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Chem 332L

CHEM 332L PHYSICAL CHEMICAL MEASUREMENTS
Spring 2016

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Office Hours: Thursday 10-11 am or on appointment

Course Goal: The laboratory course complements the Physical Chemistry lecture series. The lab introduces key skills in instrumentation, signal detection, data collection and analysis as well as illustrating core physical chemistry concepts. In particular, the lab serves to support objectives 4 and 5 (Application and Analysis, Evaluation and Judgment) from learning outcomes defined for chemistry department majors. http://chem.usc.edu/undergraduate/learning_outcomes.html

Lectures: Lecture and discussion will be on Tuesday at 9:00a.m. Topics covered will include data and error analysis, report writing, electrical, optical, and vacuum systems, computer use, statistical tests of data, and specific instruments. The individual experiments will not always be discussed in detail, though specific methods involved in them will be.

Text: You will be given a laboratory manual at the first class meeting: the lab manual contains detailed material on each of the experiments available in the 332L laboratory as well as reference lists to provide additional information related to the experimental works.

It will be useful for you to refer to Experiments in Physical Chemistry by Shoemaker, Garland and Nibler (or a similar text). A few copies of Shoemaker are available in the lab.

Course Outline: The course consists of lectures, discussions, laboratory work and presentations. The lectures will cover both theoretical material and techniques related to the laboratory experiments based on the first of the texts given to you.

<table>
<thead>
<tr>
<th>Lab reports</th>
<th>70%</th>
</tr>
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<tbody>
<tr>
<td>Presentations</td>
<td>30%</td>
</tr>
</tbody>
</table>

Each student is to complete six (6) of the experiments listed below, two experiments from each of the groups I, II and III. There will also be a preliminary experiment on signal measurements with an oscilloscope. Due dates for experimental reports will be posted.
During the lectures, students will give an oral presentation (~20 min.) about the experiment which he/she will perform (or currently performing). Any appropriate professional type of presentation is acceptable; blackboard presentation, overhead projection, and PowerPoint have been used in the past.

Laboratory: Though the laboratory is formally scheduled in three segments, it will be open without breaks during the day. You will plan your work so you may use this time to your advantage. The laboratory will close promptly at 6:00 p.m., and may close earlier if no students are working; you must arrange your work with this in mind, and must keep the instructor informed if you leave the laboratory and plan to come back later in the day.
Experiment List:

I. Spectroscopic Experiments:
   1. Electronic spectrum/dissociation energy of Iodine
   2. Excited state properties of 2-naphthol
   3. Spectrofluorimetry and fluorescence quenching
   4. Infrared spectrum of HCl/DCI

II. Solution chemistry:
   5. Conductance of electrolytes (KCl, HCl, KAc, HAc)
   6. Magnetic susceptibility of transition metal ions
   7. EMF (Pt/Hydrogen//AgCl/Ag)

III. Chemical Kinetics:
   8. Pulsed NMR kinetics
   9. Monte Carlo Simulation of a Lennard-Jones Fluid
   10. Pulsed laser fluorescence and quenching
   11. Physical adsorption of gases

Computers: Computers are available in the lab for data processing and for direct data acquisition on a few experiments. Computer use is a part of the course. It will be assumed that students are able to use a spreadsheet program for data processing. OriginLab, a particularly useful program for data processing and plotting, is installed on each of the computers and will be briefly introduced. Certain programs will be available for use on students’ computers.

Notebooks: Each student must have a bound duplicate-style laboratory notebook. All raw data (balance readings, volumes, meter readings, control settings, etc.) must be entered directly in ink in the notebook. It should be possible to find every bit of information needed to obtain final results from the entries in the notebook; nothing should be ‘from memory’. The notebook should have duplicate pages which are to be turned in to the TA at the end of each laboratory period.

Reports: Your lab report should be submitted as a Word document or PDF by email to Prof. Takahashi, susumuta@usc.edu.

Assignments & Information: All information including assignments as well as changes to the schedule will be announced via email. It is your responsibility to check frequently.

Academic Integrity: USC seeks to maintain an optimal learning environment. General principles of academic honesty include the concept of respect for the intellectual property of others, the expectation that individual work will be submitted unless otherwise allowed by an instructor, and the obligations both to protect one’s own academic work from misuse by others as well as to avoid using another’s work as one’s own. All students are expected to understand and abide by these principles. SCampus, the Student Guidebook, contains the Student Conduct Code in Section 11.00, while the recommended sanctions are located in Appendix A: http://www.usc.edu/scampus/. Students will be referred to the Office of Student Judicial Affairs and Community Standards for further review, should there be any suspicion of academic dishonesty. The review process can be found at: http://www.usc.edu/student-affairs/SJACS/.
**ABSORPTION SPECTRUM AND DISSOCIATION ENERGY OF IODINE**

**References:**

**Summary:**
The electronic spectrum of iodine vapor has played a central role in testing the consistency of quantum mechanics and explaining observed spectroscopic fine structure, and the results have been summarized in master fashion by Mulliken (2). Analysis of the low-resolution absorption spectrum has become a classic advanced undergraduate experiment, and a number of fine expositions are available in the literature (2-4). A useful review of the theory is to be found in McNaught's paper (1).

