Physical Chemistry Laboratory

Department of Chemistry and Biochemistry

University of Wisconsin-Milwaukee

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CHEMISTRY 563-801

PHYSICAL CHEMISTRY LABORATORY

LABORATORY MANUAL

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Summary of Laboratories

Experiment [1]	Title	Notes
IR[2]	Infrared spectrum of diatomic molecules	Check with TA for which IR spectrometer to use.
AE[2]	Activation Energy	
BBR[2]	Blackbody radiation laws	
FEM	Free Electron model	
6	Heats of Combustion	Operation manual on electron reserve in library [4]. Use EITHER solid or liquid samples. Consult TA before selecting 2 "unknowns"
8[2]	Heats of Ionic Reaction	Operation manual on reserve [4]
13B	Vapor pressure of pure liquid	Use acetone. Our equipment is different to that shown in Figure 2 (Page 203 of text)
9	Partial Molal Volume	Use Weld pycnometers
10	Cryoscopic determination of molecular weight and freezing point depression of strong and weak electrolytes	Use the digital thermometer. Determination of the molecular weight of naphthalene.
3B	Heat capacity ratio for gases	Use air, N_2, CO_2 and He.
15[2]	Binary solid-liquid phase diagrams	Use Bi-Cd
26	Surface tension of solutions	Use capillary rise method
MR[2]	Acid dissociation constant of methyl red	Use the procedure in Tobey [3].
DSC[2]	Differential scanning calorimetry	TA will assign hydrates.
STM[2]	Scanning tunneling microscopy of silicon and graphite	Experiment carried out in the basements STM laboratory under the supervision of a TA.

1. The outline for most of these experiments is in the textbook
2. See the corresponding section in this manual
3. S.W. Tobey, *J. Chem. Educ.,* **35,** 514 (1958)
4. URL: http://www.uwm.edu/Library/ERES/sorensen/CHEM563.html

Syllabus

Introduction:

The object of this course is to introduce the student to some of the basic techniques and operations of physical chemistry and the formal reporting of experimental results. The class meets on Tuesday and Thursday from 9:00 am to 11:50 am in Room 470.

Textbook:

The course textbook is "Experiments in Physical Chemistry" by D.P. Shoemaker, C.W. Garland, and J.W. Nibler published by McGraw-Hill. Most of the experiments are described in this book except as noted in the table on page 3 of this manual. The experiments not described in the book are outlined in this manual.

The Laboratory:

1. Each experiment has a number and definite location. Do not remove it from there. Do not use any material from the other section. Before you do a laboratory, make sure all materials are present.

2. Standard solutions are located in the area of your experiment or should be made up as needed. All other chemicals as well as additional equipment have to be obtained from the stockroom. Inform the stockroom personnel when you are running low on a solution.

3. All waste must be properly disposed of.

    1. Organic waste disposal bottles are located in the prep room.
    2. Broken glass, **EXCEPT BROKEN THERMOMETERS**, should be placed in the sharp object box.
    3. Safe powders should be placed in the box provided.
    4. Mercury spills require special clean-up procedures. Follow the posted procedures and contact the instructor and/or stockroom personnel immediately.

4. Handle flammable and poisonous materials in the hood.

5. Keep your work area clean, handle the equipment carefully.

6. Inform the instructor if any apparatus becomes defective, or breakage occurs.

7. All equipment has to be returned to its original place **10 -- 15 minutes prior** to the end of the laboratory periods; it should be kept clean. Such equipment should be clearly labeled and stored in a special place.

Safety:

1.   Know the location of fire extinguishers, the emergency shower, emergency eyewash station, and emergency telephone.

2.   Smoking, eating, and/or drinking are prohibited in the laboratories.

3.   Eye shields, required by Wisconsin statute, must be worn at all times.

4.   Other hazards specific to a particular experiment are described in the textbook.

5.   No student is permitted to work in the laboratory without the supervision of an instructor. If for exceptional reasons you have to work during some other physical chemistry lab section, you must have the permission of your instructor and the corresponding instructor in charge.

Reports:

A good report should concisely describe **IN YOUR OWN WORDS** the experiment so that a chemist can easily follow the objectives of the work and repeat it. Use secondary literature and do not simply copy your textbook. The purpose and results of the experiment should be clearly stressed. Quote all outside sources by complete references. The pages and graphs should be stapled together. The use of the Laboratory Research NoteBook (National 43-649) is recommended. All pages will be numbered. Use a fine ball pen for all entries. Do not erase in your notebook. False entries should be crossed out but still remain legible: you never know when you might need the data. Diagrams should be generated by computer or produced using appropriate graph paper (log or semi-log paper where necessary). The original of each is subject to collection by the instructor at all times. When the Laboratory Research NoteBook is used, the **ORIGINAL** is to be handed in.

The following topics should be used:

1.   Your name, course section number, date on which the experiment was performed, when it was submitted, and all pages should be numbered.

2.   Title: name and number of experiment.

3.   Abstract: a short introduction as to what is to be investigated and how it is to be carried out and a brief summary of your results (use between 2 and 5 sentences).

4.   Introduction: Describe the goal of the work and indicate why the experiments are being done and what will be learned.

5.   Theory: describe concisely, in your own words, the theoretical background, the purpose of the experiment and the experimental method (about 600 words). Equations must be numbered and all symbols defined.

6. Experimental Outline: under this heading the experimental procedure to be followed is outlined. This outline should be complete enough so that you can perform the experiment **WITHOUT REFERENCE TO THE TEXT, OR OTHER PRINTED INFORMATION**.

7. Experimental Results: set up neat, concise, and carefully thought-out tables before lab time, ready to use for recording experimental data in the laboratory. Column headings should contain the name of the quantity, the internationally accepted symbol, and the dimensions (for example, Temperature T K). All data must be entered in the notebook as you obtain it. Do NOT record your data on other bits of paper and then transfer it, after appropriate modifications, to your notebook.

8. Calculations and Error: refer to equations, tables, and graphs by consecutive numbers. Define all symbols when you introduce them. Each equation should be part of a sentence. Give a 'typical sample calculation' to illustrate how you did it. Error analysis will depend on the experimental procedure. A typical error calculation should include: determination of standard deviations for 3 or more determinations of the same quantity and propagation of errors.

9. Discussion: state clearly the final results in the context with the topics of the experiment. Compare it with literature and theoretical values. The error analysis should be used to explain discrepancies. Include comments on how the experiment might be improved. You should look at the published literature for examples of style and content.

10. Conclusions: Briefly summarize the results and conclusions of your paper.

11. References: cite completely. See the Bibliography for examples.

Prerequisites:

A grade of C or better in CHM 221 or 223 AND a grade of C or better in CHM 561.

Assignments:

Eight experiments will be performed. Students will work in pairs. You will be given an opportunity to choose your partner during the first class. If you do not wish to do so, you will be assigned a partner. Following completion of the laboratory, you will discuss your results with either the TA or the faculty in charge and grades will be assigned partly on this basis. During the course of the semester, you will choose two of your experiments to write up as a formal paper. The final grade will be based on both the laboratory interviews and the reports.

Each laboratory write-up will be graded on the basis of 100 points. It will be graded as follows:

Points   Section

20   Theory and Experimental Procedures.

20	Experimental Results.
40	Calculations and Error.
20	Discussion and Abstract.

Make Up Work: Make up work is NOT allowed.

Grading: Because the laboratory grade is essentially a performance grade, a grade of F in the laboratory will result in an F for the course. Final grade will be 80% laboratory discussions, 20% write up.

Dropping: You may only drop this course during the first two weeks of class.

Policies: Department Policies have been posted on bulletin boards next to the door in room 271, across from room 195, and adjacent to room 164.

CHEMISTRY 563

Physical Chemistry Laboratory

IR

Infrared Spectrum of Diatomic Molecules

OBJECTIVE

To measure the bond lengths and force constants of heteronuclear diatomic molecules.

