PHYSICAL CHEMISTRY 352
LABORATORY MANUAL

FALL 2005

Physical Chemistry 352 Lab Manual

352L LABORATORY SCHEDULE

Experiments	Number of Lab Periods
Bomb Calorimeter	2
Vapor Pressure of a Pure Liquid	2
Phase Diagram for a Three-Component System	2
Liquid-Vapor Equilibrium in Binary Systems	2
Reduction of Cr(VI) by Glutathione (Consecutive Reaction Kinetics)	2
Excited-State Properties of 2-Naphthol, Part I	2
Excited-State Properties of 2-Naphthol, Part II	2
Analysis of the Infrared Spectrum of HCl	2
Infrared and Raman Spectrum of Carbon Disulfide	2
Cyclic Voltammetry Studies of Hydrogen Bonded Quinones	1
Temperature Dependent NMR Spectroscopy of Dimethylformamide	1

BOMB CALORIMETER

PURPOSE

In this experiment the student will study the operation and use of a commercial type of bomb calorimeter by determining the heat of combustion of an organic substance.

DISCUSSION

The commercial bomb calorimeter is a self-contained instrument used in the determination of heats of combustion of certain fuels and pure organic substances. The results obtained are sufficiently precise to make them of extreme importance in most commercial and laboratory procedures concerned with heats of combustion.

The combustion bomb, made of corrosion-resistant metal, holds the sample whose heat of combustion is to be measured. The sample is held in a cup as shown in Figure 1. This figure also shows how the fuse wire, used to ignite the sample, is threaded into an electrical circuit. After the sample and the wire have been properly placed in the bomb, it is charged with oxygen gas from a commercial cylinder to the pressure of about 25 atm.

The assembled bomb is placed in the bucket as shown in the figures. The bucket contains a specified quantity of water. The temperature rise accompanying the combustion is read from a thermometer whose bulb is immersed in the water. A stirrer effects an even distribution of the water. The bucket in turn is surrounded by an insulating air space, which prevents, as far as possible, heat leakage to the surroundings.

First, it is necessary to obtain the heat capacity of the calorimeter system. This is the number of calories necessary to raise the temperature of the entire calorimeter system by one degree centigrade. This is found by burning a sample of material of known heat of combustion. Benzoic acid of high purity is usually employed. The temperature rise due to the sample is noted, and the number of joules of heat released in the combustion is calculated. These two values enable one to calculate the heat capacity of the calorimeter system. This is then used to calculate the heat of combustion of the assigned material.

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

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

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

$$C_6H_5COOH(s) + 7.5O_2(g) \rightarrow 7CO_2(g) + 3H_2O(l)$$

and Δn is equal to 7 minus 7.5, or minus 0.5. Hence for the combustion of one mole of benzoic acid at 25^oC

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

APPARATUS AND CHEMICALS

Parr calorimeter system including firing mechanism, stirrer, etc...; pellet press; two special thermometers calibrated in 0.01 degree intervals; fuse wire; oxygen cylinder; benzoic acid; naphthalene, sucrose, or other organic substances.

PROCEDURE

Pellet Formation

Care must be taken to avoid overcharging the bomb for it must be realized that the peak pressure developed during a combustion is proportional to the size of the sample and to the initial oxygen pressure. Pellet size should be limited to not more than 1.1 grams.

1. Weigh out approximately 1.0 gm. of sample. Grind it in a clean mortar and pestel.

2. Use the pellet press to make a pellet. Weigh it.

3. Carefully place it in the sample cup.

Ignition Wire

1. Measure out approximately 10-11 cm of wire and weigh. It will be necessary to weigh any unburned wire after combustion since this is an important factor in the calculations.

2. Set the bomb head in the support stand and attach the length of nichrome fuse wire as illustrated in Figure 1. A pair of tweezers may be helpful in attaching the wire to the electrodes. If the electrodes resemble those in Figure 2, insert the wire through each eyelet then slide each cap downward to complete the connection.

3. Place the sample cup (with sample sitting in the center of the cup) in the cup holder and bend the nichrome wire in a v shape. Position the wire so that it almost touches the surface of the pellet (about 1 mm separation). Figure 3 illustrates the proper threading of the electrodes and sample placement.

Liquids In The Bomb

1. Pipet 1.0 ml of deionized water into the bomb to absorb the oxides of nitrogen formed from nitrogen present in the oxygen mixture.

Closing The Bomb

1. Care must be taken not to disturb the sample when sealing and charging the bomb. Slide the head assembly into the bomb cylinder, screw open the vent cap on the head assembly to allow air to be expelled, and push the head down as far into the cylinder as it will go.

2. Close the vent cap tightly. A tight seal is needed to prevent pressurized oxygen from leaking.

Installing The Oxygen Connection

1. Carefully place bomb in bench clamp and secure.

2. Slip on the oxygen tank connection hose to the pin on the head assembly.

Filling The Bomb

1. Open the oxygen tank valve. Open the regulator valve SLOWLY and watch the gauge as the bomb pressure rises to the desired filling pressure (25-30 atm.). Once this pressure is reached close the control valve and then the tank valve. Note: If the bomb is filled too quickly you can blow your sample out of the sample cup.

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

Problems:

1. If there is a continual escape of gas from the bomb head connections once the oxygen tank valve is unscrewed the bomb is defective and should not be used.

2. If the bomb will not hold pressure and you can hear oxygen escaping around the vent cap, then the cap is not sealed tightly enough. Tighten down the screw cap by hand again and try to pressurize the bomb. If you are not successful after one or two attempts use a new bomb.

3. If too much oxygen should accidentally be introduced into the bomb, don't proceed with the combustion. Unscrew the oxygen tank connection and exhaust

the bomb in the hood. This can be done by pressing opening the vent cap. Reweigh the sample before repeating the filling procedure.

Operating The Calorimeter

1. Remove the lid and place on the ring stand. Check to see that the bucket is resting properly in the jacket, noting the four pegs on the bottom of the jacket which hold the bucket in place.

2. Carefully place the charged bomb in the bucket, noting that it rests on the raised circular area on the bottom of the bucket.

3. Connect the ignition wire to the terminal socket on the bomb head. Prepare 2 liters of water that is between $24^o - 25^o C$. To obtain this, start with deionized water and add warm tap water or ice chips, as needed. Fill the bucket with the 2 liters of water. Be careful not to spill it. Make sure that the initial temperature can be read by the thermometer.

4. Set the cover on the jacket. The screw attached to the lid fits into the screw hole in the ledge of the jacket.

5. Turn the stirrer by hand to be sure that it runs freely, then slip the drive belt onto the pulley. If the belt does not work properly, rubber bands can be used.

6. Place the thermometer in the support and then attach the thermometer support to the calorimeter (screws into lid). Adjust the rubber washer on the thermometer so that the bulb does not touch the bottom of the bucket.

7. Connect the two lead wires on the ignition unit to the calorimeter. Don't press the firing button unless the lead wire inside the jacket is connected to a bomb.

8. Plug in the calorimeter, ignition unit and timer. If the stirrer does not turn automatically check to see that it is turned on.

9. Let the stirrer run for 5 minutes to reach equilibrium. At the end of this period start the timer and read and record the temperature at one minute intervals for 5 minutes. At the start of the sixth minute stand back and fire the bomb by pressing the ignition button and holding it down for about 5 seconds.

Caution: Don't have any parts of the body over the calorimeter when firing the bomb. Continue to stand clear for 30 seconds.

10. The temperature should start to rise within 20 seconds of firing. Take the first temperature reading at 30 seconds and continue to take temperature readings every 15 seconds for a period of 2 minutes. The temperature should be read to the nearest $0.02^o C$. The reading lens is not required at this point.

11. After this 2 minute period record the temperature to the nearest tenth with the aid of the reading lens at one minute intervals until the difference between successive readings is zero (or perhaps becomes negative). This will be approximately five minutes. Accurate time and temperature observations must be recorded to identify certain points needed to calculate the calorific value of the sample. Usually the temperature will reach a maximum, and then drop very slowly.

Problems:

1. No significant temperature rise (1 C within 1 minute). Check to see that the ignition unit is plugged in and all electrical connections are tight. Ignite the bomb again.

2. If this does not solve the problem it will be necessary to turn off all electrical connections, discharge the bomb in the hood and open it up. Place bomb in hood and open the valve to release the pressure. If pellet is still intact but fuse wire is partially burned re-wire the bomb, weigh the pellet again, charge the bomb and ignite it again. If the pellet is only partially burned then start over.

12. After the last temperature reading, turn off all electrical connections, remove drive belt, and place cover in support ring. Remove ignition wire from bomb, lift bomb out of the bucket and wipe off any excess water. Open the valve cap and discharge the bomb in the hood. Unscrew the cap, lift the head out of the cylinder, and place it on the support stand.

13. Remove and weigh the unburned fuse wire still attached to the electrodes. Ignore "globules." Examine the interior of the bomb for soot or other evidence of incomplete combustion. If such evidence is found then the test will have to be discarded.

UTILIZATION OF DATA

Plot the temperature time data for each run as illustrated in Figure 5. The following data should be collected for each run:

a = time of firing

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

T_a = temperature at beginning of period (after initial temp. rise and before firing) in which the rate of temperature change became constant (see Fig. 5).

T_c = temperature at time c

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

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

e_3 = correction in joules for heat of combustion of wire, found by multiplying the weight of fuse wire which burned by the constant given on the fuse wire package. (1400 cal./gm. for Parr 45C10 nickel chromium fuse wire, 1 cal = 4.184 joules)

NET CORRECTED TEMP. RISE:

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

ENERGY EQUIVALENT FACTOR(W) OF THE CALORIMETER:

This factor denotes the energy required to raise the temperature of the calorimeter one degree. The data obtained from the trials with benzoic acid will be used for the determination.

$$W = \frac{(nQ + e_3)}{\Delta T}$$

W= energy equivalent (heat capacity) of the calorimeter in Joules/^{o}C

Q = heat of combustion of the standard benzoic acid sample in kilojoules per mole (given as -3226.9 KJ/mol.) This is obtained from the literature value of the molar enthalpy of combustion, minus the ΔPV correction.

n = moles of the benzoic acid pellet.

ΔT = net corrected temperature rise in ^{o}C

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

Note: Fuse Wire Correction

The wire used as a fuse for igniting the sample is partly consumed in the combustion. Thus the fuse generates heat both by the resistance it offers to the electrical current and by the heat of combustion of that portion of the wire which is burned. The heat generated by the resistance is constant and small and thus can be neglected. However, the amount of wire consumed will vary from test to test and therefore a correction must be made to account for the heat of combustion of the metal.

After determining W, one can use this value (average of the runs) to calculate the gross heat of combustion of the sample in question in joules per mole.

Gross Heat of Combustion:

$$Q = \frac{(\Delta T)(W) - e_3}{n}$$

Molar Heat of Combustion at Constant Pressure ΔH:

When expressed in joules per mole, $Q = \Delta U$. By definition, a change in enthalpy ΔH is related to the corresponding change in internal energy ΔU by the equation:

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

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

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

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

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

ΔU = gross heat of combustion, Q. R is the ideal gas constant and T is the temperature of the products if they were returned to the initial temperature of the experiment at the time of firing.

FIGURE 1

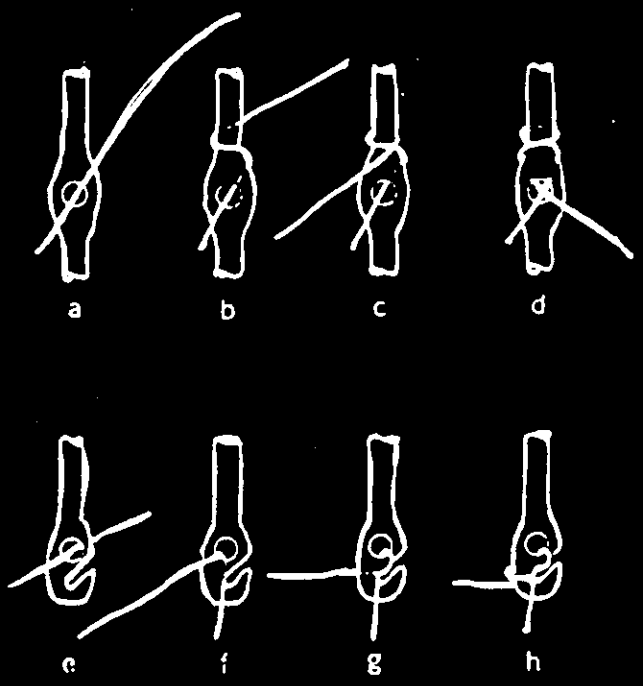


FIGURE 2

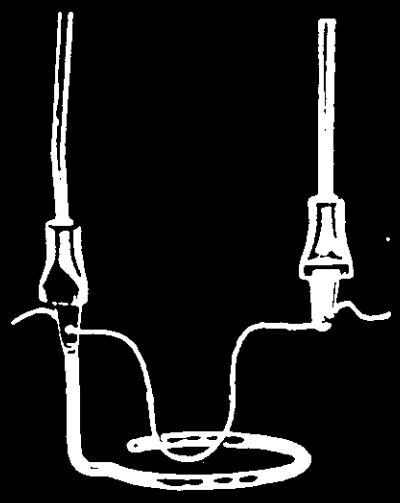
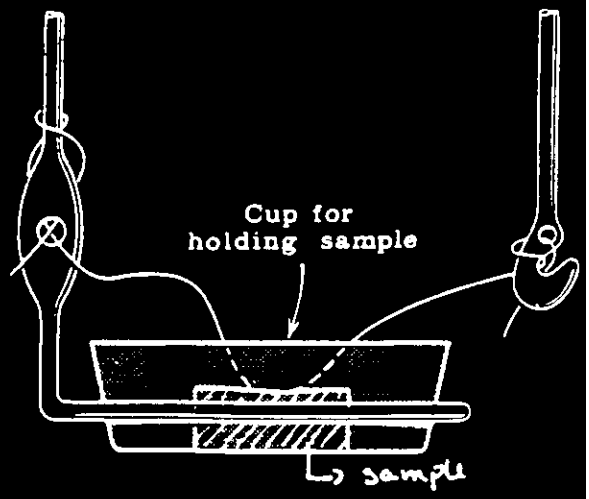
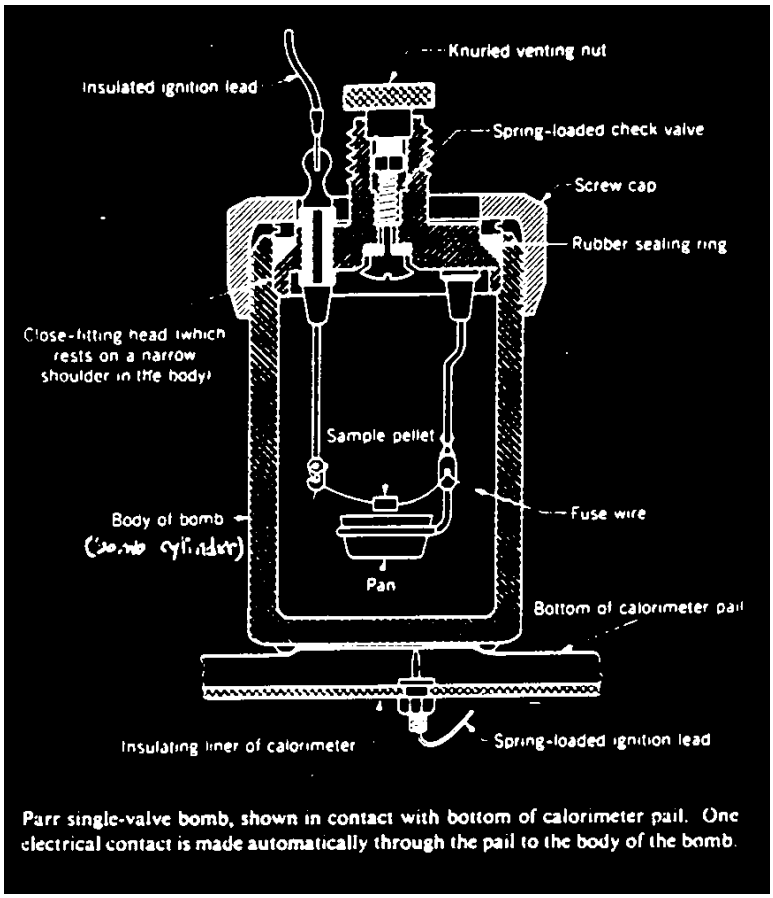
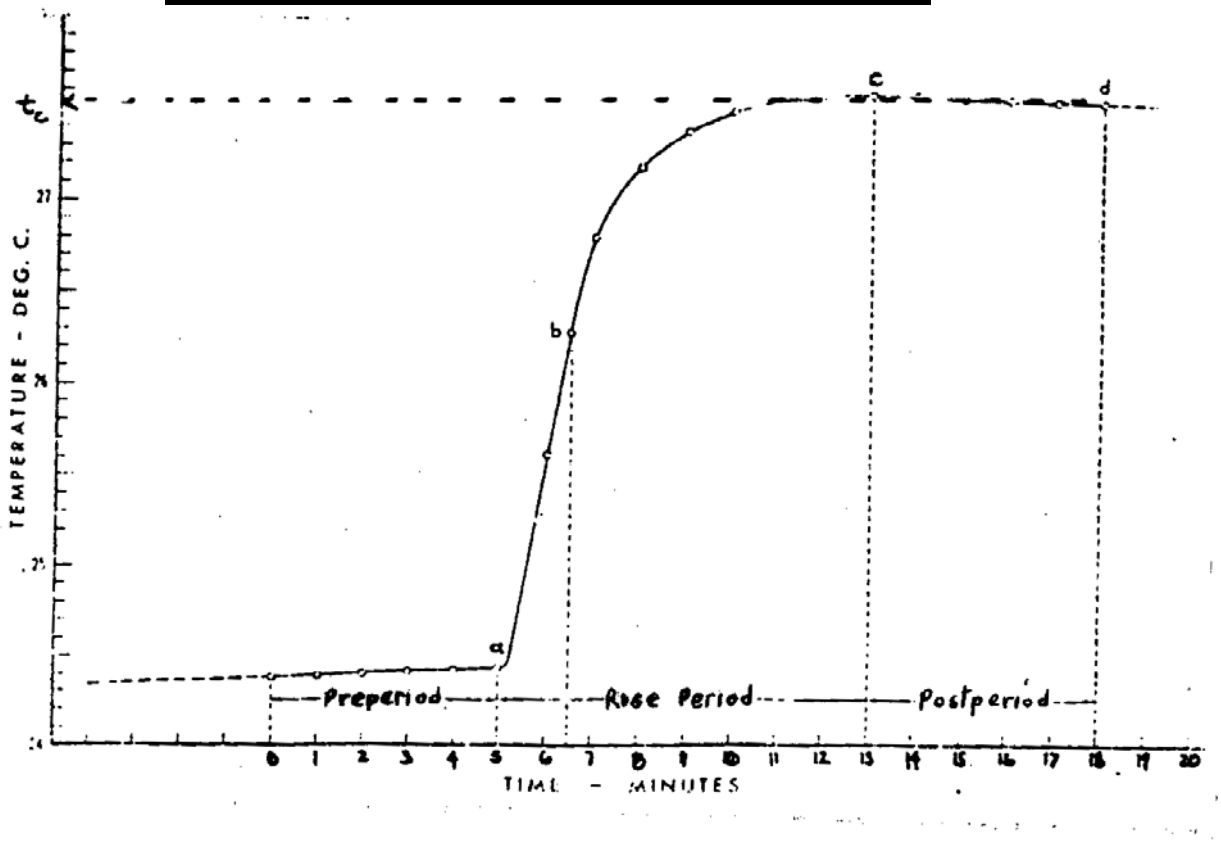


FIGURE 3





Parr single-valve bomb, shown in contact with bottom of calorimeter pail. One electrical contact is made automatically through the pail to the body of the bomb.

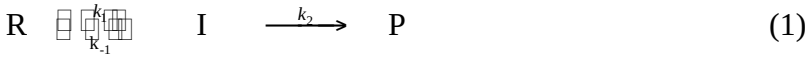


Consecutive Reaction Kinetics: The Reduction of Cr(VI) by Glutathione

Objective To study the first order decay kinetics of the reactant Cr(VI) which absorbs at 370 nm. To study the first-order evolution and first-order decay kinetics of the thioester intermediate which absorbs at 430 nm. To estimate all rate constants graphically and then use those values as best guess values to initiate the analytical nonlinear regression calculation using Kaliedagraph software.

Introduction Most of the rate processes that take place in biochemical systems cannot be described by the fundamental, textbook-type kinetic models, such as simple first order or second-order reactions. Recognizing that fact, many physical chemistry textbooks devote a separate section to the kinetics of complex reactions. Reversible, multistep, consecutive reactions are examples of such kinetic models. They are often relevant to biological reactions; moreover, they exhibit fascinating kinetic behavior. In addition, the experimental data are amenable to rigorous interpretation if straightforward computer-assisted data acquisition and analysis techniques are used.

Consider the reaction mechanism in which the reactant, R, reversibly forms an intermediate, I, that in turn, is irreversibly converted to the product, P. The **mechanism** is shown in the following scheme:



(1)

We will assume that each elementary step in the mechanism is first order in the corresponding reactant species. The coupled **differential equations** that account for the rate of change in the concentrations of the three species are as follows:

$$\frac{d[R]}{dt} = -k_1[R] + k_{-1}[I] \qquad (2)$$

$$\frac{d[I]}{dt} = k_1[R] - (k_{-1} + k_2)[I] \qquad (3)$$

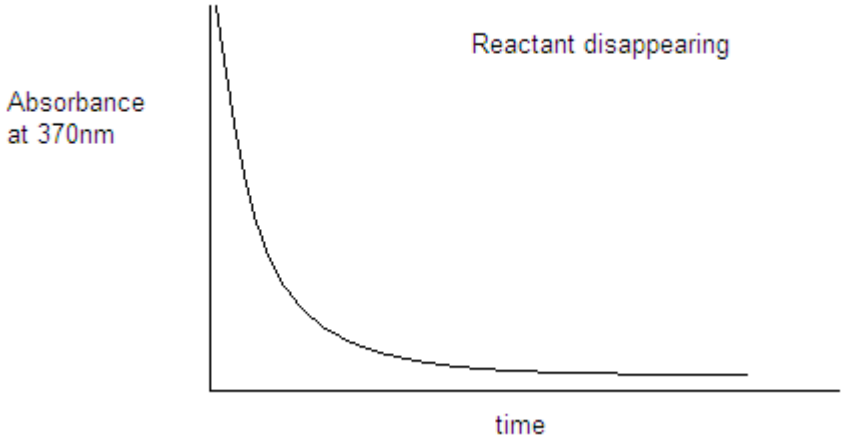
$$\frac{d[P]}{dt} = k_2[I] \qquad (4)$$

When these differential equations are solved exactly, the resulting **integrated equations** for the reactant, R, and intermediate, I, are:

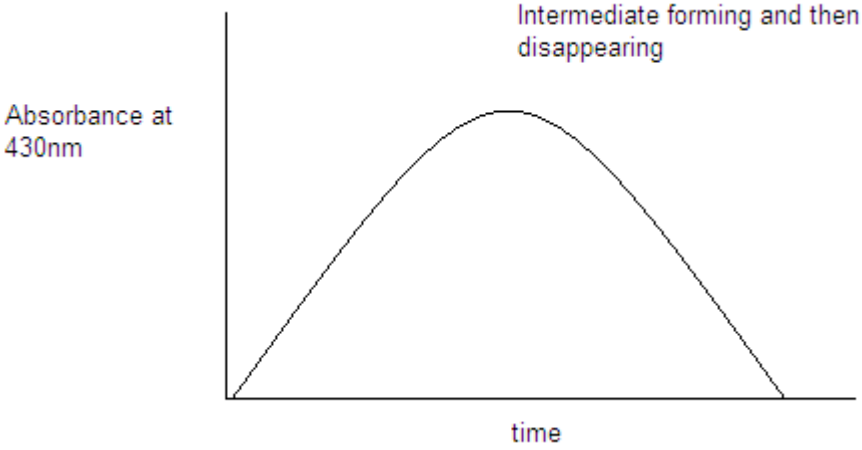
$$[R] = \underbrace{A\left(e^{-k_1 t}\right)}_{decay} + \underbrace{B\left(e^{-k_{-1} t}\right)}_{rise} \quad (5)$$

$$[I] = \underbrace{C\left(e^{-k_2 t}\right)}_{decay} - \underbrace{D\left(e^{-k_1}\right)}_{rise} \quad (6)$$

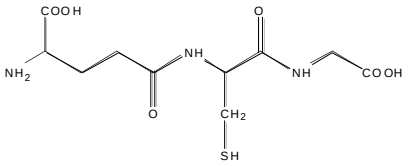
The reactant follows two simple first-order decay processes associated with the forward and reverses reactions and the intermediate exhibits a rise term and a decay term. The magnitude of the decay rate constant of the reactant should match the magnitude of the rise constant of the intermediate, since the intermediate evolves from the reactant. However, the decay constant of the reactant will have a negative sign and the rise constant of the intermediate will have a positive sign.



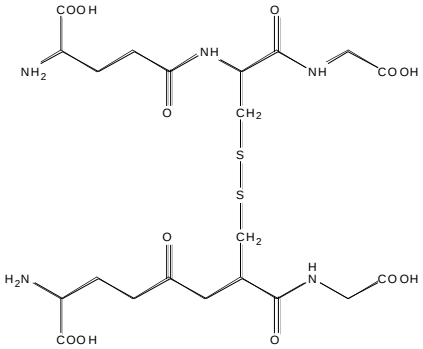
Graph of the evolution (rise) and decay of the intermediate



The Reaction In this experiment, the kinetic behavior of the redox reaction that takes place between the tripeptide glutathione, γ-L-glutamyl-Lcysteinylglycine (or GSH) and Cr(VI) at near-neutral pH is studied. Two GSH units are coupled together through the thiol groups, thus being oxidized to glutathionyl disulfide, GSSG. In the process, Cr(VI), which symbolizes the aquated chromium ion in the +6 oxidation state, is reduced to Cr(III).



GSH



GSSG

The reaction is described by the following stoichiometric equation:

$$2CrO_4^{2-} + 6GSH + 10H^+ \rightarrow 2Cr^{3+} + 3GSSG + 8H_2O$$

This reaction is believed to account, in part, for the toxicity and carcinogenicity of chromium (VI). GSH and GSSH function as a redox couple, both in intracellular and plasma environments. An enzyme regulates the appropriate proportion of the oxidized GSH to the reduced GSSH species, both of which are involved in other intracellular redox reactions. GSH also functions as a detoxifying agent that scavenges reactive species, such as free radicals and peroxides. Thus Cr(VI) has the ability to interfere with these processes by causing a depletion of GSH.

The reaction mechanism is believed to involve the reversible formation of a chromium (VI) thioester intermediate. There is a subsequent redox step between this intermediate and a second molecule of GSH, resulting in the ultimate products, Cr(III) and GSSG.

$$CrO_4^{2-} + GSH \rightleftharpoons CrO_4^{2-} + GSH\,(\text{thioester})$$
$$\text{Thioester} + GSH \rightarrow\!\rightarrow GSSG + Cr^{3+}$$

Thus R, I and P are the symbols of Cr(VI), the Cr(VI)-GSH thioester intermediate, and Cr(III), respectively.

Experimental Method A nice feature of this reaction is that reactant Cr(VI) and the thioester intermediate have reasonably different absorption spectra, rendering the spectroscopic study of the reaction very easy and convenient. This very common experimental strategy is based on the linear relationship between the absorbance, A, of a specie and its molar concentration, C. At a given wavelength, λ, we may write

$$A = \varepsilon bC$$

where ε is the molar absorptivity coefficient, and b is the pathlength of the absorption cell (usually 1 cm.)

The time dependence of the Cr(VI) concentration can be followed by monitoring its absorbance at 370 nm. The evolution and decay of the thioester intermediate can be followed at 430 nm. The reaction rate is highly dependent on pH, the nature of the buffer, as well as the buffer concentration. Hence, the reaction conditions have to be chosen carefully in order for the system to exhibit well-resolved kinetics.

Safety Precautions Hand protection must be used when working with chromium compounds. After the experiment, dispose of all chromium-containing solutions in a heavy-metals waste container.

Procedure You will be given the following aqueous stock solutions:

$0.40\,M\ K_2HPO_4$	(The buffer)
$5.0\times10^{-3}\,M$ HCl	(To adjust the pH)
$1\,M$ HCl and $1\,M$ NaOH	(To trim the pH)
$8.0\times10^{-3}\,M$ GSH	(The reductant)
$1.6\times10^{-3}\,M\ K_2Cr_2O_7$	(The oxidant)

Note: Since GSH solutions undergo slow oxidative degradation in air, prepare the stock solution in a 50 mL volumetric flask on the day of the experiment and store it in a refrigerator if necessary. Small volumes (<10 mL) of the first three solutions are needed; 20 mL of the GSH solution is required.

1. Trim the pH. The pH of the reaction medium must be brought to a value of 6.0. Pipet 20 mL of the GSH solution into a test tube or other convenient vessel, such as a small beaker or flask into which a pH electrode can be inserted. Into that vessel pipet 4 mL of the K_2HPO_4 buffer and 6 mL of the HCl solution. Mix thoroughly, and measure the pH. Add dropwise sufficient 1 M HCl (or NaOH) to bring the pH to 6.0.

2. Turn on the Hewlett-Packard Diode Array UV-vis absorption spectrometer. Wait for a minute and then turn on the computer. Press Ctrl, Alt, and Del simultaneously, enter the password: ChemUVVis. Click START, PROGRAM, HPUV, and then INSTRUMENT 1 ONLINE.

