow A + Q'$$

For this system, we can write fluorescence quantum yield as

$$\Phi = \frac{k_f}{k_f + k_{nr} + k_q |Q|}$$  \hspace{1cm} (2)

Thus,

$$\frac{\Phi_0}{\Phi} = 1 + \frac{k_q}{k_f + k_{nr}} |Q|$$  \hspace{1cm} (3)

The relative quantum yield in this expression can be replaced by the relative fluorescence intensity $\frac{I_0}{I}$, which can be easily measured.

In order to determine the quenching rate constant $k_q$, the $k_f + k_{nr}$ must be determine. The lifetime of the molecule in the absence of quencher, $\tau_0$, can be written as

$$\tau_0 = \frac{1}{k_f + k_{nr}}$$  \hspace{1cm} (4)

Thus we can rewrite the equation 3 as

$$\frac{I_0}{I} = 1 + k_q \tau_0 |Q|$$  \hspace{1cm} (5)

Thus by plotting $\frac{I_0}{I}$ vs $|Q|$ one can determine the quenching rate constant, $k_q$, when $\tau_0$ is known.

In this experiment we will first measure the absorption and fluorescence spectrum of anthracene molecule then we will measure the rate constant of fluorescence quenching of anthracene by CCl$_4$ in ethanol.

**Equipment and supplies**

Spectrofluorimeter, Fluorescence cuvette, 7 x 25 ml volumetric flasks, 1 x 50 ml volumetric (for anthracene stock solution), 2 x 100 ml volumetric (for anthracene and CCl$_4$ stock solutions), pipets: 2, 3, 5, 10, 15 ml, anthracene, CCl$_4$, Ethanol

**Procedure**

Excitation and emission spectra of anthracene

Your first task is to record the absorption spectrum of anthracene in ethanol. Choose the wavelength corresponding to the maximum absorption. It is important that the absorbance of the solution is not more than about 0.2. The concentration anthracene should be 10 μM. Since the concentration of anthracene is so small, the stock solution should be made up in two steps. For example, first make a 5.0 x 10$^{-4}$ M
solution of anthracene by diluting about 9 mg of anthracene to the mark with ethanol in a 100 ml volumetric flask. Now dilute this by 5 by transferring 10 ml of this solution to a 50 ml volumetric and diluting to the mark, giving a 10 µM stock solution. Then measure the emission spectrum by exciting the anthracene molecule in that chosen wavelength. The emission spectrum shows the intensity of light emitted as a function of the emission wavelength, for a selected excitation wavelength.

Fluorescence quenching

Prepare 6 different solution of anthracene of the above mentioned concentration with 0.2 M, 0.4 M, 0.8 M, 1.2 M, 1.6 M, 2.0 M CCl₄ in ethanol. It is important to keep these solutions out of bright light so that the fluorescence intensity measurements take place before any of the fluorescing molecule disappears through the photochemical reaction. Make sure to rinse the fluorescence cuvette several times with the new solution before taking its spectrum.

Determine the rate constant of fluorescence quenching using equation 5. Given, the lifetime of anthracene in ethanol is 5 ns.
Experiment No. 7(a)

Rate of the hydrolysis of sucrose using polarimeter

Theory:
In this experiment you will determine the pseudo first order rate constant governing the acid catalyzed hydrolysis of sucrose to glucose and fructose:

Thus the rate of change at any time is proportional to the concentration of sucrose. If the initial concentration is \( a \), at time \( t \) the sucrose concentration will be \( a - x \) (\( x \) being the amount of sucrose hydrolyzed) and the rate of the reaction will be

\[
\frac{dx}{dt} = -k(a-x) \quad ; \quad k \text{ is the rate constant}
\]

Integration of equation 1 yields

\[
\int_0^x \frac{dx}{a-x} = \int_0^t k \, dt \quad ; \quad \text{or} \quad \ln \frac{a}{a-x} = kt
\]

therefore,

\[
k = \frac{1}{t} \ln \frac{a}{a-x}
\]

A linearly polarized light can be visualized as the result of two circular rotations, right (dextrorotation; designated as \( d \)) and left (levorotation; designated as \( l \)). An optically active substance can be considered a medium that has different refractive indices in the different directions. When linearly polarized light passes through an optically active medium, the planar projection of the two circular components reaches a phase difference (as velocity of one component became greater than the other). The recombination of these components causes a linear polarized light that is not in the same direction as the original one, but is rotated at a certain angle.

The optical rotation of the polarimeter, \( \alpha \), in degrees is given by

\[
\alpha = \frac{Lc\vert\alpha\vert_D}{100}
\]

\( L \) is the path length of the light through the solution in decimeters, \( c \) is the concentration of the solute in grams per 100 ml in solution, and \( \vert\alpha\vert_D \) is the specific rotation of solute (for sucrose \( \vert\alpha\vert_D = +66.48^\circ \text{ ml} / (\text{dm g}) \) at \( t = 25.0^\circ \text{C} \), using the Na "D" line (an unresolved doublet at 589.0 nm and 589.6 nm) as a light source).
The sucrose is dextrorotatory, but the resulting mixture of glucose and fructose is levorotatory because the levorotatory fructose has a greater molecular rotation than the dextrorotatory glucose. As the sucrose is used up and the hydrolysis products are formed, the angle of rotation to the right becomes less and less, and finally the light rotated to the left. The reaction proceeds too slowly to be measured in pure water, but it is catalysed by hydrogen ion.