BACKGROUND

The rotational energies of a *rigid* rotor are given by:

$$E_J = B\,J(J+1),$$

where J is the rotational quantum number and may take any integral value. The rotational constant $B = \hbar^2/2I$, where I is the moment of inertia of the diatomic molecule ($I = \mu r^2$; where r is the bond length of the diatomic molecule and μ the reduced mass). In principle, measurement of the positions of the rotational energy levels can yield a value of B and hence the bond length (through I). These transitions generally occur in the *microwave* region of the spectrum and the selection rule in this case is $\Delta J = \pm 1$.

Rotational motion of the molecule can also couple with the vibrational motion to yield a *rotational-vibrational spectrum*, and the transitions in this case appear in the infrared region of the spectrum. It can be shown for a *Morse potential* (which closely resembles the true interatomic potential) that the energy levels are:

$$E_v \;=\; (v+1/2)\hbar\omega \;-\; (v+1/2)^2\,x_e\,\hbar\omega,$$

where x_e is the anharmonicity constant and ω the angular frequency of vibration of the diatomic molecule. The selection rules for a *harmonic* oscillator (i.e., one where x_e is very small) is $\Delta v = \pm 1$. The selection rules can be relaxed for a non-harmonic (i.e., anharmonic) oscillator so that rotational-vibrational transitions with $\Delta v = \pm 2, \pm 3,$ etc. are also allowed (these are called *overtones)*. The intensity arising from these transitions is generally much weaker than those for which $\Delta v = \pm 1$ (which is called the *fundamental)*. The frequency of the oscillation is related to the force constant k via $\omega = \sqrt{k/\mu}$. In principle, measurement of the positions of the vibrational energy levels can provide information on the bond strength.

An additional complication for "real" diatomic molecules is that they are rarely rigid; as the rotational quantum number J increases, the rotational angular momentum increases so that the centripetal force increases. This has the effect of stretching the bond for higher J values and so increasing I and decreasing B. This gives rise to unequally spaced lines in the rotational-vibrational spectrum, which must be taken account of in measuring bond lengths from B. A more detailed outline of this experiment in included in "Experiments in Physical Chemistry" by Shoemaker, Garland and Nibler (Page 397). In addition, you should read the section on Infrared Spectrophotometers in this book (beginning on page 679) before doing this experiment.

EXPERIMENTAL

Filling Infrared Cells

The infrared cells are filled using a vacuum line from the gas bottles. The infrared cells have KCl windows, which are transparent to infrared radiation but are also very soluble in water. This means that several precautions must be taken to ensure that they are not damaged:

(i) They should not be touched since perspiration can etch the windows. They cannot be cleaned like glass by just rubbing!

(ii) The exposure to water vapor in the air must be minimized. They are therefore stored in a desiccators when not being used.

If you are uncertain how to use the vacuum system for filling the bottles, please ask the laboratory staff for assistance. Attach the infrared cell to the vacuum line and initially evacuate using the rotary pump. Isolate the pumping system and carefully introduce the gas from the lecture bottle to the desired pressure (a few hundred Torr should be sufficient). Do not open both valves on the cylinder simultaneously; this will cause the vacuum line to explode. Close off the valve to the infrared cell, and pump away any residual gas from the line. This must be done because many of the diatomic gases used for this experiment are poisonous (particularly CO). Isolate the pump from the line and slowly introduce air to enable you to remove the cell. Evacuate the gas line ready for the next user and transfer the filled cell to the infrared spectrometer.

For the measurements a computer controlled Fourier transform spectrometer is used. The software should be self explanatory, but if you have any doubts, consult the T.A., faculty or

laboratory staff. A sheet of instructions should be close to the apparatus to help you to find your way through the software. First perform a "wide scan" (between 400 and 4000 cm^{-1}) to ascertain where the peaks in the spectrum are. Identify the rotational-vibrational region of the spectrum and focus on this region. You should collect spectra for, at least two gases (CO and NO). You should also search the region at twice the frequency of the fundamental (if accessible) to search for overtones. If there are none visible, the molecule is, to a good approximation, a harmonic oscillator.

ANALYSIS OF RESULTS

- Draw a rotational-vibrational energy level diagram for a diatomic molecule and use this to establish the form of the rotational vibrational spectrum that you expect.

- The vibrational frequency of the molecule is determined straightforwardly from the spectrum by using the energy level diagram you should have already constructed. If the molecule is harmonic, this correspond directly to the vibrational frequency.

You will notice that the rotational lines in the spectrum are not equally spaced. Assign values of J to the peaks in the rotational vibrational spectrum and measure the line spacing (which corresponds to $2B$) as a function of J. You should do this manually from the hard copy and not using the cursor on the software since this is not sufficiently accurate. Extrapolate this back to $J = 0$ to get the value of B for a non-rotating molecule. Use this value to calculate the bond length of the molecule.
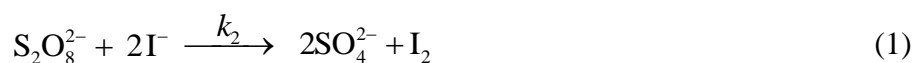
CHEMISTRY 563

Physical Chemistry Laboratory

AE

Activation Energy

OBJECTIVE

In this experiment the reaction of persulfate and iodide ions is used to illustrate the dynamics of ionic reactions in solution. The influence of temperature on the specific rate constant will be evaluated.

BACKGROUND

The reaction

$$S_2O_8^{2-} + 2I^- \xrightarrow{k_2} 2SO_4^{2-} + I_2 \tag{1}$$

is bimolecular and follows a second order rate law. If the reaction is carried out in the presence of thiosulfate ions, the iodine liberated in (1) is rapidly consumed according to

$$I_2 + 2S_2O_3^{2-} \xrightarrow{k_i} 2I^- + S_4O_6^{2-} \tag{2}$$
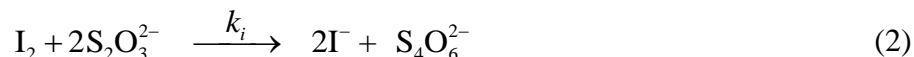
Thus, the iodide ions are regenerated continuously according to reaction (2). Therefore, the reduction of the persulfate proceeds at a constant iodide concentration $[I^-]_0$, provided that

$$\left[S_2O_3^{2-}\right]_0 \geq 2\left[S_2O_8^{2-}\right]_0 \tag{3}$$

In this case, all iodine produced in the reaction (1) would continue to react according to reaction (2). An indicator sensitive to I_2 (such as thiadene or a standard starch solution) would not cause a color change. On the other hand, if

$$\left[S_2O_3^{2-}\right]_0 < 2\left[S_2O_8^{2-}\right]_0 \,, \tag{4}$$

the system will develop color as soon as the $S_2O_3^{2-}$ is used up and the first trace of I_2 is produced by reaction (1). Since $k_i \gg k_2$, the time required for this to happen is thus a simple inverse measure of the reaction rate constant, at constant temperature and constant iodide concentration $[I^-]_0$. Under these conditions, the rate law reduces to a pseudo first-order reaction with a reaction rate given by

$$rate = -\frac{d\left[S_2O_8^{2-}\right]}{dt} = k_2\left[I^-\right]\left[S_2O_8^{2-}\right] = k_1'\left[S_2O_8^{2-}\right], \tag{5}$$

with

$$k_1' = k_2 \left[I^- \right]_0 \tag{6}$$

k_1' has units of reciprocal time, and the subscript "0" indicates the concentration at time "0". Integrating Eqn. (5) and rearranging yields

$$k_1' = \frac{1}{t} \ln \frac{\left[S_2O_8^{2-} \right]_0}{\left[S_2O_8^{2-} \right]_t}. \tag{7}$$