3. In the menu at the top of the screen, check that the MODE is set for KINETICS. Click on SETUP. Set the wavelength at 430 nm, the absorbance at 0.0 and 0.3, the time at 2400 sec (or 1800 if time is short), and the cycle at 5 sec. Click OK.

4. Pipet 3 mL of the pH trimmed reaction solution into a stopper-fitted 1-cm path length spectrophotometer sample cell. Insert into the sample compartment of the Hewlett-Packard Diode Array spectrometer. Push down the lever. When the instrument is set to display 430 nm time behavior, the 370 nm decay of the reactant will be recorded simultaneously, and can be viewed later. Click on BLANK and take the background spectrum. Pull the lever up, remove the cell, Click on TIME BASED MEASUREMENT push START and name the spectrum, (e.g. SC370r1.kd). Now inject 200 µL of the $K_2Cr_2O_7$ solution into the cell solution, stopper it, invert it several times, and quickly place it into the cell compartment. Quickly press START again. Take data for approximately 40 min.

5. Repeat the procedure if time allows.

6. With the 430 data on the screen, click on the 430 nm spectrum, then go to **file** and choose **export selected data**. Name it as a **.csv** file. Repeat for the 370 nm data.

Print the Spectra

1. Click on the title bar above the spectrum. It will turn blue. Go to FILE to PRINT. Choose either SELECTED WINDOW (for a bigger plot) or CURRENT VIEW (which will print a small plot). The bigger plot is ideal for estimating rate constants. Plot your 370 and 430 nm spectra for both kinetic runs.

2. Exit the program. From your plotted spectra, estimate the values of k_1, k_2, const, C and D for the 430 nm curve. Estimate the values of k_1, k_{-1}, const, A and B for the 370 nm run.

Computer Analysis

1. Open the Kaliedagraph nonlinear regression program. Choose: **open, C, hpchem, 1, data**. Open the .csv file at this point.

2. In order to get to the curve fitting program, choose: **gallery, linear, line, x = t, y = A. Click new plot, curve fit, general, fit 1**, **absorbance** (put an **x** in the box).

3. Enter the form of the equation. Enter your estimated values for the constants**.** Let the program run. Compare your estimated constants to the calculated values.

Data Analysis for the 430 nm rise and fall data

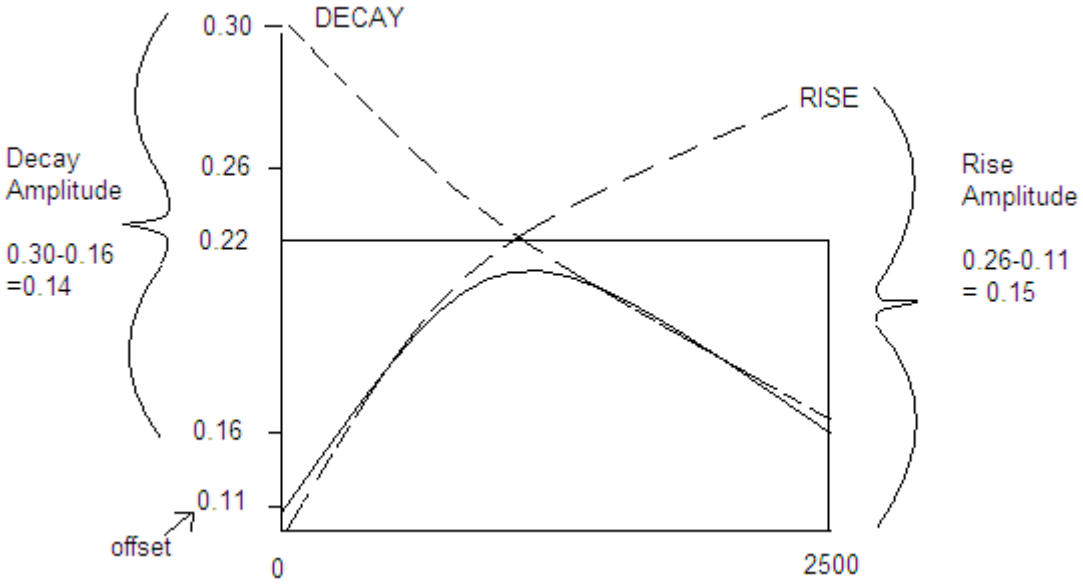
$y = \text{const} + C\exp(-k_1 t) + D\exp(-k_2 t)$ Where C is positive to fit the decay and D is a negative value to fit the rise

The language of the program will be:

m1 + m2*exp(-1*m3*m0) + m4*exp(-1*m5*m0); m1 = ; m2 = ;m3 = ;m4= ;m5=

From your data, estimate the half-lives of the decay (i.e. the time it takes for the concentration to decrease by half) and the rise (i.e. the time it takes for the concentration to double.) Calculate the estimated rate constants from the half-lives. Use $k = 0.693/t_{1/2}$. These will be the values of m3 and m5. Estimate the amplitudes (C and D) for the individual rise and fall curves. These will be the values for m2 and m4. Estimate the absorbance offset (the const) of the data at time t=0. This will be the value for m1. Enter your estimated values for m1,m2,m3,m4, and m5. Remember m4 will be a negative value. Run the program. The computed values will appear along with the error.

Your estimated values will be determined as follows:



RISE	$t_{1/2} = 1500\,\text{sec}$	$k = \frac{0.693}{1500} = 0.00046$
DECAY	$t_{1/2} = 2500\,\text{sec}$	$k = \frac{0.693}{2500} = 0.00027$

$$y = 0.11 + \underbrace{(0.14)e^{-(0.00027)t}}_{decay} + \underbrace{(-0.15)e^{-(0.00046)t}}_{rise}$$

Data Analysis for the 370 nm data, this is the sum of two exponential decays

$$y = \text{const} + A\exp(-k_1 t) + B\exp(-k_{-1} t)$$

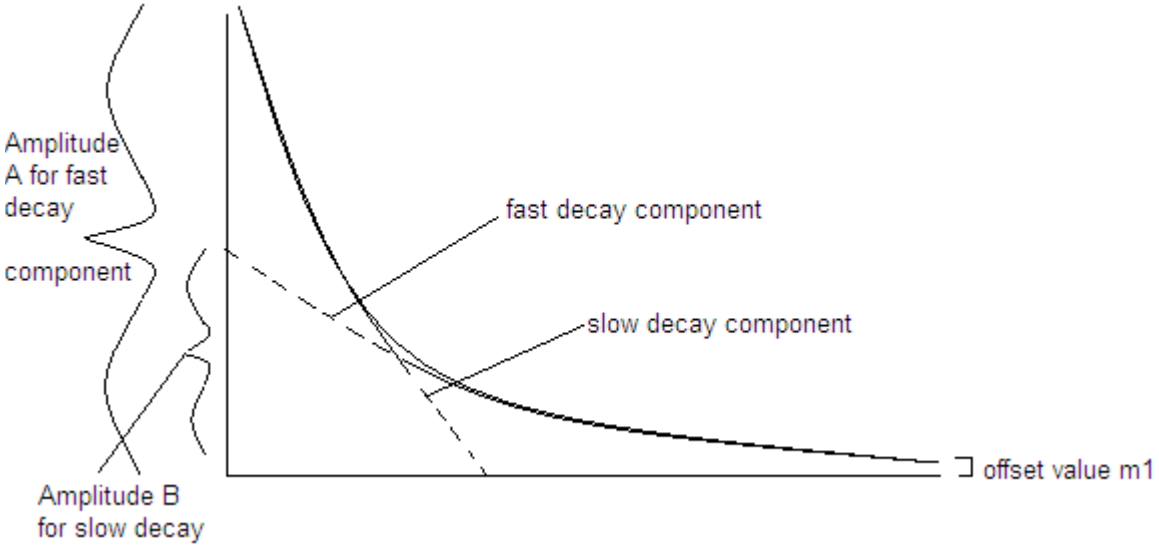
Where A and B are positive values to fit the two decay contributions.

The language of the program will be:

m1 + m2*exp(-1*m3*m0) + m4*exp(-1*m5*m0); m1 = ; m2 = ;m3 = ;m4= ;m5=

From your data, estimate the half-lives of the two decays (i.e. the time it takes for the concentration to decrease by half). One will be evaluated at early time, the other will be evaluated at late time. Calculate the estimated rate constants from the half-lives. Use $k = 0.693/t_{1/2}$. These will be the values of m3 and m5. Estimate the amplitudes (A and B) for the two decay curves. These will be the values for m2 and m4. Estimate the absorbance offset (the const) of the data at time t=0. This will be the value for m1. Enter your estimated values for m1, m2, m3, m4, and m5. Run the program. The computed values will appear along with the error.

Your estimated values will be determined as follows:



Determination of Hydrogen Bonding Constant, Hydrogen Bonding Numbers using Cyclic Voltammetry

Voltammetry is a collection of electro-analytical techniques in which information about the analyte or a physical processes is derived from the measurement of current as a function of applied potential obtained under conditions that encourages polarization of an indicator or working electrode. It is widely used by chemist for nonanalytical purposes including fundamental studies on redox processes, adsorption processes on surfaces, electron transfer mechanism, and electrode kinetics.

Voltammetric measurements are carried out using an electrochemical cell made up of three electrodes immersed in a solution containing the analyte and also an excess of a nonreactive electrolyte called the supporting electrolyte. One of the three electrodes is the micro electrode or the working electrode whose potential is varied. Its dimensions are kept small in order to enhance its tendency to become polarized. The second electrode is a reference electrode (commonly a silver/silver chloride electrode or calomel electrode) whose potential remains constant throughout the experiment. The third electrode is a counter electrode, which is often a platinum wire that simply serves to conduct electricity from the signal source through the solution to the working electrode.

Figure 1 shows the nature of the triangular waveform that is applied to the working electrode. After applying a linear voltage ramp between t_0 and t_1, the ramp is reversed to bring the potential back to its initial value at time t_2. Figure 2 illustrates a typical cyclic voltammogram. In the part of the wave labeled A, B, and C, the voltage is applied and an increasing amount of current is observed. This is the cathodic part of the wave, where reduction of the quinone molecules is occurring. Maximum flow of electrons is observed at point D. After point D, voltage is still applied, but the current associated with the reduction decreases due to a depletion of quinone molecules at the electrode. Quinone diffusion toward the electrode must occur before reduction. Diffusion is slower than reduction, therefore there is a reduction in the current flow in part c of the figure. Parts G, H, I, J, and K describe the reverse process. The voltage is decreased, the reverse oxidation process occurs, and the quinone molecules are returned to their initial state. Figure 3 is a typical cyclic voltammogram for the two-electron reduction of a compound.

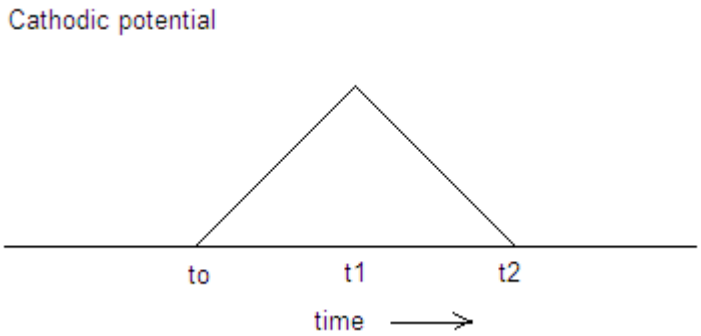
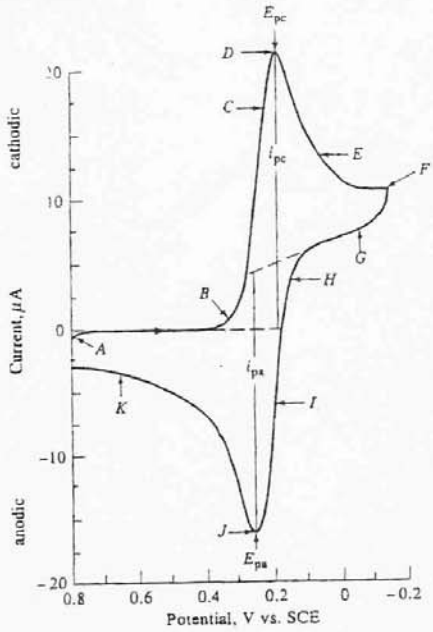
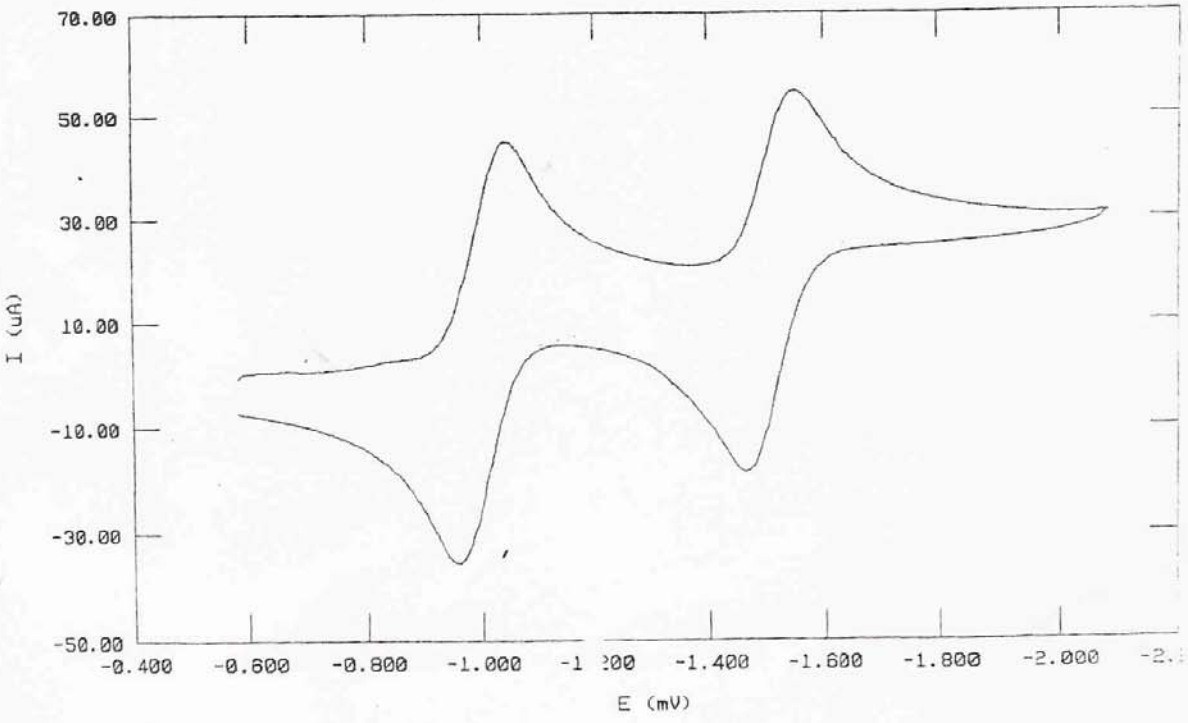


Figure 1

FIG 2


E_{pc}
D
C
i_{pc}
E
F
G
H
B
A
i_{pa}
K
I
J
E_{pa}
cathodic
anodic
Current, μA
20
10
0
-10
-20
0.8
0.6
0.4
0.2
0
-0.2
Potential, V vs. SCE

3


70.00
50.00
30.00
10.00
-10.00
-30.00
-50.00
I (uA)
-0.400
-0.600
-0.800
-1.000
-1.400
-1.600
-1.800
-2.000
E (mV)

Introduction The importance of hydrogen bonding in physico-chemical processes is enormous (e.g. the liquid state of water, helical structure of DNA etc. are attributed to H-bonding). The purpose of this experiment is to directly show the effect of hydrogen bonding and evaluate the hydrogen-bonding constant and the hydrogen-bonding number.

Benzoquinone and substituted quinones (Q) undergo two step-wise one electron reversible reactions in solvents like acetonitrile, benzonitrile, dimethylsulfoxide, dimethylformamide, etc:

$$Q + e^- \Leftrightarrow Q^- \qquad (1)$$

$$Q^- + e^- \Leftrightarrow Q^{2-} \qquad (2)$$

In the presence of a protic solvent, like ethanol, steps 1 and 2 are affected. The experiment will show that step 2 is dramatically affected. The voltammogram peaks shift anodically, i.e. more positive, as a result of the hydrogen bonding. From these peak shifts the hydrogen-bonding parameters can be evaluated. The various equilibria are:

$$Q + e^- \Leftrightarrow Q^- \qquad (1)$$

$$Q^- + n\,EtOH \Leftrightarrow Q^-(EtOH)_n \qquad (2)$$

$$Q^-(EtOH)_n + e^- \Leftrightarrow Q^{2-}(EtOH)_n \qquad (3)$$

$$Q^{2-}(EtOH)_n + (m-n)EtOH \Leftrightarrow Q^{2-}(EtOH)_m \qquad (4)$$

Use of the following equation will allow the determination of the values of hydrogen-bonding equilibrium constant, $K_{eq}^{(1)}$, and the hydrogen-bonding number, n, that characterize the first two steps illustrated above.

$$E_p - E_p^{\,0} = \left(\frac{RT}{F}\right)\ln K_{eq}^{(1)} + (n)\left(\frac{RT}{F}\right)\ln[EtOH] \qquad (5)$$

E_p^o is the peak potential of the quinone obtained in the absence of ethanol. E_p is the potential of the same quinone peak obtained in the presence of ethanol. Several values of E_p will be obtained corresponding to increasing amounts of added ethanol. By plotting the experimentally determined value of (E_p - E_p^o) for the first peak versus ln [EtOH], one can obtain the values of $K_{eq}^{(1)}$ from the intercept and n from the slope. R= 8.314 J/mol K, T= room temp, F= 9.65 x 10^4 Coulombs/mol electrons.

Similarly for the second peak, we can obtain

$$E_p - E_p^{\,0} = \left(\frac{RT}{F}\right)\ln K_{eq}^{(2)} + (m-n)\left(\frac{RT}{F}\right)\ln[EtOH] \qquad (6)$$

By plotting the (E_p - E_p^o) for the second peak vs. ln [EtOH] we will get (m – n) . Taking n from the first step we can obtain m. $K^{(2)}_{eq}$ can be evaluated from the intercept.

Instrument and materials:

Instrument:A PAR Potentiostat / Galvanostat 273A controlled by a P.C. through a software Power Suite or Electrochem.bat. The sofware has a provision for carrying out Cyclic Voltammatry , storing ,overlaying and printing graphs.

Electrodes: Working Glassy Carbon (Bioanalytical System, 6mm diameter), Auxiliary Electrode. Custom made Gold Electrode (diameter 1mm, length 1.5 cm), Reference Electrode: Custom made Quasi Reference Silver wire Electrode. A standard Ag/AgCl, SCE or Ag/AgNO3 can also be used.

Chemicals: Quinone (1,4 Duraquinone), Tetra-n- butyl ammonium hexafluorophosphate (TBAHFP), Acetonitrile, Ethanol (d = 0.725 at 25 C).

General: You will record CVs of a 2mM solution of quinone. You will add successive amounts of dry ethanol to the solution in the cell (Fisher reagent grade ethanol will be dried over molecular sieves) to make 0.05M, 0.1M, 0.2M, 0.5M and 1.0M in ethanol. Purge the oxygen with bubbled nitrogen then record CV's after each successive addition of EtOH.

Procedure

1) Prepare 25.0 mL of a 2.0mM solution of quinone with 0.1M TBAHFP as the supporting electrolyte in acetonitrile using 25-mL volumetric flask.NOTE: Do Not wash any thing with water.

2) Make sure the solution is mixed well and that all solids have been dissolved 3)

(a) Assemble the reference electrode. Insert the jacket of Reference electrode in one of the holes of the stopper. If the silver wire is not shiny use a fine emery paper to clean the surface and then wipe it with with Kimwipe.

(b) Deliver 10.0 mL of the 2.0mM solution to a voltammetric cell. Before delivering the solution in the cell have a look at the working electrode surface . If the surface is not shining report to the Instructor. The electrode needs polishing: Put a drop of distilled water on a 1500 grade emery paper and gently rub the electrode surface on the emery paper rotating it in counter clock and then counter-clock directions 5-6 times . Wash the surface of the electrode and dry with kimwipe. See if the electrode is mirror like shiny or not. If not, the electrodes needs more polishing

(c) Insert the two — the counter and working - electrodes in the two holes of the stopper. Stopper the cell. Inset the reference electrode in the jacket (of the reference electrode.

(d) Bubble the solution with N_2 for 5-7 minutes.

3) Make the following settings in the Electrochem.bat software: Click on Electrochem.bat, then PAR... Press any key to continue. Click SETUP, EDIT, and EDIT MENU. Set PURGE TIME = 0.0, SCAN RATE = 50.0, INITIAL PLOT = 0.0, VORTEX 1 POT = -1.50, and FILTER = 5.3 Hz. Scan the solution at 50 mV/s, save and print a copy of the resulting voltammogram. Locate the two peaks by clicking on GRAPH, CURVE, and FREE CURSOR. Bring the cursor to the two peak positions and read the x axis values. Write your values on the printed curve.

4) Using a microsyringe, add the proper amount of dry ethanol to the solution in the cell to make it 0.05 M ethanol, bubble the solution for 1 -2 minutes with N_2 gas, and scan the solution at 50 mV. Save and print a copy of the voltammogram.

5) Using the microsyringe, deliver the proper amount of ethanol to the same solution in the cell to increase the total ethanol concentrations to 0.1M, 0.2M, 0.5M and 1.0M; Making sure to deoxygenate with nitrogen and scan at 50mV/s for each concentration. Make sure to save each voltammogram. Overlay the curves to see the trend. Print the overlaid curves.

6) For each voltammogram, save it with a file name, record the filename in your notebook, and and print it. Make sure to write the filename on each printed voltammogram. Evaluate the two E_p^o peak positions for the two waves in the absence of ethanol and the two E_p peak positions for each voltammogram corresponding to added amounts of ethanol.

7) Using the first peak data and equation 5, plot the experimentally determined values of $(E_p - E_p^o)$ versus ln [EtOH] and calculate values of the values of $K_{eq}^{(1)}$ from the intercept and n from the slope. R= 8.314 J/mol K, T= room temp, F= 9.65 x 10^4 Coulombs/mol electrons.

8) **Optional:** Using the second peak data and equation 6, plot the experimentally determined values of $(E_p - E_p^o)$ versus ln [EtOH] and calculate values of the values of $K_{eq}^{(2)}$ from the intercept and (m-n) from the slope. Once (m - n) has been determined, use the value of n determined from the first graph to determine m.

Lab Cautions for Cyclic Voltammetry

1. Contamination of reagents, glassware or electrodes can be a serious problem in this experiment. Make sure that only the pure reagents identified for this experiment are used and that all glassware and electrode surfaces are thoroughly clean before proceeding.

2. When you are finished using the electrode assembly, thoroughly rinse the cell and electrodes, clean the working electrode by rubbing it very gently with a very fine emery paper, washing it with deionized water and then with acetonitrile or ethanol. Clean the jacket of the reference electrode by throwing out the contents of the jacket and rinsing acetonitrile. Also wash the silver wire and counter electrode with acetonitrile.

3. The last person in the lab using the nitrogen gas for purging should close the valve to the tank before leaving**.**

Reference. N. Gupta and H. Linschitz, J. Am. Chem. Soc. 1997, 119, 6384.

Acknowledgment: The CSUN Chemistry Department wishes to thank Dr. M. Mohammad and Stephen Toner for their preparation of this lab experiment and writeup for the manual.

SUPERCONDUCTIVITY OF YTTRIUM BARIUM COPPER OXIDE

TABLE OF CONTENTS

SUPERCONDUCTIVITY OF YTTRIUM BARIUM COPPER OXIDE

LABORATORY OVERVIEW

This laboratory consists of two experiments which will be done over three three-hour laboratory sessions. One experiment includes preparation of a sample for electrical measurement using a helium cryogenic set-up. The other experiment employs a commercially available superconducting sample for electrical measurement using a liquid nitrogen set-up, hereby denoted as the Mickey Mouse (MM) set-up. To complete both experiments, proceed as follows:

Session I: 09:00 to 12:00hrs

09:00 to 10:00hrs Sample preparation for the He set-up
10:00 to 11:00hrs Sintering of the sample for the He set-up
11:00 to 12:00hrs Calibration of the MM set-up: Ohm's Law

Session II: 09:00 to 12:00hrs

09:00 to 10:00hrs Sample connections and evacuation for the He set-up
10:00 to 12:00hrs T_c measurement of the commercial sample using the MM set-up

Session III: 09:00 to 12:00hrs

09:00 to 12:00hrs T_c measurement of the prepared sample using the He set-up

PURPOSE

To explore the magnetic and electrical superconducting properties of yttrium barium copper oxide (Y-Ba-Cu-O or 1-2-3 as denoted by the subscripts in $YBa_2Cu_3O_x$) ceramics by:

1. Testing for the Meissner Effect
2. Measuring the critical or transition temperature, T_c

INTRODUCTION

History

Superconductivity's unusual electrical and magnetic properties have fascinated people since their discoveries in the early 20th century. Many materials show superconductivity, however, their transition or critical temperatures, T_c's, are either very low, or the form they are in are not conducive to work with on a practical level. Generally, metals have T_c's lower than 5K, elements are <10K, binary compounds and alloys are slightly higher, organic compounds are >30K, and oxides are >90K. Typically semiconductors and insulators show an increase in resistivity as temperature decreases, whereas metals show a decrease in resistivity as temperature decreases.

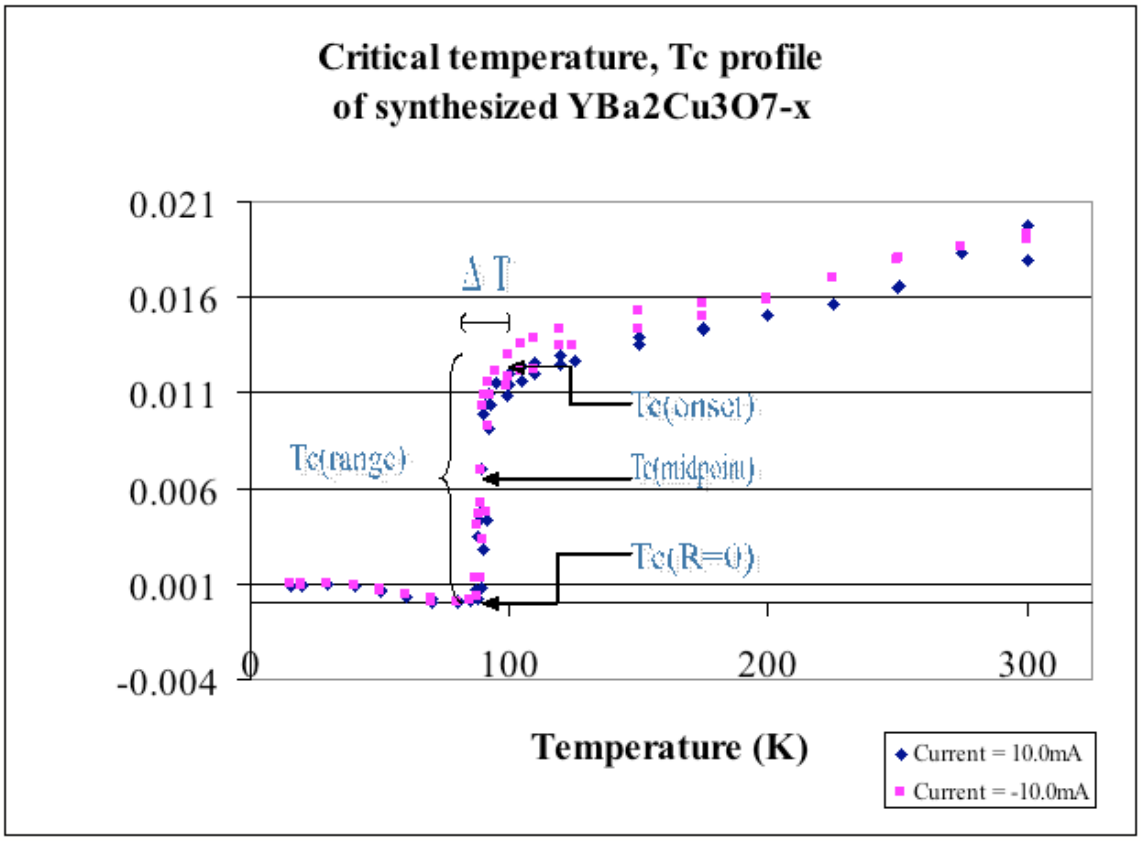


***Figure 1**, (1-2-3) profile of f(temperature)= resistance*

Relevance

The discovery of the more potentially practical high T_c superconductors such as that of the perovskite structured $YBa_2Cu_3O_x$ and the hexagonally structured MgB_2 in 1987 and 2000, respectively, has shown great promise in profoundly affecting many scientific, technological, and industrial applications; certainly a room-temperature or even "dry ice" temperature T_c superconductor would revolutionize the areas of electronics, transportation, medicine, and energy, and bring great fame and fortune to those researchers involved. One such application, nuclear magnetic resonance, NMR, a technique for organic analysis of molecular structure, uses high temperature superconducting Y-Ba-Cu-O and $Bi_2Sr_2CaCu_2O_{8+\delta}$ magnets and solenoids to provide the strong magnetic fields needed for improved resolution, sensitivity, and signal to noise ratio--commercial instruments operate at 900MHz hydrogen frequency at 21.1T central field (the Earth's field is approximately 20μT).