Let, specific rotation of

Sucrose = $S$
Glucose = $G$
Fructose = $F$

If there are ‘$a$’ moles of sucrose initially present in solution, and after time ‘$t$’, ‘$x$’ mole have been hydrolyzed to give ‘$x$’ moles of each glucose and fructose, then,

Optical rotation at $t = 0$ \[ \alpha_0 = \frac{L a S}{100} + \frac{L 0 G}{100} + \frac{L 0 F}{100} = \frac{L a S}{100} + 0 + 0 \] (5)

Optical rotation at $t = t$ \[ \alpha_t = \frac{L (a-x) S}{100} + \frac{L x G}{100} + \frac{L x F}{100} \] (6)

Optical rotation at $t = \infty$ \[ \alpha_\infty = \frac{L 0 S}{100} + \frac{L a G}{100} + \frac{L a F}{100} = 0 + \frac{L a G}{100} + \frac{L a F}{100} \] (7)

Therefore,

\[ \alpha_t - \alpha_\infty = \frac{L S}{100} (a-x) + \frac{L G}{100} (x-a) + \frac{L F}{100} (x-a) \] \[ = (a-x) \frac{L}{100} (S-G-F) \] \[ = a \frac{L}{100} (S-G-F) \] (8)

Dividing equation (9) by equation (8), we have

\[ \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty} = \frac{a}{a-x} \] (10)

Substituting the value of $\frac{a}{a-x}$ in equation 3, we have,

\[ k = \frac{1}{t} \ln \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty} \quad \text{or} \quad \ln \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty} = kt \] (11)

Therefore, a plot of $\ln \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty}$ vs $t$ should give a straight line passing through the origin with a slope (= $k$).

Equipment and Supplies

Hydrochloric acid (2 and 4 Molar), Sucrose, Sodium lamp, Polarimeter, Polarimeter tube, Volumetric flasks (100 mL), Graduated cylinders (25 mL), deionized water.
Procedure:

1. The sodium lamp should be turned on at the beginning of the lab and positioned on the lab bench. The lamp takes 20-30 minutes to warm up, so this should be done first.

2. Dissolve 20 g of pure cane sugar in distilled water and make up to 100 ml

3. Quantitatively prepare at least 100 ml of a 2.00 M/4.00 M HCl solution (dilute concentrated HCl to ~ 4 M and then standardize this solution against standard base to a phenolphthalein endpoint)

4. Disassemble the polarimeter tube, clean the windows (be careful not to break them), and reassemble the polarimeter tube filled with distilled water. When filling the polarimeter tube you should make sure that there are no air bubbles in the tube and that the tube does not leak, as either of these problems can degrade the optical path through the tube. In this regard it is especially important that the polarimeter tube be thoroughly rinsed with the solution that is to be filled with.

5. Adjust the polarimeter so that it indicates zero rotation with the water filled polarimeter tube in it (use of the polarimeter will be demonstrated by the instructor).

6. Measure optical rotation of 10% sucrose solution by diluting the 20% sucrose.

7. Estimate the specific rotation of sucrose.

8. Empty the polarimeter tube and thoroughly wash it out with distilled water.

9. Pipette 25.00 ml of sucrose solution into a 100-150 ml beaker. Now pipet (use a different pipet) 25.00 ml of the 2N HCl solution into the beaker containing the sucrose solution. (In another experiment use 4N HCl).

10. Carefully, but quickly (since the rate of change of optical rotation with time will greatest early in the reaction, rinse and then fill the polarimeter tube with this reaction mixture (again insuring that there are no bubbles or leaks), place the tube in the polarimeter, and take a reading of the degree of optical rotation by the solution.

11. Initially take readings every 5 minutes. As the reaction slows down you can take reading less frequently. Continue to take readings until the degree of optical rotation has fallen to about -5°.

12. Determine the rate constant for the reaction when 2N and 4N HCl is used for the preparation of the reaction mixture.

Precautions:
1. Polarimeter tube must be rinsed before the experiment with the experimental solution.
2. Any air bubbles must be removed from the tube.
3. Weighing and dilution must be done correctly.
4. Polarimeter eye-piece must be properly focused before using.
5. Make sure that the sodium lamp has been turn on about 15 mins before taking any reading.
**Experiment No. 7(b)**

**Polarizability from refractive index measurements**

Theory:

When a molecule is placed in an electrical field between two condenser plates, the applied electrical field is reduced. The reason is that the field polarizes the molecule in such a fashion that the positive end of the molecule aligns itself with the negative plate and vice versa. This total polarization of the molecule can be measured by the dielectric constant, which is the ratio of the capacitances of the dielectric compound in question to that of vacuum at the same geometric setting of the condenser.

\[
\frac{C}{C_0} = \varepsilon
\]

The total molar polarization of the compound is given by equation 2.

\[
P_T = P_I + P_P = \frac{4\pi N \alpha}{3} + \frac{4\pi N \mu^2}{9 kT} = \frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{\rho}
\]

where \(P_T\) is the total molar polarization; \(P_I\) is the induced molar polarization; \(P_P\) is the molar polarization due to the permanent dipole moment, \(\mu\); \(M\) is the molecule weight; and \(\rho\) is the density of the compound in question. The \(\alpha\) is the polarizability of the molecule (in cubic centimeters), which indicates how much distortion is induced by the field in the nuclear and electronic charge distribution. The \(N\) is Avogadro’s number, \(K\) is the Boltzmann constant and \(T\) is the absolute temperature.