Now consider the case where the initial concentrations are

$$\left[S_2O_3^{2-} \right]_0 = \left[S_2O_8^{2-} \right]_{-0}, \tag{8}$$

which means the amount of $S_2O_3^{2-}$ is insufficient to prevent a color change. At the time when $S_2O_3^{2-}$ is used up we have

$$\left[S_2O_8^{2-} \right]_{t_{1:1}} = \left[S_2O_8^{2-} \right]_0 - \frac{1}{2}\left[S_2O_3^{2-} \right]_0, \tag{9}$$

where $t_{1:1}$ indicates the time for color change for the 1:1 mixture. Evaluating Eqn. (7) for this case and employing condition (8) yields

$$k_1' = \frac{1}{t_{1:1}} \ln \frac{\left[S_2O_8^{2-} \right]_0}{\left[S_2O_8^{2-} \right]_0 - \frac{1}{2}\left[S_2O_3^{2-} \right]_0} = \frac{1}{t_{1:1}} \ln \frac{\left[S_2O_8^{2-} \right]_0}{\left[S_2O_8^{2-} \right]_0 - \frac{1}{2}\left[S_2O_8^{2-} \right]_0} = \frac{1}{t_{1:1}} \ln 2. \tag{10}$$

Note that for this case $t_{1:1}$ is the half-life of the (pseudo) first-order reaction. In general, if

$$\left[S_2O_3^{2-} \right]_0 = \frac{1}{\alpha}\left[S_2O_8^{2-} \right]_0 \quad \text{(with } \alpha > 1/2 \text{)}, \tag{11}$$

we obtain the following expression

$$k_1' = \frac{1}{t_{1:\alpha}} \ln \frac{\left[S_2O_8^{2-} \right]_{-0}}{\left[S_2O_8^{2-} \right]_0 - \frac{1}{2}\left[S_2O_3^{2-} \right]_0} = \ln \frac{\left[S_2O_8^{2-} \right]_0}{\left[S_2O_8^{2-} \right]_0 - \frac{1}{2\alpha}\left[S_2O_8^{2-} \right]_0} = \frac{1}{t_{1:\alpha}} \ln \frac{2\alpha}{2\alpha - 1}. \tag{12}$$

Keep in mind that as soon as iodine starts to appear, all of the $S_2O_3^{2-}$ is used up. Therefore, Eqn. (9) is valid for all mixing ratios (provided that $\alpha > 1/2$).

The temperature dependence of a specific rate constant $k = k_1'$ is given by the Arrhenius expression

$$k_1' = AT^m \exp\left(-\frac{E_a}{RT} \right)$$

where E_a is the so-called the activation energy, R is the gas constant, and T is the (absolute) temperature. The prefactor of the exponential function is the product of the so-called frequency factor A and the m-th power of the absolute temperature. Often we have *m=0*. For this case, taking the logarithm of Eqn. (13) yields

$$\ln k_1^{'} = \ln A - \frac{E_a}{RT} \quad .$$

(14)

When Eqn. (14) is valid, that is, if the prefactor shows no temperature dependence, a plot of $\ln k_1^{'}$ versus *1/T* will be a straight line with slope E_a/R. Thus, E_a can be calculated from the slope of such a plot.

EXPERIMENTAL:

In all of the following experiments, maximum efficiency is achieved by running several reactions at the same time. Replications may be useful to determine the precision with which you can detect indicator color change.

1.   Place in a test tube 20 ml of 0.5M KI and 10 ml of 0.01M $Na_2S_2O_3$. In a second test tube place 20 ml of 0.01M $Na_2S_2O_8$ and several drops of thiadene or starch indicator solution. Both tubes should be thermostated in the large Dewar flask containing water at the desired temperature. If possible, stir the thermostat. Vary initial concentrations to study the concentration dependence.

2.   At time zero, rapidly mix the contents of the 2 tubes and return to the thermostat. Measure the elapsed time for the appearance of a dark blue or brown color. Enough points should be taken to permit a statistical analysis of the data and to determine the rate constant $k_1^{'}$ at a number of different temperatures. Duplicate runs may be made at each temperature.

ANALYIS OF RESULTS:

1.   Verify the validity of the rate law (5) by plotting the proper function of $S_2O_8^{2-}$ versus time. Be sure to label each axis, including the units!

2.   Calculate the activation energy E_a.

3.   Evaluate the Arrhenius frequency factor A.

REFERENCES:

1.   D.A. House; *Chem. Rev*., <u>62</u>, 197 (1962).

2.   K.J. Laidler; "Chemical Kinetics"; Chap. 5; McGraw Hill (1965).

CHEMISTRY 563

Physical Chemistry Laboratory

BBR

Blackbody Radiation Laws

OBJECTIVE

To measure the total amount of radiation energy emitted by an object as a function of its temperature.

BACKGROUND

The early ideas in quantum mechanics arose out of a failure by classical mechanics to predict correctly several experimental phenomena. One of the most important of these was the spectrum emitted by a non-reflective object (i.e., a black body) at various temperatures.

In particular, classical physics predicted that the amount of radiation should increase asymptotically to infinity as the wavelength became shorter; the so-called *ultraviolet catastrophe*. A result of this prediction was, for example, that an incandescent light bulb should emit large quantities of x-rays and γ-radiation. This is clearly not the case. Planck was able to resolve this problem by postulating that the radiation modes of various frequencies could be excited to only a discrete set of energies (i.e., they were *quantized*). This energy depended on the frequency ν of the mode. Planck found that if the energy E was given by $E = nh\nu$ (where h is Planck's constant), he could then calculate the energy spectrum $U_\lambda \, d\lambda$ (i.e. the energy emitted in a wavelength range between λ and $\lambda + d\lambda$) and found that the result agreed well with that obtained experimentally.

It is found both theoretically (using the above energy quantization condition) and experimentally that the maximum wavelength of the emitted radiation, λ_{max}, and the total energy emitted, U_{tot}, depend on temperature. The first is given by the Wien displacement law

$$T \, \lambda_{max} = k \, , \tag{1}$$

where k is a constant. The total emitted power per unit area S_{tot} is given by Stefan's law

$$S_{tot} = \sigma \, T^n \, , \tag{2}$$

where σ is also a constant. T is the absolute temperature in both cases, and n is an integer

theoretically equal to 4. The aim of the experiment is to determine the value of *n*.

<u>EXPERIMENTAL</u>

The radiation emitted from a heated "blackbody" is detected using a "thermopile" to measure the radiation emitted as a function of the sample temperature.

The blackbody consists of a brass block with a cone-shaped hole at one end that constitutes the region from which radiation is emitted. This shape is selected to minimize reflection of any incident radiation. The blackbody is placed within a tube furnace that is resistively heated and the heating current is controlled using a Variac (which is a continuously variable transformer). The temperature is measured by means of a thermocouple inserted into the rear of the blackbody, and the sample temperature is read directly using a meter that automatically converts the thermocouple voltage output to temperature.

A water-cooled baffle with a hole in it is placed in front of the blackbody aperture to prevent extraneous radiation from the furnace from entering the detector.

The heat energy detector (a thermopile) operates on the same principal as the thermocouple used to measure the furnace temperature: a potential difference (voltage) is generated when a junction of two dissimilar metals is heated. In order to increase the sensitivity of the thermopile, a number of thermocouples are attached in parallel. The voltage produced is therefore proportional to the incident infrared radiation (heat) energy.

The experiment is housed in a darkened room to minimize the amount of stray radiation reaching the detector. Line up the detector so that it points at the aperture in the cooling baffle and turn on the cooling water and voltmeter. Allow for the temperature to stabilize for a few minutes. Leave the door of the laboratory closed, and make sure that it is closed when any readings are taken. Read the "background" voltage prior to turning on the thermopile. Turn on the Variac to ~80% and wait until the temperature has stabilized at a reasonable value. This will probably take ~2 hours. Read the voltage on the thermopile meter and the temperature. Turn the Variac down (~70%) and again allow the temperature to stabilize and again record the blackbody temperature and thermopile reading. Repeat as often as suitable.