Theory

Methodology

While materials that superconduct may be affected by external magnetic fields, current, and temperature, the two factors defining superconductors are the exhibition of perfect diamagnetism and the conduction with zero electrical resistivity. In this laboratory, two characterization techniques will be employed on $Y\text{-}Ba_2\text{-}Cu_3\text{-}O_x$ samples--the Meissner Effect and the transition or critical temperature, T_c measurement. The **Meissner Effect** is the repelling magnetic force a superconducting sample exerts on an external magnet at or below the T_c.

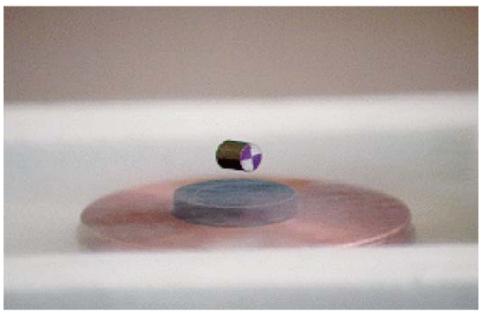


***Figure 2**, the Meissner effect*

Determining the T_c involves cooling of the sample until a dramatic drop to zero resistance is measured. To measure the resistance of the sample with depth **t** without having to consider the contact resistance as in a two-probe method, a **four-probe technique**, which measures the voltage difference, will be used. With this technique, four parallel, equidistant leads are adhered to the sample with spacing **s**. The outer two leads connect to a galvanostat which provides a constant current source **I**. The current flow, ideally, to eliminate dc polarisation, should be switched in direction for each measurement. The inner two leads connect to a multimeter to measure the resulting voltage **V**.

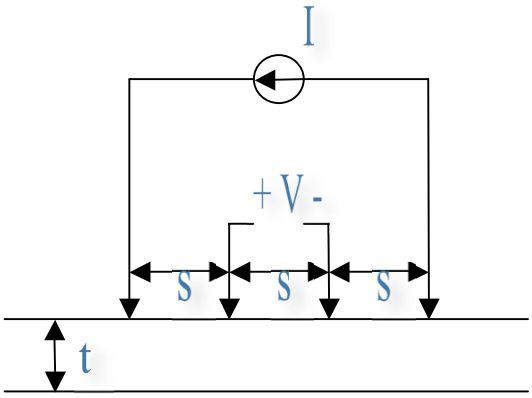


***Figure 3**, diagram of the four-probe method*

Through Ohm's Law, V=IR, the resistance, or resistivity can be calculated. Resistivity, ρ (Ohm m), is the electrical resistance between the parallel faces of a cubic meter of sample such that R = ρ(length/cross-sectional area); conductivity is the reciprocal of resistivity. Thus, resistivity for the following materials can seen as such:

an *infinite slab* of material

$$\rho = 2 \pi s V / I \quad \text{Ohm-meters for } t \gg s$$
$$\rho = (\pi t / \ln 2) V / I \quad \text{Ohm-meters for } s \gg t$$

a *shallow layer/sheet resistance* as

$$R_s = \rho / t = (\pi / \ln 2) V / I = 4.53 V / I \quad \text{Ohm-meters for } s \gg t$$

an *arbitrarily shaped sample sheet resistance* (Van der Pauw's method)

$$\exp (-\pi t R_{AB,CD} / \rho) + \exp (-\pi t R_{BC,DA} / \rho) = 1,$$

where A, B, C, and D are peripheral contacts such that

$$R_{AB,CD} = V_{CD} / I_{AB} \text{ and } R_{BC,DA} / V_{DA} / I_{BC}$$

a *symmetrical structure*, e.g., square or circle

$$R_{AB,CD} = R_{BC,DA} \text{ so } R_s = \rho / t = (\pi / \ln 2) V_{CD} / I_{AB}$$

Resistance, Resistivity, Conductivity

The proportionality between the current, **I** (Amperes), in a metal conductor and applied potential difference, **V** (Volts), is termed as Ohm's law. It is represented as

$$\mathbf{V = IR} \qquad \mathbf{(1)}$$

where **R** (Ohms) is the resistance to the passage of the current.

Resistance depends on the conductor's dimensions length ***l*** and area ***a***, such that

$$\mathbf{R = \rho\ (\ \mathit{l} / \mathit{a}\ )} \qquad \mathbf{(2)}$$

where ρ (Ohm m) is the sample's resistivity.

The reciprocal of resistivity, conductivity, κ ($Ohm^{-1}m^{-1}$), is a characteristic property of a material, e.g. density, specific heat, etc.

$$\mathbf{\kappa = 1 / \rho} \qquad \mathbf{(3)}$$

Electrical conductivity, notated as κ_E, is related to the thermal conductivity, κ_T; the number of conducting electrons, n_s (or charge density, n_s **e**); the relaxation time τ (or characteristic or relaxation frequency **ν**); and the activation energy of "conduction":

$$\mathbf{\kappa_T / \kappa_E = (\ 12 / \pi\ ) (\kappa_B / e\ ) T} \qquad \mathbf{(4)}$$

where κ_B is the Boltzmann constant = 1.380658(12) X 10^{-23}J K^{-1}, and **e** is the electronic charge.

Relaxation Frequency and the Activation Energy

Theory of the movement of electrons in metals relates κ_E to the charge density n_s **e** and to the relaxation time τ as

$$\mathbf{\kappa_E = (n_s e^2 \tau\ ) / m_e = b\ \tau} \quad \mathbf{(}\text{where } \mathbf{b = n_s e^2 / m_e\ )} \qquad \mathbf{(5)}$$

and to the number of electrons n_s as

$$\mathbf{\kappa_E = (8\ e^2 / h\ ) (\pi /3\ )^{2/3}\ n_s^{1/3}} \qquad \mathbf{(6)}$$

where **h** is the Planck constant = $6.6260755(40)\times10^{-34}\ J\ s$ and m_e is the mass of an electron = $9.1093897(54)\times10^{-31}\ kg = 5.48579903(13)\times10^{-4}\ m_u$. The relaxation frequency $\mathbf{1 / \tau = \nu}$, may be considered as the "hopping" frequency of an electron from one site to another.

This relaxation or "hopping" frequency **ν, i**s related to the ("hopping") activation energy $\mathbf{E_a}$ as

$$\nu = \nu_o e^{[-E_a / RT]} \qquad \textbf{(7)}$$

where $\mathbf{\nu_o} \cong 10^{14}\, s^{-1}$. Combining the equations (2, 3, 5, and 7) gives

$$\mathbf{R} = \left(\frac{l}{\mathbf{a}}\right)\left(\frac{\mathbf{\nu}_o}{\mathbf{b}}\right)\mathbf{e}^{[-\mathbf{E_a}/\mathbf{RT}]}$$

or

$$\mathbf{R} = \mathrm{L}e^{[-E_a / RT]} \qquad \textbf{(8)}$$

where **L** is a constant provided *l, a,* and n_s vary insignificantly with temperature. $\mathbf{E_a}$ can be determined from a plot of **ln R** vs. **1/T**.

Thus, the measurement of resistance (at various temperatures), along with the transition temperature T_c, can give other valuable information ($\boldsymbol{\tau}$**,** $\mathbf{n_s}$, $\mathbf{E_a}$, and $\boldsymbol{\kappa_T}$).

Sample Purity and the Superconducting Phase

The sample volume $\mathbf{V_0}$ that is found in the superconducting phase can be estimated from the relation

$$\mathrm{V_o} = \mathrm{V}\left(\frac{\mathrm{R_o}}{\mathrm{R}}\right)^2 \qquad \textbf{(9)}$$

where **V** is the total volume of the sample, and $\mathbf{R_0}$ and **R** are the sample resistances in the superconducting and non-superconducting states, respectively.

Another indication of the impurity phase is the purity factor **P. F.**, and is estimated to be

$$\mathrm{P.F.} = \frac{\Delta \mathrm{T}}{\mathrm{T_c}} \qquad \textbf{(10)}$$

where $\mathbf{\Delta T}$ is the width of the resistance vs. temperature transition curve, and $\mathbf{T_c}$ for this laboratory, is the midpoint of the transition curve (resistance $\mathrm{R} \neq 0$). The width $\mathbf{\Delta T}$, can be considered as the temperature range from the onset temperature $\mathbf{T_{c(onset)}}$ (or 95% of the onset) to the zero resistance (or near zero resistance or 5% of the zero resistance) temperature $\mathrm{T_{c(R=0)}}$**.**

EXPERIMENT (Helium set-up)

MATERIALS

- Alfa Aesar Stock#39534 Yttrium barium copper oxide (1-2-3) 99.9% metals basis 1-6 micron powder, $YBa_2Cu_3O_x$
- Weighing paper
- Soft cloth or lens paper
- Spatula
- Brush
- Liquid nitrogen
- Magnets: Neodymium-iron-boron $Nd_2Fe_{14}B$
- Fisher Brand 01-213-3 Aluminum foil
- Apiezon Type N cryogenic high vacuum grease
- Apiezon Type H high temperature vacuum grease
- SPI# 05062-AB 05063-AB Silver Paste Plus TM Silver Paste
- Sample connections made from: heat shrink; Belden bus bar AWG18 tinned wire; MWS copper magnet wire SPN-155; Radioshack 64-029 Lead-Free Silver-Bearing Solder 96%Sn/4%Ag)
- 3M Scotch^{TM} Permanent-Linerless Double-Coated Tape 665
- VWR Aluminum foil tape without liner

EQUIPMENT

- ICL 0009-491 Agate mortar and pestle 95mm OD
- AG204 Mettler Toledo analytical balance
- Carver Laboratory Press Model B 0 to 24000LBS Load
- ICL 0012-2477 Macro/Micro KBr 13mm diameter evacuable pellet die set
- Vacuum system: Welch 1400 DuoSeal Vacuum Pump; Varian 801 MilliTorr tc vacuum gauge; Nalgene tubing
- Fisher 10-470-18 ceramic combustion boat
- Fisher Scientific Isotemp Programmable Muffle Furnace 750-14 with 10550P Port Kit
- Dewar
- Plastic tweezers
- Glass Petri dish or Styrofoam insulation
- Awl
- Tweezers
- Razor blades
- Lamp
- Computer; printer; shielded GPIB cables and software
- Scientific Instruments Temperature Controller Model 9700-1-7 with G.U.I.
- Agilent 34401A Digital Multimeter
- Princeton Applied Research 263A-2
- Neslab Coolflow CFT-75 Refrigerated Recirculator
- Air Products HC-2
- Air Products Displex DE-202-O.S. P. AA1214-101 and cryogenic sample chamber with quartz window; sample platform and electrical connections; radiation shield; temperature sensors (Scientific Instruments Si410NN Silicon Diode Thermometer; Gold-Chromel thermocouple).
- Vacuum system with diffusion pump set-up: glassware; diffusion pump with aluminum heat vane and Corning diffusion pump oil; heater; ceramic plate; dewar; nitrogen trap; Varian Torr cold cathode vacuum gauge 860A-2; Varian MilliTorr Tc vacuum gauge 801; power conditioner; Laboratory Craftsmen Solid State Control S-22 Powermite; Welch 1400 DuoSeal Vacuum Pump; Nalgene tubing.

SAFETY

Safety goggles
Gloves
Dust mask
Laboratory coat
Fume hood

Cautionary Notes:

Alfa Aesar Stock#39534 Yttrium barium copper oxide (1-2-3):

Avoid inhaling this black, odorless, 1-6 micron size powder. Wear appropriate gloves and face dust mask. Wash hands immediately after using. Keep stored in a tightly sealed container in a cool, dry place. Dispose appropriately.

SPI #5063 Silver paste plus:

To minimize loss of the carrier solvent, keep the tube stored vertically with the opening pointed downwards.

PROCEDURE

Laboratory I:

Sample preparation

1. Because yttrium barium copper oxide (1-2-3) is moisture sensitive, keep the precursor powder and sample in a dessicator when not in use. Obtain ~630mg of the (1-2-3) powder. The powder should be as fine and homogenous as possible—pulverize, using an agate mortar and pestle to remove any agglomeration. A spatula, weighing paper, and/or brush may be used to transfer the powder.

2. The evacuable pellet die set has five main visible parts: two anvils, a plunger with an o-ring, a base with hose barb/evacuation tube and o-ring, a cylinder, and a transparent lucite or acrylic pellet extractor ring. Make sure the base and cylinder that has a bore for the pellet are assembled.

***He Figure 1**, ICL evacuable pellet die*

3. The polished sides of the anvils should face the sample powder. In the barrel, drop in one anvil with the polished side up. If available, position a paper insert over this

anvil and fill the paper insert with the sample powder. Transfer and evenly distribute the sample powder into the barrel over the anvil. Avoid getting sample powder on the walls of the bore. Tapping the side of the cylinder or slowly turning the plunger over the powder two turns may help in distributing the sample powder. Drop the other anvil with the polished side down into the barrel over the sample powder. Slide the lubricated o-ring down the plunger away from the beveled end. Drop the plunger into the barrel, so that the beveled end is up and the o-ring forms a seal.

4. Position the assembled pellet die set in the center of the platform of the laboratory press. Tighten the knob (turn clockwise) and check that the platform is level. Move the lever up and down just until there is enough pressure to hold the pellet die set in place. The load should be approximately 5000lbs. Grease the evacuation tube if necessary. Fit the Nalgene tubing over the hose barb. Plug in both the vacuum gauge and vacuum pump. Turn the vacuum pump on. When the vacuum gauge reads ≤ 100 mTorr, wait for two minutes before slowly pressing to 15000lbs (the 13mm pellet die set has a recommended 5 to 8 tons of pressure range; 1 ton = 2000lbs). If needed, fit the steel pipe over the lever to extend the length. The lever may need to be adjusted while holding the pressure at 15000lbs for two minutes. Note the vacuum gauge reading, e.g. 60 mTorr, before turning the vacuum pump off. Remove the Nalgene tubing. Release the pressure knob (turn counterclockwise) so that the press platform lowers just enough to remove the pellet die assembly.

5. Disassemble the pellet die by first removing the plunger, and then twisting off the base from the cylinder. Slide the o-ring towards the beveled end of the plunger and place the plunger with the beveled end down. Invert the cylinder over the plunger. Place the extractor ring on top of the cylinder. Holding all three parts, gently push out the anvils and sample pellet. Alternatively, leave the plunger in place, after removing the base. Invert the cylinder and plunger, place the extractor ring over the cylinder cavity, place this assembly in the press, and lightly apply a load across the plunger and extractor ring until the sample pellet can be seen. The sample can be extracted with plastic or bamboo tweezers.

6. Clean the pellet die set with a soft cloth or lens paper. Grease the o-rings if they are stiff with vacuum grease. Avoid getting hydrocarbon or other solvents on the black anodized section of the base.

7. Note the appearance and take the dimensions of the sample pellet (diameter and thickness). Use a multimeter to determine the two-probe resistance of the sample.

Sintering

1. Sintering, an irreversible thermal treatment at or below the main constituent's melting point of a powder compact, is usually the last step in a solid-state synthesis process for strengthening, hardening, distributing and averaging of grain number, size, and shape, increasing densification and grain growth, and eliminating of porosity with diffusional mass transport. Further cooling under controlled atmospheres can affect the composition of the final product.
2. Refer to the Fisher Scientific Isotemp Programmable Muffle Furnace 650-750 Series Instruction Manual when necessary. The Fisher Isotemp Programmable Muffle Furnace with injection port average temperature uniformity is $\pm 5^{o}$, with a temperature stability of $\pm 1^{o}$. Because of the furnace's limitations, the actual temperatures may not follow the set temperatures, and the ALARM LED will be on when the actual temperature exceeds the set temperature by 25°C until the actual temperature falls within 5°C of the set temperature. The set display, actual display, heat LED, alarm LED, and Run LED's should all be monitored throughout the heating program. When the program is running, the status of the current program step can be viewed in the following order by successively pressing the MENU key End set point, rate, elapsed jump count, step, hour, min, sec, actual and set temperatures.
3. The furnace power should be switched on and the circulating fan switched off (0). The fumehood should be on. Place the sample pellet horizontally over the ceramic combustion boat, open the furnace door, position both in the center of the furnace chamber on the hearth plate, and close the furnace door.
4. Furnace programming:
    4.1 The sintering will be done under an air atmosphere. The furnace program cycle will start at room temperature, then go to 950°C at a rate of 50°C/min., then remain at 950°C for 6 hours, and finally, go to 25°C at a rate of 1°C/min. This program will take approximately 1 hour and 45 minutes to reach 950°C, will hold at 950°C for 6 hours, and will take approximately 18 hours to get close to room temperature.
        4.1.1 The MENU key functions as an "enter" key. The UP and DOWN arrow keys can be used to adjust the values/settings displayed.
        4.1.2 If the RUN key is on, press it until it goes off. Press the MENU key [no Prog]. Press the UP-arrow key [1 Prog]. Press the MENU key to enter Program 1.
        4.1.3 Verify the furnace Program 1 has the following program:
            4.1.3.1 [1 Step] MENU [SP Styp] MENU [950 SP] MENU [50.0 rate] MENU [no retn] MENU
            4.1.3.2 [2 Step] MENU [Soak Styp] MENU [6 hour] MENU [0 min] MENU [0 sec] MENU [no retn] MENU
            4.1.3.3 [3 Step] MENU [SP Styp] MENU [25 SP] MENU [1.0 rate] MENU [no retn] MENU
            4.1.3.4 [4 Step] MENU [End Stop] Menu [Off End] MENU [1 SAVE] MENU [Actual ˚C OFF]
5. Running the furnace program:

5.1 Press the RUN key. The Run light will flash. Press the MENU key until the display shows [1 Prog]. Press the UP key to display [1 Step]. Press RUN key. The Run LED will constantly be on.

6. When the program has finished, remove the sample from the furnace. Note the physical characteristics and dimensions (thickness, diameter, mass). Measure the 2-probe resistance with a multimeter.
7. Test for the Meissner Effect:
   7.1 Wrap the sample pellet in aluminum foil and place this sample in the insulated Petri dish.
   7.2 Pour liquid nitrogen (b.p. 77K) from the dewar into the Petri dish over the sample.
   7.3 Bring a magnet near the sample and observe if there is a repulsive effect. If the sample and magnet repel each other, then there is a strong indication that the sample will be superconducting.
   7.4 After drying the aluminum foil covering the sample, remove the aluminum foil from the sample.

Laboratory II:

Sample connections

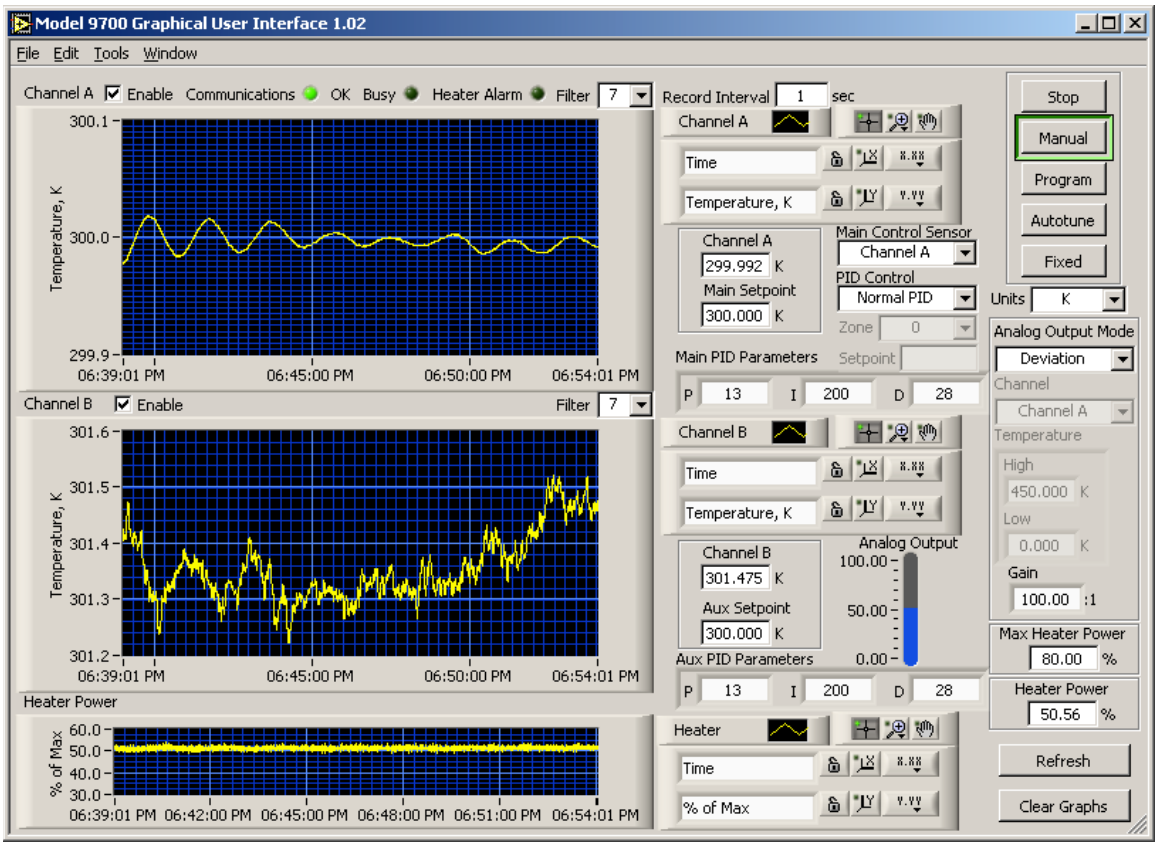
1. For the four-probe method, obtain four wire connections—the two other leads will pass the constant current supply, and the inner two leads will be used to measure the voltage difference. Using a razor blade, scrape off enough insulation so the wire can be adhered to the sample. Place a piece of double-sided tape on a piece of weighing paper. Position the sample on top of the double-sided tape.
2. The awl and tweezers may help in positioning the wires and in applying the necessary amount of silver paste to the sample and bare wire to make four equidistant parallel connections. To cure the silver paste more quickly, radiate these connections with a lamp. The cured silver paste should be lighter in color and harder. Check the connections with a multimeter.
3. Measure the dimensions—the thickness of the sample pellet, the length of the sample wire adhered to the sample, and the distance between the two outer leads.
4. Make sure the vacuum to the sample chamber is closed. The vacuum in the sample chamber can be released by pulling out the rod held in place by a screw. Remove the quartz window on the vacuum shroud before pulling it off. Unscrew the radiation shield to reveal the sample mount and probe. Unwind enough aluminum foil tape to remove the previous sample.
5. Connect the four sample connectors by fitting the bus wire end of the connectors to the appropriate lead sockets that match the measurement leads that come out from the pin head of the Displex and then connect to the instruments. Replace the double-sided tape on the sample mount if needed, and gently press the sample and wires onto the taped mount for heat sinking. Using a multimeter, check the connections from the sample to the instruments. Place another piece of double-sided tape over the sample. Position the silicon diode over the taped sample and press gently. Check that the temperature controller has a room temperature reading.
6. Rewrap aluminum foil tape over the wire connectors and sample, screw on the radiation shield, and push the vacuum shroud back on. Make sure the vacuum release is secure and that the window opening is horizontal. Reposition the quartz window so that it closes the sample chamber; add grease to the o-ring if needed.

7. Hold the vacuum shroud in place while slowly opening the vacuum. Monitor the vacuum pressure with the gauges. When the Varian 801 milliTorr tc vacuum gauge reads 100mTorr, the diffusion pump can be used.
8. Start the diffusion pump by pressing the Green start button on the power conditioner. Turn the dial of the Powermite to about 40% to start the heater; the oil in the diffusion pump should reflux. Fill the dewar surrounding the trap with liquid nitrogen. When the Varian 801 milliTorr tc vacuum gauge reads below zero, the pressure can be monitored by the Varian 860A-2 Torr cold cathode vacuum gauge. When the Varian 860A-2 Torr cathode vacuum gauge gets to 10^{-5} Torr, the Powermite can be turned off.
9. Perform the Critical temperature, T_c initial settings if time allows.

Laboratory III:

Critical Temperature, T_c Initial settings

1. The Scientific Instruments Model 9700 temperature controller, the Agilent 34401A digital multimeter, and the Princeton Applied Research (PAR) Galvanostat Model 263A-2 instruments should be on. In Windows, open the Scientific Instruments Graphical User Interface G.U.I. LabView 2003 Version 1.02b program on the computer by clicking on the Start menu. Select Programs, select Scientific Instruments, select M9700. The G.U.I. should appear. Click on the Manual button in the top right of the window.
2. To switch the other instruments to local control, press the blue shift button on the Agilent 34401A, press the black F5 button on the PAR263A-2. Press the Agilent 34401A function button DC V. For the PAR263A-2 front panel, make sure the Cell light is off; press the black Mode button until the display reads [Galvanostat]; turn the silver knob until the display reads CURRENT = -0.2mA; and press the up or down buttons until the light is on 100mA.
3. Return to the G.U.I. window and check the settings. Setting values can be changed by clicking in the box, typing in the value, and pressing Enter. Remember to change both settings for each of the active temperature sensors (Channel A is the silicon diode; Channel B is the gold-chromel thermocouple).



***He Figure 2**, S.I. Model 9700 G.U.I.*

4. Turn on the Neslab Coolflow CFT-75 Refrigerated Recirculator, and then turn on the Air Products HC-2.
5. Return to the G.U.I. window. When the temperature has stabilized, click on the Autotune button to start a 9 cycle autotune procedure that can be monitored on the front panel display of the temperature controller. A window will appear that with the old and new PID parameters. Accept or enter the new PID parameters for the sensors. When the temperature has stabilized, the T_c measurement process may begin.

Critical Temperature, T_c Measurement

1. Decide on a constant current and the temperatures at which the measurements will be taken given the allotted laboratory class time. Thermal equilibrium time is faster at higher temperatures and slower at lower temperatures. Be aware that the silver adhesive may not withstand dramatic temperature changes. The temperature can be changed through the Scientific Instruments G.U.I. and monitoring can be done for Channel A, the silicon diode temperature sensor. The voltage will be measured using the Agilent 34401A. The current settings must be manually changed through the front panel of the PAR263A-2. At each set temperature, the actual voltage reading, actual temperature, set current, and applied current should be recorded.
2. Given the class time allotted, the instructor or assistant will take data measurements for the temperatures (K) 300, 250, 200, and 150. **Recommendations are as follows:**

applied current via the galvanostat = cell off at 300 K and cell on at +10mA. Leave the current at +10mA for the remaining measurements at set temperatures (K) = 100, 95, 93, 91, 90, 89, 87, 85, 83, 81, 79, 77, 75, and 70. The system, when the set temperature is 0 K, will go to approximately 14 K (b.p. of helium is 4.2K). Temperature stabilization after a setting change is approximately 20 minutes, and settling time for a measurement is approximately 2 minutes. For a three hour laboratory period however, 14 temperature settings will allow for ~ 12 minutes to be given for each measurement setting. A dramatic change in the voltage reading and thereby, resistance via Ohm's Law, is indicative of the T_c region. Graph the data.

3. The class instructor or assistant will bring the temperature back to room temperature and remove the sample.

EXPERIMENT (Mickey Mouse MM set-up)

MATERIALS

- Superconductivity sample obtained from Arbor Scientific with dimensions: 22mm diameter, 4mm thickness
- Arbor Scientific Supercon. Economy Demo Kit

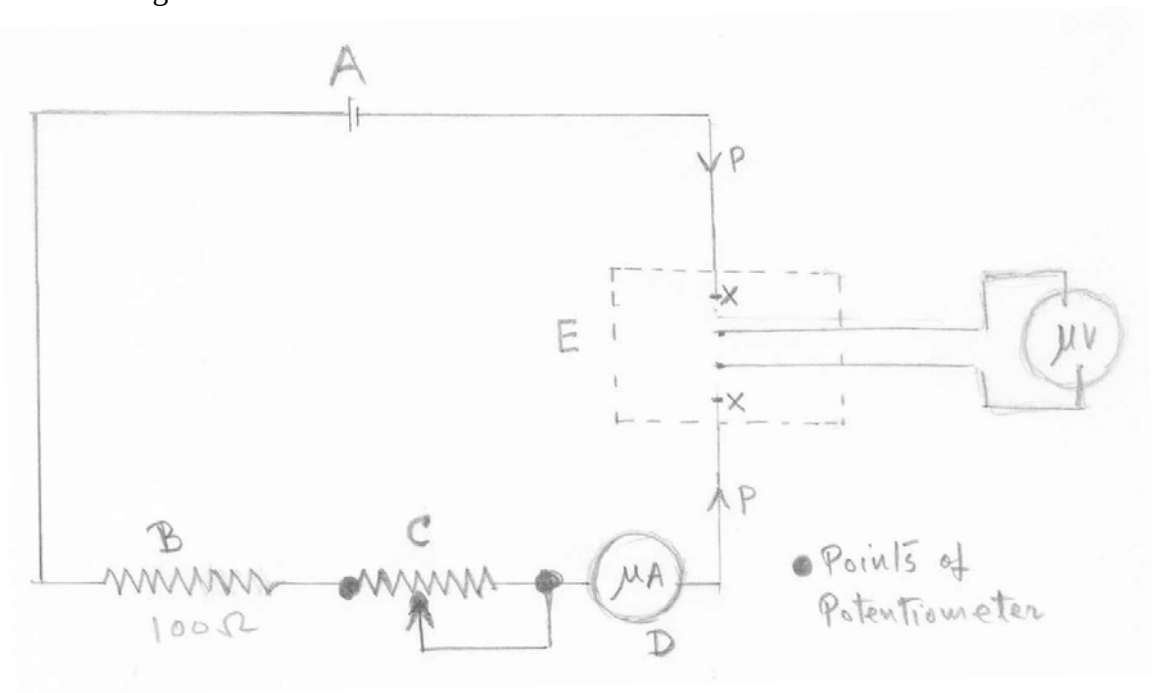
EQUIPMENT

- 10 point Temp scanner (Extech Co) used as a temperature sensor (needs calibration).
- Fluke 8600 multimeter, limit 10μV, used as μ voltmeter.
- Multimeter (Triplett Elec. Instrument Co. USA) used as a DC milliammeter.
- Constant current Power supply (custom built).
- Sample Immersion Probe (custom built).
- 10 or 25 L liquid nitrogen dewar.
- J-type thermocouple wire.
- Miscellaneous: electrical wires, alligator clips, on/off switch, rubber stopper, clip, scotch and masking tapes.