When the refractive index \(n_0\), of a compound is measured in the visible region, the light can be considered a field of high frequency, and the Maxwell relationship holds.

\[
n_R^2 = \varepsilon_{\infty}
\]

where \(n_R\) is the refractive index measured and \(\varepsilon_{\infty}\) is the dielectric constant at high frequencies.

The atomic polarization, which can be measured in the infrared region, is difficult to determine experimentally. In the cases in which it has been measured, it was found to be 3 to 10 percent of the value of the electronic polarization, \(P_E\). Hence as a first approximation, to evaluate the polarizability of a molecule one can neglect the contribution of the atomic polarization and calculate \(\alpha\) from the following equation.

\[
P_E = \frac{4\pi N \alpha}{3} = \frac{n_R^2 - 1}{n_R^2 + 2} \frac{M}{\rho} = R
\]

The second part of this equality is called the Lorenz-Lorenz equation and \(R\) is the Lorenz-Lorenz molar refraction.

Since the refractive index is both temperature and frequency dependent, it is necessary to specify the experimental conditions. \(R_D^{20}\) refers to a molar refractivity with the sodium D line as the light source at 20°C. The molar refractivity is a characteristic of the molecular structure and it was long thought to be an additive property of its parts. However, the increments are dependent not only on the atoms but also on the types of chemical bonds between the atoms; hence the property is both additive and constitutive.
Upon mixing two liquids one would expect the additivity to be operative; hence

$$R_{\text{add}} = X_1 \frac{n_1^2 - 1}{n_1^2 + 2} \frac{M_1}{\rho_1} + \left| 1 - X_1 \right| \frac{n_2^2 - 1}{n_2^2 + 2} \frac{M_2}{\rho_2}$$  \hspace{1cm} (5)

The experimental molar refractivity has the following formula;

$$R_{\text{exp}} = \frac{n^2 - 1}{n^2 + 2} \left( X_1 \frac{M_1}{\rho} + \left| 1 - X_1 \right| \frac{M_2}{\rho} \right)$$  \hspace{1cm} (6)

In equations 5 and 6 the subscripts 1 and 2 refer to components 1 and 2 and the quantity without is the property of mixture measured. The $X_1$ is the mole fraction of compound 1.

The difference between the experimental and the predicted values demonstrates the deviation from additivity.

$$\Delta R = R_{\text{exp}} - R_{\text{add}}$$  \hspace{1cm} (7)

when $\Delta R$ exceeds 0.1 cc, one may assume that strong interaction forces between components 1 and 2 cause electronic deformations. Similarly, when the refractive indices of the mixtures vs. mole fraction or volume fraction are plotted, the data often fit straight lines. In cases of strong interaction between two components two straight lines are obtained and their intersection gives the molal ratio corresponding to the complex.

In using equation 4 in attempting to obtain a polarizability value, $\alpha$, for either of the pure liquid components or for a mixture, two important facts should be kept in mind. First, the induced polarization, hence the polarizability as obtained from refractivities, is in error because of the neglect of atomic polarization. Second, the single value of $\alpha$ obtainable from equation 4 represents merely an average of the polarizabilities in various directions.

Material and Equipment

Dimethyl sulfoxide (DMSO) (or Dimethyl formamide, Acetone, Dioxane, or other compound): thermostat with heater, thermoregulator, and stirrer; circulating pump; Refractometer; Thermometer; lens paper, Ethanol.

Experimental

The Abbe and Pulfrich type refractometers are the ones most commonly used. Both measure the critical angle of refraction relative to a glass prism. When a light passes from one isotropic medium to another (m $\rightarrow$ M) both its direction and its velocity will change unless it is normal to the boundary separating m from M. The relation between the angle of incidence; $\theta_m$, and angle of refraction, $\phi_M$, is given by Snell’s law.

$$n = \frac{\sin \theta_m}{\sin \phi_M} = \frac{V_m}{V_M}$$  \hspace{1cm} (8)

In this case n is the refractive index of M relative to m. Usually the reference substance, m, is air or, more properly, vacuum, which has a refractive index of 1.00. In measuring critical angles of refractions one must consider that a liquid sample, m, is resting on the surface of a prism, P, which has a greater refractive index than m. Rays entering medium m at different angles have corresponding angles of refraction according to Snell’s law (equation 8). If we follow different angles of incidence, $\theta_{m}$, from the normal to the glancing incidence, i, we find that the angle of refraction
increases. At the glancing incidence we obtain the critical angle of refraction, which is the last angle that lets light passed through the prism. Any higher angle of refraction will provide a dark field. They can be seen by following the reverse path of an angle of refraction that is higher than the critical angle. In practice, not one point but the whole prism surface is illuminated with the glancing incident light and a telescope collects all the refracted rays with the same φ into one line in the focal plane. Thus a sharp boundary is seen in the telescope between the dark field and the bright field illuminated by the monochromatic light source.