<u>ANALYSIS OF RESULTS</u>

The thermopile records voltages that are proportional to the detected power P_{tot}. Determine a calibration factor (with units W/V) using Fig. 8 on page 602 of "Experiments in Physical Chemistry" by Shoemaker, Garland and Nibler for the conversion of the measured voltages into the total powers P_{tot}. Using the area of the aperture (that is, the effective area of the emitting blackbody) calculate total power emitted per unit area S_{tot}. S_{tot} depends on the temperature T according to equation (2):

$$S_{tot} = \sigma T^n .$$
(2)

We wish to measure n. Taking logs of both sides gives:

$$\log S_{tot} = n \log T + \log \sigma .$$
(3)

Thus, plotting $\log(S_{tot})$ versus $\log(T)$ should yield a straight line of slope n. A linear regression of Eqn. (3) will yield the slope directly.

Note: For unpolarized radiation, S_{tot} is related to total emitted energy per volume u_{tot} according to

$$u_{tot} = \frac{8\pi}{c} S_{tot}$$

CHEMISTRY 563

Physical Chemistry Laboratory

FEM

Free Electron Model

<u>OBJECTIVE</u>

The absorption of visible light by a molecule indicates the presence of an excited electronic state lying between 1.55 eV (800 nm) and 3.10 eV (400 nm) above the ground electronic state. Molecules containing conjugated single- and double- bonds generally meet this requirement. The electronic structure of such molecules may be regarded as a linear combination of equally weighted valence bond structures. In terms of molecular orbitals, the σ electrons form localized bonds, while the π electrons are delocalized. Absorption of a photon of suitable wavelength may cause excitation of an electron from the highest occupied π molecular orbital (usually a bonding orbital) to the lowest empty π orbital (usually antibonding).

In this experiment the energies and intensities of such transitions are calculated for a series of polymethine dye molecules containing conjugated chains using the so-called free electron molecular orbital model (FEMO).[1,5] Experimental spectra are then obtained for these molecules, and compared with the predictions of the model.

<u>BACKGROUND</u>

The assumption is made that a linear conjugated chain may be treated as a 1-dimensional box of length L, and that the potential of an electron is zero inside the box, and infinite outside. The one-electron Schrödinger equation for this situation is:

$$\frac{-h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2} = E\psi , \qquad (1)$$

where E is the energy eigenvalue, m the electronic mass and $\psi = 0$ at x = 0 and $x = L$ (boundary conditions). Solving equation (1) yields the wavefunction

$$\psi = (2/L)^{1/2}\sin\frac{\pi\,nx}{L} \qquad (2)$$

with the energy eigenvalues

$$E_n = \frac{h^2 \, n^2}{8 \, m \, L^2} \qquad n = 1, 2, 3 \ldots \qquad\qquad (3)$$

h is Planck's constant.

The energy levels may now be filled with π electrons such that 2 electrons with opposite spins are placed in each level according to the Pauli principle. If the molecule contains N π-electrons, the highest filled level will have the quantum number $n = N/2$, while the lowest vacant level will have the quantum number $n+1$.

The energy for an electronic transition from the highest filled level to the lowest vacant level is given by

$$E_{(n+1)} - E_{(n)} = \frac{h^2}{8 \, m \, L^2} (2n+1) = \frac{h^2}{8 \, m \, L^2} (N+1) \qquad\qquad (4)$$

The question now arises how the length L of the one-dimensional box is determined. Consider for example the polymethine dye 3,3'-diethylthiacarbocyanine iodide[4,5]:
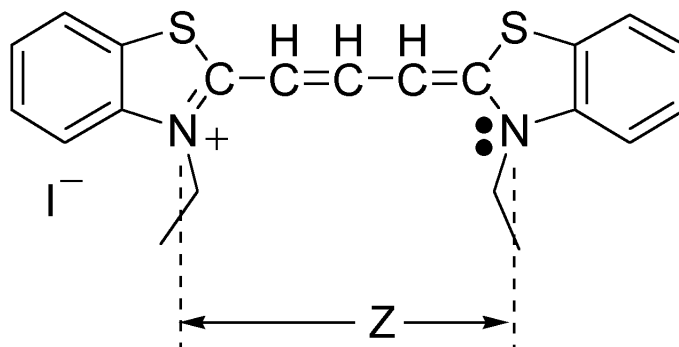

Figure 1

For this molecule the number Z of resonant double-bonded atoms in the chain is $Z = 7$. The number j of double bonds over the distance Z is $j = 3$, while the number N of π-electrons in chain is given by $Z + 1$ (3 from N; 1 from each C).

The length of the box L models the extent of the conjugated π-electron system of the molecule. Looking at the molecular structure, one is tempted to take just the length L' of the "quasi" linear portion of the molecule ranging from N^+ to N along the chain. However, the molecular wavefunction is not likely to abruptly terminate at the nitrogens, but extends beyond them. A common procedure to account for this fact is to add to nitrogen-nitrogen distance one

average bond length l on either end.[2,6] Using this assumption, we can write for L

$$L = (Z-1)\, l + 2l = (Z+1)\, l , \tag{5}$$

Using the fact that for the class of molecules that are investigated in this experiments $N = Z+1$, we can rewrite the expression for the transition energy (Eqn. (4)) as

$$E_{(n+1)} - E_{(n)} = \frac{h^2}{8ml^2} \frac{N+1}{N^2} . \tag{6}$$

In the experiment, the wavelength λ of the light that induces a transition between highest filled π-level A and the lowest empty π-level B is measured. The wavelength is related to the energy difference $E_B - E_A$ between these states via

$$\lambda = \frac{hc}{E_B - E_A} , \tag{7}$$

where c is the speed of light.

EXPERIMENTAL

The following polymethine dyes are available for study in the laboratory.

I.   3,3' diethylthiacyanine

3,3' diethylthiacarbocyanine

3,3' diethylthiadicarbocyanine

3,3' diethylthiatricarbocyanine

II: 1,1'-diethyl-2,2'-cyanine

1,1'-diethyl-2,2'-carbocyanine

1,1'-diethyl-2,2'-dicarbocyanine

1,1'-diethyl-2,2'-tricarbocyanine

Structural formulas are given in reference 4. A reference sheet with all of the structures is available in the laboratory.

1.   Prepare experimental solutions of one series of dyes in methanol by diluting the stock solutions by a factor of 50 with reagent grade methanol.

2.   Measure the absorption spectra of the diluted solutions over the full range of the spectrometer against a methanol reference, using one of the spectrometers in the laboratory.

3.   Plot of absorbance (or transmittance) vs. wavelength for each dye solution.

ANALYSIS OF RESULTS

1.   For each solution, calculate E_B - E_A from the wavelength λ_{max} of the absorption maximum.

2.   If you obtained results for a second series of dyes, discuss any changes, which may have arisen because of changing end groups attached to the conjugated chain.

3.   Compare the results of the measured value of E_B - E_A with the results predicted theoretically from the particle-in-a-box model.

4.   According to equation (6), plotting the measured wavelengths λ_{max} of the absorption maxima vs. $N^2/(N+1)$ should produce a straight line. Determine from the slope of this line the average (effective) bond length l for this class of molecules.

DISCUSSION

You should comment on whether you think that this model for conjugated hydrocarbons is reasonable. Is the average bond length l a reasonable number? The discussion can be brief, but should include

(1) the influence of estimated uncertainties in your work on values you obtained for λ_{max} ;

(2) how your values of λ_{max} compare with those of Kuhn, and possible reasons for significant differences.