COMPONENTS

Constant Current Power Supply (custom built)

A Rayvok heavy duty 6 volt battery was used as a source of current. The current was regulated through a circuit board which was used in earlier coulometry experiment. The circuit board has a "pot" potentiometer and for use in galvanostatic mode. The circuit is shown in Figure 1.



***MM Figure 1**, the circuit.*

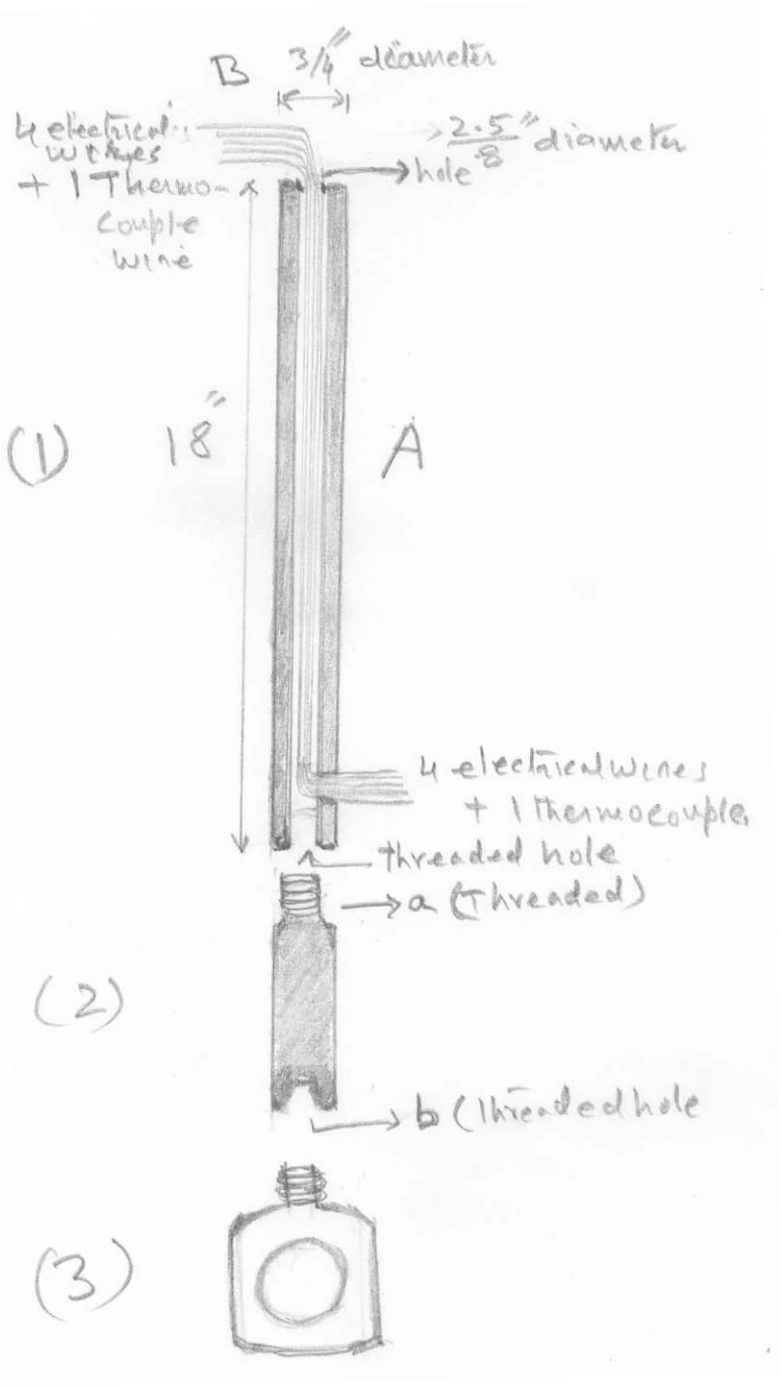
A = Rayvok heavy duty 6 volt battery (cell)
B = 50 or 100 Ω resistors.
C = Pot potentiometer used as Rheostat with max R = 500 Ω

D = a milliammeter
P = (wires) to the 4 probe measurement device to X
E = 4 probe device showing power supply (current) connection at X's (the end-connection of two yellow wires of the probe), and
F = Fluka micro-voltmeter connected to the inner two red wires of the probe.

Sample Immersion Probe (custom built)

The probe essentially has three parts (see **Figure 2**):

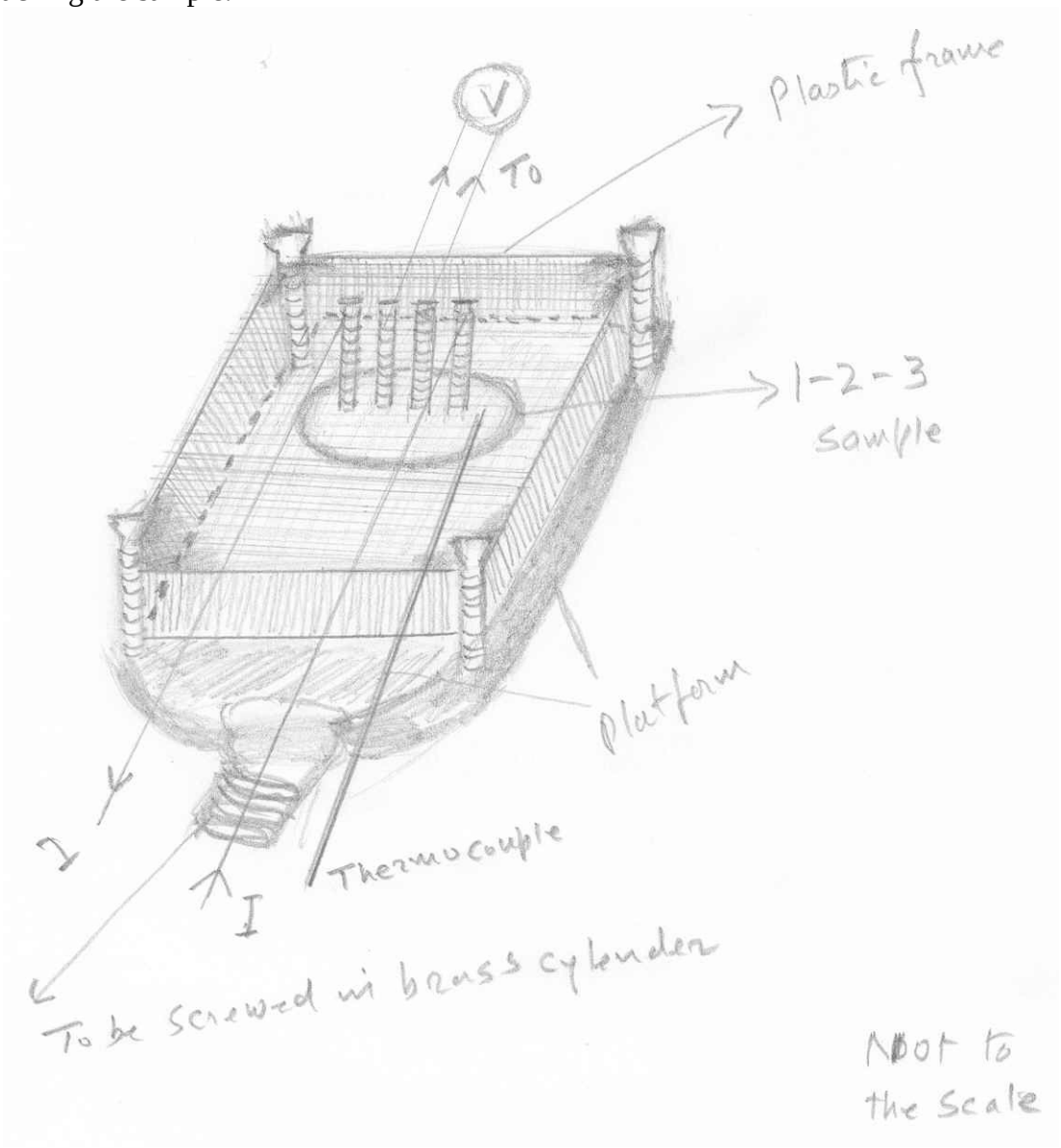
1. **A hollow plastic handle.** Length = 18"(A); diameter = ¾" (B); diameter of the hole 2.5/8" (C); and hole D for four electrical and one thermocouple wires to come out.
2. **Solid brass cylinder.** Length 4.25 "; diameter ~ .75 " with threads at both ends (a and b). End **a** fits in the hole on one end of plastic handle, the other end, **b**, is a threaded hole to which a platform screws in. This part of the brass cylinder acts as a heat sink.
3. **Platform**. Taken from an old Displex system where a CsI disc platform was used. The gap was filled with an aluminum disc adhered with Scotch tape for insulation; Scotch tape conducts heat at low temperatures.



MM Figure 2, *the sample probe.*

4. **The fourth part, a plastic frame** (see **Figure 3**). In a true sense, this piece is not a part of the platform. This plastic rectangular piece frame (28mm x 28 mm x 3mm(thick)) has four screws at the four corners and is screwed to the platform with corner screws. It also has four collinear holes in the center for screws. These (collinear) screws, after the frame is screwed on to the platform, can be screwed down to touch the superconductor sample (these screws are then glued to the superconductor sample with silver conducting epoxy (see Procedure)). The four collinear screws are then connected to the four-probe

wires--the yellow ones to the end screws and the red or inner ones to the center two screws. The thermocouple wire end is kept on the surface of the sample platform or touching the sample.



***MM Figure 3**, the sample frame and platform.*

PROCEDURE

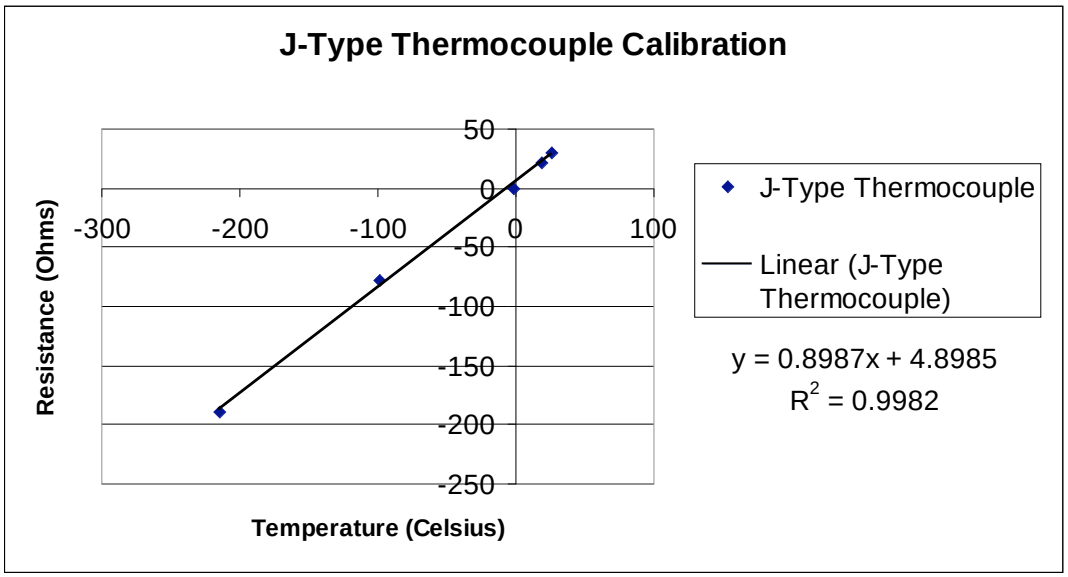
The experimental assembly has been completed, and students should only do the specified steps—the circuit connections, the room temperature verification of Ohm's Law, and the cryostatic measurements of resistance..

Calibration of the thermocouple temperature scanner

1. The temperature scanner was made for high temperature measurements for a tube furnace. It used a different thermocouple wire, a K-type. For low temperature, a different thermocouple wire (J-type) was used. The following temperature points/baths can be used to calibrate the system: room temperature, ice, dry ice, and liquid nitrogen, and these readings were obtained at various times:

Temperature (K/°C)		Temperature scanner reading (/°C)
Room temperature	291/21	19
Ice	273/0	-1
Dry ice	194.8/-78.2	-99
Liquid nitrogen	77/-197	-214

Students can use the plotted graph (**Figure 4**).



***MM Figure 4**, calibration curve of the J-type thermocouple and Extech temperature indicator.*

A new calibration curve may be drawn if and when needed.

2. A new calibration curve may be drawn if and when needed with the following procedure:
   - 2.1 The red lead of thermocouple to be connected to negative "-", the other lead to the positive "+" of any channel connection, say #1 of temperature scanner.
   - 2.2 The other end of the thermocouple is to be exposed to the environment (room temperature, ice bath, dry ice bath, liquid nitrogen).
   - 2.3 After letting the thermocouple equilibrate to give a stable temperature reading on the scanner, record the temperature.

Electrical connections to the superconductor sample

1. This procedure was the trickiest part. The published stainless steel strip connection between screws and the superconductor ceramic did not work. This procedure is not to be done by the students. They will be given the assembled apparatus.
2. Four collinear screws were "glued" to the ceramic with silver epoxy (Alfa Aesar Silver two part conductive adhesive; purchased in 2000 and stored in a refrigerator). A small, tiny amount of silver epoxy was put on the tip of each screw. The plastic frame was screwed to the platform, taking care that the collinear screws did not touch the sample. The four collinear screws were then lowered (screwed in) until the tip of each screw touched the ceramic. It is unnecessary to tighten the screws, but it doesn't hurt if they are slightly tightened.
3. The connecting leads were wound around the collinear screws, near the heads of the screws. The two yellow wires connect to the outside screws, and the red wires connect to the inner two screws (see Figures 3 or 4). Some silver epoxy was also put around each wire to prevent loose connections.
4. The platform (with the sample ceramics) which was already screwed in the brass sink tip, and the frame and wires attached to the screws were all left overnight to let the silver epoxy dry (for curing).

Laboratory I

Circuit connections

1. Check the following connections:
   - 1.1 The two red wire clips are connected to the clips of voltmeter.
   - 1.2 The two yellow wire clips are connected to the clips of black and multicolor leads of power supply system.
   - 1.3 The red lead of thermocouple wire is connected to the negative terminal "–", and the other wire is connected to the positive terminal "+" of the temperature scanner. These connections will enable one to read the temperature in Celsius (Note: the calibration graph is to be used to know the actual temperature of the sample).

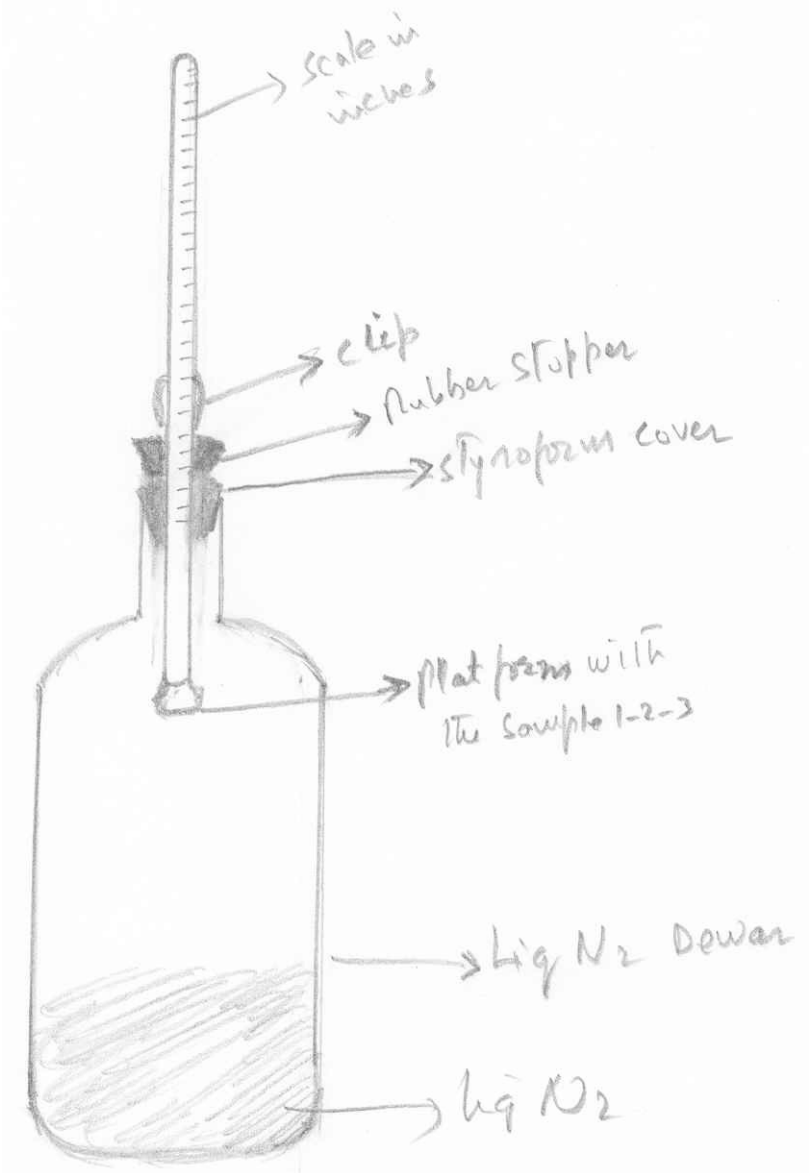
Room temperature verification of Ohm's Law

1. With the help of the "pot" potentiometer, the applied current to the sample can be increased or decreased, and the corresponding voltage can be noted from voltmeter.
2. Starting with 10mA (read the value on the voltmeter/multimeter), record the voltage (mV) for every 10mA increments up to 50 mA. The five points--10mA, 20mA, 30mA, 40mA, and 50mA—should be sufficient to draw a graph to see if the system follows Ohm's Law.

Laboratory II

Cryostatic measurements of resistance

1. Approximately 3-5 liters of liquid nitrogen in the 10-25 L dewar should work for this procedure as there are two factors to consider—the probe should be lowered slowly into the dewar and there should not be too much liquid nitrogen in the dewar.
   1.1 The immersion probe carrying the sample is not to be directly immersed in liquid nitrogen in the dewar. To handle and control the length of the probe to be put in the dewar, the custom built probe has been provided with a styrofoam cover, a rubber stopper and a large clip. All these three components can slide on the probe "handle", enabling adjustment in height as shown in **Figure 5**.



***MM Figure 5**, probe immersion into a liquid nitrogen filled dewar.*

1.2 The amount of liquid nitrogen in the dewar could affect the measurement in the sense that, if there is plenty of liquid nitrogen in the dewar, the temperature inside the dewar even near the top could be quite low. A very rapid decrease in temperature of the sample once in the dewar could disrupt the screw-sample-silver epoxy connection and cause the connection to break.

2. **Students should follow this procedure**:

2.1 Fill the dewar to its $1/3^{rd}$ capacity with liquid nitrogen.

2.2 Lower the probe, not more than six inches initially. Let the temperature stabilize. Read the temperature (on the temperature scanner) and the voltage. These values should be recorded for all the temperature points.

2.3 Lower the probe by 2-3 inches and read the temperature and voltage; when readings on the Temp. Scanner and voltmeter stabilize, the voltage may fluctuate +/- 0.01 mV.

2.4 When the system reaches around $-205^{o}C$ temperature (on the Temperature Scanner), lower the probe 1 more inch. This temp may be close to the critical temperature. In previous experiments, the critical temp was found to be $-209\ ^{o}C$ to $-210\ ^{o}C$ reading on the Temperature Scanner). The middle point Tc would therefore be -209.5 (+/- 0.5) ^{o}C. Go down to the limit—the liquid nitrogen temperature. Read the temp from the scanner and the voltage from the voltmeter. It should display the value at the instrument's limit.

2.5 Now reverse the procedure by lifting the immersion probe 1-inch at a time while reading the stabilized temperature and voltage. When $-205\ ^{o}C$ is reached, the probe can be removed 3-4 inches at a time. Keep recording the stabilized temperature and voltage. This reversed procedure will give the hysteresis curve of the V vs. T plot. Ideally, the T_c obtained by going down the temperature should be the same as going up the temperature scale.

DATA ANALYSIS

Experiment (He set-up)

Critical Temperature, T_c

1. Plot a graph of temperature (K) vs. resistance R (Ohms).
2. Determine the T_{onset}, $T_{c(midpoint)}$, and $T_{c(R=0)}$.

Resistivity, ρ

1. Use the sample dimensions to obtain a plot of the temperature (K) vs. resistivity ρ (Ohm m).

Conductivity, κ_E

1. Take the reciprocal values of the resistivity to obtain a graph of temperature (K) vs. conductivity κ_E ($Ohm^{-1}m^{-1}$).

Relaxation Frequency, ν and Activation Energy, E_a

1. Plot 1/T vs. lnR, use the $T>T_c$ region to obtain the E_a.
2. Evaluate ν for the temperatures at 300K, T_{onset}, and $T_{c\ (midpoint)}$.

Superconducting Phase Purity

1. Use the graph of temperature (K) vs. resistance R (Ohms) to determine

1. the percent of sample in the superconducting phase and
2. the sample purity factor.

Experiment (MM Set-up)

Ohm's Law, V = IR

1. Plot a graph of voltage V (Volts) and current I (Amperes).
2. Obtain the values of resistance R (Ohm) from the graph.

Critical Temperature, T_c & Other Parameters

1. Use the temperature calibration graph to get the actual temperature values
2. Plot temperature vs. voltage/resistance to evaluate T_c
3. Using the graph of 1/T vs. lnR (or lnV), evaluate E_a for the region where $T>T_c$.
4. Refer to equations 5 and 6 to determine the relaxation (hopping) frequency at room temperature, near the T_{onset}, and at the T_c (defined here as the midpoint of the transition curve; technically, resistance R 0).
5. Refer to equations 9 and 10 to obtain the phase purity of the sample.

Resistivity & Conductivity

1. Assuming
   Length l = .75 cm (= 0.015 m, the distance between the two inner screws) and
   Area a = 1.5 cm x 0.4 cm (= 0.6 cm^2 = 0.00006 m^2),

convert resistance into resistivity , and hence obtain the conductivity $_E$.

Acknowledgment: The CSUN Chemistry Department wishes to thank Dr. M. Mohammad and Young Shen for their preparation of this lab experiment and writeup for the manual.

REFERENCES

1. The Meissner effect: http://www.physics.ubc.ca
2. Neudeck, G. W. and Pierret, R.F., editors. Modular Series on Solid State Devices. Volume 5, Introduction to microelectronic fabrication by R. C. Jaeger; Addison-Wesley (1993).
3. 13mm KBr pellet die: http://www.internationalcrystal.net/icl78.htm.
4. The High-T_c Superconductivity Information Center http://www.iitap.iastate.edu/htcu/
5. Kittel, Charles; *Introduction to Solid State Physics*; John Wiley 1968.
6. Poole Jr., Charles P. et al.; *Superconductivity*; Academic Press 1995.
7. Moelwyn-Hughes, E. A.; *Physical Chemistry*; Pergamon Press 1961; Chapter XV.
8. Shabetnik, V. D.; Butuzov, S. Yu.; Paksi 0, V. I. High-temperature superconducting compound $YBa_2Cu_3Se_7$ with T_c = 371 K. *Tech. Phys. Lett. 21* (5), May **1995**; pages 382-384.
9. Fisher Scientific Isotemp Programmable Muffle Furnace 650-750 Series Instruction Manual Part No. 103770 Rev B. Published 11-2001.
10. Princeton Applied Research Model 263A Potentiostat/Galvanostat User's Manual 222688 F / 0800 and Command Set Handbook 222689D / 0103.
11. Agilent Technologies Inc., Agilent 34401A Multimeter User's Guide Manual Part Number 34401-90004 and Service Guide Manual Part Number 34401-90014, March 2000 Edition 5.
Scientific Instruments, Inc. Operation Manual for 9700 Temperature Controller 090-256.

PHASE DIAGRAM FOR A THREE COMPONENT SYSTEM

PURPOSE

The ternary system butanol-water-acetic acid will be investigated. The phase diagram for the system will be constructed and examined for conformity to the phase rule.

THEORY

Information regarding phase equilibria can be predicted by a simple rule that was originally formulated by Gibbs:

$$\mathbf{f = c - p + 2}$$

where **c** is the number of components and **p** is the number of phases present in the system. The degrees of freedom, **f**, or variance, gives the number of variables (pressure, temperature, composition, etc..) that must be fixed to completely describe the system, or locate the state of the system on the phase diagram. Gibbs defined the components of a system as *the minimum number of independent species necessary to define the composition of all phases present in the system* and he defined a phase as *a state of matter that is uniform throughout, not only in chemical composition but also in physical state.*

In a one component system such as a pure gas for example, we have c = 1 and p = 1 so that $f = 2$. This means that in order to completely describe the system, we only have to know two out of the three variables P, V, or T to completely describe the 'state' of the system. This fact becomes clear when these variables are considered in conjunction with a phase diagram, but in this case we know that we can calculate the third variable from equations of state such as the Ideal Gas Equation.

As a second example, consider water. Most physical and general chemistry books give its phase diagram. In the pure phase regions (S, L, or V) we have that f = 2, meaning that pressure can be varied independently of temperature. Along the S-L, L-V boundary, however, p = 2, and f = 1. Thus for every value of P, there can only be one specific value of T. Finally at the triple point, p = 3 and f = 0. Under these conditions the system is totally fixed, and no variation in temperature or pressure is possible without changing the 'state' of the system.

There are many examples in nature of phase diagrams and the phase rule. This experiment and the liquid-vapor experiment described in this manual are just two examples.

PROCEDURE

ALL PARTS OF THE EXPERIMENT SHOULD BE DONE IN THE HOOD

PART I

1. Place 20 ml of water in a 50 mL Erlenmeyer.flask. Cover the flask with parafilm. Poke the buret containing butanol through the parafilm. Add butanol to the water drop by drop with continuous stirring until the last drop does not dissolve in the water after five minutes of stirring. It will take less than 2 ml to reach this point.

2. Place 20 ml of butanol in a 50 mL parafilm-covered Erlenmeyer flask. Add water to the butanol drop by drop with continuous stirring until the last drop does not dissolve after five minutes of stirring. It will take more than 2 ml to reach this point. Record your results on the data sheet provided.

3a. Place 20 ml of butanol and 5 ml of water in a 200 mL parafilm-covered Erlenmeyer flask. Add acetic acid drop by drop with continuous stirring until the turbidity disappears. Record the volume of acetic acid added.

3b. Add an additional 5 ml aliquot of water to the mixture from step 3a. Again titrate with acetic acid dropwise with stirring until the turbidity dissapears.

3c. Continue adding water in 5 ml aliquots and titrating to the turbid point with acetic acid as indicated on the data sheet until a total of 30 ml of water have been added, then 10 ml aliquots of water are added.

PART II

1. Mix 25 ml of water and 25 ml of butanol. Stir for five minutes and let settle. Add 3 ml of acetic acid and again stir for five minutes and let settle. Place in a separating funnel and separate. Determine the mass of each phase. Titrate the bottom phase with standardized 1.0 M NaOH. The standardization of NaOH must be done during the period that the bottom -phase titration is done since the NaOH concentration changes rapidly when carbon dioxide is absorbed from the atmosphere. Use the HCL solution provided. High precision is not crucial here. Obtain an average of three runs.

CALCULATIONS

1. For each solution determine the weight percent of each component. Take the densities of H_2O, butanol, and acetic acid to be 0.9970, 0.8098, and 1.046 g/ml, respectively. Plot the data on the triangular graph paper provided. Show one set of sample calculations.

2. From the results of Part II determine the weight percent of the three components in each phase. Put these two points on the curve and draw a line between them.

FURTHER CALCULATIONS AND QUESTIONS

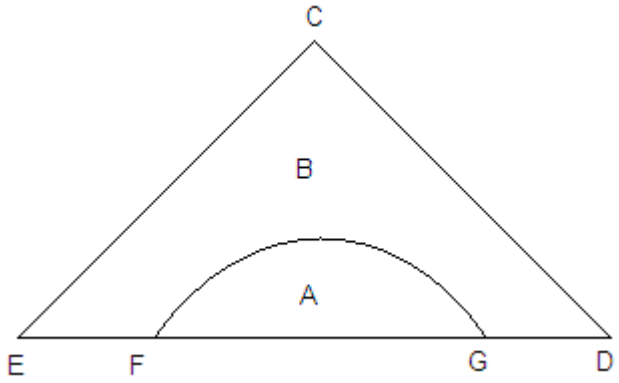
1. For the two solutions with no acetic acid calculate the mole fraction of water and butanol in each. Give a qualitative explanation as to why butanol is rather insoluble in water while water is rather soluble in butanol.

2. If two moles of water and one mole of butanol are mixed, will two phases result? If so, what will be the mole fractions of water and butanol in each of the two phases? Which has a lower free energy, a single solution containing two moles of water and one mole of butanol or a two phase system resulting from mixing two moles of water with one mole of butanol?