Earlier objectives (2) for student study were quite restricted, usually including only determination of the vibrational frequency and anharmonicity in the excited electronic state and the dissociation energy of the molecule. With the availability of computers now it is possible to perform a more sophisticated analysis and obtain more information about the iodine molecule and gain insight into a wider range of quantum mechanical concepts (4).

This experiment determines the molecular electronic and vibrational properties of iodine vapor, the dissociation energy of iodine in its ground and excited electronically states, and some information on the change in bond length of iodine upon electronic excitation.

**Equipment:**
Monochromator with associated light source, photomultiplier detector, power supplies, pre-amplifier, mercury lamp, digital storage oscilloscope, cell containing solid iodine with heating mantle.

**Experimental:**
There are two parts to the experiment: checking the wavelength accuracy of the monochromator and recording the absorption spectrum of iodine vapor. Before turning on the spectrometer and light source talk with a TA to make sure you understand the controls. The photomultiplier voltage should be kept in the 600-800 V range; the sensitivity control and slit width may be used for additional adjustment of sensitivity. Don't turn up the light source to get more light; with proper alignment of the optics there is plenty of light. Talk with someone about starting the spectrometer drive in the correct way to eliminate backlash in the gears!

(a) **Wavelength calibration:** Light from a Hg penlight is allowed to enter the slits of the monochromator to study the emission spectrum of Hg. The range from 490 to 630 nm is covered, since this is the region of interest for iodine. A number of lines appear, and short regions should be recorded covering single lines or small clusters of lines; run each region two or three times as
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a measure of reproducibility. Take particular care to synchronize the digital scope and the spectrometer (talk with a TA about this, since there are tricks to improve precision). DO NOT record the whole 490-630 nm range as you will wind up with a lot of useless blank space. Adjust the instrument sensitivity for each small region so the line(s) is of appropriate intensity. Use a slit width of about 30 μm and a chart speed of perhaps 50 A/min. Some of the lines are 'second order' lines, appearing at twice their true wavelengths, since the mercury spectrum contains intense lines in the UV. (Make sure you understand what this means!)

**Caution: the Hg penlight emits a great deal of UV light, and should not be looked at directly for more than an instant!**

Prepare a table of careful readings of the line positions against true line wavelengths (you should have seven points or so), with a column of differences (true - observed). The values of the differences are fitted to a polynomial in the observed wavelength; choose the order of the polynomial as appropriate. This polynomial then serves as a calibration function, with which observed wavelengths may be converted to true values. Care must be taken to insure that proper accuracy is obtained in measurement-taking and recording as well as during the curve-fitting.

(b) The absorption spectrum: Check the alignment of the optics to make sure a reasonable amount of light is getting through to the detector, and adjust the sensitivity for a reasonable signal at the wavelength of maximum intensity (near 530 nm). Some experimentation with slit width, scan speed and sensitivity are necessary (covering only a short region of the spectrum) to obtain optimum results on the shapes of features in the spectrum. The iodine (I₂) cell must be heated to obtain sufficient vapor pressure to yield reasonable absorption.

See the additional instructions "Preliminary Instructions, Iodine spectrum, using Large Spectrometer and Data Logger" for details on setup and running the spectrum. Record the spectrum in the range 620 to 490 nm.

In the spectrum, the absorption peaks are superimposed on a broad emission of the tungsten light source, and readings are to be taken of the peak absorption wavelengths. You will notice that the absorptions rise sharply on the low-wavelength side. (Why?) Correct the wavelengths, using the calibration equation obtained above, to get the true wavelengths. Use of Origin data processing software will help you obtain the positions of the peaks as a data file. Peak positions are then converted to wavelengths using your calibration function and knowledge of the digital recording settings.

**Analysis:**
(a) **Interpretation of the spectrum:** Absorption transitions are from the ground electronic state (X), vibrational level v"=0,1,2... to the excited state (B), vibrational level v'. The vibrational quantum number v' may take on quite large values (see the Theoretical section below). A small number of v" values are possible (roughly how many?), due to thermal population of the vibrational levels before absorption of light. Thus the first problem is the assignment of v",v' values to the absorption peaks.
For a series of absorptions originating on from a single value of \( v'' \), the peaks will come closer together with increasing \( v' \) because of vibrational anharmonicity (see Theoretical section). It is very useful to prepare a copy of the observed spectrum and mark it with the \( v'',v' \) assignments in the following way: a horizontal line is drawn for each value of \( v'' \), and vertical lines are drawn from it at the wavelength of each peak which originates in that value of \( v'' \). These vertical lines are labeled with the \( v' \) value. Assignment of the \( v'',v' \) values is quite difficult without other experiments, so to help get you started some assignments are provided in a table on page 9. The figure there also indicates what a bit of your spectrum should look like.