Make up ten different mixtures of Dimethyl sulfoxide (DMSO) and water (Dimethylformamide DMF and water, acetone and water, dioxin and water, and so on). The densities of these solutions are obtained as described in experiment 3. Be sure that the thermostat is stable at 25°C for at least five minutes before the first measurements are taken. Clean the surface of the prism with ethanol and wipe it with soft lens paper. Use lintless paper so as not to leave lint on the surface of the prism rinse it with water and wipe it with lens papers and wipe it with lens paper. Place about 0.5 ml water on the surface. Spread it evenly and clamps the two prisms together. If the prism surface is not completely covered with liquid no clear separation of dark and light field can be achieved. Allow one to two minutes for thermal equilibrium. Tilt the mirror or move the light source to give maximum illumination. Move the scale to 1. Looking through the telescope, adjust screw H to achromatize the boundary by rotating the compensator. The boundary is achromatized when it becomes sharp and divides the field into dark and light halves. Focus the eyepiece if necessary. Adjust the scale so that the boundary passes through the cross hair. Take a few readings by removing the boundary and bringing it back to the cross hair. Average the readings.

Repeat the procedure with the other samples, finally proceeding to pure DMSO.

Calculations:
Calculate $R_D^{20}$ for water and DMSO. Calculate $R_{\text{exp}}$ and $R_{\text{add}}$ from equations 5 and 6 for the different mixtures. Plot $R_{\text{exp}}$ and ΔR vs. mole fraction and also $n^2$ vs. mole fraction. Calculate the average polarizabilities and plot vs. mole fraction and volume fraction.
Experiment No. 8(a)

Determination of pKa of poly-basic acid with the pH meter

Theory:

The glass electrode functions in both oxidizing and reducing media and in the presence of protein and sulfur compounds, all of which interfere with the use of platinised-platinum. The glass electrode consists of a thin membrane of soft glass enclosing a dilute solution of KCl and CH₃COOH in which is immersed a platinum wire coated with AgCl. The variation of the potential of the glass electrode with hydrogen-ion concentration is the same as that of a hydrogen electrode. A saturated calomel electrode is used in conjunction with the glass electrode, so that the cell may be represented diagrammatically as follows:

$$\text{AgCl, KCl, CH}_3\text{COOH} || \text{unknown solution} || \text{KCl(sat):Hg}_2\text{Cl}_2\cdot\text{Hg}$$

The glass electrode potential changes 0.05916 volt/pH unit at 25°C and pH meter graduated directly in terms of pH. The standard pH buffer solutions are needed for standardization of glass electrode.

The pH of a mixture of a weak acid or base and its salt may be calculated with a reasonable degree of precision from the ordinary mass-action equilibrium formulation

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

where HA is weak acid \(1\)

Taking logarithm of this equation and rearranging, we obtain

$$pK_a = pH - \log\frac{[A^-]}{[HA]}$$

\(2\)

If the concentration of the acidic and basic forms of the buffer are equal, i.e. \([A^-] = [HA]\) then, \(pH = pK_a\). This fact may be used to determine ionization constants weak acids and bases.

The titration of a polybasic acid such as phosphoric acid, using a pH meter, may used to evaluate the ionization constants. The successive ionization of phosphoric acid can be represented as follows:-

$$\text{H}_3\text{PO}_4 \leftrightarrow \text{H}_2\text{PO}_4^- + \text{H}^+; \ K_{a1} = \frac{[H^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$$ \(3\)

$$\text{H}_2\text{PO}_4^- \leftrightarrow \text{HPO}_4^{2-} + \text{H}^+; \ K_{a2} = \frac{[H^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$ \(4\)

$$\text{HPO}_4^{2-} \leftrightarrow \text{PO}_4^{3-} + \text{H}^+; \ K_{a3} = \frac{[H^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}$$ \(5\)
The third dissociation takes place at such a high pH that it can not be studied in dilute solutions. The first two end points can be recognized by large change in pH for a small addition of base.

The pH, at which the second acid group is half neutralized, the hydrogen-ion concentration is equal to the equilibrium constant $K_{a2}$.

Apparatus and materials

Apparatus:
pH meter with electrode, 50ml burette and stand, 150ml clean beakers.

Material:
0.1M Phosphoric acid, 0.5M NaOH, standard buffer solutions

Preparation of standard buffer solution:

<table>
<thead>
<tr>
<th>Buffer solution</th>
<th>pH at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05M Potassium hydrogen phthalate</td>
<td>4</td>
</tr>
<tr>
<td>38 ml of M/15 KH$_2$PO$_4$ + 62ml OF M/15 Na$_2$HPO$_4$</td>
<td>7</td>
</tr>
<tr>
<td>0.1M of Borax solution</td>
<td>9.2</td>
</tr>
</tbody>
</table>

Titration of phosphoric acid

Procedure:
Switch on the pH meter; bring it to the pH mode. Calibrate with the supplied buffer solutions.

Experiment:
50 ml of 0.1M H$_3$PO$_4$ is titrated with 0.5N NaOH. The pH is measured after each addition of 0.2 ml of the base at the initial stage, then 0.1 ml near to the end point.

Calculation:
The pH of the solution is plotted versus volume of sodium hydroxide added and the acid dissociation constants are calculated.
Determinación de la transportación de número por el método de la frontera móvil

Teoría:

En presencia de un gradiente potencial, la corriente se transporta por la migración de iones, los iones positivos se mueven hacia el catodo y los iones negativos se mueven hacia el ánodo. La carga total liberada en el catodo y el ánodo son iguales pero la fracción del total de la corriente llevada por los cationes y aniones a través de la solución no es necesariamente igual. La fracción de la corriente llevada por cada iones migrante se llama el número de transporte de ese iones. La fracción de la corriente llevada por los cationes y aniones se representan por \( t_+ \) y \( t_- \).