3. If two moles of butanol and one mole of water are mixed, will two phases result? If so, what will be the mole fraction of water and butanol in the two phases? Which has a lower free energy, a single solution containing two moles of butanol and one mole of water or a two phase system resulting from mixing two moles of butanol with one mole of water?

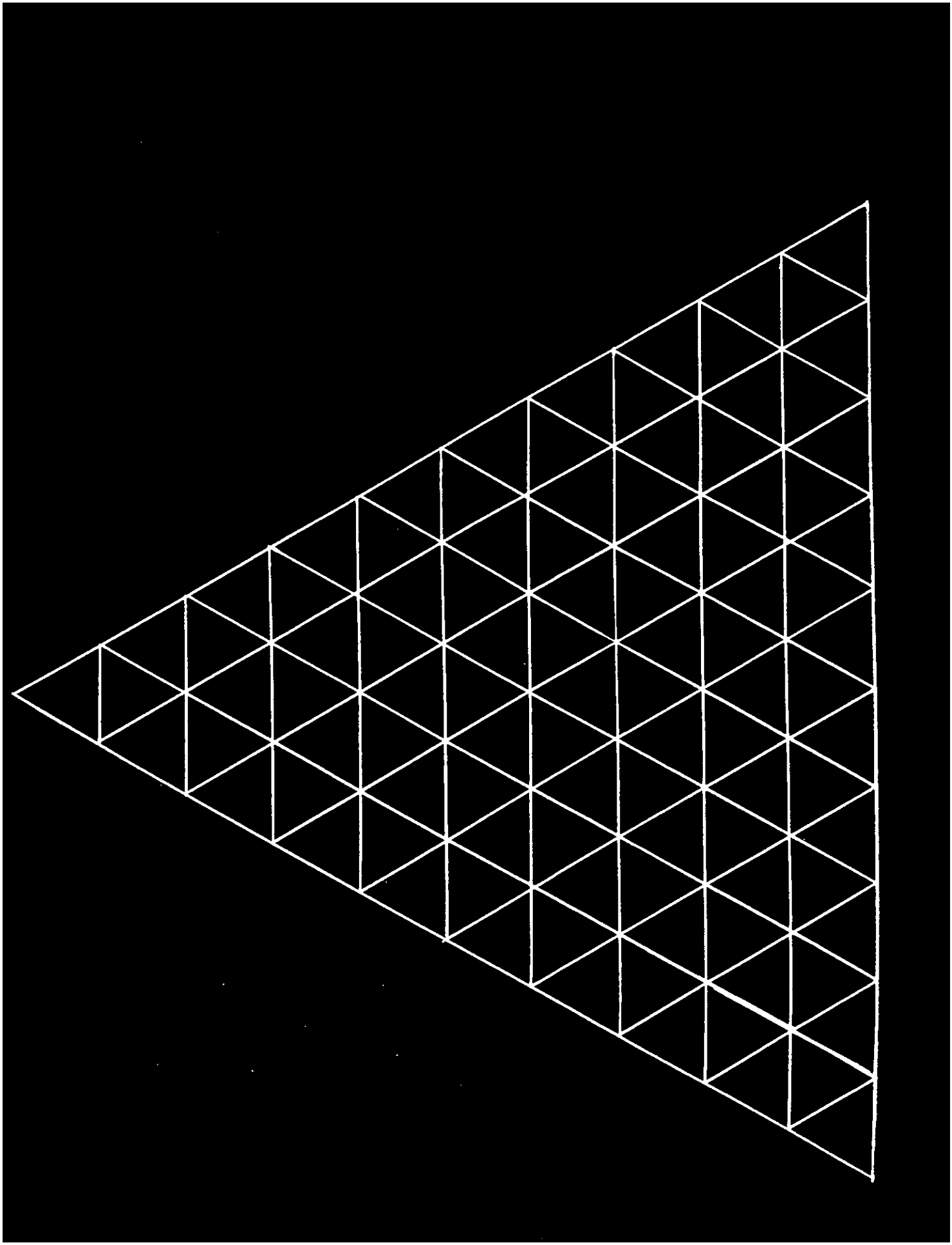
4. Qualitatively explain why the addition of acetic acid makes a two phase mixture of butanol and water into a one phase system. Answer this question in terms of "like dissolves like" instead of free energy.

5. Determine the C (# of components), p (# of phases), and v (variance) of the system in each region of the phase diagram.



Region A
Region B
Line EC
Line CD
Line EF
Line GD
Line FG
Points C, D, E

BuOH Total Volume	H_2O Total Volume	HAc Total Volume	BuOH Mass, g	H_2O Mass, g	HAc Mass, g	% BuOH	% H_2O	% HAc
20.00 mL	0 mL	0 mL						
20.00	5.00							
20.00	10.00							
20.00	15.00							
20.00	20.00							
20.00	25.00							
20.00	30.00							
20.00	40.00							
20.00	50.00							
20.00	60.00							
20.00	70.00							
20.00	80.00							
20.00	90.00							
20.00	100.00							
20.00	110.00							



EXCITED-STATE PROPERTIES OF 2-NAPHTHOL

PART I: ACIDITY CONSTANT

OBJECTIVE

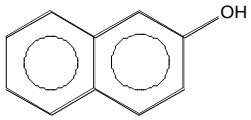
To determine the acidity constants of the ground and lowest electronically excited states of 2-naphthol (or β -naphthol) in aqueous solution.

INTRODUCTION

The electronic structure of a molecule determines such physical and chemical properties as its charge distribution, geometry (therefore dipole moment), ionization potential, electron affinity, and of course, chemical reactivity. If the electronic structure of a molecule were to be changed, one would expect its physical and chemical properties to be altered. Such a rearrangement in electronic structure can, in fact, be brought about (and very rapidly, -10^{-13} s) if the molecule is raised to an electronically excited state via the absorption of a quantum of light (photon) whose energy matches the gap between the molecular ground and excited state energy levels.

For most organic molecules that contain an even number of electrons, the ground state is characterized by having all electron spins paired; the net spin angular momentum is zero, and such an arrangement is called a singlet state. When considered in terms of molecular orbitals (mo), electronic excitation involves the promotion of an electron from a filled mo to a higher, vacant mo. This new orbital configuration, which characterizes the electronically excited state, may be one in which the two electrons in the singly occupied mo's have opposite spins. Accordingly, this electronically excited state is also a singlet. The ground, and lowest electronically excited, singlet states are often denoted as S_0 and S_1, respectively. Higher excited singlet states are referred to as S_2, S_3, ..., S_n. This experiment deals with excited singlet states.

Although measurements of the physical and chemical properties of a molecule in its ground state can be carried out, more or less, at leisure (assuming that the molecule is thermally stable), the examination of these properties in its excited states is severely hampered by the fact that these states are very short-lived. For most molecules, S_1 states have lifetimes ranging from 10^{-6} - 10^{-11} s. Excited states are metastable; they undergo decay processes that dissipate the energy they possess relative to more stable products. For example, the excited state of a molecule may, in general: spontaneously return to the ground state via photon emission (fluorescence), convert electronic excitation into ground state vibrational energy (heat), undergo bond dissociation or rearrangement or a change in electron spin multiplicity. Because spontaneous emission from an excited state (i.e., fluorescence) often takes place very rapidly, fluorescence can be used as a probe, or measurement, of excited state concentration (e.g., fluorescence assay). In addition, fluorescence studies can provide information about the physical and chemical properties of these short-lived singlet states. This field of experimentation is called photophysics. In this experiment, some ground and excited state properties of the organic molecule, 2-naphthol (ArOH) will be determined.



2-naphthol (ArOH)

In aqueous solution, ArOH behaves as a weak acid, forming the hydronium ion and itsconjugatebase, the naphthoxy ion, ArO^-.

$$ArOH + H_2O \rightleftharpoons H_3O^+ + ArO^-$$

It is instructive to measure the acidity constant of ArOH in its lowest excited electronic state, denoted as K_a^* , and to compare this value with that of the ground state K_a. This information indicates how the change in electron structure alters the charge density at the oxygen atom. The experimental method is best introduced in terms of the energy-level diagram shown in figure 1.

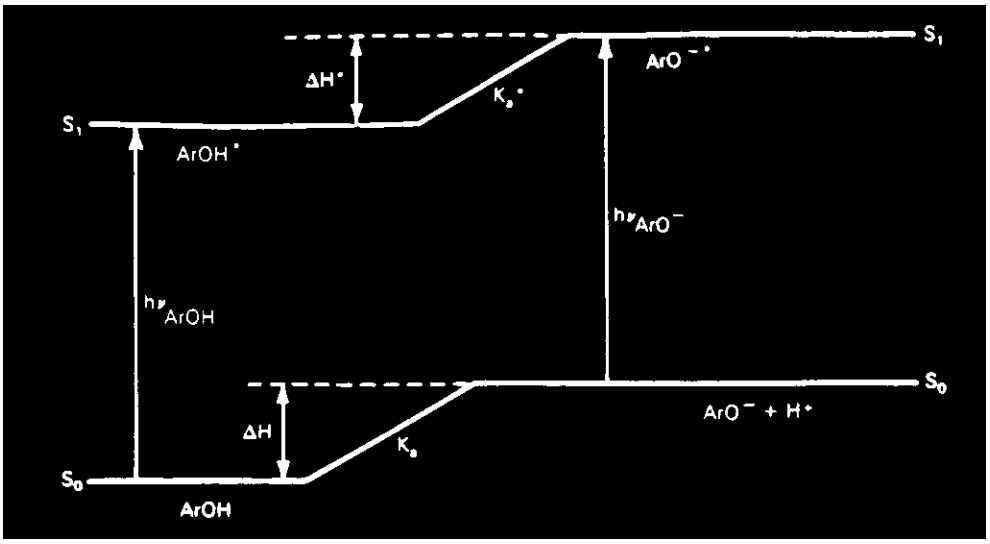


Figure 1. Schematic diagram of the ground and first excited singlet state energies of free naphthol and its conjugate base, the naphthoxy ion, in aqueous solution.

The relative energies of the free acid and its conjugate base (the naphthoxy ion) are indicated for both the electronic ground (S_o) and (lowest) excited (S_1) states in aqueous solution. Each anion is elevated with respect to its free acid by an energy, ΔH and ΔH^*, respectively. These are the enthalpies of deprotonation. Both the ground state acid and its conjugate base can be transformed to their respective excited states via the absorption of photons of energy $h\nu_{ArOH}$ and $h\nu_{ArO^-}$. For simplicity, these absorptive transitions are shown to be equal to the fluorescence from the excited to the ground states of the acid and conjugate base. (The ground and excited state vibrational levels that are involved in the transitions are not indicated.)

The free energy of deprotonation of ArOH can be expressed in terms of the enthalpy and entropy of deprotonation and the equilibrium (ionization) constant

$$\Delta G = \Delta H - T\Delta S = -RT \ln K_a \qquad (1)$$

and

$$\Delta G^* = \Delta H^* - T\Delta S^* = -RT \ln K^* \qquad (2)$$

for the S_o and S_1 states, respectively. If we make the assumption that the entropies of dissociation of ArOH and $ArOH^*$ are equal, it follows that

$$\Delta H \quad - \Delta H^* \quad = \; - RT \ln\left(\frac{K_a}{K_a^*}\right) \tag{3}$$

and thus from Figure 1, using a Hess' law approach, it can be deduced that

$$\Delta H + N_A h\nu_{ArO^-} = N_A h\nu_{ArOH^+} + \Delta H^+ \tag{4}$$

where *h* is Planck's constant. Avogadro's number, N_A, has been included to put each energy term on a molar basis. Combining equations (4) and (3) and rearranging gives

$$\ln\left(\frac{K_a^*}{K_a}\right) = \frac{N_A h\left(\nu_{ArOH} - \nu_{ArO^-}\right)}{RT} \tag{5}$$

Thus knowledge of the energy gap between the ground and first excited states for both the free acid and its conjugate base leads to an estimate of K_a^*, if K_a is known. The analysis presented above, which accounts for the observed thermodynamic and spectroscopic energy differences, was first developed by Th. Forster (1949, 1950). This approach is thus often referred to as a *Forster cycle*. Equation (5) can be recast into a more convenient form
where c, the speed of light has been incorporated in the expression to convert the transition frequencies of ArOH and ArO^- into *wavenumbers* (cm^{-1}, ~v), a common spectroscopic energy unit. h is Planck's constant, N_A is Avagadro's constant, R is the ideal gas constant (in Joules), and T is the room temperature. The acidity constants are expressed as **pK** values, where $pK_a = -\ln K_a$.

$$pK_a^* = pK_a + \frac{N_A hc}{2.303RT}\left(\tilde{\nu}_{0-0}\left(ArO^-\right) - \tilde{\nu}_{0-0}\left(ArOH\right)\right)$$

or (6)

$$pK_a^* = pK_a + \frac{N_A hc}{2.303RT}\left(\Delta\tilde{\nu}_{0-0}\right)$$

The question now is how to obtain the spectroscopic energy difference $\left(\tilde{\nu}_{0-0}\left(ArO^-\right) - \tilde{\nu}_{0-0}\left(ArOH\right)\right)$ or $\left(\Delta\tilde{\nu}_{0-0}\right)$, pertinent to the Forster cycle in 2-naphthol. One useful method provides the value of $\left(\Delta\tilde{\nu}\right)$ that best represents the energy difference between S_1 and S_0 implied in the Foster cycle, $\left(\Delta\tilde{\nu}_{0-0}\right)$. Unfortunately $\left(\Delta\tilde{\nu}_{0-0}\right)$cannot be determined directly in all cases (such as ArOH), but it can be estimated from an analysis of *both* the absorption and fluorescence spectra. This is shown schematically in Figure 2 for a single species (ArOH or ArO^-). The absorption and fluorescence spectra are both plotted on a common wavelength axis. Furthermore, the spectra are presented so that they are normalized to have complementary maxima with equal heights. The point of intersection of these spectra can be approximated, in units of wavenumbers, as the energy gap in units of cm^{-1} between S_0 and S_1.

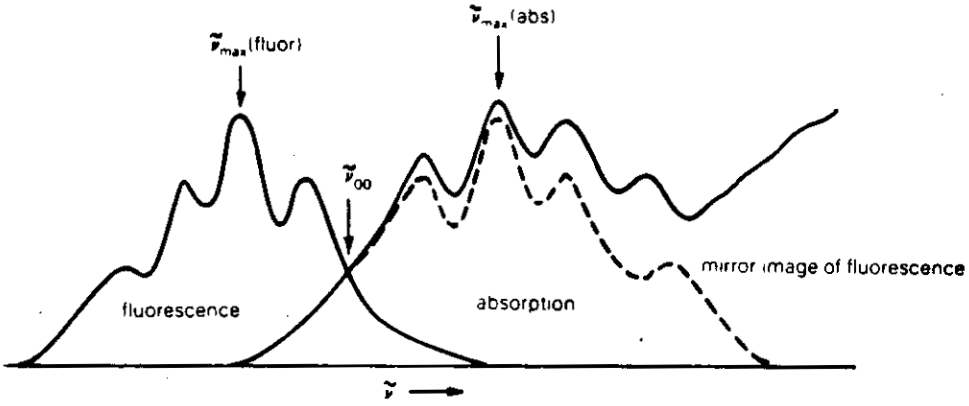


Figure 2. Schematic diagram of the absorption and fluorescence spectra of a molecule. It is assumed that these transitions are between the same two electronic states, i.e., S_o <==> S_1.

PROCEDURE.

FIRST LAB PERIOD

1. In this experiment, K_a will be determined from the **pH** dependence of the absorption spectrum of aqueous 2-naphthol. You willtake absorption spectra of ArOH at high pH, low pH and at three intermediate pH values. It is important to prepare fresh solutions. Using the 1.00 mL autopipet, carefully pipet 1.00 mL of the 2.0 x 10^{-3} M 2-naphthol stock solution into each of five 25-mL volumetric flasks. In an acidic solution, the protonated 2-naphthol must predominate. Fill the first flask with the HCL solvent. In a basic solution, the deprotonated 2-naphthol must predominate. Fill the second flask with the NaOH solvent In the remaining three solutions, a mixture of the protonated and deprotonated forms will be present at intermediate pH levels. This can be obtained by using the provided ammonium chloride buffer solutions (NH_4OH/NH_4Cl) as solvents for the three remaining flasks with the following concentrations: 0.1 *M*/0.1 *M*, 0.1 *M*/0.2 *M*, and 0.2 *M*/0.1 *M*. For the five prepared solutions the new $[ArOH]_o$ concentrations are approximately $8.0\times10^{-5}\,M$. Absorption spectra of all five solutions should be obtained using the Perkin-Elmer uv-vis absorption spectrometer. Each spectrum should be saved individually on the computer. Then the five spectra should be overlaid on the computer screen. For these spectra a 290-400 nm range can be used. It is *essential* that the 2-naphthol concentrations be identical (and accurately known) in each case-- **pipet carefully**. Immediately after the spectra are recorded, measure the actual **pH** of the solution using a properly calibrated **pH** meter. If the *bulk* ArOH concentration, e.g., $[ArOH] + [ArO^-]$, is invariant, the spectra, when properly overlapped, should intersect at a common wavelength called the *isosbestic point* (equal extinction). The presence of an isosbestic point, in this case, indicates that the system is closed, consists of two species in equilibrium and is a function of the one variable, **pH**. In order to satisfy the isospestic point condition, you may need to remake some solutions and retake their spectra. When you are satisfied that the isospestic point condition is fulfilled for your five solutions, plot your overlaid results on one graph.

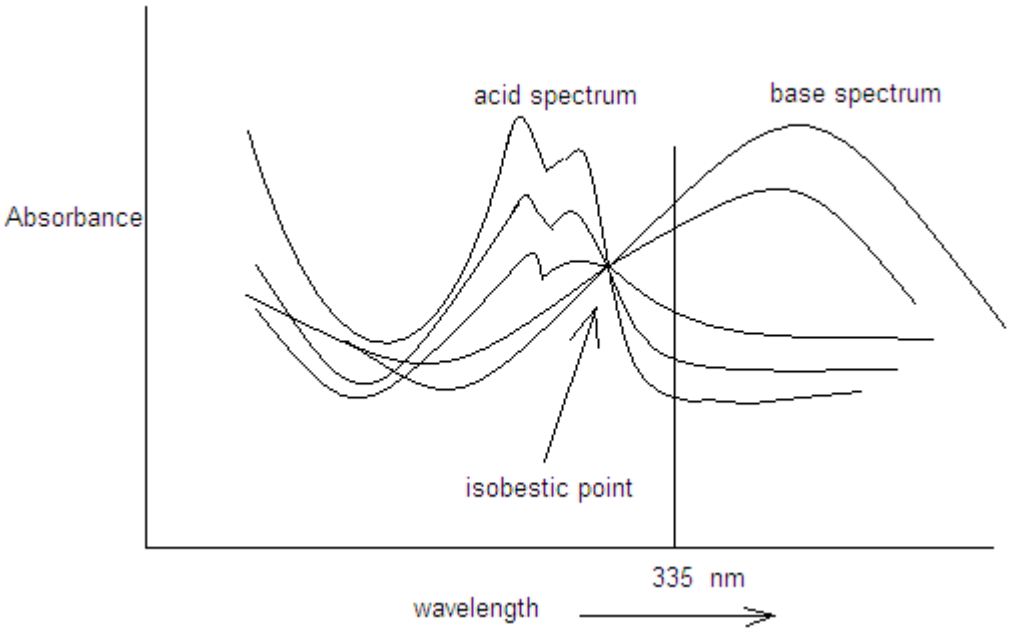
MEASUREMENTS FOR ABSORPTION

Perkin-Elmer Lambda 14 UV-Vis Absorption Spectrophotometer

1. Switch on the Lambda 14.
2. Turn on the computer.
3. Click WINLAB
4. Click SCAN 1 MISC
5. Set wavelength START=420, END = 290 nm
6. Put the ordinate on 1.40
7. Click AUTOZERO
8. Click START to sample
9. Fill each cuvet with water (you could do air vs air also) and place in the sample compartments.
10. Click BACKGROUND
11. Put your sample that you are tesing in the front cell holder and click START.

12. After the spectra is recorded, focus on the longest wavelength band. Expand that portion of the spectrum by making a box around the spectrum and them clicking in it, or go to VIEW, then FORMAT GRAPH, enter a value of 0.2, for example, Press OK.
13. Go to FILE and SAVE. Save each individual spectrum. Then overlay the five spectra and look for the isospestic point.
14. PRINT (if necessary change the box switch behind the printer to B)
15. Get the numerical absorbance values by clicking on the crosshairs icon. With the mouse place the crosshairs at the 335 nm position and read the absorbance value that is indicated at the bottom of the screen. Repeat for each spectrum. Record the absorbance values in your table as described below. Proceed to calculate the pK_a .

First Lab Period



After determining the extinction coefficients for the acid and base solutions at 335 nm, set up the following table:

Solution Number	pH of Solution	Experimental Absorbance at 335 nm	Calculated [ArOH] from equation 9	Calculated [ArO^-] from equation 7	Calculated K_a from equation10
1					----------
2					
3					
4					
5					----------

CALCULATIONS

Since the bulk naphthol concentrations, $[ArOH]_o$ are identical in each of the solutions studied, the following material balance applies:

$$[ArOH]_o = [ArOH] + [ArO^-] \qquad (7)$$

Under the condition that both the free acid and conjugate base absorb at 335 nm, the wavelength near the maximum absorption for ArOH, and that Beer's law holds

$$ABS(\lambda_{355} ArOH) = \varepsilon_{ArOH}[ArOH] + \varepsilon_{ArO^-}[ArO^-] \qquad (8)$$

where *ABS* is the absorbance (for a one cm path length), and ε_{ArOH} and ε_{ArO^-} are the extinction coefficients of the free acid and conjugate base at $\lambda_{355} ArOH$, respectively. Combining equations (7) and (8) produces

$$ABS(\lambda_{355} ArOH) = (\varepsilon_{ArOH} - \varepsilon_{ArO^-})[ArOH] + \varepsilon_{ArO^-}[ArOH]_o \qquad (9)$$

This relation allows the five values of [ArOH] to be determined from the measured absorbances of the solutions with varying pH from spectra gathered in step 3. Best results are obtained at 335 nm, where all five solutions have significant absorption. Remember to obtain the extinction coefficients from the acid and base solutions at 335 nm as well. Once this is known, the value of [ArO^-] at the same pH can be obtained from equation (7). Since the acidity constant is

$$K_a = \frac{[H_3O^+][ArO^-]}{[ArOH]} \qquad (10)$$

Take the average of the three K_a values. Calculate the average pK_a also. Compare your results with the literature values.

SECOND LAB PERIOD

1. The value of pK_a* can be calculated from the pK_a determined from the first lab period and the measured values of $\Delta\tilde{\nu}_{0-0}$ for the protonated and deprotonated forms of 2-naphthol. In order to get the $\Delta\tilde{\nu}_{0-0}$ values use the acid and base solution absorption spectra from the first lab period and the fluorescence spectra as described in the next paragraph.

2. For the fluorescence spectrometer a more dilute sample must be prepared. Pipet exactly 1 mL of the basic 2-naphthol solution prepared in the first lab period into a 25 mL volumetric flask; dilute to the mark with 0.02 M NaOH. Into a second 25 mL volumetric flask, pipet 1mL of the acidic solution prepared in the first lab period and dilute to the mark with 0.02 M HCl solution. The 2-naphthol concentration of these solutions should now be 3.2×10^{-6} M. (The volumetric dilutions must be performed carefully for the actual concentration must be accurately known). Both the Perkin-Elmer LS 50 B Luminescence (fluorescence) Spectrometer and the Perkin-Elmer (Lambda-14) UV-VIS (absorption) Spectrometer are PC driven machines and both allow spectral plots to be saved on 3.5" disks: it is recommended that spectra obtained are so saved.

3. For the determination of the $\Delta\tilde{\nu}_{0-0}$ for the acid and base systems, the following settings may be used:

Absorption Spectra $\left(Conc. = 8.0 \times 10^{-5} M\right)$	Acid: 220 -435 nm	Perkin Elmer λ-14
	Base: 220 - 435nm	Perkin Elmer λ-14
Fluorescence Spectra $\left(Conc. = 3.2 \times 10^{-6} M\right)$	Acid: 320 - 535 nm	Perkin Elmer LS50B
	Base: 320 - 535 nm	Perkin Elmer LS50B

USE OF FLUORESCENCE DATA TO CALCULATE pK_a^*

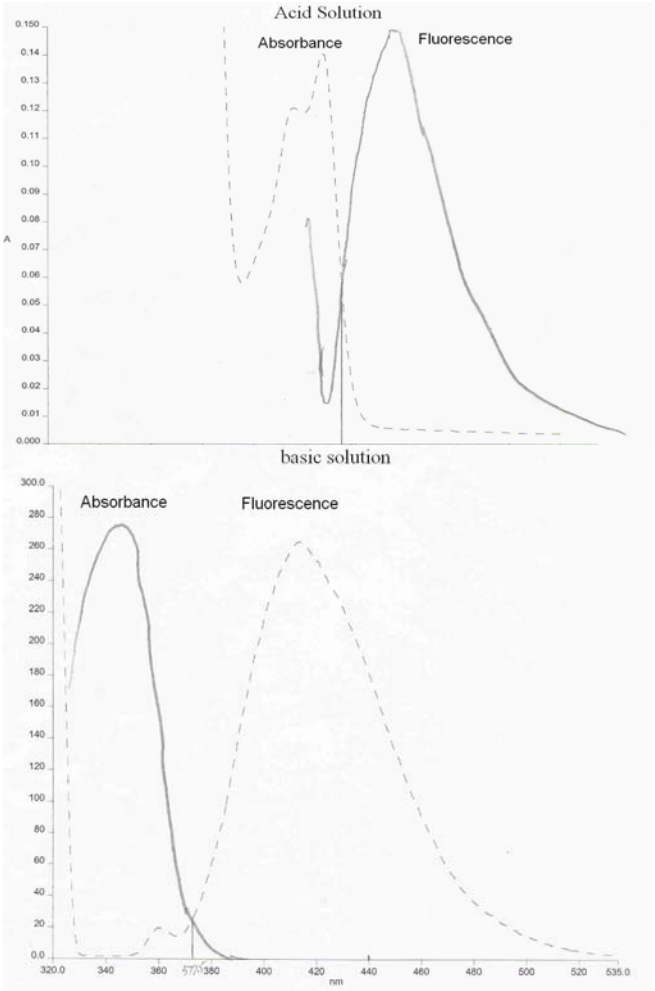
Perkin Elmer Fluorescence Spectrometer LS50B

1.Switch on instrument. Turn on computer.
2. Click on FLWinlab. Click on 2-naphthol fluorescence.
3.Fix wavelength at 320 and 500 nm.
4.Click on EXCITATION WAVELENGTH. Set it t 320 nm.
5.Use the four clear sided quartz cell.
6. Click green button
7. Click the autoexpand button

8. Collect the spectrum. The huge emission band at 320nm is a scattering band and it can be ignored.
9. Go to the XY coordinates icon. Click it and enter an emission counts value that will maximize your peak intensity on the screen. Print the spectrum.

Plot the 2-naphthol absorption and fluorescence spectra for the acid and base solutions on four separate pages. Insure that the height of the four curves are the same and that they are plotted with the same wavelength divisions. Overlay the absorption and fluorescence curves for the acid solution. Repeat for the basic solution. Match the wavelengths. The position of the intersection is the zero-zero point. Obtain the crossing wavelengths for the acid and base solution spectra. Convert to wavenumbers. Subtract the wavenumber values (base minus acid) to get $\left(\tilde{\nu}_{0-0}\left(ArO^{-}\right)-\tilde{\nu}_{0-0}\left(ArOH\right)\right.$. Finally, calculate pK_a^* from equation (6) for $(ArOH)^*$ from the pK_a value obtained above and the value for $\Delta\tilde{\nu}_{0-0}$. Compare these values. Discuss the errors that the primary measurements have on the derived value of pK_a^*

SECOND LAB PERIOD



QUESTIONS AND FURTHER THOUGHTS

1. In comparing the values of K_a and K*a, what can you deduce about the change in electron density at the O atom in 2-naphthol in the electronically excited state relative to the ground state?

2. Other molecules that can be studies using this technique are 2-naphthoic acid, acridine, and quinoline. Indicate the protolytic reactions for these molecules, i.e., write the aqueous acid-base reactions.

3. Can you predict before doing an experiment whether the excited state of a molecule is a stronger or weaker acid relative to its respective ground state? What information would you need to perform such an assessment?

FURTHER READINGS

Th. Forster, Naturwiss., 36, 186 (1949)
Th. Forster, Z. Electrochem., 54, 531 (1950)
C. Parker, “Photoluminescence of Solutions,” pp. 328-341, Elsevier (Amsterdam), 1968
J. Van Stam and J. E. Loefroth, J. Chem. Educ., 63, 181 (1986).
A. Weller, in G. Porter, ed., "Progress in Reaction Kinetics," vol. 1, pp. 189 - 214, Pergamon (New York), 1961.
R.A. Alberty, "Physical Chemistry," 7th ed., pp. 543 - 547, Wiley (New York), 1987.
P. W. Atkins, "Physical Chemistry," 3rd ed., pp. 471 - 475, W. H. Freeman (New York), 1986.
G. N. Castellan, "Physical Chemistry," 3rd ed., pp. 889 - 896, Addison-Wesley (Reading, Mass.), 1983.

EXCITED-STATE PROPERTIES OF 2-NAPHTHOL

PART II: DEPROTONATION/PROTONATION RATE CONSTANTS

OBJECTIVE

To determine the deprotonation and protonation rate constants of 2-naphthol in its lowest excited singlet state in aqueous solution.