A very convenient presentation is called the Deslandres Table, which consists of an array of the wavenumbers of the observed peaks in columns labelled by \( v'' \) and rows labelled by \( v' \). The wavenumber of a peak is the reciprocal of the wavelength expressed in cm, and is directly related to the energy of the transition. For instance, the wavenumber of the band head at 571.6 nm (assigned as \( v',v''=18,1 \) in the table) is 17493 cm\(^{-1}\). The energy of the corresponding transition is the wavenumber multiplied by Planck's constant, \( h \), and by the velocity of light, \( c \) (\( E=hc\nu \)), in this case 3.477x10\(^{-12}\) ergs. This Deslandres table checks consistency of assignments, since all differences between two particular columns should be the same, as should all differences between two particular rows. (Ensure that understand why this is so before starting the experiment. This will tell you and others that you know what you’re doing.)

(b) Data treatment: Once the table of assignments is available, the pure electronic transition frequency (\( v''=v'=0 \)), the vibrational frequencies, and anharmonicities for the two electronic states should be obtained. This may be done graphically or better yet by fitting the data to a theoretical expression. (See reference 4 in particular.)

You will observe that the absorption peaks (\( v'' = 0 \)) come closer and closer together as one moves toward the blue end of the spectrum. At a certain point, the vibrational spacing goes to zero; this is the point where the upper level in the transition reaches the dissociation limit of the upper electronic state. If this energy (\( E^* \)) can be measured, it is possible to extract the dissociation energy of the iodine molecule (its bond energy). The traditional way to do this is by use of a Birge-Sponer plot of the separation of successive peaks (with the same \( v'' \)) versus \( v' \), extrapolating to zero separation. This yields a good value for iodine. An alternate is to use an analytical expression for the transition frequencies, with the \( v'',v' \) assignments, to calculate \( E^* \) from each observed absorption peak, thus giving an illustration of the probable error in the result from the scatter of the values of \( E^* \) obtained. Of course the analytical expression itself may be fitted by least squares on the computer (and this is the best way!).

Further details of the background of the data treatment are included in the theoretical section. McNaught (1) tells of the other information which can be obtained from the experimental data, in particular the change in internuclear distance between ground and excited electronic state; his paper is well worth reading for full information on the experiment.
Theoretical Background

Imagine two atoms, their energies determined by their electronic states, brought together from infinite separation. As they begin to interact, they will experience either attraction or repulsion. In the case of attraction, the energy of the system goes down; for repulsion, the energy goes up. When attraction occurs, the atoms eventually reach a minimum, stable energy before the energy begins to go up again. A bond is thus formed with a length equal to the distance apart of the atoms at the stable minimum energy. Starting with two atoms in particular electronic states, it is possible to form more than one bonding or non-bonding molecular state. For each of these states, the energy will go steadily up for non-bonding molecular states, and will go down and pass through a minimum for each bonding molecular state. The distance for which the energy has a minimum is called the equilibrium bond length. These bond lengths, as well as the shapes of the energy $E$ plotted versus the distance “r”, are generally different for different molecular electronic states.

The lowest molecular state is called the ground state, and given the symbol X; the next higher state is called A, the next B and so on (sometimes there are states a, b, etc. also). In addition, there is a nomenclature system used to describe the molecular states in terms of quantum numbers, similar to that used for atomic states. It's not necessary to be familiar with the nomenclature for the purposes of this experiment, but it is fully set forth in (6).

Figure 1. Shows potential energy curves which represent schematically the situation found in iodine. Notice that two molecular states (X and A) are shown relating to iodine atoms in their ground electronic states, while a further (B) state relates to one ground-state plus one excited-state atom. Remember that these curves show the potential energy of two atoms in the molecular state as a function of their separation. The spectra observed in this experiment involve transitions between the vibrational levels of electronic states X and B.

Vibrational Energy:
A molecular oscillator is quantized; vibrational energy levels can only be found at specific energies. The vibrational energies are usually expressed as *term values*, which are the energies divided by $\hbar c$ ($\hbar c=$Planck's constant times the velocity of light), and thus are in wavenumber units. They can be written as

$$G(v) = \omega_v(v+1/2) - \omega_v\omega_n(v+1/2)^2$$

where $\omega_v$ is the frequency for infinitesimal amplitudes of vibration and $\omega_v\omega_n$ is an anharmonicity constant. $v$ is the vibrational quantum number. If the potential energy curve were accurately represented by a quadratic function (as for a harmonic oscillator), the first term of Eq. 1 alone would be an exact result. The subscript “e” refers to the electronic state of the molecule, and the constants in Eq. 1 may have different values for different electronic states.
Equation 1 shows that the vibrational states are not equidistant (as they would be for a harmonic oscillator); some vibrational energy levels are shown in Figure 1 (only the first few in each electronic state). As one approaches the energy corresponding to the separated atoms, the vibrational levels come closer together, eventually reaching almost zero separation. In fact, only a finite number of levels can exist in a given molecular electronic state. For the X and B states, respectively, $\omega_e$ is about 210 and 130 cm$^{-1}$.