Podemos escribir,

\[
\begin{align*}
    t_+ &= \frac{I_+}{I} = \frac{u}{u+v} \quad (1) \\
    t_- &= \frac{I_-}{I} = \frac{v}{u+v} \quad (2)
\end{align*}
\]

Donde, \( u \) y \( v \) son las velocidades de cation y anion respectivamente.

En este experimento, el método de la frontera móvil se utiliza para estudiar una solución acuosa de HC1. Aunque es más limitado en aplicabilidad, este método tiene la gran ventaja de proporcionar una precisión excelente y una indicación visual directa del movimiento de un iones especie en la solución.

Declarar el número de transporte de \( \text{H}^+ \) y \( \text{Cl}^- \) iones en una solución acuosa de HC1 se denota por \( t_{\text{H}^+} \) y \( t_{\text{Cl}^-} \) respectivamente. Considere un tubo vertical de sección uniforme, con corriente eléctrica fluviando hacia arriba. Para cada \( N \) faradays de electricidad que pasan por un plano horizontal estacionario en el tubo, \( N t_{\text{H}^+} \) equivalentes de \( \text{H}^+ \) pasan por el plano avanzando hacia arriba y \( N t_{\text{Cl}^-} \) equivalentes de \( \text{Cl}^- \) pasan el plano avanzando hacia abajo. Si hubo en el tubo una definida línea inferior por debajo de la que los iones eran ausentes (otro cation presente en su lugar), esta línea se movería hacia arriba como los \( \text{H}^+ \) iones se mueven hacia arriba. La posición de la línea puede ser determinada como la posición en la que hay una diferencia en alguna propiedad de la solución, como el pH (mostrado previamente por una indicación adicionada a la solución HC1) o índice de refracción. Bajo condiciones apropiadas la línea permanece afilada; la composición de la solución por encima de la línea es uniforme, y la velocidad media de migración hacia arriba de los \( \text{H}^+ \) iones pueden ser tomados como igual a la velocidad observada hacia arriba de la línea.

Cuando la línea avanza a través de un volumen \( V \) en un tiempo \( t \), un número de equivalentes de \( \text{H}^+ \) ion igual al número contenido en ese volumen avanza a través de un plano horizontal fijo durante ese tiempo. Si la corriente eléctrica total fluviando hacia arriba a través del tubo tiene el valor constante de 1 amp durante este tiempo, este número de \( \text{H}^+ \) iones es igual a \( \frac{1000}{F} t_{\text{H}^+} \). Por lo tanto

\[
\frac{VC_{\text{H}^+}}{1000} = \frac{it_{\text{H}^+}}{F} \quad \text{or}, \quad t_{\text{H}^+} = \frac{FC_{\text{H}^+}}{1000} \frac{dV}{dt} \quad (3)
\]

Donde \( C_{\text{H}^+} \) es la concentración de \( \text{H}^+ \) iones en equivalentes por litro, \( V \) es el volumen en mililitros avanzado a través de la línea por el tiempo en \( t \) segundos, y \( F \) es el constante de Faraday.
The transference number of the chloride ion can be determined from the relation $t_{H^+} + t_{Cl^-} = 1$.

Experimental

The transference cell, is constructed from a 1-ml Mohr capillary pipette, with a reservoir at the top and a metallic cadmium electrode which can be inserted at the bottom. The cell is surrounded by a jacket in which water should be placed to absorb the heat generated by the passage of electric current through the cell and thus prevent a significant rise in the temperature of the solution. The temperature of the jacket water should be checked occasionally during the run. Into the reservoir at the top is introduced an Ag-AgCl electrode, made by anodizing a silver wire in HCl solution. This is surrounded around the sides and bottom by a glass cup, which serves the dual purpose of preventing AgCl particles from falling down into the capillary and of retarding the more concentrated HC1 solution (accumulating by Hittorf transference at that electrode) from convectively mixing with the solution in the capillary.

Procedure:

Do not connect the standard cell or plug into the DC mains until an instructor has checked your circuit. The switch on the DC control box should be off, and the 100K rheostat should be set at maximum resistance. Prepare the solution by pipetting 5.0 ml of Bromophenol blue indicator solution into a 100 ml volumetric flask. Make up to the mark with 0.3N HCl. Note the exact concentration of stock HC1 solution, and calculate the concentration of $H^+$ in your solution. This solution will be yellow in color.

Remove the cadmium electrode from the bottom of the cell, clean the cell with detergent if necessary, rinse several times with distilled water, and thoroughly rinse with the HC1 solution prepared above. Reinsert the cadmium electrode carefully and fill with a small amount of the HC1 solution so that the meniscus is on scale in the capillary part of the cell. Dry the bottom of the cell around the cadmium electrode, and watch for several minutes to see if any leaks are present. A slow leak can be best observed by a change in level of the solution in the capillary. If no leaks are present, fill the cell to the top of capillary with HC1 solution. During filling, bubbles may be trapped in the capillary section. These can be removed easily with a length of thin plastic tubing. Insert the glass cup and add enough HC1 solution to cover the rim of the cup, then insert the Ag-AgCl electrode. Fill the outer jacket with water at about 22°C. Avoid air bubbles on the walls of the water jacket, as they will make readings of the capillary scale more difficult. Do not allow the Ag-AgCl electrode to become dry. When not in use, store it in the vial in which it was issued.

Plug into the 110-V dc line and turn on the switch. While current is being passed through the cell, be careful of shock from any exposed contacts. The boundary should appear as a sharp line of demarcation between the yellow solution above and a pale blue solution below. A white background placed behind the jacket of the cell will make this boundary more clearly observable. When a satisfactory boundary is obtained and the current has the desired value, continuously maintain this current.