REFERENCES

1.   S.P. McGlynn, "Introduction to Applied Quantum Chemistry", Holt, Rinehart, and Winston, Inc., New York, 1972

2.   H. Kuhn, *J. Chem. Phys.*, <u>17</u>, 1198 (1949).

3.   C.N.R. Rao, "Ultraviolet and Visible Spectroscopy", Butterworth, London, 1975

4.   F.M. Hamer, "Cyanine Dyes and Related Compounds", Interscience Publishers, New York, 1964

5.   H. Kuhn, *Helv. Chim. Acta*, <u>31</u>, 1441 (1948).

6.   K. Ruedenberg and C.W. Scherr, *J. Chem. Phys.*, <u>21</u>, 1565 (1953).

CHEMISTRY 563

Physical Chemistry Laboratory

15

Phase Diagram of a Binary System

<u>OBJECTIVE</u>

The phase diagram of a Bismuth-Cadmium binary system is to be determined and plotted by means of a series of cooling curves obtained from seven portions of the melt of the two metals with different compositions.

<u>BACKGROUND</u> [1,2]

It is possible to depict equilibrium conditions of a binary system by means of a phase diagram. This diagram will show at what temperature solid and liquid phases are present for a given composition, providing the pressure of the system remains constant.

The simplest type of phase diagram is generated from a binary system where the substances mix in all proportions in the liquid state (total liquid-liquid intersolubility), and do not form compounds in the solid state (negligible solid-solid intersolubility). Such a diagram is depicted in Figure 2a (page 217 in text). From such a diagram the eutectic point of the two component systems can be calculated. The eutectic point corresponds to the lowest possible melting point for a two-component system. A eutectic mixture is the alloy with a composition corresponding to the eutectic point. As can be seen from the diagram, during cooling, a mixture of two components will not be totally solidified until this temperature is attained.

The data necessary for the construction of a phase diagram is obtained from a series of cooling curves of the two components in various composition ratios. Cooling curves have the shapes shown in Figure 2b (page 217 in text). After the component has been heated above its melting point and then allowed to cool, the temperature of the melt drops gradually until the melting point is reached. It will remain flat as long as the solid-liquid equilibrium is attained. The temperature corresponding to this plateau is the melting point of the system. A cooling curve of a composition   ratio other than the eutectic mixture (Figure 2b III, page 217 in text) may appear as depicted in Figure 2b I and II (page 217 in text). At the point in the cooling curve where the slope decreases (at T_A) the solid, whose side of the eutectic point the composition ratio

is on, will separate out. This change in slope is due to the release of latent heat of fusion during the solidification of the component. The decline in the slope will continue until flatness occurs, indicating the formation of the eutectic.

The cooling curves are obtained from using an analog-to-digital (a/d) converter in conjunction with an Iron-Constantan (Type J) thermocouple. A thermocouple [3,4] will record temperature in terms of mV due to the observation that, when a circuit is formed between two dissimilar metals with one junction maintained at a higher temperature than the other, a potential difference is developed. Thermocouples are arranged so that the measuring junction can easily be introduced to the source of temperature to be observed and the reference junction is maintained at ROOM TEMPERATURE.

EXPERIMENTAL

Materials: Iron-Constantan thermocouple, computer with a/d converter, stand for crucibles, clamp to support thermocouple, stirring rods for crucibles, and seven crucibles with various composition ratios. The seven crucibles have the following composition:

Crucible Number	% Bismuth	% Cadmium
1	0	100
2	20	80
3	40	60
4	60	40
5	80	20
6	90	10
7	100	0

PROCEDURE

The temperature is measured by means of a thermocouple, where the thermocouple temperature (that is converted automatically into °C) are read directly as a function of time using a digital-to-analog converter. This is run from a program called "EUTECTIC". This will record the thermocouple voltage as a function of time at 2 s intervals (this can be adjusted from 0.5 to 5 s) and then stored as an ASCII table. In order to obtain a cooling curve, after the experiment is complete, these numbers can be imported into a spreadsheet program (i.e. Microsoft Excel).

Note that each of the seven crucibles is fitted with its own argon bonnet and thermocouple, which should not be moved. In going from one crucible to the next, it is only necessary to transfer the argon gas line, and switch the plugs at the reference junction of the thermocouple.

To obtain a cooling curve, start the data collection program. Heat the crucible IN THE HOOD only until the temperature readout is nearing a maximum (from 330 to 350 °C). Be sure the thermocouple hot junction is in the melt. To minimize formation of unwanted oxides, do not heat too strongly and DO NOT sir the melt! When a homogeneous melt is obtained, start the recording program. Remove the flame. Turn off the argon flow. When the voltage drops below 100EC, stop the program. Obtain at least three cooling curves for each of the seven crucibles.

ANALYSIS OF RESULTS

From the obtained cooling curves, determine the eutectic and the point where solid first began to separate out. Then make a plot of temperature vs composition of the points where solid first began to separate out. From this plot, determine experimentally the eutectic point and eutectic mixture composition.

REFERENCES

1.   Hugh S. Taylor, *A Treatise on Physical Chemistry,* (Van Nostrand, New York, 1931), Vol. I, 539.
2.   E. B. Millard, *Physical Chemistry for Colleges,* (McGraw-Hill, New York, 1921), 283.
3.   Hugh W. Salzburg, *Laboratory Course in Physical Chemistry* (Academic Pres, New York, 1966), 51.
4.   William Oelke, *Laboratory Physical Chemistry*, (Van Nostrand-Reinhold, New York,

1969), 153.

CHEMISTRY 563

Physical Chemistry Laboratory

MR

Acid Dissociation Constant of Methyl Red

This laboratory was adapted from Experiment 17 in Daniels [1] and the article by Tobey [2] that should be consulted for additional details.

THEORY

Methyl red is a zwitterion in aqueous solution. The protonated form of methyl red (HMR) exists in acid solution and is red. The ionized form (MR-) is yellow and may be derived from HMR by addition of base. These two forms absorb light in different regions of the electromagnetic spectrum. The equilibrium constant for the reaction is

$$HMR \equiv H^+ + MR^- \qquad (1)$$

$$K_c = \frac{[H^+][MR^-]}{[HMR]} \qquad (2)$$

A convenient form of this equation is

$$pK_c = pH - \log \frac{[MR^-]}{[MHR]} \qquad (3)$$

Thus, the ionization constant may be calculated from measurements of the ratio [MR-]/[HMR] at known pH values. Since both forms of methyl red absorb strongly in the visible range, the ratio [MR-]/[HMR] may be determined spectrophotometrically. The absorption spectra of methyl red in both acid and basic solution are determined, and two wavelengths are selected to analyzing mixtures of the two forms. These wavelengths (8_1 and 8_2) are chosen so that at one the acidic form has a large absorbancy index compared to the basic form, and at the other the situation is reversed. The absorbancy indices of HMR and MR- are determined at both of these wavelengths, using several concentrations to determine whether Beer's law is obeyed.

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The composite mixture of HMR and MR- may be calculated from the absorbances A_1 and A_2 at the wavelengths 8_1 and 8_2 using, at unit cell thickness

$$A_1 = \alpha_{1,HMR}[HMR] + \alpha_{1,MR^-}[MR^-] \qquad (4)$$

$$A2 = \alpha_{2,HMR}[HMR] + \alpha_{2,MR^-}[MR^-] \qquad (5)$$

PROCEDURE

Use the procedure described in Tobey [2] (on reserve in the library).

CALCULATIONS

Plots are prepared of absorbance *versus* wavelength and absorbance *versus* concentration of dye in acidic and basis solutions at 8_1 and 8_2 . The values of the various absorbancy indices are calculated.

The concentrations of the acidic and basic forms of the dye in the various buffer solutions are calculated using Eqs (4) and (5).

Equation (3) is used to calculate the pK value for the dye. As a means of testing and averaging the data log ([MR$^-$]/[HMR]) may be plotted *versus* pH. An average value from the literature [3] is 5.05 ± 0.05 for the 25 to 30EC temperature range.