In addition to vibrational motion, the molecule can also rotate. The energy levels for rotation are also quantized, with quantum number $J$. Except for a rather small effect on the shapes of the absorption peaks, rotational motion does not enter into this experiment. The rotational energy levels are so close together that we can't separate them, so we will not consider them further here.

**Spectroscopic Transitions:**

We call the term values for electronic energy at the equilibrium bond distance (the energies at the bottoms of the potential wells) $T_e$. Further, it is customary to indicate the upper energy level in a transition by putting single primes on its energy parameters and quantum numbers, while the lower level gets double primes. Thus the vibronic (vibrational plus electronic) energy of a particular upper state and lower state would be given by (remember, everything is in cm$^{-1}$ units):

\[
E' = T_e' + \omega_e'(v'+1/2) - \omega_e'x_e'(v'+1/2)^2 \\
E'' = T_e'' + \omega_e''(v''+1/2) - \omega_e''x_e''(v''+1/2)^2
\]

and the spectroscopic frequency (in cm$^{-1}$) would be

\[
\nu = E' - E'' = \nu_e + \omega_e'(v'+1/2) - \omega_e'x_e'(v'+1/2)^2 \\
- \omega_e''(v''+1/2) + \omega_e''x_e''(v''+1/2)^2
\]

where $\nu_e$ is $T' - T''$. One such transition is shown in Figure 1, in going from $v'' = 1$ of the X state to $v' = 2$ of the B state.

From Eq. 3 it would appear that a specific $(v'',v')$ vibronic transition should appear in the spectrum as a sharp line at the frequency calculated. In fact, the rotational transitions among the various J levels which are populated at finite temperatures broaden the transitions. In the case of iodine, this has the effect of making each $v'',v'$ transition appear as a rough triangular peak, steeper on the blue side than on the red. If one could resolve the rotational fine structure, more accurate wavelengths could be obtained, but with our instrumentation it is probably best to take the peak absorption to give the vibronic transition wavelength.

**Data Treatment:**
The classical method for determining the vibrational constants $\omega_e$ and $\omega_e x_e$ from data such as these on iodine is to use a Birge-Sponer Plot (6), of $\Delta G$ versus $v'$, where $\Delta G$ is the spacing of successive absorption peaks originating on a specific state $v''$ (usually $v''=0$). From Eq. 3 this plot should be a straight line, eventually reaching $\Delta G = 0$ at some high value of $v'$. Regardless of
whether the theory leading to Eq. 3 is exact, and thus whether this plot is a straight line, it's clear that the area under the plot, beginning at $v''$, is just the sum of the $\Delta G$ values, and thus is the energy $E^*$ of transition from $v''$ to the dissociation limit of the upper (B) state.

Find $E^*$. If the plot is a straight line, find $\omega_e'$ and $\omega_e'x_e'$. Or try to find the limiting slope (at low $v'$) to get $\omega_e'x_e'$. Another good method for finding these parameters is to obtain from the theory in (4) an equation for the $\Delta G$ values, or from Eq. 3 an equation for the wavenumbers of transitions themselves, and then to fit all the data to a quadratic or cubic equation to get the parameters. You can also find for the ground (X) state $\omega_e''$ and $\omega_e''x_e''$. All the parameters you find should be summarized in a single table.

**Dissociation Energy:**
The value of $E^*$ obtained above for lines originating on the $v''=0$ level may be used to obtain the dissociation energy for iodine. This *dissociation energy* is given by

$$D_0'' = E^*(v''=0) - E(I^*) \quad (4)$$

where $E(I^*)$ is the energy of excitation of the iodine atom. This is true because the B state of iodine dissociates to form one normal and one excited iodine atom, while $D''$ refers to two normal iodine atoms (see Figure 1). The energy $E(I_2^*)$ is known from atomic spectroscopy to be 7589 cm$^{-1}$, and it is indicated by a vertical line near the right hand side of Figure 1. Knowing the ground state (X) constants $\omega_e''$ and $\omega_e''x_e''$ one can also get the theoretical *pure electronic dissociation energy*, $D_e$, given by

$$D_e'' = D_0'' + \omega_e''/2 - \omega_e''x_e''/4 \quad (5)$$

The value of the excited state dissociation energies $D_0'$ and $D_e'$ can also be obtained of course.