INTRODUCTION

In the previous experiment, acidity constants for aqueous 2-naphthol (ArOH) were determined for both the ground and lowest excited (singlet) states. These constants pertain to the equilibrium

$$ArOH + H_2O \underset{k_p}{\overset{k_d}{\rightleftharpoons}} ArO^- + H_3O^+$$

where the rate constants for the forward (deprotonation) and reverse (protonation) reactions are indicated as k_d and k_p, respectively. Similar equilibrium expressions can be written for the excited state species,

$$ArOH^* + H_2O \underset{k_p}{\overset{k_d}{\rightleftharpoons}} ArO^{-*} + H_3O^+ \qquad (2)$$

in which the values of the forward and reverse rate constants may be different from those in the ground state because of differences in the properties of the 2-naphthol in these two states (e.g., different K_a values).

The ratio of the concentrations of free acid and the conjugate base can be expressed as a function of the pH, by the following equation,

$$\log\left(\frac{[ArOH]}{[ArO^-]}\right) = pK_a - pH \qquad (3)$$

where molar concentrations are used to approximate activities. An analogous equation,

$$\log\left(\frac{[ArOH^*]}{[ArO^{-*}]}\right) = pK_a^* - pH \qquad (3a)$$

applies to excited state species. Equations (3) and (3a) show that if the pH of the solution is less than pK_a of naphthol (in either electronic state), the free acid form will predominate over that of conjugate base, i.e., $[ArOH] > [ArO^-]$. Likewise, if $pH > pK_a$, then $[ArO^-] > [ArOH]$.

Suppose that by using a suitable buffer, the pH of the medium is established to be less than pK_a but greater than pK_a^*. The ground state of the system will then consist primarily of ArOH. Electronic excitation via light absorption will "instantaneously" (~10^{-13} s) transform ArOH into $ArOH^*$. We may assume that in this experiment, the buffer holds the pH of the medium constant during and after electronic excitation. This is a valid assumption because the number of photons absorbed per unit volume is much less than the ground-state concentration of ArOH. Thus $[ArOH^*] < [ArOH]$; however, $ArOH^*$ will spontaneously dissociate to form $[ArO^{-*}]$ in order to establish new equilibrium conditions. Under these circumstances, $[ArO^{-*}]$ must be greater than $\left[ArOH^*\right]$ because $pH > pK_a^*$ [see equation (3a)]. In fact, most of the fluorescence observed from $\left[ArO^{-*}\right]$ takes place from species that were formed via $ArOH^*$ deprotonation after electronic excitation. As excited state equilibrium is approached, the $ArOH^*$ concentration decreases, while that of ArO^{-*} increases. The strategy of this experiment in determining k_d and k_p is to measure the dependence of $\left[ArOH^*\right]$ on the pH of the solution. $\left[ArOH^*\right]$ is monitored through its fluorescence intensity, I_f, assuming that it is proportional to $\left[ArOH^*\right]$ (see below). The pH is varied (and established) using an ammonium acetate buffer.

KINETIC ANALYSIS

$$ArOH + h\nu_{abs} \rightarrow ArOH^*$$

Because in this experiment $pH < pK_a$, only absorption by the protonated form, ArOH, is considered

The $ArOH^*$ thus produced is (like any excited state) metastable and in relaxing, undergoes a number of different decay processes, e.g.:

$$ArOH^* \xrightarrow{k_f} ArOH + h\nu_{fluor}$$

$$\text{fluorescence rate} = r_{fluor} = k_f \left[ArOH^*\right] \qquad \text{(I)}$$

$$ArOH^* \xrightarrow{k_{nr}} ArOH + heat$$

$$\text{nonradiative decay rate} = r_{nr} = k_{nr} \left[ArOH^*\right] \qquad \text{(II)}$$

$$ArOH^* \xrightarrow{k_d} ArO^{-*} + H^+$$

deprotonation rate = $r_d = k_d \left[ArOH^* \right]$ (III)

$$ArOH^* + Ac^- \xrightarrow{k_{Ac^-}} ArO^{-*} + HAc$$

deprotonation rate via Ac^- = $r_{Ac^-} = k_{Ac^-} \left[ArOH^* \right] \left[Ac^- \right]$ (IV)

In addition to radiative (fluorescence) decay (I) and non-radiative relaxation (II), $ArOH^*$ can undergo "unassisted" (III) and "acetate-assisted" (IV) deprotonation. This distinction is significant because the rate of deprotonation will be *enhanced* in the presence of Ac^- in the bimolecular step indicated above in (IV). Undoubtedly, solvent plays a role in the unassisted deprotonation (III), but this step can be considered pseudo-first-order in $ArOH^*$ because the concentration of "solvent" is so much larger than $[ArOH^*]$. The reverse steps of the deprotonation processes, which are bimolecular and proportional to $[H_3O^+]$ and [HAc]-- see steps (III) and (IV), respectively-- are ignored because under these experimental conditions, $[H_3O^+]$ and [HAc] are very small.

If the pH of the solution is much lower than pK_a^* (e.g., in the presence of sulfuric acid), deprotonation by either process will be suppressed, and fluorescence from $ArOH^*$ predominates. In this case, the *fluorescence intensity*, I_f^o, which is proportional to the ratio of the rate of radiative decay to the *total* $ArOH^*$ decay rate, is

$$I_f^o = \frac{CK_f \left[ArOH^* \right]}{k_f \left[ArOH^* \right] + k_{nr} \left[ArOH^* \right]} \qquad (4)$$

or, canceling $[ArOH^*]$,

$$I_f^o = \frac{Ck_f}{k_f + k_{nr}} \qquad (5)$$

where *C* is an instrumental constant.

On the other hand, when $pH > pK_a^*$ (but less than pK_a), i.e., under **NH_4Ac** buffer conditions, the deprotonation steps become kinetically important, and thus the denominator of equation (4) will contain the additional terms, $k_d[ArOH^*]$ and $k_{Ac}\text{-}[ArOH^*][Ac^-]$. Therefore the $ArOH^*$ fluorescence intensity, now denoted as I_f, becomes [see equation (5)]

$$I_f = \frac{Ck_f}{k_f + k_{nr} + k_d + k_{Ac^-} \left[Ac^- \right]} \qquad (6)$$

The deprotonation of $ArOH^*$ causes a diminution of its fluorescence intensity; thus $I_f < I_f^0$. Assuming that [$ArOH^*$] is identical in all the solutions studied, the ratio of $ArOH^*$ fluorescence intensity in a solution containing sulfuric acid (low pH) to that containing ammonium acetate buffer (high pH) is obtained by dividing equation (5) by (6); thus

$$\frac{I_f^0}{I_f} = \frac{k_f + k_{nr} + k_d + k_{Ac^-}\left[Ac^-\right]}{k_f + k_{nr}} \qquad (7)$$

Equation (7) can be rearranged to the more convenient form

$$\frac{I_f^o}{I_f} = 1 = \frac{k_d}{k_f + k_{nr}} + \frac{k_{Ac^-}\left[Ac^-\right]}{k_f + k_{nr}} \qquad (8)$$

or,

$$\left(\frac{I_f^o}{I_f}\right) - 1 = \mathrm{T}_o k_d + \mathrm{T}_o k_{Ac^-}\left[Ac^-\right] \qquad (8a)$$

where $\mathrm{T}_o = 1/\left(k_f + k_{nr}\right)$ and is called the "lifetime" of $ArOH^*$ in the absence of significant deprotonation. A plot of $\left(I_f^o / I_f\right) - 1$ vs. [Ac^-] (called a *Stern-Volmer* plot) should be linear with a slope of $\mathrm{T}_o k_{Ac^-}$ and an intercept of $\mathrm{T}_o k_d$. In order to determine k_d, T_o must be determined separately.The information provided by the Stern-Volmer plot (a time-independent, or steady-state, method) could be obtained directly using a transient, or kinetic approach by monitoring the fluorescence *decay* of $ArOH^*$. After instantaneous photo excitation (< ca. 10^{-9} s), the $ArOH^*$ fluorescence intensity follows the decay law:

$$I_f(t) = \left[ArOH^*\right]_o e^{\left(-\left(k_f + k_{nr} + k_d + k_{Ac^-}\left[Ac^-\right]\right)\right)} \qquad (9)$$

where [$ArOH^*$]$_o$ is the concentration of photoexcited ArOH produced immediately after excitation (at $t = 0$), and t is the time after excitation. It should again be noted that equation (9) represents the proportionality between fluorescence intensity and excited state concentration. Equation (9) also indicates that $ArOH^*$ decays via a net first-order process; the coefficient of t in equation (9) is the reciprocal of the *lifetime* of $ArOH^*$, $\left(1/\mathrm{T}_{Ac^-}\right)$, *in the presence* of the NH_4Ac buffer. By plotting $1/\mathrm{T}_{Ac^-}$ *vs* $\left[Ac^-\right]$, the information provided by the Stern-Volmer plot, i.e., equation (8), could directly be obtained. This approach can be carried out using a nanosecond (10^{-9} s) fluorescence spectrometer, a sophisticated and expensive apparatus.

In this experiment, k_d will be obtained using the steady-state approach previously described. The value of T_o will be provided from data for the time dependence of $ArOH^*$ fluorescence

intensity determined from a fluorescence kinetic experiment (see the appendix). It should be emphasized again that in deriving equations (4) to (8), it is assumed that throughout the series of fluorescence intensity measurements, first in sulfuric acid, and then in different NH_4Ac buffer solutions, the concentration of $ArOH^*$ is *invariant*. This condition requires that the amount of light absorbed by ArOH per unit time be constant; thus not only must the formal concentration of ArOH be identical in each of the samples, but also the excitation source must not fluctuate. Satisfying these conditions is crucial for the success of the experiment.

Once a value of k_d is obtained from the analysis of the data as discussed above, the value of k_p (the ArO^{-*} protonation rate constant) can be determined from K_a^*, since

$$K_a^* = \frac{k_d}{k_p} \tag{10}$$

for this set of elementary reactions.

PROCEDURE

1. Prepare a series of aqueous solutions, each having the *same* ArOH concentration (about $3.2\times10^{-6}\,M$). See the procedure in Part I for the preparation of this solution. One solution will be ca. 0.02M H_2SO_4 (for I_f^o), and another ca. 0.02M NaOH (in order to observe predominantly ArO^{-*} fluorescence). The remainder of the solutions will have varying NH_4Ac between ~0.01 and ~0.10 M. Study at least five NH_4Ac containing ArOH solutions.

PROCEDURE USING SCANNING FLUORIMETER

2. Using an excitation wavelength of 320 nm, obtain the fluorescence spectra of the ArOH solutions starting with the solution containing NaOH. Maximize the instrument settings so that there is a 90% reading at the fluorescence maximum; then all other readings will be relative to this. Next obtain the fluorescence spectrum of the H_2SO_4 containing solution; then proceed with the NH_4Ac-containing solutions in order of increasing NH_4Ac concentration. It is desirable to record these spectra on the same chart paper. If the excitation source remains steady and the solutions have the same bulk ArOH concentrations, a distinct *isostilbic* point (equal brightness) should be produced. This is the common wavelength point of all the ArOH fluorescence spectra.

DATA ANALYSIS

1. Using the time dependent fluorescence intensity data provided in the appendix for ArOH in 0.10 M H_2SO_4, determine T_o, the reciprocal of the decay constant. The fluorescence quantum efficiency of ArOH under these conditions has been determined to be 0.18; this is equal to $k_f T_o$. Report values of both k_f and k_{nr} for ArOH.

2. Tabulate I_f^o and I_f values for the samples and construct a Stern-Volmer plot indicated by equation (8). Determine the values of k_d and k_{Ac^-} using linear (first-order) regression. Consider the error in T_o [obtained in equation (1)] in your error analysis of the rate constants.

3. Determine k_p from your previously obtained value of K_a^* [see equation (10)].

4. Tabulate all the rate constants determined and include the respective error limits.

FURTHER READINGS

R. Boyer, G. Deckey, C. Marzzacco, M. Mulvaney, C. Schwab, and A.M. Halpern, J. Chem. Educ., 62, 630, 1985.

J. Van Stam and J.E. Loefroth, J. Chem. Educ., 63, 181 (1986).

R.A. Alberty, "Physical Chemistry," 7th ed., pp. 543-547, Wiley (New York), 1987.

P.W. Atkins, "Physical Chemistry," 3rd ed., pp. 471-475, W.H. Freeman (New York), 1986.

G.N. Castlellan, "Physical Chemistry," 3rd ed., pp. 889-896, Addison-Wesley (Reading, Mass.), 1983.

I.N. Levine, "Physical Chemistry," pp. 725- 729, McGraw-Hill (New York), 1983.

J.N. Noggle, "Physical Chemistry," pp. 754- 760, Little, Brown (Boston), 1983.60

N.J. Turro, "Modern Molecular Photochemistry," Benjamin/Cummings (Menlo Park, Calif.), 1978.

APPENDIX

Fluorescence Decay Data for 2-Naphthol in 0.10M H_2SO_4 at 25^oC	
Time (ns)	Intensity (Photons emitted per unit time)
0.00	21753
1.00	18907
2.00	16380
3.00	14171
4.00	12432
5.00	10757
6.00	9288
7.00	8138
8.00	7083
9.00	6014
10.00	5350
1 ns = 10^{-9}s.	

DYNAMIC NMR SPECTROSCOPY

Introduction

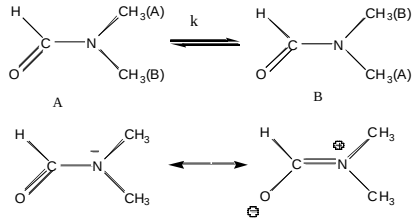
While the main objective of Dynamic NMR Spectroscopy is to introduce the technique of DNMR and the valuable information that can be derived from it, our secondary aim is to observe the increase in rate constant that occurs for methyl exchange in conditions of elevated temperature for dimethylformamide, DMF. The rate constants can be related to the activation energy of rotation for the double bond in DMF.

Proton NMR spectroscopy is based on the theory that if a proton is placed in an extenal magnetic field, its magnetic moment can be aligned either with or against the field. Just how much energy, in the radio frequency range, is needed to flip the proton depends on the magnetic field strength. The NMR spectrum is a plot of intensity of absorption versus the frequency of the of the absorption, with a constant magnetic field strength. The frequency at which a proton absorbs energy depends on the magnetic field strength which the proton "feels" . The effective field that is "felt" by the proton depends on the presence of electrons in the molecule which tend to shield the proton from the external field. Protons with the same electronic and nuclear environment absorb at the same applied field strength while those with different environments do not.

When two nuclei, A and B, occupying positions with different shielding values absorb radiation in the presence of a magnetic field, two lines appear in the NMR spectrum.
When the nuclei exchange positions due to a rotation or molecular motion, both nuclei "see" the same environment, and thus one absorption band appears.

In the proton NMR spectrum of dimethylformamide (1) at 22.5 C, two methyl signals are observed at 2.83 ppm and 2.87 ppm. Above 100 C these two signals broaden, then at 120 C they coalesce into one broad band. On raising the temperature further this again becomes a narrow peak, whose position is exactly midway between the original peaks.

From the temperature-dependent behavior of the signals it can be concluded that at room temperature the two methyl groups are differently shielded, whereas at the higher temperatures they become equivalent. The reason for this is well understood. The CN bond has a high proportion of double bond character, which results in the rotation being hindered, so that methyl groups A and B are in different magnetic environments. The representation in terms of mesomeric canonical forms makes this clear (Scheme I, A and B) shown below.



When the temperature is raised, the barrier to rotation is overcome, and if the rate at which the two methyl groups exchange places becomes sufficiently rapid they can no longer be distinguished by NMR spectroscopy, only one signal is observed.

The two extreme cases- slow exchange and rapid exchange-can be understood from what we already know, but why do the signals become broad in the intermediate temperature range? Theory provides an explanation of this, and the relevant results will be considered in the next section.

The dynamic process exemplified by dimethylformamide (1) is the simplest case of a first-order reversible reaction, which is described by the forward and reverse rate constants, k_f and k_r :

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$$

The rate constants k_f and k_r for the forward and reverse reactions are equal, since the two rotamers A and B in the equilibrium are equal in energy.

From the temperature dependence of the resonance lines one can obtain rate constants and activation parameters. The spectral curve, or lineshape, is the functional relationship between signal intensity and frequency. When dynamic processes are involved the lineshape also depends on the exchange rate k, and thus on the time τ spent by the nuclei in a particular environment. For a first-order reaction we have

$$k = \frac{1}{\tau}$$

The lifetime, τ, is determined from the reciprocal of the full width of the band measured at half of the maximum intensity, or FWHM, given by the symbol $\Delta\nu_{1/2}$.

Procedure

The technique used here requires more computer expertise than laboratory skills. A 10 mL solution of 0.02 M dimethylformamide is prepared using perdeuterated nitrobenzene as the solvent. A small quantity is placed in an NMR tube which is then placed in a ceramic spinner to calibrate the exposed length. Once it is properly prepared, it is placed in the NMR instrument. The sample temperature is measured by a thermocouple. The temperature is changed by blowing liquid nitrogen boil-off gas around the sample at various rates, i.e., the faster the flow, the colder the sample is.

The NMR spectra are taken by the Brucker AMX400 instrument. This is a variable temperature, high resolution instrument capable of measuring spectra of many nuclei, including hydrogen. When the sample spectrum is desired, first one must first maximize the absorption signal by first ensuring that the magnetic field is uniform. To do this one must adjust the shims of the magnet and then lockk the signal. Second the signal can be maximized through various amplification procedures.

Spectra can be taken at approximately 298, 313, 343, 373, 393, and 413 K. After the bands are recorded be sure to note the frequency of the band maxima and the FWHM values. Calculate the rate constants associated with spectra taken at all of the temperatures. Categorize the rate constants as falling into the three temperature regimes, i.e., below, at, and above the coalescence temperature. Use the “below coalescence” data to calculate the activation energy for rotation about the double bond. The equations associated with the three regimes are given below.

Quantitative Calculations

The following steps illustrate how to treat the data obtained at various temperatures. When measuring the FWHM and absorption frequencies, measure in units of Hz directly form the instrument.

1. Rate Constant and Lifetime in the Low Temperature Limit - absence of site exchange

The proton NMR spectrum of dimethylformamide at a temperature below its coalescence point will show two methyl signals indicating that the two sets of protons are in different environments. Either band may be evaluated for the FWHM, given by the symbol $\Delta\nu_{1/2}$.

$$\tau = \frac{1}{\Delta\nu_{1/2}}$$

Where $\Delta\nu_{1/2}$ is the full width at half max (FWHM) of the peak intensity, and

$$k = \frac{1}{\tau}$$

2. Rate Constant and Lifetime at the Coalescence Temperature, T_c

When the rate of magnetic site exchange increases so as to affect the NMR spectrum, the situation is treated by invoking the Uncertainty Principle. The uncertainty in the energy of absorption due to the site exchange is $\Delta E = \frac{(\sqrt{2}/\pi)h}{\Delta t} = \frac{(\sqrt{2}/\pi)h}{\tau_c}$. Thus, using $\Delta E = h\nu$ and rearranging the equation, one obtains

$$\tau_c = \frac{\sqrt{2}}{\pi(\nu_A - \nu_B)}$$

Also

$$k_c = \left(\frac{\pi}{\sqrt{2}}\right)(\nu_A - \nu_B)$$

Here $\Delta\nu$ is the separation in Hz between the two signals in the absence of exchange

3. Rate Constant and Lifetime above the Coalescence Temperature – fast exchange limit

Even though you will probably not take the sample to very high temperatures to observe the sharpening of the coalesced band, information will be included here for the sake of completeness.

Under the conditions of low temperature, i.e., the slow exchange limit, one observes two band centered at ν_A and ν_B. At the opposite extreme of high temperature in the fast exchange limit, a single sharp band of double intensity occurs at the frequency of $\nu = (1/2)(\nu_A + \nu_B)$

The relevant equations are:

$$k_f = \frac{\pi(\nu_A - \nu_B)^2}{2\Delta\nu_{1/2}}$$

$$\tau = \frac{1}{k_f}$$

4. The Arrhenius Activation Energy, E_A

By applying the Arrhenius equation it is possible to graphically determine the activation energy E_A for the dynamic process being studied. Use the rate constants, k, from measurements made at a series of temperatures, T, below the coalescence temperature.

$$k = Ae^{-(E_A/RT)}$$

$$\ln k = \ln A - E_A/RT$$

Plotting ln k versus 1/T will yield a straight line whose slope is $-E_A/R$. This is the activation energy, E_A, for rotation about the double bond in dimethyl formamide. A is the Arrhenius A factor, which is related to the entropy of activation.

VAPOR PRESSURE OF A PURE LIQUID

Introduction

In this experiment the vapor pressure of a pure liquid is measured at several temperatures. The enthalpy of vaporization is calculated using the **Clausius-Clapeyron** equation.

Theory

When the temperature of a liquid is raised, the vapor pressure of a liquid increases, because many more molecules gain sufficient kinetic energy to break away from the surface of the liquid. When the vapor pressure becomes equal to the pressure of the gas space, the liquid boils. The temperature at which the vapor pressure reaches 760 mmHg is the **Standard Boiling Point**.

According to the Clapeyron equation, the temperature coefficient of the vapor pressure of a liquid is given

$$\frac{\partial P}{\partial T} = \frac{\Delta \overline{H}_{vap}}{T\left(\overline{V}_v - \overline{V}_l\right)}$$

where $\Delta \overline{H}_{vap}$ = enthalpy of vaporization at temperature T

$\overline{V}_v, \overline{V}_l$ = molar volumes of vapor and liquid

The Clausius - Clapeyron equation

$$\ln P = -\frac{\Delta \overline{H}_{vap}}{RT} + \text{constant}$$

is derived from this exact equation with the following three assumptions: (a) the volume of a mole of liquid is negligible in comparison with a mole of vapor at its saturation pressure; (b) the vapor behaves as an ideal gas; and (c) the enthalpy of vaporization is independent of temperature. Although the Clausius-Clapeyron equation leads to a very simple interpretation of experimental data, the values of $\Delta \overline{H}_{vap}$ calculated in this manner may disagree significantly with the directly determined calorimetric values.

Instructions for using the Vapor Pressure Apparatus

1. Read and record the room temperature and barometric pressure from the instruments behind the laboratory door. Inspect the vapor pressure apparatus. The valves **#1**, **#2**, and **#3** should be closed completely. Now read and record the temperature of the vapor pressure apparatus and the heights of the left and right sides of the mercury column. The menisci of the mercury columns

should be level, or at least within a few millimeters of each other. The mean value of the heights should be recorded.

2. Turn on the vacuum pump using switch **#7**.

3. Very slowly and carefully begin to open valve **#2**. This will evacuate the glass tubing above the left side of the mercury column.

4. When fully evacuated, close valve **#2.** Read and record, using the meter stick in the center of the apparatus, the heights of the left and right sides of the mercury column. Subtract the larger from the smaller; the difference should be approximately-- within a few millimeters-- of the current barometric pressure recorded earlier.

5. **Read this step completely before you begin.** Very slowly and carefully begin to open valve **#3**. As the glass tubing above the right side of the mercury column is evacuated the right side will begin to rise as the left falls. If the glass tubing is evacuated completely, the columns will rise and fall until they reach the mean height. For the purposes of this experiment, a pressure differential of about **100 mmHg** is desirable. When the meniscus of the left side falls to a height of the mean height (recorded in step 1) plus 50 mmHg, close valve **#3**. If the liquid in the round bottom flask begins to boil before a **100 mmHg** differential is reached, close valve **#3** immediately. Record the heights of both sides of the mercury column.

6. Examine the contents of the round bottom flask. It should be liquid. If the evacuation of the glasswork was performed rapidly, it may be solid and the round bottom flask will feel cold to touch. If this is the case, the liquid has been *freeze-dried*-- a process made famous in coffee TV commercials. Chemically speaking, if considering a phase diagram of a pure liquid, the pressure and temperature changes have fixed the system somewhere near the gas phase-solid phase interface.

7. Wait an additional ten minutes. After ten minutes, record the heights of the mercury columns. If there is a significant change-- more than **10 mmHg**-- notify your lab instructor.

8. Turn on the cold water valve which supplies the condensing tube. It is located about shoulder height to the right of the vapor pressure apparatus at the adjacent vent hood work bench.

9. Turn the dial of the autotransformer marked **#6** to a setting of about **30 volts** and allow the heating element to come to temperature. As the liquid begins to boil, watch the lower end of the thermometer bulb. Eventually, liquid will begin to drip from it. The thermometer bulb is headed by radiation from the flask and by condensation of the vapor; it is cooled by evaporation of the liquid. A steady-state of these heating and cooling processes is necessary in order to record the boiling temperature of the liquid at a pressure and unaffected by super heating. Steady-state conditions should be assumed when the time interval between the drops falling from the thermometer bulb is **5 - 10 seconds**.

10. When steady-state conditions have been achieved, record the temperature and heights of the mercury columns.

11. Very slowly and carefully open valve **#1** until the pressure of the system increases by an additional **100 mmHg**. Close valve **#1**.

12. Allow the system to achieve steady-state conditions as above. It may be necessary to increase the voltage output of the autotransformer to achieve steady-state conditions. Record the temperature and column heights as before.

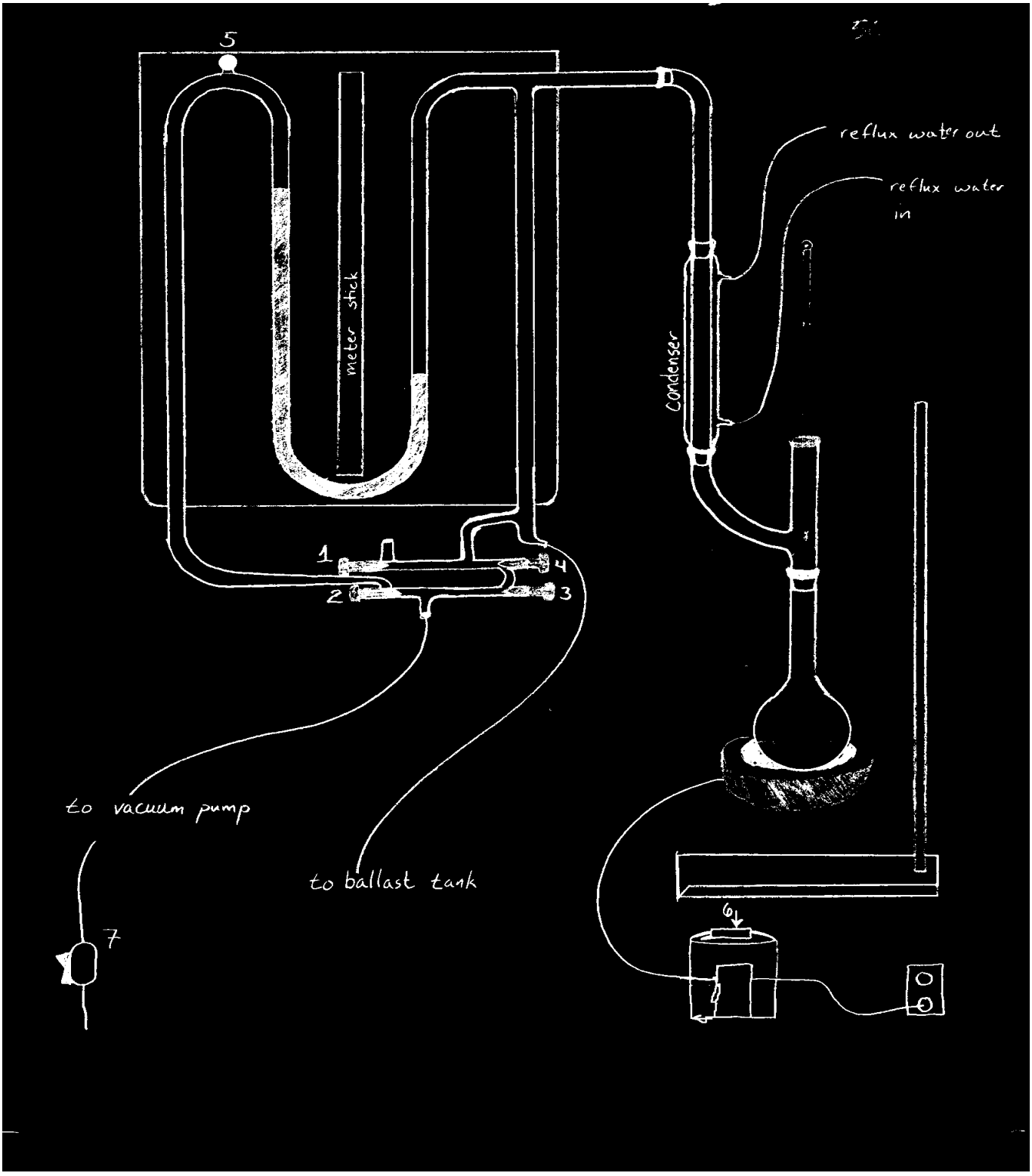
13. Repeat steps **12** and **13** several times until the system is returned to atmospheric pressure. The entire experiment should be repeated three times.

14. After the last measurement has been recorded, the vapor pressure apparatus must be returned to its initial state. Turn the voltage dial (**#6**) of the auto transformer to **0 volts**. Lower the heating element approximately 1 to 2 centimeters from the round bottom flask.

15. Very slowly and carefully open valve **#1**. Turn off the vacuum pump. Very slowly and carefully open valve **#3**. As air is introduced, the gas space of glass tubing above the right side of the mercury column will return to atmospheric pressure. Slowly open valve **#2**. When the menisci of the mercury columns are level and still, tightly close valves **#1–3**. Turn off the cold supply valve feeding the condenser.