Make a repeat run after rinsing and refilling the cell. To empty the cell, remove the Ag-AgCl electrode and glass cup, turn the cell upside down, then remove the Cd electrode, and let the cell drain. When the experiment is finished, empty the cell and rinse thoroughly several times with distilled water, leaving the cell dry. Be
sure to record the complete potentiometer setting and the precise value of the standard resistor.

Calculations

Calculate the current $I$ in amperes which was passed through the coil. Also plot the volume displacement of the boundary in milliliters vs. time in seconds. Draw the best straight line through these points and obtain the slope $\frac{dV}{dt}$. Calculate $t_{H^+}$ and $t_{Cl^-}$ for the two different HC1 concentrations of ~0.3 N and ~0.1N with two different current of 2.5 mA and 5 mA.
Experiment No. 9:

IR and Raman Spectra of solvent mixtures

Theory: Infrared (IR) spectroscopy and Raman spectroscopy are two popular techniques for identifying molecules by probing their molecular vibrations. Whereas the IR spectrum represents the intensity of light transmitted through a sample, the Raman spectrum represents the light scattered by the sample in a direction perpendicular to that of the incident beam. For typical low resolution spectra, the peaks corresponding to differences in vibrational states are broadened due to transitions involving different rotational states. A high resolution Raman spectrophotometer can be used to identify shifts in the incident wavelength (Stokes and Anti-Stokes lines), but this is not possible in the lower resolution instruments.

For both IR and Raman spectroscopy, the location of the peak corresponds to a specific vibrational mode and the intensity of the peak is proportional to the concentration of the species giving rise to the vibration. However, IR and Raman spectroscopy have different gross selection rules. Thus there are certain vibrational modes which might not be active for IR or Raman. These are dependent on the symmetry of the molecule and can be identified using group theoretic techniques.

In this experiment, you will carry out IR and Raman spectroscopic studies of solvent mixtures of carbon disulphide and carbon tetrachloride of varying concentrations. The peak intensities and peak locations can be used to detect the compositions of the mixtures and study their interactions. For example, if solvent A shows a peak at $\nu_A$ and solvent B shows a peak at $\nu_B$, then the mixture of solvents will show peaks close to both $\nu_A$ and $\nu_B$. The relative intensities of the peaks for different solvent mixtures is proportional to the concentrations of the respective solvents. Let $I_A$ and $I_B$ are the intensities of the peaks at $\nu_A$ and $\nu_B$ for the solution with mole fractions $X_A$ and $X_B$ (=1-$X_A$), then we have

$$\frac{I_A}{I_B} \propto \frac{X_A}{X_B}.$$  

This relation assumes that the extinction coefficient of the two solvent peaks do not change in the presence of the other solvent. However, if the solvents interact strongly with each other, this will not be the case. In this case, it is also possible that the location of the peaks of the individual solvents shift a little because of the presence of the other solvent. The shift of the solvent peaks from $\nu_A$ and $\nu_B$ in the mixtures is a signature of interaction between the solvents causing a change in the vibrational energies.

Procedure: Prepare solvent mixtures of CS$_2$ and CCl$_4$ of varying compositions, 0%, 25%, 50%, 75% and 100% by volume. Record the IR and Raman spectra of all the solutions. It is very important that the sample cell for IR spectrum should be very clean and free of water. You can also record IR spectrum of liquid solvents by dropping them on KBr pellets. In this case, it is very important to set the reference spectrum for the KBr pellet as the zero and measure all peak intensities relative to it. This has to be done for each solvent mixture since the KBr pellet is prepared for each spectrum. It is also recommended that this experiment should be repeated to make sure that the observed spectra are not affected by residual impurities in the sample holder. Locate the prominent peaks of CS$_2$ and CCl$_4$ in the spectrum of the pure solvents. Choose one peak for each solvent that is well separated from the other peaks. Track the intensities and locations of these peaks as a function of composition. Plot the ratio of the intensities of the two solvent peaks as a function of composition. Repeat the experiment if necessary to confirm your results.
Questions to be answered in the Report:

1. Index the three most intense peaks in the IR and Raman spectra of the pure solvents. Compare with the standard values reported in literature.
2. Plot the relative intensities of the two well-separated peaks as a function of concentrations and track their locations. Analyze your results and discuss.
3. From literature, identify the vibrational modes in CS$_2$ and CCl$_4$ that are Raman and IR active. Compare with your results and discuss reasons for any discrepancy.
Experiment No. 10

Computing potential energy surface of molecules using quantum mechanics

Using ab initio quantum mechanical calculations compute the following:
- Potential energy surface for the rotation in $\text{H}_2\text{O}_2$ molecule
- Compute the potential energy difference of staggered and eclipsed ethane molecule
- Calculate the HNH bond angle of Ammonia molecule and the barrier for umbrella rotation of ammonia.