REFERENCES

1.   F. Daniels, *Experimental Physical Chemistry,* (Seventh Edition, McGraw-Hill, New York, 1970)
2.   S. W. Tobey, *J. Chem. Educ.,* **35,** 514 (1958).
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CHEMISTRY 563

Physical Chemistry Laboratory

DSC

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is divided into two areas: heat-flux and power-compensated. For this experiment, we will be interested in the area of heat-flux differential scanning calorimetry only. The difference between these two experimental methods is in the way the sample and reference are heated and therefore how)T, the difference in temperature, is calculated. In heat-flux DSC, both a sample and a reference material are subjected to the same controlled flow of heat. In power compensation DSC, the sample and reference are isolated from each other and are heated separately. See Figure 1. The reference material in both applications must possess three qualities [2]. First, the reference material should not undergo thermal events, (like melting or a phase transition), over the temperature range of heating in the experiment. Second, it should not react with the sample holder. Third, both the thermal conductivity and the heat capacity of the reference should be similar to those of the sample. For our experiment, the reference will be an empty aluminum crucible. Because aluminum has a melting point of 660.45EC, it is out of the heating range of this experiment and will work nicely for our purposes.

A characteristic heating curve on a DSC will most likely be a curve with several peaks that correspond to exothermic or endothermic events within the sample crucible. There are two ways that these curves can be oriented so that the data obtained may be analyzed. That is, the curve may be oriented so that an exothermic reaction is positive and endothermic negative-on the graph output or oppositely, an exothermic reaction may be negative and an endothermic reaction may be positive. Respectively, these are the DIN (Deutsche Industrie Norm) and ICTA (International Confederation of Thermal Analysis) methods of curve presentation. The machine in this lab is capable of either of these modes but it is probably easiest to use the ICTA method to keep in line with the idea that a positive enthalpy describes a system to which heat is being added while a negative enthalpy implies that the system is losing heat.

The theory of the heat-flux DSC is provided by Goose van der Platts [1]:

The heat flow to the sample (s), given by)Q/)t and expressed in mW, originates from the cell surface (c) and the reference (r). Therefore, the following equation holds:

$$Q_s = Q_{cs} + Q_{rs} = K_{cs}(T_c - T_s) + K_{rs}(T_r - T_s) \tag{6}$$

where K_{cs} is the heat transfer coefficient between c and s, K_{rs} the heat transfer coefficients between r and s, T_c the temperature of the furnace, T_s the temperature of the sample, T_r the temperature of the reference, Q =)Q/)t, and)t the unit of time. Note that the heat transfer coefficient K is equal to $1/R_{th}$ with R_{th} being the thermal resistance. All equations are approximations, but give clear insight as to the principle of measurement.

The heat flow is used for heating the sample. Taking the heat of reaction or transition into account gives:

$$Q_s = C_s\left(\frac{dT_s}{dt}\right) + q \tag{7}$$

where C_s is the heat capacity of the sample and the sample crucible and q is the heat of reaction (or transition). Combining equations (6) and (7) yields:

$$Q_s = C_s\left(\frac{dT_s}{dt}\right) + q = K_{cr}(T_c - T_s) + K_{rs}(T_r - T_s) \tag{8}$$

A similar equation can be derived for the heat flow to the reference, Q_r

$$Q_r = C_r\left(\frac{dT_r}{dt}\right) = K_{cr}(T_c - T_r) + K_{rs}(T_s - T_r) \tag{9}$$

The heat of reaction, q, is not taken into account because the reference is inert. The approximation is made that:

$$K_{cs} = K_{cr} = K' \tag{10}$$

Combining equations (8) and (9), after simplification, yields:

$$C_s\left(\frac{dT_s}{dt}\right) - C_r\left(\frac{dT_r}{dt}\right) + q = (K' + 2K_{rs})(T_r - T_s) \tag{11}$$

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Using $T_s=T_r-(T_s-T_r)$ and $K'+2K_{rs}=K$ it follows that:

$$(C_s - C_r)\left(\frac{dT_r}{dt}\right) - C_s\left(\frac{d(T_r - T_s)}{dt}\right) + q = K(T_r - T_s)$$

(12)

or that:

$$(T_r - T_s) = \Delta T = \left(\frac{C_s - C_r}{K}\right)\frac{dT_r}{dt} - \left(\frac{C_s}{K}\right)\frac{d\Delta T}{dt} + \frac{q}{K}$$

(13)

The term $((C_s - C_r)/K)(dT_r/dt)$ originates from the difference in heat capacities of the reference and sample and gives rise to a shift in the baseline when a measurement is started. The term (d)T/dt) is the slope of the DSC curve. This is not equal to zero during a transition. The term (C_s/K) is the time constant ϑ. The term q/K is the resultant heat flow due to a reaction or transition. In the case of a complete reaction, q is zero and the decay to the baseline follows:

$$(\Delta T)_t = (\Delta T)_{max,t=0}(e^{-t/\tau})$$

(14)

Figure 3 shows a graphic representation of equations (13) and (14).

METTLER DSC12E DIFFERENTIAL SCANNING CALORIMETER

This list of directions is a general set for a wide range of experiments. These directions are compiled mainly to describe the workings of the computer interface and the operations associated with calculations of enthalpy changes and temperatures.

Experiments that can be performed with the DSC fall into one of two areas. The experiments will either seek to determine a specific melting temperature, or an enthalpy change. Some important parameters of the DSC in this lab should be attended to in order to insure that the experiment you choose is one that yields good data.

Heating range: -40EC to 400EC

Accuracy: ± 0.4EC

Heating rate: 1 - 20EC/minute

Crucible: Aluminum, 40 µl effective volume

EQUIPMENT

Computer, monitor, Mettler differential scanning calorimeter, curved tweezers, spatula, sample, analytical balance, welding press, aluminum crucibles, thumbtack, and hydrates.

PROCEDURE

1   Turn computer and monitor on.

2   Go to sink next to the DSC and turn water on so that there is a steady stream coming out of the hose. The DSC is hooked up to the left nozzle. This flow must be checked periodically due to air bubbles in the water line.

3.   Run the program "DSC"

4.   Turn on the Mettler DSC.

SAMPLE PREPARATION

These preparations are best done at the balance to minimize the chance that your sample will spill.

1.   Weigh out between 5 and 10 milligrams of your sample directly into the bottom of an aluminum crucible. The difference between the bottom and the top of the crucible is easy to see. The bottom has a deeper well than the top. The top of the crucible is rounded whereas the bottom is not so smooth. This is a very important step that will insure that the correct heating ratio is achieved for the DSC. If the sample is too large, the peak sizes and temperature gradients will be too large and the resolution of the graph will suffer. Each experiment may recommend a sample weight and this should be strictly adhered to.

2.   Find a lid for the crucible bottom and with the curved tweezers, place this lid on top of the crucible bottom.

3.   Again, with the curved tweezers, place the entire crucible flat on the welding press platform. Make sure that the lid is centered on the bottom half of the crucible.

4.   Once situated on the platform, turn the handle of the press clockwise or counterclockwise a full 360E. This will insure that the crucible is sealed.

5.   Using a stickpin or other sharp pointed object, poke a small hole in the lid of the crucible if needed. Before doing this however, be sure that the experiment you are doing specifies whether or not the sample should be exposed to the atmosphere. If there is supposed to be a hole in the crucible lid, the diameter of a thumbtack is sufficient for the size hole that is required.

6.   Using the tweezers again, remove both the outer and inner lids of the DSC. Throughout the experiment, nothing other that tweezers should be used to remove the lids. **They can be very hot**! When taking crucibles and lids out of the furnace cell, set these items on the metal portion on top of the DSC until they have cooled.

7.   Using the tweezers again, place your sample (lid up) on the left hand platform in the DSC. There should already be a crucible in the DSC on the right hand side platform. This is the reference and should not be tampered with.

8.   Replace both the inner and outer lids making sure that they are in the correct order and that both are seated properly.

EXPERIMENT EXECUTION AND DATA COLLECTION

1. First you need to enter the experimental parameters on the Mettler DSC.
2. After the Mettler DSC has been switched on it will show the start temperature in the left-hand box. > and < mean that the measurement parameter is active, namely that it is ready for entry.