**Summary of Data Treatment:**
(a) **Mercury Calibration:** Measure the wavelengths of the observed mercury lines from the chart. Prepare a table of observed and true wavelengths, and of corrections at each observed wavelength. Useful wavelengths of mercury spectrum lines include:

- Lines observed in 1$^{\text{st}}$ order: 4358.35 Å, 5460.72 Å, 5769.70 Å, 5790.66 Å
- Lines observed in 2$^{\text{nd}}$ order: 2536.52 Å, 2967.28 Å, 3125.65 Å

Find a correction formula for the observed wavelengths.

(b) **Corrected Iodine Wavelengths:** Measure as many absorption peaks as you can. Use your mercury calibration function to obtain corrected values. Convert wavelengths to wavenumbers. Prepare a Deslandres table and make assignments of as many peaks as you can to $v',v''$ values. Note that high $v'$ peaks are important for an accurate dissociation energy.

(c) **Dissociation Energy and Molecular Parameters:** Using the techniques best suited to your needs, including making a Birge-Sponer plot, determine $E^*(v''=0)$ and the dissociation energy of
iodine. Use either the Birge-Sponer method or a polynomial least-squares fit to obtain the vibrational parameters and anharmonicity parameters.

Figure 2. Segment of the spectrum of I₂. Absorption lines point down, i.e. to less light intensity transmitted through sample cell. The figure covers roughly 5650 to 5750 Å in wavelength, and includes the transitions indicated originating on levels \( v''=0 \) and \( v''=1 \).

Table 1. Some \( v'',v' \) assignments for iodine

<table>
<thead>
<tr>
<th>( v' )</th>
<th>( v'' )</th>
<th>Wavelength (Å)</th>
<th>( v' )</th>
<th>( v'' )</th>
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EXCITED STATE PROPERTIES OF 2-NAPHTHOL

References:

Summary:
The absorption and fluorescence spectra of 2-naphthol in aqueous solution are obtained as a function of pH. The acidity constants of the ground and lowest electronically excited states are determined.

Introduction and Theory:
The electronic structure of a molecule determines the physical and chemical properties such as charge distribution, geometry, dipole moment, ionization potential, electron affinity, and chemical reactivity. If the electronic structure of a molecule is changed by exciting it to an electronically excited state we expect the physical and chemical properties to be altered.

Electronic excitation via absorption of light raises the typical organic molecule from a singlet ground state (all electrons paired) to another singlet state (electrons still paired, but one electron raised to a higher molecular orbital. The excited state has a very short lifetime (typically $10^{-6}$ to $10^{-9}$ s), so study of the properties of the excited state is not a matter of ordinary chemical experimentation. However, investigation of the absorption and fluorescence spectra provides a tool by which such information may be obtained. In this experiment the acid dissociation constants of 2-naphthol ($C_{10}H_7OH$, or ArOH) in both its ground and excited states are determined.

In aqueous solution, ArOH behaves as a weak acid dissociating to form its conjugate base ArO$^-$ according to

$$\text{ArOH} \leftrightarrow \text{ArO}^- + \text{H}^+ \quad (1)$$

We shall measure the equilibrium constants for the reaction: $K_a$ in the ground state $S_0$ and $K_a^*$ in the first excited state $S_1$. An energy level diagram for the ArOH molecule (in solution) shows relationships between the energies of the species involved in the equilibria, where $\Delta H$ and $\Delta H^*$ are respectively, the enthalpies of the acid dissociation in the $S_0$ and $S_1$ states. Both the ground state acid and its conjugate base can be excited via absorption of photons of energy $h\nu$ (ArOH) and $h\nu$ (ArO$^-$).

The free energy of dissociation of ArOH in terms of enthalpy and entropy is:

$$\Delta G = \Delta H - T\Delta S = -RT \ln(K_a) \quad (2)$$

and similarly for ArOH$^*$. If we assume that the entropies of dissociation are equal for ArOH and ArOH$^*$, then it follows that $\Delta H - \Delta H^* = -RT \ln(K_a^*/ K_a)$. From the energy level diagram below we see that
\[ \Delta H + N_a hc \nu(\text{ArO}^-) = \Delta H^* + N_a hc \nu(\text{ArOH}) \]  

(3)

where Planck's constant \( h \), Avogadro's number \( N_a \), and the speed of light \( c \) have been introduced in order to use wavenumber units for the frequencies.

\[
\begin{align*}
\text{ArO}^- + H^+ & \rightarrow \text{ArO}^- + H^+ \\
\Delta H^* & \rightarrow \text{ArO}^- + H^+
\end{align*}
\]

\[
\begin{align*}
\text{ArOH}^* & \rightarrow \text{ArOH}^* \\
\nu(\text{ArO}^-) & \rightarrow \nu(\text{ArOH})
\end{align*}
\]

\[
\begin{align*}
\Delta H & \rightarrow \text{ArO}^- + H^+
\end{align*}
\]

ArOH

Rearranging equations gives

\[
\ln \left( \frac{K_a^*}{K_a} \right) = N_a hc/RT \left[ \nu(\text{ArO}^-) - \nu(\text{ArOH}) \right]
\]

(4)

Thus, knowledge of the energy gap between the ground and first excited states for both the free acid and the conjugate base yields an estimate of \( K_a^* \) if \( K_a \) is known\(^1\).