Theory:

The basis of most quantum chemical approaches is the time-independent Schrödinger equation:

$$\hat{H}\Psi = E\Psi \quad (1)$$

where $\hat{H}$ is the Hamilton operator, $\Psi$ is the wavefunction and $E$ is the energy of the system. The wavefunction $\Psi$ contains all information about the quantum system. $\hat{H}$ is an operator representing the total energy of the system. It can be expressed (in atomic units) for a system of $N$ nuclei and $n$ electrons as,

$$\hat{H} = -\sum_{I=1}^{N} \frac{1}{2M_{I}}\nabla_{i}^{2} - \sum_{i=1}^{n} \frac{1}{2\mu_{i}}\nabla_{i}^{2} - \sum_{I=1}^{N} \sum_{i=1}^{n} \frac{Z_{I}}{r_{II}} + \sum_{i<j}^{n} \frac{1}{r_{ij}} + \sum_{J=1}^{N} \sum_{J=1}^{n} \frac{Z_{I}Z_{J}}{R_{IJ}} \quad (2)$$

Here $M_{I}$ is the mass and $Z_{I}$ is the atomic number of a nucleus $I$. The first two terms describe the kinetic energy of the nuclei and the electrons, respectively. The remaining three terms define the potential part of the Hamiltonian and represent the attractive electrostatic interaction between the nuclei and the electrons and the repulsive potential due to the electron-electron and nucleus-nucleus interactions, respectively. $r_{ij}$ is the distance between the electrons $i$ and $j$, $r_{II}$ is the distance between nucleus $I$ and electron $i$, and $R_{IJ}$ is the distance between the nuclei $I$ and $J$.

The Schrödinger equation Eq.1 can be further simplified by the Born-Oppenheimer approximation. Its basic assumption is that the kinetic energy of the nuclei can be neglected. Therefore the potential energy due to nucleus-nucleus repulsion is a constant. It is therefore convenient to reduce the Hamiltonian Eq.2 to the electronic Hamiltonian

$$H_{el} = -\sum_{i=1}^{n} \frac{1}{2\mu_{i}}\nabla_{i}^{2} - \sum_{I=1}^{N} \sum_{i=1}^{n} \frac{Z_{I}}{r_{II}} \quad (3)$$

The electronic Schrödinger equation with $\hat{H}_{el}$, replacing $\hat{H}$ in Eq.1 is

$$\hat{H}_{el}\Psi_{el} = E_{el}\Psi_{el} \quad (4)$$

The solutions of this equation are the electronic wavefunction $\Psi_{el}$ and the electronic energy $E_{el}$. The total energy $E_{tot}$ of the system is the sum of the electronic energy and the constant nuclear repulsion term.

$$E_{tot} = E_{el} + E_{nuc} \quad (5)$$

where

$$E_{nuc} = \sum_{J=1}^{N} \frac{Z_{I}Z_{J}}{R_{IJ}} \quad (6)$$

In other words, by employing the Born–Oppenheimer approximation, we can write the potential energy or total energy $E_{tot}$, as a function only of nuclear coordinates only, provided we can find the $\Psi_{el}$

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1 I. N. Levine, *Quantum Chemistry*
which can provide the least possible $E_{\text{tot}}$. Thus for a given nuclear coordinate, potential energy $E_{\text{tot}}$, can be computed solving time independent Schrödinger equation. For a given molecule, a structure (i.e. position of atoms) with least possible potential energy will be the most stable configuration.

The Schrödinger equation has only been solved exactly for simple model systems. Except hydrogen all elements in the periodic table and all neutral molecules are many-electron systems where the motion of each electron is coupled to the motion of all other electrons. To study these systems approximations are unavoidable. One possibility is represented by the Hartree-Fock method\textsuperscript{2}. It is based on the assumption that every electron moves in a potential created by the nuclei and the average potential of all the other electrons.

Various computer programs are available for doing Hartree–Fock based calculations, and the one which you will be using is the GAUSSIAN\textsuperscript{3} program suite.

**Procedure**

**Potential Energy Surface for Rotation in H$_2$O$_2$ Molecule**

Constructing Input File for GAUSSIAN

As a first step, we have to define the structure of H$_2$O$_2$ and other required keywords in an input file. This input file will be read by GAUSSIAN, and it computes the potential energy ($E_{\text{tot}}$) using the Hartree–Fock method. The format of input file is specific to GAUSSIAN program and is explained below.

The input file of GAUSSIAN contains several sections, as described in Table 1, and see Fig 1 for the corresponding sketch of the molecule.

![Fig 1. Sketch of hydrogen peroxide molecule showing different distances and angles corresponding to the Z-matrix in Table 1.](image)

\textsuperscript{2} A. Szabo and N.S. Ostlund, *Modern Quantum Chemistry.*

\textsuperscript{3} www.gaussian.com
<table>
<thead>
<tr>
<th>Description</th>
<th>Input</th>
</tr>
</thead>
<tbody>
<tr>
<td>Memory Allocated for the program</td>
<td>%Mem 1GB</td>
</tr>
<tr>
<td>Name of scratch/checkpoint file</td>
<td>%chk=h2o2.chk</td>
</tr>
<tr>
<td>Specify Job type and model</td>
<td>#RHF 6-31G(d)</td>
</tr>
<tr>
<td>Blank Line</td>
<td></td>
</tr>
<tr>
<td>Title of the Job</td>
<td>Energy Calculation of H2O2 molecule</td>
</tr>
<tr>
<td>Blank Line</td>
<td></td>
</tr>
<tr>
<td>Charge &amp; Multiplicity</td>
<td>0 1</td>
</tr>
<tr>
<td>Z-matrix (molecular specification)</td>
<td>O</td>
</tr>
<tr>
<td></td>
<td>O 1 dOO</td>
</tr>
<tr>
<td></td>
<td>H 1 dOH 2 aHOO</td>
</tr>
<tr>
<td></td>
<td>H 2 dOH 1 aHOO 3 tHOOH</td>
</tr>
<tr>
<td>Blank Line</td>
<td></td>
</tr>
<tr>
<td>Specify Parameters</td>
<td>dOO=1.475</td>
</tr>
<tr>
<td></td>
<td>dOH=0.95</td>
</tr>
<tr>
<td></td>
<td>aHOO=101.0</td>
</tr>
<tr>
<td></td>
<td>tHOOH=90.0</td>
</tr>
<tr>
<td>Blank Line</td>
<td></td>
</tr>
</tbody>
</table>

Pay attention to the exact syntax including spaces.