3. Enter the start temperature: 25 °C. As soon as you enter 3, > and < change to black rectangles. The numbers move across the input field. If you have made an error, enter the complete value again. If you enter an inadmissible value, the box displays ????. Once you have entered the correct value, press **ENTER**.

4. Input the ending temperature. The DSC in this lab has a maximum temperature of 400EC so the experiment you choose is somewhat constrained by this.   Remember, the maximum temperature must be chosen such that all thermal activity of interest is exhausted for your sample over the chosen temperature range. This will have ocured by 225 °C. Thus, enter the end temperature: 225 °C, in a similar way. Then press **ENTER**.

5. Input the desired heating rate. A general rule of thumb for choosing heating rates is that for the determination of the purity of a sample, a slower heating rate is desirable. For the determination of any transitions in a sample, a higher rate of heating may be more desirable. This is a parameter that has a lot of freedom and it is recommended that it be varied several times for each sample so that an optimum resolution is achieved. A suitable value of the heating rate is 5 °C/min. Input this value and again press **ENTER**..

6. Since an isothermal part of the experiment is not needed, enter 0, and press **ENTER**.

7. You then need to enter the measurement range. 200 µV should be sufficient but may need to be adjusted during subsequent runs. Press **ENTER**.

8. The values that you have selected are then displayed. If they are **not** correct, press **ENTER** and the system will go back to step 3.

9. Measurement procedure: You are now ready to start an experiment. The data will be collected by plotting the output voltage versus time into an Excel spreadsheet. The data collection will **not** start automatically, and data collection must be initiated manually.

10. When all measurement parameters are correct, press the **run**/hold key.

11. The status line displays the message "Scanning to T start". Here the furnace is cooling from the standby temperature (50 °C) to the start temperature.

12. The status line then displays "Settling". After the furnace reaches the start temperature, the system stabilizes for about 10 s.

9.   The status line then displays "Heating" and the **up** indicator lights up and the **furnace control** indicator is green. **Start** the data collection program. You can follow the sample

temperature on the **temperature** display.

10.   The status line then displays "Ready" and you should then **stop** the data collection.

11.   The status line then displays "Standby" and the instrument is cooling to the start temperature.

VIEWING THE HEATING CURVE

1.   Move the arrow to "view" and click once.

2.   Move arrow to "running" and click once. Note, the graph may not appear immediately because the DSC may be settling. Once the DSC starts heating, the curve should appear.

3.   The graph may be expanded by clicking once on the graph border and "dragging" the graph to a larger configuration.

4.   Once the measurement is finished, click once on the gray box marked "OK".

GRAPH EVALUATION

1.   The data collection program will store the results in an Excel file. Save this file in the folder named "P Chem Lab" with your name in the file name for future reference.

2.   The Y column of the spreadsheet is the output voltage which you need to scale to the maximum value you entered in section 7 above.

3.   This is converted into mW (milliWatts) by using the conversion factor of 3.4 µV/mW.

4.   The X column is the time in seconds. This is converted to temperature using the initial temperature (a t = 0) and the heating rate or final temperature entered above.

5.   Initially plot your data and Power on the Y axis versus temperature along the X axis in Excel.   The initial portion of the graph should be at 0 mW. You should then offset the data to make sure that this is the case.

6.   Once the curve has been properly calibrated in Excel, you can transfer it to Origin (by copying and pasting), and plot the graph. You can also add axis labels for later plotting. You can evaluate the peak temperatures by using the cursor (+) and placing it at the minima.

To calculate the area under the curve (Enthalpy Change) using Origin.

1. Using Origin, define and baseline and integrate under the peak to give you an energy in mJ (milliJoules). Consult with the TA if you do not know how to use Origin

2. Obtain a hard copy by printing the graph.

QUESTIONS:

1. Calculate the corresponding enthalpy, at standard temperature, for each peak using the CRC Handbook of Chemistry and Physics. How close do these literature values come to the value calculated by the computer?

2. Explain any differences.

REFERENCES

1. G. van der Platts, *The Practice of Thermal Analysis.*

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CHEMISTRY 563

Physical Chemistry Laboratory

STM

Scanning Tunneling Microscopy of Silicon and Graphite

OBJECTIVE

To measure the surface structure and tunneling potential of graphite and silicon surfaces.

BACKGROUND

The scanning tunneling microscope relies on the observation that, in quantum mechanics, a particle, in this case an electron, with an energy E can exist in a region of potential energy V when the potential energy is greater than the total energy. In classical mechanics, this would be energetically impossible, while in quantum mechanics it can occur. The Schrődinger equation for a particle mass m in a region where the potential is V is given by:

$$-\frac{\hbar^2}{8\pi^2 m}\frac{d^2\Psi}{dx^2} + V\Psi = E\Psi \qquad (1)$$

Taking a trial solution for this equation as $\Psi = Ae^{\alpha x}$, substituting into equation (1) yields a solution when $\alpha^2 = \frac{8\pi^2 m}{\hbar^2}(V - E)$. In the classically allowed region, when $E>V$, then α is an imaginary number given by: $\alpha = \pm i\sqrt{\frac{8\pi^2 m(E - V)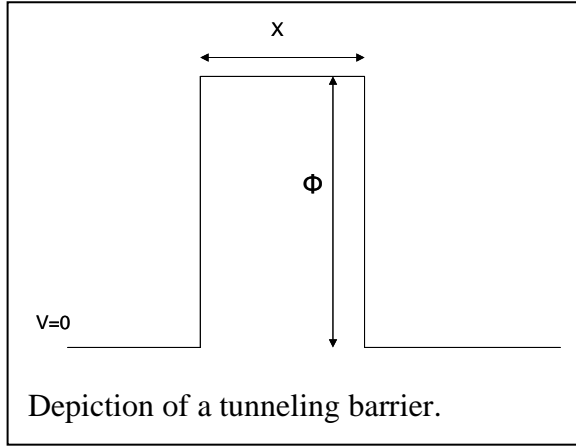}{\hbar^2}}$ so that the wavefunction is represented by a sine or cosine wave. However, in the classically forbidden region, when $E<V$, the value of α given by: $\alpha = \pm\sqrt{\frac{8\pi^2 m(V - E)}{\hbar^2}}$. The positive solution corresponds to an exponentially growing function, which will tend to infinity with increasing values of x and is therefore not physically realistic. The negative solution corresponds to an exponentially decaying wavefunction given by:

$$\Psi \sim \exp(-\sqrt{\frac{8\pi^2 m(V-E)}{\hbar^2}}x) \qquad (2).$$

This demonstrates that the particle has some probability of existing within the classically forbidden region and also shows that that the smaller the mass of the particle m, the further that it can penetrate the forbidden region. If we now imagine an electron of energy E incident on a narrow potential barrier of height Φ and width x shown in the figure, the electron can exist inside this region with a wavefunction given by equation (2). If the barrier is sufficiently narrow, the wavefunction at the other side of the barrier will be non zero, and the electron will be able to tunnel through the barrier. A reasonable

Depiction of a tunneling barrier.

approximation for the current I passing through a barrier of width x and height Φ is given by:

$$I = C\exp(-A\sqrt{\Phi}x) \qquad (3)$$

where the constant $A = 1.025\sqrt{eV}$ / Å.

If a sharp metallic tip is moved very close to a sample, at a distance x away from it, a tunneling current will pass depending on the distance x and the height of the barrier Φ. However, the height of the barrier will depend on the electron density in the sample beneath the tip. Since the wavefunction of the sample will depend on position the tunneling current depends on the lateral position of the (sharp) tip. Thus, scanning the tip back and forth across the sample will produce an image of the sample below and, if the tip is sufficiently sharp, will be capable of imaging the atoms in the sample. Obtaining a sufficiently sharp tip is not trivial, but it is not as difficult as might be thought because of the exponential decay in current with distance shown in equation (3). Thus, if there is one atom that protrudes slightly further than the rest at the end of the tip, because of the exponential decay (equation (3)), the majority of the tunneling will occur through this atom.