Several approaches may be used to obtain the spectroscopic energy differences. The simplest is to use the difference between the absorption maxima for the two species; this method, however, is only approximate since it ignores the contribution of vibrational energy to the spectroscopic transition. The best method, which you should employ, is to determine the energy difference implied in the Förster cycle, \( \Delta \nu_{00} \). The subscript 0-0 indicates the transition frequency between the zero vibration levels of the two electronic states. This value cannot be observed in all cases (specifically for \( \text{ArOH} \)), but it may be estimated from analysis of both fluorescence and absorption spectra. The two spectra are plotted on the same scale, with the intensities of their maxima adjusted to be equal. Then the intersection of the spectra gives a good value of the 0-0 frequency. This measurement must be done on both the parent acid and the conjugate base. Instead of the absorption spectrum, the fluorescence excitation spectrum may be used.

Be sure to have the TA check you out on the UV-VIS and fluorescence spectrometers before you start this experiment.
Equipment:
Perkin Elmer LS55 fluorescence spectrometer, Varian 50Bio UV-VIS spectrometer, optical cells, 2-naphthol (C_{10}H_{7}OH), solutions of HCl, NaOH, NH_4OH and NH_4Cl.

*Caution: 2-naphthol is an irritant. Use gloves if you work with the solid material.*

The optical cells are delicate and expensive. They are sensitive to the natural oils found on your hands. Touch them only at the top and bottom, never on the sides, so as to avoid leaving etch-marks of your fingerprints on them. Clean them carefully, with a final ethanol rinse, and put them away in their box when you have finished with them.

Procedures:
Familiarize yourself with the spectrometers. You should have the help of an instructor when you first start working with them.

Prepare an aqueous solution of about 0.0002 M 2-naphthol. Make other solutions as needed. Sufficient time is required to dissolve naphthol in water.

Absorption spectra:
(a) Obtain absorption spectra of 2-naphthol (ArOH, about 0.0002 M) in solutions which are made acidic and basic by addition of HCl or NaOH, respectively. The HCl or NaOH concentration should be approximately 0.02 M. **It is important that the two ArOH solutions have identical concentrations.** This will give spectra of the acid and conjugate base forms of the naphthol, ArOH and ArO^−, respectively.

(b) Obtain absorption spectra of ArOH (also at 0.0002 M) in solutions at intermediate pH values by using ammonium chloride buffer solutions (NH_4OH/NH_4Cl) showing both acid and base forms. Obtain at least three spectra, choosing appropriate ratios of NH_4OH and NH_4Cl. You may also use your aqueous stock solution as an intermediate solution because the buffer solutions provide high pH values. If possible, measure the pH of each solution immediately after use. Label and save the solutions.

If the total ArOH concentration is constant, the spectra at various pH values, when properly overlapped, should intersect at a common wavelength called the *isosbestic point*. **What does the isosbestic point imply?**

Fluorescence spectra:
Using the same solutions as in step (a) and (b) above, obtain the fluorescence spectra of ArOH and ArO^−. **In the settings of the method for the spectrofluorimeter, be sure to tell the program to save the data as ASCII file before scanning otherwise data will be lost.**

Analysis:
Analyze the data to obtain $K_a$, using absorption data for the various buffer solutions. You will be able to find the ratio (ArO^−)/(ArOH) from the spectra, using your results on the acidic and basic solutions in (a) above.
Analyze the fluorescence and absorption data to obtain the 0-0 frequency difference and thus the value of $K_a^*$. 
FLUORESCENCE SPECTRUM OF ANTHRACENE

References:

Summary:
The absorption spectrum and fluorescence spectra of anthracene in ethanol solution are obtained in the visible and near-ultraviolet regions and analyzed. The fluorescence spectrum is studied as a function of concentration to determine the sensitivity of this technique for detecting anthracene. Quenching of the fluorescence of anthracene by chloroform is also measured.

Equipment:
Perkin Elmer LS55 fluorescence spectrometer, Varian 50Bio UV-VIS spectrometer, optical cells, anthracene (C_{14}H_{10}), absolute ethanol (CH_{3}OH), chloroform (CH_{3}Cl).

The optical cells are made of silica, and are delicate and expensive. They are sensitive to the natural oils which are found on your hands. Touch them only at the top and bottom, never on the sides, so as to avoid leaving etch-marks of your fingerprints on them. Clean them carefully, with a final ethanol rinse, and put them away in their box when you are finished with them.

Procedure:
Familiarize yourself with the spectrometers. You should have the help of an instructor when you first start working with them. Use the instructor's recommendations concerning instrument settings (sensitivity, etc) for the majority of this work.