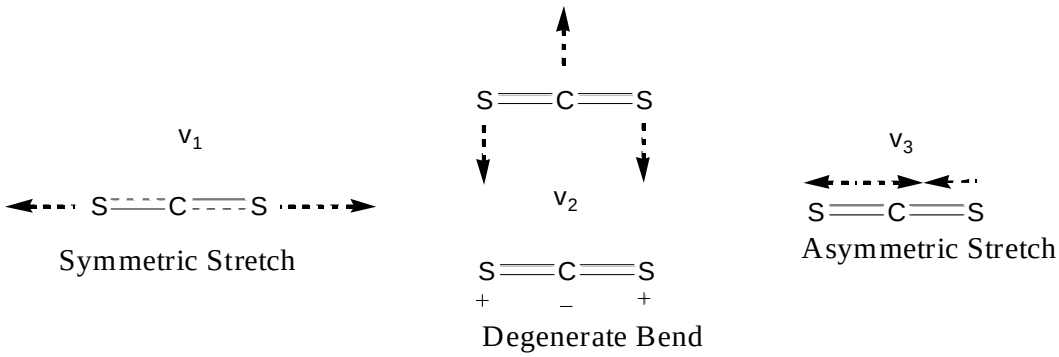
CALCULATION

Plot the vapor pressure and temperature data. The first graph, Figure 1, should be a plot of **P(mmHg) vs. T(C)**. In the second, Figure 2, a plot of **ln P(mmHg) vs. 1/T(K)**should be linear. From the slope of the second graph, determine the molar heat of vaporization for cyclohexane using the Clausius-Clapeyron equation. The assumptions made in the derivation of the Clausius-Clapeyron equation limit the accuracy of the heats of vaporization calculated in this manner.


5
meter stick
reflux water out
reflux water in
condenser
1
2
3
4
to vacuum pump
to ballast tank
7
6

THE VIBRATIONAL SPECTRUM OF CS_2

A linear triatomic molecule like CS_2 has three vibrational degrees of freedom. These vibrations



are the symmetric stretching mode, ν_1, the bending mode ν_2 , and the antisymmetric stretching mode ν_3 .

When a molecule is excited from the ground state to a state where only one of these vibrations are excited by a single quantum number, the vibrational band is referred to as a fundamental vibration. If a molecule were an exact harmonic oscillator, only fundamental vibrations would be allowed by the quantum mechanical selection rules. While the molecule is not exactly a harmonic oscillator, and therefore it is possible to excite more than one vibration simultaneously (referred to as combination mode) , or excite a single vibration by more than one quantum number (referred to as an overtone band), in general the most intense bands in both the infrared and Raman spectra are the fundamental bands. In order for a vibration to be observable in the infrared the vibration must cause a change in the dipole moment, while the corresponding rule for the Raman spectrum is that the vibration should cause a change in the polarizability of the molecule. To a first approximation, the polarizability of a molecule is proportional to its volume, therefore if a vibration changes the volume of the molecule it will be Raman active. Based on these rules it is clear that the ν_1 vibration will be Raman active and not infrared active, while the ν_2 and ν_3 vibrations will be infrared active. It can be shown by symmetry arguments that in fact the latter two are only infrared active but not Raman active. In fact for molecules that have a center of symmetry we have the so called law of mutual exclusion, that says that any fundamental band may only be observed, in either the infrared or the Raman spectrum but never in both. Please remember that this rule holds **only for molecules with a center of symmetry** .

ASSIGNMENT OF THE FUNDAMENTAL BANDS.

You should now look at the observed spectra by the two techniques. You will note that the infrared spectrum has two very intense bands, one which is barely observable because it lies just below the frequency range of the instrument, and a second at around 1500 cm^{-1} . In general the

stretching modes occur at a higher wavenumber than the bending modes because stretching force constants are larger than bending ones, therefore the lower wavenumber fundamental band must

be the bending mode ν_2 , while the band at about 1500 cm^{-1} must be the antisymmetric stretching mode ν_3 . Since your instrument does not give you an accurate reading for ν_2 we will give this to you. It occurs at 397 cm^{-1} . Now record the value of ν_3 from your infrared spectrum. The Raman spectrum shows only one very strong band which must be the ν_1 band. Record the value of ν_1 from your Raman spectrum. Compare your values, with those given in the literature. Remember to cite the reference.

ASSIGNMENT OF OVERTONES AND COMBINATIONS.

The vibrational energy of a molecule expressed in wavenumber units is given by the expression:

$$G(v_1, v_2 \ldots) = \sum_i \omega_i \left(v_i + \frac{1}{2} \right) + \sum_i \sum_{k \geq i} x_{ik} \left(v_i + \frac{1}{2} \right) \left(v_k + \frac{1}{2} \right) \qquad (1)$$

In this expression ν_i are the vibrational quantum numbers, ω_i are the harmonic wavenumbers, and x_{ik} are the so called anharmonicity constants. There are additional anharmonic terms that have been neglected. In general the harmonic wavenumbers are much larger (of the order of hundreds or thousands of wavenumbers) than the anharmonicity constants which are of the order of several wavenumbers. If one were to neglect the anharmonicity constants , the value of the first overtone wavenumber would be twice the fundamental wavenumber (which in turn would be the same as the harmonic wavenumber). Similarly, if one were to neglect the anharmonicity constants, the combination wavenumber $\nu_i + \nu_j$ would equal the sum of the harmonic wavenumbers. Using this information, you should now assign the remaining observed peaks in both the infrared and Raman spectra that you observed, and compare them to those found in the literature. Before you do so there is one additional fact that you should note. While most bands in the infrared and Raman spectra arise from the molecule jumping from the ground vibrational state to an excited vibrational state, there are some exceptions. In particular, if a molecule possesses a low wavenumber fundamental band, there will be an appreciable number of molecules in this vibrational state at room temperature. It will then be possible to observe transitions originating from such an excited vibrational state to a higher vibrational state. Such transitions are referred to as difference bands or hot bands. In the absence of anharmonicity, the vibrational wavenumber for the transition $v_i + v_j \leftarrow v_j$ should be the same as the wavenumber for the $v_i \leftarrow 0$ transition, except that its intensity will be weaker than that of the fundamental transition $v_i \leftarrow 0$, because the Boltzman factor in the ν_j state is lower.

CALCULATION OF FORCE CONSTANTS

The potential energy for a symmetric linear triatomic molecule may be written as follows:

$$V = \frac{1}{2} k_{rr} \left(\Delta r_1^2 + \Delta r_2^2 \right) + k_{rr'} \Delta r_1 \Delta r_2 + k_\alpha \Delta \alpha^2 \qquad (2)$$

where the k-s are force constants and Δr-s are changes in bond length and $\Delta\alpha$ is the change in the bond length. The vibrational wavenumbers for the molecule depend on the force constants , atomic masses and the geometric parameters for the molecule. In order to show the relationship between force constants and wavenumbers it is customary to introduce a frequency parameter λ , where $\lambda_i = 4 \pi^2 c^2 \nu_i^2$, where c is the velocity of light, and ν_i is the wavenumber of the vibration. Ideally, one should use the harmonic wavenumber ω_i rather than ν_i , but the difference between

the two is very small. It can be shown that for the linear symmetric triatomic molecule CS_2 , the following relationship exist between λ_i and the force constants:

$$\lambda_1 = \frac{(k_{rr} + k_{rr'})}{m_s}$$
$$\lambda_2 = \frac{2(m_C + 2m_S)k_\alpha}{m_S m_C r^2} \qquad (3)$$
$$\lambda_3 = \frac{(k_{rr} - k_{rr'})(m_C + 2m_S)}{m_S m_C}$$

In these expressions m_S is the mass of sulfur atom, m_C is the mass of carbon atom, and r is the C=S bond length. Using your measured fundamental frequencies, calculate the values for the force constants of this molecule, and compare them to those given in the literature. You will need to look up the value of the C=S bond length. Please watch your units when you do the calculation.

CALCULATION OF THE ANHARMONICITY CONSTANTS x_{ik}

If one measures the overtones, combinations and fundamental wavenumbers one may calculate the anharmonicity constants. Using equation (1) one can show that the following relationships exist:

$x_{ik} = (\nu_i + \nu_k) - \nu_i - \nu_k$, where $(\nu_i + \nu_k)$ is the combination band wavenumber while ν_i and ν_k are the fundamental wavenumbers, and

$2x_{ii} = (2\nu_i) - 2\nu_i$, where ($2\nu_i$) is the overtone wavenumber and ν_i is the fundamental wavenumber. Use your measured overtones, combinations and fundamental to calculate as many anharmonicity constants as you can from your data, and compare them to those found in the literature.

ANALYSIS OF THE INFRARED SPECTRUM OF HCl

PURPOSE:

The purpose of this experiment is to determine the equilibrium bond distance and the force constant of HCl from its infrared spectrum. The analysis also permits the evaluation of the anharmonicity constant, the vibration-rotation interaction constant, and the centrifugal distortion constant.

DISCUSSION:

The energy levels of a diatomic molecule may be discussed in terms of electronic levels, vibrational levels, and rotational levels. The translational energy is quantized into such infinitesimally small increments that it may be considered to be a continuous distribution. In this experiment the molecules remain in the ground electronic state. Since changes in electronic and transnational energies are not observed in this experiment one may write

$$\Delta E_{total} = \Delta E_{vib} + \Delta E_{rot} \qquad (1)$$

As a first approximation the analysis of the spectrum is developed for a model in which the diatomic molecule is considered to have the energy levels of a rigid rotor in each of the vibrational levels of a harmonic oscillator. Then simple refinements are introduced to give a more accurate model.

Vibrational Levels

The energy levels of a harmonic oscillator are given by

$$E_{vib} = \left(v + \frac{1}{2}\right) h\nu_e \qquad v = 0,1,2..... \qquad (2)$$

where

$$\nu_e = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} \qquad (3)$$

and μ ,the reduced mass, is defined by

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \qquad (4)$$

for a diatomic molecule composed of masses m_1 and m_2 separated by an equilibrium bond distance r_e. The force constant is denoted by k. The energy levels are illustrated in Figure 1. The vibrational levels of HCI are so widely spaced that only the ground state, $v = 0$, is populated. Thermal energies around room temperature are not sufficiently high to populate even the first excited state, $v = 1$. The excited vibrational states are reached by absorption of photons in the infrared region of the electromagnetic spectrum. The selection rule which is applicable to these transitions is $\Delta v = +1$.

Rotational Levels

The energy levels of a rigid rotor are given by

$$E_J = J(J+1)\frac{h^2}{8\pi^2 I_e} \qquad J = 0,1,2,..... \qquad (5)$$

where

$$I_e = \mu (r_e)^2 \qquad (6)$$

is the moment of inertia. The rotational quantum number is J. Each vibrational level has an array of rotational levels beginning with $J = 0$ and increasing in rotational energy according to equation (5). It is convenient to define energy quantities in units of cm^{-1} since the spectrum may be read directly in these units. This is accomplished by dividing energy in Joules by hc, where c is the speed of light. Accordingly, the rotational constant is

$$B_e = \frac{h}{8\pi^2 c I_e} \qquad (7)$$

and

$$\overline{v}_J = \frac{E_J}{hc} = J\left(J+1\right)B_e \qquad (8)$$

For absorption or emission of photons for changes in rotational energy, the selection rule is $\Delta J = \pm 1$.

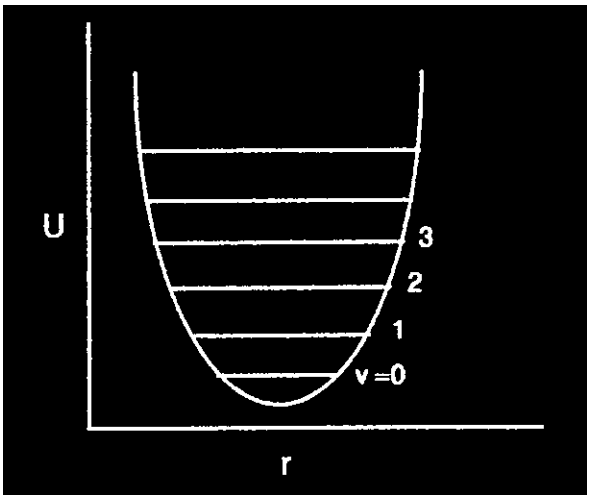


FIGURE 1: Potential energy, U, of a harmonic oscillator. Vibrational energy levels are also shown; rotational levels are not shown

Figure 2 shows a few of the lower lying rotational levels for each of the vibrational levels $v = 0$ and $v = 1$. On the lefthand side of Figure 2, vertical arrows show some of the allowed transitions for $\Delta J = +1$. On the righthand side vertical arrows indicate some of the allowed transitions for $\Delta J = -1$. The observed vibration-rotation transitions are given by

$$\overline{v} = \frac{\Delta E}{hc} = \left(v' - v''\right)\overline{v}_e + \left(J'\left(J'+1\right) - J''\left(J''+1\right)\right)B_e \qquad (9)$$

where the prime is used to refer to the higher or final energy state while the double prime is used to refer to the initial state.

Since for this experiment $v'' = 0$and $v' = 1$, we have
for $J' = J'' + 1$,

$$\overline{v} = \overline{v}_e + 2\left(J''+1\right)B_e \qquad J'' = 0,1,2,.... \qquad (10)$$

and for $J' = J'' - 1$

$$\overline{\nu} = \overline{\nu}_e - 2J''B_e \qquad J'' = 1,2,3,... \tag{11}$$

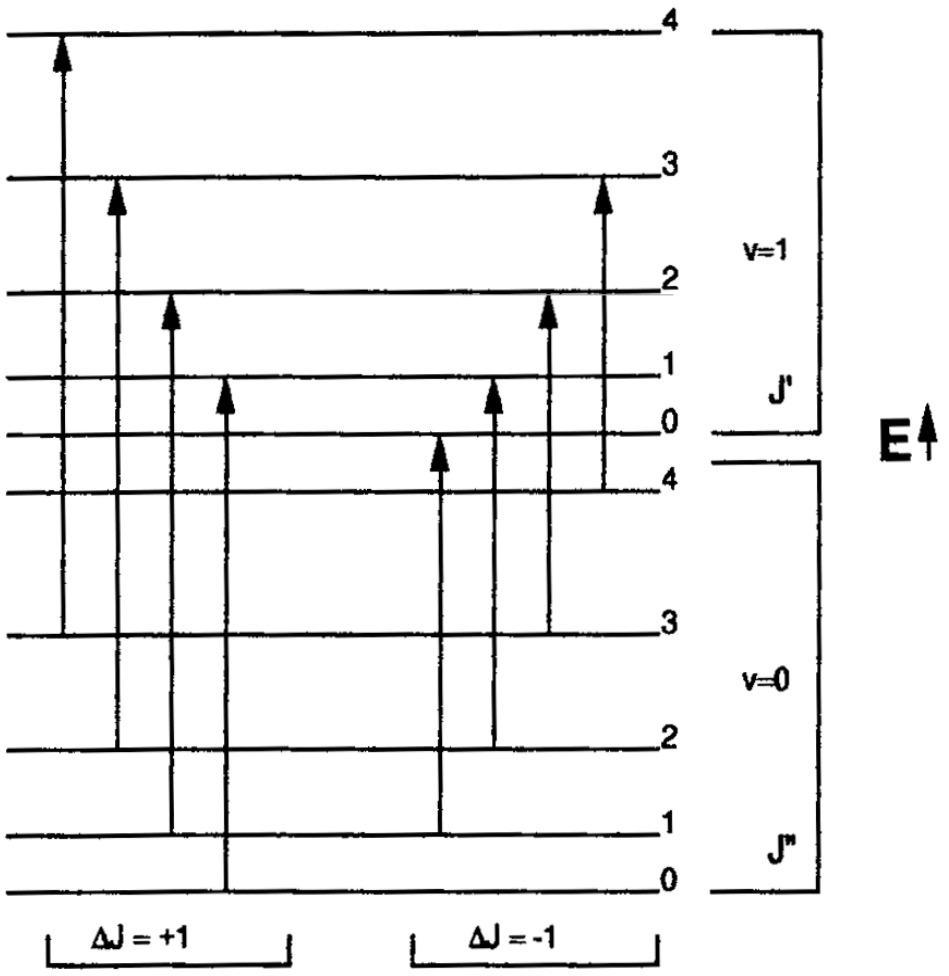


FIGURE 2: Rotational energy levels for the vibrational levels $v = 0$ and $v = 1$ in a diatomic molecule. The transitions observed in the vibration-rotation spectrum are also shown

Equation (10) describes the quantum jumps denoted by the vertical arrows on the lefthand side of Figure 2, while equation (11) describes those denoted by the arrows on the righthand side. Thus the idealized model leads to a spectrum with absorption frequencies spaced as indicated in the stick plot of Figure 3. We have here a series of absorption lines breaking naturally into two sets, one set separated from the other by $4B_e$. Each set has lines separated by $2B_2$. The sets are referred to as branches, the R branch occurring at energies higher than $\bar{\nu}_e$ and the P branch occurring at lower frequencies. The heights of the absorption lines in this figure are drawn to indicate the relative intensities of a typical vibration-rotation spectrum.

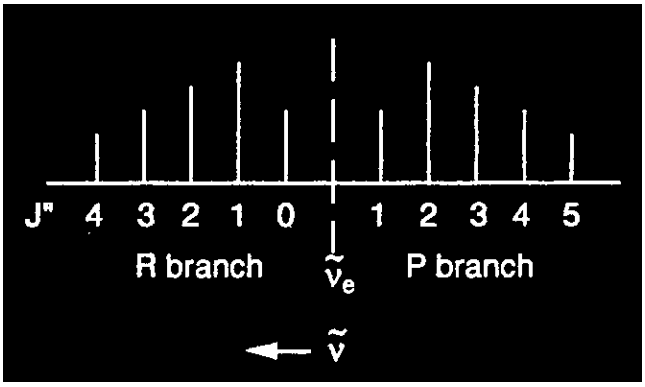


FIGURE 3: Schematic diagram showing the relative intensities of absorption in the vibration-rotation spectrum.

Corrections to the Model

Since the real diatomic molecule is not a rigid rotor undergoing harmonic oscillation, corrections must be made to our model. The anharmonic nature of the vibration changes the potential energy function. The new potential energy function for a diatomic molecule is illustrated in Figure 4.

The effect of the anharmonicity is to lower each vibrational energy level below that of the harmonic oscillator. The vibrational levels approach each other as v increases. Another result is that the selection rule is now $\Delta v = \pm 1, \pm 2, \pm 3, ...$ Thus in addition to the fundamental absorption band, $v" = 0 \rightarrow v' = 1$, overtone bands such as $v" = 0 \rightarrow v' = 2$ or $v" = 0 \rightarrow v' = 3$ may be observed. The overtone bands are usually much less intense than the fundamental band.

A sufficiently complete account of all effects which need to be considered in this experiment is given by

$$\bar{\nu} = \left(v + \frac{1}{2}\right)\bar{\nu}_e - \left(v + \frac{1}{2}\right)^2 x_e \bar{\nu}_e + J(J+1)B_e - J(J+1)\left(v + \frac{1}{2}\right)\alpha_e - J^2(J+1)^2 D_e$$

The first and third terms have been discussed. The second term contains the expression $x_e \bar{\nu}_e$, the anharmonicity constant, which is related to the bond dissociation energy. The term in α_e represents the vibration-rotation interaction which may be associated with the change in the effective moment of inertia as the vibrational energy is increased. The term in D_e is the centrifugal distortion term which is associated with the increase of the internuclear distance as the rotational energy is increased. If the third and fourth terms of equation (12) are combined by defining the rotational coefficient

$$B_v = B_e - \left(v + \frac{1}{2}\right)\alpha_e \qquad (13)$$

one obtains

$$\bar{\nu} = \left(v + \frac{1}{2}\right)\bar{\nu}_e - \left(v + \frac{1}{2}\right)^2 x_e \bar{\nu}_e + J(J+1)B_v - J^2(J+1)^2 D_e \qquad (14)$$

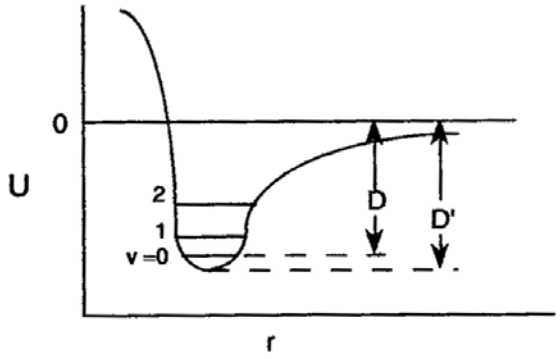


Figure 4. Potential Energy U of a diatomic molecule plotted against the internuclear separation. The difference between the shape of the curve here as compared to Figure 1 is due to the anharmonic correction.

The Use of Selection Rules

For $v'' = 0$ and $J' = J'' + 1$, the equation for the frequencies of the R branch becomes

$$\bar{\nu}_R(J'') = \nu'\left(1 - (\nu'+1)x_e\right)\bar{\nu}_e + 2B_{\nu'} + J''\left(3B_{\nu'} - B_o\right) - J''^2\left(B_{\nu'} - B_o\right) - 4(J''+1)^3 D_e \qquad (15)$$

for J'' = 0,1,2,….

For v'' =0 and J' = J'' + 1, the equation for the P branch becomes

$$\overline{v}_P\left(J''\right) = v'\left(1-\left(v'+1\right)x_e\right)\overline{v}_e - J''\left(B_{v'} + B_o\right) + J''^2\left(B_{v'} + B_o\right) + 4J''^3 D_e \qquad (16)$$

for J'' = 1,2,3...

The first term on the right in equations (15) and (16) is referred to as the **band origin**. When $\overline{v}_e$ is solved from this expression, the frequency corresponds approximately to the center of the spectrum where no absorption occurs, i.e. the center of the Q branch when J' = J'' and corresponding to a forbidden transition for this molecule.

Use of Equations 15 and 16 to Calculate the Molecular Parameters

To facilitate the calculation of the molecular parameters, three combinations of these equations are presented. If one considers only the members of the R and P branches which have the same value of J", i.e., components which have the same initial state, one obtains

$$\overline{v}_R\left(J''\right) - \overline{v}_P\left(J''\right) = 2\left(2J''+1\right)B_{v'} - 4\left(\left(J''+1\right)^3 + J''^3\right)D_e \qquad J'' = 1,2,3,.. \qquad (17)$$

$B_{v'}$ and D_e can be obtained from equation (17). From components of R and P which have the same final state for each of the two transitions one obtains

$$\overline{v}_R\left(J''\right) - \overline{v}_P\left(J''+2\right) = 2\left(2J''+3\right)B_o - 4\left(\left(J''+1\right)^3 + \left(J''+2\right)^3\right)D_e \qquad J'' = 0,1,2,..... \qquad (18)$$

Values of B_o and D_e thereby can be obtained. Inspection of equations (15) and (16) reveals that an equation which involves the band origin can be derived from the addition of components of the two branches. The most convenient sum is one in which the D_e terms cancel.

$$\overline{v}_R\left(J''\right) - \overline{v}_P\left(J''+1\right) = 2v'\left(1-\left(v'+1\right)x_e\right)\overline{v}_e + 2\left(J''+1\right)^2 \qquad J'' = 0,1,2,..... \qquad (19($$

If plotted, this yields a value for the band origin, $v'\left(1-\left(v'+1\right)x_e\right)\overline{v}_e$, as the y-intercept and a value for difference $\left(B_{v'} - B_o\right)$ as the slope.

APPARATUS AND CHEMICALS:

High resolution infrared spectrophotometer with scale expansion capability; gas cell with NaCl windows; vacuum manifold for filling cell; gas cylinder of HCl; calipers or other accurate millimeter scale.

EXPERIMENTAL PROCEDURE:

Introduce HCl gas to the desired total pressure into the gas cell. This is conveniently done with a two-stopcock cell. Connect one side of the cell to a vacuum line and connect the other side to a lecture bottle of HCl. Open both stopcocks and evacuate the cell and the connection to the lecture bottle. Fill the cell with gas to the pressure needed for the particular cell and spectrophotometer being used. Close stopcocks and disconnect the cell. Record the spectrum from about 3150 cm^{-1} to about 2550 cm^{-1}. A scale expansion which gives about 20 cm^{-1}/10 mm is satisfactory.

UTILIZATION OF THE DATA

Follow the general instructions in the CSUN Chemistry Department Excel program manual for building the spreadsheet and for entering the data and formulae. Then use the **Trendline** function to plot the data.

SPREADSHEET:

For your data, construct a spreadsheet with nine columns (A-I) in which column A contains the rotational quantum number J" for the state in which the transition originates (e.g., for cell A8, J"=0; for cell A9, J"=1: etc....).

Columns B and C should contain, respectively, the values $\overline{v}_R\left(J"\right)$ and $\overline{v}_P\left(J"\right)$

Column D should contain the values obtained from the calculation of $\frac{0.5\left(\overline{v}_R\left(J"\right)-\overline{v}_P\left(J"\right)\right)}{2J"+1}$, beginning with D9. e.g. $0.5*\left(B9-C9\right)/\left(\left(2*A9\right)+1\right)$

Column E should contain calculations of $\frac{2\left(\left(J"+1\right)^3+J"^3\right)}{\left(2J"+1\right)}$, beginning with E9.

Column F should contain calculations of $\frac{0.5\left(\overline{v}_R\left(J"\right)-\overline{v}_P\left(J"+2\right)\right)}{\left(2J"+3\right)}$, beginning with F9.

Column G should contain calculations of $\frac{2\left(\left(J"+1\right)^3+\left(J"+2\right)^3\right)}{\left(2J"+3\right)}$, beginning with G9.

Column H should contain calculations of $0.5\left(\overline{v}_R\left(J"\right)-\overline{v}_P\left(J"+1\right)\right)$, beginning with H9.

Column I should contain calculations of $\left(J"+1\right)^2$, beginning with I9.

GRAPHING:

Equation 17 suggests that a plot (Graph 1) of column D versus column E should yield a straight line of slope $-D_e$ and an intercept of $B_{v'}$

Equation 18 suggests that a plot (Graph 2) of column F versus column G should yield a straight line of slope $-D_e$ and an intercept of B_o .

Equation 19 suggests that a plot (Graph 3) of column H versus column I should yield a straight line of slope $(B_{v'} - B_o)$. These values of $B_{v'}$ and B_o should be consistent with those calculated using equations 17 and 18, respectively. Similarly, the two values of $-D_e$ produced by equations 17 and 18 should also be in agreement.

Important: See note below on using Excel.

B_e and α_e may be calculated from equation 13 and the values of $B_{v'}$ and B_o. This is done by setting up two versions of equation 13 with $\upsilon = 0$ and $\upsilon = 1$ and solving the simultaneous equations. Using equations 6 and 7, r_e. In order to solve for $\overline{\nu}_e$ and $x_e\overline{\nu}_e$, the equation for the band origin is used. The values of two band origins and a set of simultaneous equations are required. The equations for the band origins are equations 15 and 16. Use the experimental value from the intercept of the third graph along with one of the values from Table 1. Once the value of $\overline{\nu}_e$ is known, the force constant can then be computed from equation 3. Equation 24 in the Appendix below suggests that the dissociation energy may be computed using the calculated values of $\overline{\nu}_e$ and $x_e\overline{\nu}_e$. This yields only a very crude estimate because of the approximations employed. Compare $r_e, \overline{\nu}_e$ and k with literature values.

(NOTE on using Excel: When moving columns to a new place on the spreadsheet for graphing, choose **Full Menu** from the options menu. Then, under **Edit**, use **Paste Special** instead of **Paste** when designating the new position for the column. In **Paste Special** choose **Values**. Also, when moving columns for the plot of D vs. E, block out starting with cell 9 and ending with one less than your last entry.)

Tables 1*	
UNDERLINE nu'	UNDERLINE { nu bar nu' (cm SUP -1)}
2	5668.05
3	8346.98
4	10923.11
5	13396.55
*Band origins for $'H^{35}Cl$ overtones. (Karplus and Porter, Atoms and Molecules, p. 477)	

APPENDIX:

FURTHER CORRECTIONS TO THE MODEL

D' is the energy required to separate the nuclei of a diatomic molecule by an infinite distance. Molecules in the lowest vibrational state possess "zero point energy" of

$$\frac{h\nu_e}{2}$$

The spectroscopic dissociation energy D is then

$$D = D' - \frac{h\nu_e}{2} \tag{20}$$

The potential energy curve may be approximated by the simple empirical Morse function

$$U = D'\left(1 - e^{-\beta(r-r_e)^2}\right) \tag{21}$$

where the constant β is

$$\beta = \nu_e \left(\frac{2\pi^2\mu}{D'}\right)^{1/2} \tag{22}$$

The anharmonicity of the HCl molecule is adequately treated as a first order approximation by substituting the Morse function into the Schrodinger equation. The energy levels then are given by

$$E_{vib} = \left(v + \frac{1}{2}\right)hc\bar{\nu}_e - \left(v + \frac{1}{2}\right)^2 hcx_e\bar{\nu}_e \tag{23}$$

and the anharmonicity constant is

$$x_e\bar{\nu}_e = \frac{h\bar{\nu}_e^2 c}{4D'} \tag{24}$$

Reference**:** Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules., D. Van Nostrand Co, Inc., 1950, p. 534.

PRINCIPLES OF ERROR ANALYSIS

I. THE METHOD OF LEAST SQUARES

Let us suppose that the experimental measurement of the quantities x and y yields the data of Table 9.