Although the principles of the STM are straightforward, the implementation is not. It first relies on being able to precisely manipulate the tip. This is accomplished using piezoelectric

materials that have the property of changing their dimensions when a voltage is applied [1]. This effect is generally very small and piezoelectric coefficients are typically nanometers/Volt.

Typical experimental arrangement for the scanning tunneling microscope.
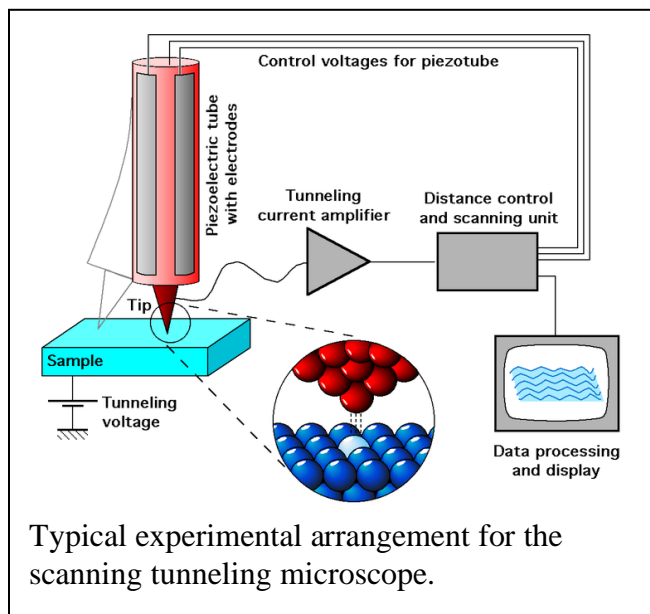
However, these are exactly the values required to scan with atomic resolution. A typical experimental arrangement for a scanning tunneling microscope (STM) is shown in the figure. The tip can be moved in the x, y and z directions by means of piezo scanners, where the distance is controlled by applying a voltage to the piezo elements. An image of the sample is collected by bringing the tip, to which some potential V is applied, slowly towards the surface. When the tip is sufficiently close to the surface, a tunneling current can be measured. The experiment is generally carried out by fixing the applied voltage and tunneling current, and moving the tip in the vertical (z) direction to maintain a constant current. As the tip moves over atoms in the surface, it must move up and down to maintain this constant current and this is done by applying a voltage of the z piezo. The tip is then "rastered " over the surface, that is, moved back and forth at slightly different positions in the same way a television image is made up by rastering an electron beam over the screen.

EXPERIMENTAL

In order to obtain a sufficiently clean surface to enable atomic-resolution images to be collected, the experiments must be carried out in vacuum. Using kinetic theory of gases, and assuming that every molecule that collides with a surface will adsorb on that surface, calculate the number of molecules will adsorb per square centimeter at pressures of 10^{-6}, 10^{-7}, 10^{-8}, 10^{-9} and 10^{-10} Torr. A hexagonal graphite surface has carbon-carbon bonds lengths intermediate between a double and single bond – measuring this value will be part of this experiment. Calculate the number of carbon atoms per square centimeter on the surface. How long will it

take for the surface to be completely covered at the above pressures? What is the best pressure for carrying out these experiments?

The experiments will be carried out in the ultrahigh vacuum STM laboratory in the basement and will be carried out under the supervision of the TA. The goals of the experiment are to:

1) Obtain atomic-resolution images of a graphite surface.

2) Measure the tunneling current versus distance from the surface for graphite.

3) Obtain atomic-resolution images of a silicon surface.

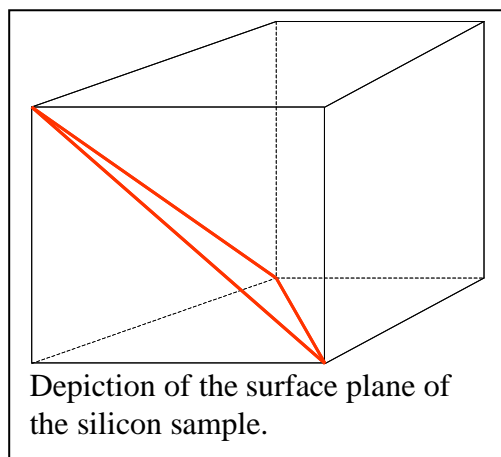4) Measure the tunneling current versus distance for silicon.

With the help of the TA:

1. Move the graphite sample, which has already been mounted onto a sample holder, onto the experimental stage.

2. Bring the STM head down onto the sample holder.

3. Using the UHV STM software, bring the tip into contact with the surface.

4. Set the tip voltage and the tunneling current to the values given to you by the TA. These have been selected to yield the best images.

5. Collect the STM image of graphite, with the system in "feedback".

6. With the feedback "off", use the software to measure a current versus distance curve.

7. Repeat these experiments for the silicon sample.   In this case, you will have to heat the sample to remove any contaminants that have adsorbed on the surface to obtain a clean silicon sample. Resistively heat the Si(111) crystal overnight at 723 K. The temperature of the sample can be measured with an IR thermometer (also known as pyrometer). This step is performed in order to obtain a clean surface by thermally degassing the sample. Then heat the sample to 1200 K for a few seconds being very careful not to exceed a pressure of 10^{-9} Torr during this step. Place the scanner head on the sample holder and approach the tip to the surface. Constant current imaging mode will be used. Set the bias voltage and set point current and begin scanning.

8.   Store your images and curves on a memory stick for "off-line" analysis.

ANALYSIS OF RESULTS

Print out the images of the graphite surface. Measure the angle between the atoms and the lattice spacing of graphite. How do these values compare with when you would expect for graphite based on carbon-carbon bond lengths in organic compounds? Using the current versus distance results for graphite, test the validity of equation (3) and measure a value for the tunneling barrier height for graphite.

Depiction of the surface plane of the silicon sample.

Similarly, print out your images of the silicon surface. Silicon has the same structure as diamond, and is thus a cubic unit cell and the lattice parameters and structure can be found at:

http://www.webelements.com/silicon/crystal_structure.html. The silicon sample that was used in these experiments has been cut so that the exposed surface is that shown as red lines in the figure. Draw a picture of the surface, assuming that the surface atoms remain in the same position as they are in bulk silicon. Does the STM image of the surface appear the same as in you drawing? Also, using the current versus distance results for silicon, test the validity of equation (3) and measure a value for the tunneling barrier height for silicon.

REFERENCES

G. Binnig, A. Rohrer, C. Berber, E. Weibel, Appl. Phys. Lett., 40, 178 (1981)

Chemistry 563 Student Information

       Fulfillment of the following prerequisites with a minimum grade of **'C'** will be strictly enforced in all cases before a student may attend Chemistry 563. If you do not meet these prerequisites, or if they cannot be completely verified in your case, you will not be allowed in the course. Students who completed prerequisites at universities other than UWM are asked to furnish transcripts. **NOTE:** If you are currently enrolled in Chemistry 563 but will not be allowed to attend due to inadequate prerequisites it is **YOUR** responsibility to file a drop form with the registrar to avoid a final grade of **'F'**.

I.   Prerequisites (Chemistry Majors)

      Chem _____ 221 or 223 _____ (Analytical)

      Chem 561 (First semester P. Chem.)

II   Additional Information

      Materials Students

      Physics 208 (2nd sem, Physics)

      Maths 233 (3rd sem, Calculus)

I certify that the above information is complete and accurate.

Name (print): _____

Signed:_____ Date:_____

Laboratories Taken

Experiment Number	Date Started	Date Finished	Interview Taken
1._____	_____	_____	_____
2._____	_____	_____	_____
3._____	_____	_____	_____
4._____	_____	_____	_____
5._____	_____	_____	_____
6._____	_____	_____	_____
7._____	_____	_____	_____
8._____	_____	_____	_____