Prepare a solution of about 0.001 M anthracene in ethanol. Make other solutions you need by 10:1 dilutions.

(a) Absorption spectrum: Record the absorption spectrum between about 500 and 210 nm. The lowest singlet excited state is the prominent vibronic series of bands whose 0-0 band occurs at about 375 nm. Verify this!

(b) Fluorescence spectrum: Select a concentration at which light at a wavelength of 360 nm is no more than 20% absorbed in 1cm of solution, and obtain the fluorescence spectrum of anthracene excited at 360 nm. Compare the energy spacing (in wavenumbers) of the series of bands in absorption and fluorescence. You might expect the 0-0 band in fluorescence to occur at the same wavelength as it does in absorption. Does it for anthracene?

Record the entire fluorescence spectrum while exciting at several wavelengths in the absorption spectrum. Are your results consistent with rapid conversion to the 0 vibrational level of the first excited singlet state?

Record the excitation spectrum by monitoring the fluorescence at, say, the 0-1 band and scanning the excitation monochromator from 450 to 220 nm. Compare the absorption and excitation
spectra and suggest explanations for any differences noted. What is the band in the vicinity of 240-250 nm?

(c) **Sensitivity of detection:** By using more dilute solutions, determine the detectability limit of this instrument. Wash the cell a number of times with alcohol and run a fluorescence spectrum of the pure solvent. Fluorescent impurities are found in many commercial solvents. In this study you may want to change the sensitivity of the instrument as the solutions get weaker.

(d) **Quenching of fluorescence:** Use a concentration of anthracene such that the optical density is no more than 0.1, so that fluorescence intensity is uniform throughout the solution. If excitation is at 366 nm the concentration should be about 0.00003 M. It's important that sample tubes always be filled to the same level (near the top).

Your object is to measure the fluorescence of a constant-concentration solution of anthracene, with increasing concentrations of chloroform. The results are treated using the Stern-Vollmer plot to find the quenching rate constant. Carbon tetrachloride (CCl₄) may be used instead, but it is a carcinogen and must be handled with precaution. To prepare the solutions, add a fixed amount of one of your stock solutions to a volumetric flask, add a known amount of chloroform, and then add ethanol to the mark. **The solution with the largest chloroform concentration should show quenching of at least half the fluorescence and the smallest concentration should be perhaps one tenth of this.**

The intensities obtained in the quenching experiment are treated using the Stern-Vollmer equation¹. In order to obtain the quenching rate constant, you need a time measurement of some kind (none of the experiments you have done above involve time!). The fluorescence lifetime of anthracene is quite short, as indicated by the fluorescence intensity-versus-time data below; since we do not have equipment capable of measuring it, you should use the data given below to determine the fluorescence lifetime of anthracene.¹

<table>
<thead>
<tr>
<th>time (ns)</th>
<th>Intensity (photons/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>62620</td>
</tr>
<tr>
<td>1</td>
<td>50408</td>
</tr>
<tr>
<td>2</td>
<td>41250</td>
</tr>
<tr>
<td>3</td>
<td>32472</td>
</tr>
<tr>
<td>4</td>
<td>27218</td>
</tr>
<tr>
<td>5</td>
<td>21556</td>
</tr>
<tr>
<td>6</td>
<td>17708</td>
</tr>
<tr>
<td>7</td>
<td>14247</td>
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<td>8</td>
<td>11352</td>
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<tr>
<td>9</td>
<td>9193</td>
</tr>
<tr>
<td>10</td>
<td>7560</td>
</tr>
</tbody>
</table>

Table 1. Fluorescence intensity of anthracene in ethanol.
Preliminary Questions:

1. Draw a schematic of the energy levels of anthracene and indicate excitation, fluorescence, and quenching processes.

2. What causes the several peaks in the absorption/fluorescence spectrum? What does "0→0" or "0←1" band mean?

3. Write the steady state equation for the concentration of the anthracene molecules in the excited state and derive the Stern-Volmer equation.
VIBRATION-ROTATION SPECTRA OF HCl AND DCl

References:
1. Alberty & Silbey "Physical Chemistry" Ch 13.7

Summary:
Infrared absorption spectra of gaseous HCl and DCl are taken on a Nicolet Avatar Fourier Transform Infrared (FTIR) Spectrometer. The high-resolution scan resolves the $^{35}\text{Cl} - ^{37}\text{Cl}$ splittings. The line frequencies are read, and the data are used to obtain molecular constants.

Equipment:
Nicolet spectrometer, pre-filled 10 cm gas cell containing HCl and DCl at about 50 Torr. The HCl cell is kept in a dessicator because its windows are potassium bromide crystals, which are fogged by humidity and are very brittle. Replace it when you are finished, and don't touch the windows. If it seems necessary to clean them, consult a TA!