Table 9

X	y
1.00	5.4
3.00	10.5
5.00	15.3
8.00	23.2
10.0	28.1
15.0	40.4
20.0	52.8

A plot of the data, Figure 6, reveals that it is essentially linear. We shall, therefore, evaluate the slope, m, and the intercept, b, for the equation,

$$y = mx + b$$

applicable to the data.

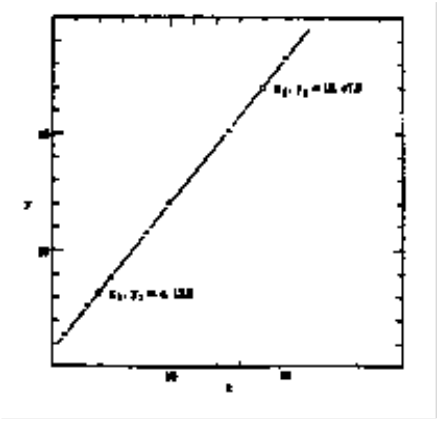


Figure 6. Data of Table 9.

In the graphical method a straight edge is used to draw the 'best straight line' for the data as plotted. Two points on this line are taken as shown in Figure 6, and the slope and intercept of the equation are calculated as follows:

$$m = \frac{y_2 - y_1}{x_2 - x_1} = \frac{47.8 - 13.0}{18.0 - 4.0} = 2.49$$

$$b' = y_2 - mx_2 = 2.98$$

$$b'' = y_1 - mx_1 = 3.04$$

The resulting equation is

$$y = 2.49x + 3.01$$

The value of b in the final equation is the average of b' and b".

The method of averages is based on the assumption that the sum of the residuals is equal to zero.

$$\sum r = 0$$

We define the residual as the difference between the experimental value of y and the value calculated from the expression (mx + b). It may be expressed mathematically in this manner:

$$r = y - (mx + b)$$

To apply the method we divide our data into two groups. This gives two equations which can be solved simultaneously for m and b. In using the data of Table 9, we shall include the first four points in one group and the last three points in another group.

First group

$$5.4 = 1.00m + b$$

$$10.5 = 3.00m + b$$

$$15.3 = 5.00m + b \qquad (17)$$

$$\underline{23.2 = 8.00m + b}$$

$$54.4 = 17.00m + 4b$$

Second group

$$28.1 = 10.0m + b$$
$$40.4 = 15.0m + b$$
$$\underline{52.8 = 20.0m + b}$$
$$121.3 = 45.0m + 3b \qquad (18)$$

Equations (17) and (18) are now solved simultaneously for m and b. When these values are substitute in the straight-line equation, we obtain

$$y = 2.48x + 3.05$$

The method of least squares is discussed in detail by Crumpler and Yoe, *Chemical Computations and Errors*, John Wiley and Sons, Inc., page 217, and the student is urged to study this reference. The principle of the method is based on the following two assumptions, which are quoted from Crumpler and Yoe: (1) "The fixed values of the independent variable are correct, and hence only the dependent variable is subject to errors of measurement." (2) "The curve of best fit is the one which makes the sum of the squares of the deviations from the curve a minimum." The deviations are the same as the residuals defined in the method of averages.

Let us see how the method is used for obtaining a best straight line. The proofs of the equations used to calculate the slope and the intercept of the best fit will not be given.

If x represents the independent variable, y the dependent variable, m the slope, and b the intercept, then the best straight line is the one for which

$$m = \frac{\sum x \sum y - n \sum xy}{\left(\sum x\right)^2 - n \sum x^2}$$

and

$$b = \frac{\sum xy \sum x - \sum y \sum x^2}{\left(\sum x\right)^2 - n \sum x^2}$$

Let us now calculate the values of m and b by the method of least squares. In Table 10 are given the values of x^2 and xy for the various value of x and y from Table 9.

TABLE 10

	x	y	x^2	xy
	1.0	5.4	1.0	5.4
	3.0	10.5	9.0	31.5
	5.0	15.3	25.0	76.5
	8.0	23.2	64.0	185.6
	10.0	28.1	100.0	281.0
	15.0	40.4	225.0	606.0
	20.2	52.8	400.0	1056.0
Sum	62.0	175.7	824.0	2242.0

Then

$$m = \frac{(62.0)(175.7) - 7(2242.0)}{(62.0)^2 - 7(824.0)} = 2.50$$

$$b = \frac{(2242.0)(62.0) - (175.7)(824.0)}{(62.0)^2 - 7(824.0)} = 3.00$$

and the equation for the best straight line is

$$y = mx + b = 2.50x + 3.00$$

A comparison of the values of m and b obtained by each of the three methods is given in Table 11.

TABLE 11

	m	b
Graphical method	2.49	3.01
Method of averages	2.48	3.05
Method of least squares	2.50	3.00

Of course, the uncertainty in the last digit of the values obtained by the graphical method is considerably greater than for the other two methods.

II. Probable Error

The reliability of a method of measurement of a quantity x is indicated by specifying the **probable error**, q_x of a single measurement. The meaning of q_x is that if a single measurement of x is made at random there is a 50-50 chance that the magnitude of the error will be less than q_x, or greater than q_x. Thus, for example, if the measurement were repeated many times and the errors listed in order of increasing magnitude, there would be just as many errors below q_x as above it. For a hypothetical Gaussian distribution, the probable error can be expressed in terms of the **variance** σ_x^2

$$q_x = 0.6745\sigma_x$$

for measurements $x_1, x_2, ...x_N$ with the mean value, $\bar{x}$, and with N approaching infinity. This follows from the fact that the area under the Gaussian probability curve lying between $\bar{x} - 0.6745\sigma_x$ and $\bar{x} - 0.6745\delta_x$ is exactly $\frac{1}{2}$.

For an actual series of measurements with finite N, σ_x^2 is replaced by s_x^2 where s_x is called the **standard deviation** (the divisor N is replaced by the 'degrees of freedom' N-1)

$$\sigma_x^2 = \frac{\sum (x_i - \bar{x})}{N}$$

$$s_x^2 = \frac{\sum (x_i - \bar{x})^2}{N-1}$$

and 0.6745 is replaced by $t_{0.5}(N)$ which is given in Tables of the "t-Test" (e.g., in the Handbook of Chem. & Physics)

N	2	3	4	5	6	55
$t_{o.5}$	1.000	0.816	0.765	0.741	0.727.....	0.674

(Many calculators are capable of giving s_x as well as $\overline{x}$ = mean)

Thus

$$q_x = t_{o.5} s_x$$

Actually, we are really interested in the **probable error of the mean** (called Q_x and not the probable error of a single measurement q_x. Increasing the number of measurements will reduce the probable error of the mean: it can be shown that Q_x is proportional to 1/N so that we finally have the result used in practice:

$$Q_x = \frac{q_x}{\sqrt{N}} = \frac{t_{0.5} s_x}{\sqrt{N}}$$

Example. What is the probable error of the mean of the following series of observations:

34.22, 34.28, 34.16, 34.41, 34.30 ? We have

$$\overline{x} = \frac{\sum x_i}{N} = 34.27$$

$$s_x = \sqrt{\frac{\left(x_i - 34.27\right)^2}{4}} = 0.0901$$

and $t_{0.5} = 0.741$. Therefore,

$$Q_x = \frac{(0.741)(0.0901)}{\sqrt{5}} = 0.02986$$

and we write

$$x = 34.27 \pm 0.03$$

which means that if we make a series of 5 measurements 100 times giving 100 means, 50 of the means will differ in magnitude from the true mean by less than 0.03 and 50 of them will differ by more than 0.03. (Some of course might differ by 0.03, so what is meant is that an *equal number* will be found with a difference of less than 0.03 and with a difference of more than 0.03.)

When the measurement is made only once, we must make an *estimate* of the probable error based on the features of the measuring device. For example, if a buret has each division = 0.1 ml and the eye can subdivide the interval between two divisions into fifths or 0.2, we get a possible total error of $(0.2 \times 0.1) = 0.02$ or a $\pm$ error of half this or 0.01; so we record the volume as equal to the

reading ± 0.01 and take $Q_v = 0, Q_v = 0.01$. Finally, if the number does not come from your measurement but is obtained from a reference such as the Handbook, then 1 in the next to last digit is the maximum error you could expect and a reasonable assumption would be to take 1/2 of this as the probable error. Thus if the Handbook gives density NaCl = 2.165, we would take $Q = 0.005$ and use 2.165 ± 0.005. As another example, you may need to get the density of water from the Handbook but you're not sure of the temperature you had during your experiment. Now the uncertainty in the temperature together with the way in which the density of water varies with temperature determines the probable error in the density rather than the accuracy of the tabulated values which have a much smaller probable error.

III. Propagation of Errors

Assume now that we have values $\overline{x}, \overline{y}, \overline{z}, \ldots$ for all the quantities *x,y,z,…..* which enter into the calculation of a desired quantity $f = f(x, y, z, \ldots)$, together with their probable errors $Q_x, Q_y, Q_{zQ_x}, Q_y, Q_z, \ldots.$ Then the best value of f is given by

$$\overline{f} = f(\overline{x}, \overline{y}, \overline{z}, \ldots.)$$

and not by the average of all the different f's calculated from the different x's, y's, etc. The question now is: what is the probable error associated with $\overline{f}$ due to the probable errors of $\overline{x}, \overline{y}, \overline{z}, \ldots.$? The answer is

$$Q_f = \sqrt{\left(\frac{\partial f}{\partial x}\right)^2 \overline{x}, \overline{y}, \overline{z}, \ldots. Q_x^2 + \left(\frac{\partial f}{\partial y}\right)^2 \overline{x}, \overline{y}, \overline{z}, \ldots. Q_y^2 + \left(\frac{\partial f}{\partial z}\right)^2 \overline{x}, \overline{y}, \overline{z}, \ldots. Q_z^2 + \ldots}$$

so that

$$f = \overline{f} + Q_f$$

It is helpful to present the calculated values in tabular form so that we can see the individual contributions to the total probable error, thus singling out the chief source(s) of error for the given experimental method.

U	$\frac{\partial f}{\partial U}$	Q_{uU}	$\left(\frac{\partial f}{\partial U}\right)^2 Q_U^2$
x			
y			
z			
			$Q_f^2 = \sum \left(\frac{\partial f}{\partial U}\right)^2 Q_U^2$

IV. Propagation Rule for Addition and Subtraction

Suppose the functional relation of f to $x, y, z,$ involves only addition and/or subtraction, for example, $f = x + y \pm x$, with coefficients of unit magnitude. Then since $\frac{\partial f}{\partial x} = 1, \frac{\partial f}{\partial y} = 1,$ $\wedge \frac{\partial z}{\partial z} = -1,$ and $\frac{\partial f}{\partial z} = -1$ we have.

$$Q_f = Q_x^2 + Q_y^2 + Q_z^2$$

So the probable error of $\overline{f}$ is the square root of the sum of the squares of the probable errors of $x, y, z,$ *rather than* simply the sum of the probable errors. The latter would give the worst possibility, corresponding to the situation where all the errors are in the same direction. The correct formula involving a Pythagorean type relationship allows for the possibility that some of the errors might be in opposite directions (in the case of addition) or in the same direction in the case of subtraction thereby cancelling out. For example, if we have two weighing say of a flask empty, $\omega_1 = 64.2793 \pm 0.0002g$ and then filled with sample, $\omega_2 = 82.9624 \pm 0.0002g$ where the estimated probable errors are taken to be $0.0002g$ based on experience acquired with balances which can be read to 0.1 *mg*, we would say the weight of sample w obtained is given by

$$\omega = \omega_1 + \omega_2 = 18.6831 \pm 0.0003g$$

since

$$Q_\omega = \sqrt{(0.0002)^2 + (0.0002)^2} = 2.8 \times 10^{-4}$$

Note, however, that if $f = x + 3y - z$, we get instead

$$Q_f = \sqrt{Q_x^2 + 9Q_y^2 + Q_z^2}$$

showing the greater importance of an error in y.

V. Propagation Rule for Multiplication and Division

Suppose the functional relation of *f* to *x, y, , z* involves only multiplication and/or division with exponents of unit magnitude, for example *f = xy/z*. Instead of the above result for the addition subtraction case where the *errors* are related, we find here that it is the *relative errors* which are related by the

Pythagorean type formula since

$$\left(\frac{\partial f}{\partial x}\right)\overline{x},\overline{y},\overline{z} = \frac{\overline{y}}{\overline{z}} = \frac{\overline{f}}{\overline{x}};\left(\frac{\partial f}{\partial y}\right)\overline{x},\overline{y},\overline{z} = \frac{\overline{x}}{\overline{z}} = \frac{\overline{f}}{\overline{y}};\left(\frac{\partial f}{\partial z}\right)\overline{x},\overline{y},\overline{z} = \frac{\overline{xy}}{\overline{z}^2} = -\frac{\overline{f}}{\overline{z}}$$

so,

$$Q_f = \sqrt{\left(\frac{\overline{f}^2}{\overline{x}^2}\right)Q_x^2 + \left(\frac{\overline{f}^2}{\overline{y}^2}\right)Q_y^2 + \left(\frac{\overline{f}^2}{\overline{z}^2}\right)Q_z^2}$$

or

$$\frac{Q_f}{\overline{f}} = \sqrt{\left(\frac{Q_x}{\overline{x}}\right)^2 + \left(\frac{Q_y}{\overline{y}^2}\right)^2 + \left(\frac{Q_z}{\overline{z}^2}\right)^2}$$

Note that if $f = \frac{x^4 y}{z}$, then $\left(\frac{\partial f}{\partial x}\right) = \frac{4f}{x}$, giving

$$\frac{Q_f}{\overline{f}} = \sqrt{16\left(\frac{Q_x}{\overline{x}}\right)^2 + \left(\frac{Q_y}{\overline{y}^2}\right)^2 + \quad + Q_z + \left(\frac{Q_z}{\overline{z}^2}\right)^2}$$

showing the greater importance of the relative error in x.

VI Illustrative General Example

Determination of the volume of a pycnometer by weighing the water it holds and observing the temperature. To allow for the buoyancy effect of weighing in air, we have

$$m_{true} = m_{app}\left(1 + \frac{d_{air}}{d_{H_2O}} - \frac{d_{air}}{d_{wts}}\right)$$

where m_{app} is the "apparent mass" read from the scale and *d* stands for density. Therefore, we have

$$V_{pyc} = \frac{m_{true}}{d_{H_2O}} = \frac{m_{app}}{d_{H_2O}}\left(1 + \frac{d_{air}}{d_{H_2O}} - \frac{d_{air}}{d_{wts}}\right)$$

We have the following data with the given probable errors:

$d_{air} = 0.001156 \pm 0.000002\, g/mL$; barometric pressure, $P = 740.0 \pm 0.2 mm\, Hg$;

$m_{app} = 24.9526 \pm 0.0003 g$; temperature, $T = 24.3 \pm 0.4 C$;

density of: $d_{H_2O} = 0.9972 \pm 0.0001\, g/mL$, $d_{wts}\,(brass) = 8.5 \pm 0.5\, g?/mL$

The probable errors were arrived at as follows: $Q_{d_{air}}$, based on tables together with errors in temperature, and barometric pressure, $Q_{m_a}\, app$, based on vernier scale and reliability of location of meniscus; $Q_{m_a}\, app$, based on estimate of 0.0002g probable error of single weighing and propagation of this error when take difference of two weighings to get weight of water; Q_T, based on scale on thermometer and observation of variation in readings during the course of the experiment; $Q_{d_{H_2O}}$, based on tables together with error in temp.; $Q -_{d_{wts}}$, based on table value only given to the tenth, so use 5 time this.

Calculating the best value for the volume of the pycnometer, we have

$$V_{pyc} = \frac{m_{true}}{d_{H_2O}} = \frac{m_{app}}{d_{H_2O}}\left(1 + \frac{d_{air}}{d_{H_2O}} - \frac{d_{air}}{d_{wts}}\right)$$

Now we need to calculate the probable error of this value, $Q_{V_{pyc}}$.

$$\frac{\partial V}{\partial_{m_{app}}} = \frac{V}{m_{app}} = \frac{25.048}{24.9526} = 1.0038\, mL/g$$

$$\frac{\partial V}{\partial d_{air}} = \frac{V}{d_{H_2O}}\left(\frac{1}{d_{H_2O}} - \frac{1}{d_{wts}}\right) = \frac{24.9526}{0.9972}\left(\frac{1}{0.9972} - \frac{1}{8.5}\right) = 22.149\, mL^3/g$$

$$\frac{\partial V}{\partial d_{H_2O}} = \frac{m_{app}}{d_{H_2O}}\left(\frac{-d_{air}}{\left(d_{H_2O}\right)^2}\right) - \frac{V}{d_{H_2O}} = -0.03 - 25.12 = 25.15\, mL^2/g$$

$$\frac{\partial V}{\partial d_{wts}} = \frac{m_{app}}{d_{H_2O}}\left(\frac{d_{air}}{\left(d_{wts}\right)^2}\right) = 0.0040\, mL^2/g$$

In tabular form, we have

U	$\frac{\partial V}{\partial U}$	Q_u	$\left(\frac{\partial V}{\partial U}\right)^2 Q_U^2$
m_{app}	$1.0038\, mL/g$	$0.0003g$	$0.1\times10^{-6}\, mL^2$
d_{air}	$22.149\, mL^2/g$	$2\times10^{-6}\, g/mL$	$0.0\times10^{-6}\, mL^2$
d_{H_2O}	$-25.15\, mL^2/g$	$0.0001\, g/mL$	$6.3\times10^{-6}\, mL^2$
d_{wts}	$0.00040\, mL^2/g$	$0.5\, g/mL$	$0.0\times10^{-6}\, mL^2$
			$Q_V^2 = 6.4\times10^{-6}\, mL^2$

Thus $Q_V = 2.5\times10^{-3}\, mL$ and therefore,

$$V_{pyc} = 25.048 \pm 0.003 mL$$

The greatest source of error, by far, was due to the uncertainty in d_{H_2O} which in turn came about because of the uncertainty of temperature (the density of H_20 is known very accurately for a given temperature. Thus the way to improve the experiment and reduce the probable error in the result is to exercise better temperature control and measure it with a better thermometer. If the probable error in the temperature of the water were reduced from the above value of 0.45 to 0.1 C, this would reduce the probable error in from 0.0001 to 0.00003, giving $\left(\frac{\partial V}{\partial d_{H_2O}}\right)^2$

$Q^2_{d_{H_2O}} = 0.6 \times 10^{-6}\, mL^2$ and $Q_V = 8.0 \times 10^{-4}\, mL$ so that we would have $V_{pyc} = 25.048 \pm 0.001 mL$. The experimenter would have to decide whether this improvement was of sufficient importance for him to go to the extra trouble of obtaining more accurate temperature data.

Diode Array UV-Vis Absorption Spectrometer Instructions

1. Turn on the spectrometer. (The switch is located at the bottom left corner)

2. Wait for one minute, then turn on the computer.

3. Press Ctrl + Alt + Del at the same time.

4. Enter the password: 3000hanover.

5. Click **START** then **PROGRAM** then **HP-UV**... then **INSTRUMENT 1 ON LINE**. When the computer asks for a password, click on **CANCEL**.

6. **MODE** (located at the top of the screen should be set at **STANDARD**.

7. For the **TASK** setting (on the left side of the screen) select **SPECTRUM/PEAK**.

8. Click on **SETUP** then cancel the **PARAMETERS** (by clicking on the X's), set the **DISPLAY SPECTRUM** to 204-380 nm, and select the **DATA TYPE** to be **ABSORBANCE**.

9. Insert the blank and push down on the lever.

10. Click on **BLANK** (located at the lower left of the screen).

11. Pull the lever up, remove the blank and insert your sample.

12. Click on **SAMPLE**.

13. After the spectrum has been obtained, get the longest wavelength band to full scale on the Y axis by dragging the box to the end of the screen.

14. To save your sample, click on **FILE**, then click on **SAMPLE AS** and type in your filename.

15. Click on **FILE**, then click on **PRINT SETUP**, and then on **LANDSCAPE**, then **OK**.

16. To select the spectrum to be plotted, click on **OVERLAID SAMPLE SPECTRUM** (located at the top of the graph). Make it blue. Then click on **FILE** then **PRINT** then **SELECTED WINDOW**.

17. To overlay spectra, click on **FILE**, **LOAD,** then **SAMPLE**.

PERKIN-ELMER LS 50B Luminescence Spectrometer

1. Turn on the spectrometer, wait one minute, then turn on the computer. Type **WIN** after the C:\> prompt.

2. Double click on the icon labeled **FLDM** under PE Applications.

3. Click on **INSTRUMENT** then select **SCAN**

4. Click on the box labeled **EMISSION**.

5. Select the emission wavelength range to be 320 to 535 nm. The excitation wavelength should be 320 nm. The slits should be 2.5. Then scan speed should be 240. In the **DESTINATION** box enter your filename (it must be five letters and add 001.sp). Place about 3 mL of your sample into the quartz cuvette (careful, they are very expensive). Place the cuvette in the instrument and close the cuvette compartment of the instrument. Click on OK.

6. Obtain your spectrum. Save the file. Go to **FILE**, then **SAVE AS,** click **OK**. (Do not use this screen to print)

7. To print, go to **FILE** and **QUIT** to **DOS**. Double click on **GRAPH BUILDER**. Go to **SPECTRUM** and click on **ADD SPECTRUM**.

8. Go to **FILENAME**: Find your filename and double click. Your graph should appear.

9. Go to **FORMAT**. Click on **FORMAT GRAPH**. Remove the X from the **AUTORANGE** box, in the **ORDINATE RANGE** box, and enter your desired range. Click on **OK.**

10. Go to **FILE**, click on **PRINT** and **OK**.

PERKIN-ELMER LAMBDA-14 UV-VIS SPECTROMETER

1. Turn on the instrument using the green switch.

2. After a minute turn on the computer.

3. Type WIN and enter.

4. Double click on LAMBDA 14.

5. A page labeled METHOD will appear.

6. Double click on SCAN 1.MSC Once the page entitled C:\UVWINLAB\METHJOD\SCAN 1.MSC appears, make the following changes: For OUTPUT, input your ordinate max, e.g., 0.300. For ordinate min, choose 0.0. Ask your instructor what the wavelength range should be. (Do not use AUTOPRINT, otherwise the wavelength scale of the uv spectrum won't match that of the fluorescence).

7. Click on AUTOZERO (both cell compartments should be empty). Wait for the green light to turn red.

8. After a few minutes you will be asked: "insert next sample: blank for auto zero". Insert your background blanks in the front and back compartments. Press OK.

9. The instrument will scan through the wavelength range selected.

10. Put your sample that you are testing in the front compartment. Leave the blank in the back compartment. Click on START

11. The computer will ask: "please insert next sample". Press OK.

12. The instrument will scan the spectra and print it out.

13. Go to FILE and PRINT the spectrum.

14. For the next sample, if the blank is not needed, insert the next sample, click on START and answer by clicking CANCEL. The instrument will scan the next sample and print it out. You may save your spectra and then overlay them if desired.

Nicolet FTIR/FTRaman Instrument Instructions

FOURIER TRANSFORM INFRARED SPECTRA

1. Fill the MCT (mercury/cadmium/telluride) detector with liquid nitrogen.

2. With the computer turned on, from the C:/ promt, choose **WIN**. Then select **OMNIC** software from the desktop.

3. Make sure the FTIR bench is activated by pulling down the **RAMAN** menu to see that the **Use Raman Accessory** is not selected.

4. Check to see that the KBr beam splitter is installed.

5. From the **WINDOW** menu, select **new window.**

6. From the **COLLECT** menu, choose **optical setup bench**, and then **align the bench.**

7. From the **COLLECT** menu **collect background.** Add this to the window.

8. From the **WINDOW** menu, select **new window.**

9. Put your sample in the sample compartment. From the **COLLECT** menu, select **collect sample.** Add this to the new window. From the **FILE** menu, select **print.**

FOURIER TRANSFORM RAMAN SPECTRA

1. Activate the Raman bench by pulling down the **RAMAN** menu. Choose the **Use Raman Accessory**. The key in the back of the instrument should be turned horizontally.

2. Install the CaF_2 beamsplitter.

3. From the **COLLECT** menu, choose the **optical setup bench**. Select **laser on. Align** the bench using the cyclohexane reference solution.

4. From the **WINDOW** menu, select **new window.**

5. Put your sample in the sample compartment. From the **COLLECT** menu, select **collect sample.** Add this to the new window. It may be appropriate to use the **Raman shift** function from the **VIEW** menu. From the **FILE** menu, select **print.**

7. From the **COLLECT** menu, choose the **optical bench setup.** Select **laser off. IT IS ABSOLUTELY ESSENTIAL THAT THE LASER IS TURNED OFF WHEN THE EXPERIMENTS ARE FINISHED**. **THE KEY SHOULD BE PLACED IN A VERTICAL POSITION.**

pH Measurement Procedure

1. Connect the electrode via the keeper cable to input marked "pH".

2. Press  to turn on the pH meter, then press  to clear. Display will show  .

3. Remove the parafilm covering the reference junction of the electrode and rinse the electrode with deionized water. Blot excess.

4. Immerse the electrode in pH 4.00 standard buffer solution. The solution must reach at least the level of the white line on the electrode. Press  .

5. Wait one minute to allow the electrode to equilibrate. Press  . When  stops flashing, display will show a pH of 4.00. In the upper right-hand corner of the display an arrow will point to 

6. Rinse the electrode with deionized water. Blot excess.

7. Immerse the electrode in pH 7.00 standard buffer solution. The solution must reach at least the level of the white line on the electrode. Wait one minute to allow the electrode to equilibrate. Press  . When  stops flashing, display will show a pH of 7.00. In the upper right-hand corner of the display an arrow will point to  . Calibration is now complete.

8. Rinse the electrode with deionized water. Blot excess.

9. Immerse the electrode in pH 10.01 standard buffer solution. The solution must reach at least the level of the white line on the electrode. Wait one minute to allow the electrode to equilibrate. Press  to turn off Auto Read function. Record this pH reading. The pH meter and electrode are now ready to use for the maleic acid titration.

10. Always keep the electrode dry when not in use. Never store in solution.

11. When measurements have been completed, rinse electrode thoroughly with deionized water and blot dry. Cover the electrode reference junction with a strip of parafilm.

FORMAT FOR LABORATORY REPORTS FOR PHYSICAL CHEMISTRY

Title of Experiment

Name of Student

Abstract.
Very brief summary of what was done, what method was used, what result was obtained, and the deviation from the literature value.

Purpose and Theory of the experiment. Simply stated together with necessary equations for treatment of data.

Experimental Procedure Brief description of actual procedure.

Data presented in tabular and/or graphical form.

Results organized in a concise form with samples of calculation.

Error Analysis including comparison with literature values.

Discussions with regard to results obtained, capability of methods used and possible improvements suggested.

References. Number your references in the text. List them at the end of the report.

Reports are due 1 week after the last day scheduled for the experiment. There will be penalties(1 point per day) in the grading of late reports.
Data should be recorded directly into a bound notebook.

SAFETY RULES AND REGULATIONS
CSUN DEPARTMENT OF CHEMISTRY

ENSURING LABORATORY SAFETY IS NOT JUST THE RESPONSIBILITY OF THE INSTRUCTOR; IT IS THE RESPONSIBILITY OF EVERYONE WORKING IN THE LABORATORY. YOU ARE EXPECTED TO BE FAMILIAR WITH THE SAFETY RULES AND TO CONDUCT YOUR LABORATORY WORK IN A SAFE MANNER AT ALL TIMES. The laboratory instructor will review the following safety rules and regulations with you and will point out the location and operation of the fire extinguisher, safety shower, eye wash, and other laboratory safety equipment available.

1.While in the laboratory, you must wear approved safety goggles. Hair and easily combustible clothing must be confined at all times.

2.Do not smoke, eat, or drink in the laboratory.

3.Before beginning work in the laboratory you should be familiar with the procedure you will be following, as well as with any special precautions or changes that the instructor may note. Report any unexpected events to the instructor.

4.No unauthorized experiments may be performed. Violators will be subject to severe disciplinary action.

5.Before leaving the laboratory wash your hands carefully.

6.In case of an accident, the laboratory instructor should be summoned.

a.If you receive a chemical burn, immediately flood the area with cold water while another student summons the instructor.

b.Treatment for injuries may be obtained from the Student Health Center.

7. CONDUCT OF EXPERIMENTS:

a.When cutting glass tubing or inserting tubing into stoppers, protect your hands by using a towel. Glass tubing should be lubricated with glycerol or water to aid insertion of the tubing into stoppers. To remove tubing from stoppers, cut the stoppers.

b.When heating or carrying out reactions in a test tube, never point the mouth of the tube at your neighbor or yourself.

c.Never taste or smell a chemical unless instructed to do so.

d.When smelling a chemical, fan vapors toward your face and inhale cautiously.

e.Never pour water into concentrated acid; slowly add the acid to the water with constant stirring in a pyrex beaker or flask, not in a graduated cylinder.

f.Never pipet liquids by mouth; use a suction bulb.

g.If objectional vapors are given off during an experiment, the experiment must be performed in a hood.

h.Unless instructed otherwise, flammable solvents with boiling points less than 100°C must be heated, distilled, or evaporated on a steam bath, not over or near an open flame. Flammable solvents should be contained in flasks rather than in open beakers.

i.Each student is responsible for cleaning up all spilled chemicals at his desk, on the reagent shelves, in the hoods,and around the balances. Consult the instructor if uncertain about the method of cleanup.

j.No chemicals should be disposed of in the sink unless instructed to do so. If chemicals are disposed of in the sink, they should be wash down with ample water for several minutes. Materials such as broken glass and towels should be placed in the receptacles beneath the sinks or in a waste jar.

k.Never dispose of sodium metal in the troughs or sinks. Consult the instructor for the method of disposal.