Check point files are machine readable files containing all information about the calculation, and useful for restarting and post-processing. You can call this file anything you want. Similarly for the title of the job. 6-31G(d) is the type of basis set, see Chapter 15 of I. N. Levine, Quantum Chemistry (6th Edition), Pearson Education, Inc. (2009), which is used to describe the wavefunction of the molecule. Multiplicity is 2S+1 where S is the total spin of the system. Here S=0, as all electrons are paired in the \( \text{H}_2\text{O}_2 \) molecule.

Z–matrix is the internal coordinate definition of the molecular structure. It contains the structural dependence of every atom with others. The first line of the Z–matrix in Table 1 says that atom number 1 is an oxygen. The second line says that atom number 2 is an oxygen, and it is far from atom number 1 by a distance of dOO °A (Note: here you define the value of dOO=1.475). Third atom is H, and it is at a distance of dOH °A from atom number 1. However, we need to define how the atom number 3 is oriented relative to atom number 2 and 1, else there are several structures possible at a fixed 3–2 distance. For that we specify the angle 3–2–1, and here it is set equal to aHOO degrees. Similarly, atom number 4 is connected to 2 at a bond distance of dOH, making an angle 4–2–1 equals aHOO degrees, and torsional angle 4–2–1–3 (i.e. angle between 4–2–1 and 2–1–3 planes) tHOOH degrees. Note that even if a fifth atom is present, you don’t require any more internal coordinate other than distance, angle and dihedral to other atoms. Notice that you can give any names you want to the variables but we give names that are consistent with the meaning. Thus, dOO is the oxygen-oxygen distance, and so on.

The definition of Z-matrix is made consistent using certain conventions about the order of angles and atoms. This will be important when you are writing the Z-matrix for Ethane molecule. If the Z-matrix is not correctly defined, then the Gaussian output file will give statements like “distance of zero
encountered”, indicating that atoms are lying on top of each other. This can happen in the case of Ethane molecule with the different hydrogen atoms attached to the same carbon atom and in the case of ammonia molecule with the different H atoms. In such cases, you should modify the input file till things work out. Note that Gaussian has other options for constructing Z-matrix. You can specify the Cartesian coordinates of each atom. Look at http://www.gaussian.org/g_tech/g_ur/c_zmat.htm to find out more about the Z-matrix construction.

To write an input file, you have to create a file with necessary keywords. For that click on the “Start/Menu” button at the left side of the screen and then go to Applications --> System --> Terminal to open a terminal window. In the terminal, type “ls” to get a listing of files in the home directory. See if there is directory called CHM423. If it is not there, then type “mkdir CHM423” to create this directory. Then type “cd CHM423” to change into this directory. Then type “mkdir GroupGG”, where you will enter your group no in GG. Then type “cd GroupGG”.In the terminal, type “xemacs h2o2 t90.inp” and enter. This will open an editor in which you can type the input file according to Table 1. Save the file and quit the program.

Running the GAUSSIAN Job

To run GAUSSIAN, in the terminal you have opened, type the following and enter: g03s h2o2 t90.inp h2o2t90.out

Output of the calculations are in h2o2t90.out. Calculation will take a while; please be patient until the prompt reappears on the terminal. If there are errors, then the program will not run properly. You can look at the log file for the errors.

Obtain Energy From the Gaussian Output File

Open the output file using xemacs by typing “xemacs h2o2 t90.out” and search to find a line having “SCF Done:”. In that line you will find the potential energy of the molecule printed in atomic units.

Generating Potential Energy Surface for Rotation

The rotation about the torsion angle tHOOH will generate structures of various energies. Repeat calculations as above using tHOOH equals 70.0, 80.0, 100.0, 110.0, 120.0, 130.0, 140.0. Note that you can use any, but different, names for the input files and output files depending on the torsional angles used. Once you get an idea of where the minimum should approximately lie, carry out calculations with smaller intervals. Make a plot of energy difference (kJ/mol) Vs torsion angle (1 a.u.=2625.87 kJ/mol). Find and report which torsional angle is having the lowest energy up to accuracy of 1 degree.

Potential Energy Difference between Eclipsed and Staggered Ethane Molecule

Construct Z–matrices and GAUSSIAN input files for ethane molecule in eclipsed and staggered form. Assume that the C-C bond length =1.54 A , C-H bond length = 1.09, and that all the HCC bond angles are 109 degrees.

Calculate the energy differences between them (in kJ/mol) using GAUSSIAN program with restricted Hartree–Fock approximation. Find which of the two conformers is the most stable one.

Ammonia Molecule: HNH bond angle and rotational barrier

Construct the Z-matrix for ammonia assuming a 3-fold rotational symmetry axis and NH bond length =1.02 A for pyramidal and planar geometries. Calculate the difference in energies between the two geometries.