Procedure:
You must have an instructional session to learn how to use the spectrometer. It is completely computer-controlled, including the calibration and presentation of line frequencies for the spectra.

After familiarization with the spectrometer you will take spectra in the regions of the infrared appropriate to the two molecules. It is best in taking the final spectra to divide the regions into two for each molecule, one covering the R-branch and the other the P-branch. This will show you the spectra in the most useful way.

The computer program which controls the spectrometer will analyze the spectrum for peak positions, and will prepare a file which lists them. Given this file, you can later analyze the frequencies as indicated below to obtain molecular parameters for the molecules. In addition, peak positions can be obtained from fitting in Origin.

Your report should include values of the parameters of the fitting equation, with their standard deviations. It should also include a table of the molecular parameters, with their standard deviations with comparison to literature values.

Theory and Data Treatment

Energy levels of HCl:
The infrared spectrum of HCl involves transitions between vibrational-rotational energy levels. In what follows, energies are expressed in wavenumbers ($E/\hbar c$ written cm$^{-1}$). The symbols $G$ and $F$ are used to designate vibrational and rotational term values (i.e. energy levels in
wavenumbers), and upper and lower states of the transitions are labeled with single and double primes, respectively.

Vibrational levels of a diatomic molecule depend on the vibrational quantum number, \( v \), and rotational levels on the rotational quantum number, \( J \). To a good degree of approximation, the vibrational terms obey the formula

\[
G(v) = \omega_e(v + 1/2) - \omega_e x_e (v + 1/2)^2 \tag{1}
\]

and the rotational terms obey

\[
F(J) = B_v J(J + 1) - D J^2(J + 1)^2 \tag{2}
\]

where \( \omega_e \) and \( \omega_e x_e \) are the harmonic frequency and the anharmonicity, respectively, and \( B_v \) and \( D \) are the rotational constant and the centrifugal stretching constant, respectively. The parameter \( \alpha \) is the vibration-rotation parameter, which allows for the change in apparent rotational constant \( B_v \) with vibrational state. The vibrational frequency, \( \omega_e \) (about 3000 cm\(^{-1}\) for HCl), is at least one hundred times as great as the rotational constant, roughly 10 cm\(^{-1}\); this large ratio is typical for most molecules, and the energy levels should be thought of as a set of widely separated vibrational states, each with its own collection of closely-spaced rotational levels. Include an illustration of this in your report.

**Vibration-rotation line frequencies:**

A given spectroscopic transition involves a change in both vibrational and rotational states (and thus in both \( v \) and \( J \)). There are selection rules for these changes, which can be derived theoretically or just looked on as empirical rules. They are (for diatomic molecules) that \( v \) and \( J \) may both change by one unit; thus

\[
v' = v'' \pm 1; \quad J' = J'' \pm 1 \tag{3}
\]

Writing the energy level (term value in wavenumbers) for a single vibration-rotation level using Eqs. 1 and 2 above, one has (this equation applies to either the initial or final state)

\[
T_vJ = \omega_e(v + 1/2) - \omega_e x_e (v + 1/2)^2 + B_v J(J + 1) - D J^2(J + 1)^2 \tag{4}
\]

Finally, for absorption of light, \( v \) must increase by one, while \( J \) may either increase or decrease by one. Thus, two possibilities arise for transitions from a given initial level \( (v'',J'') \); if \( J'' \) goes to \( J''+1 \) the line is called an \( R \)-branch line, while if \( J'' \) goes to \( J''-1 \) it is called a \( P \)-branch line. Taking the differences between two level formulas (two equation 4’s), with the selection rules applied, one obtains the frequencies of the two branches as follows for the \( v''=0 \) to \( v'=1 \) vibrational change (given that \( v'' = 0 \) is the only thermally populated vibrational level at room temperature for HCl):

\[
R(J'') = \omega_e - 2 \omega_e x_e + 2B' + (3B' - B'')J + (B' - B'')J^2 - 4D(J + 1)^3 \tag{5}
\]
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\[ P(J'') = \omega_e - 2\omega_x\chi_e - (B' + B'\prime)J + (B' - B'\prime)J^2 - 4DJ^3 \quad (6) \]

where \( J \) takes on the values 0,1,2,3... in the R-branch and 1,2,3... in the P-branch. **You should draw an energy level diagram with arrows connecting a number of levels between which transitions are allowed by the selection rules; this drawing should convince you that the J-numbering of the lines is as stated above.**

It is useful in analysis to have all lines represented in terms of a single "index number"; this may be accomplished if one sets \( m = (J + 1) \) in the R-branch and \( m = -J \) in the P-branch. Then \( m \) takes on the values 1,2,3... in the R-branch and -1,-2,-3... in the P-branch. With this definition of \( m \), all the lines are given by a single formula:

\[ \nu(m) = \omega_e - 2\omega_x\chi_e + (B' - B'\prime)m^2 + (B' + B'\prime)m - 4Dm^3 \quad (7) \]

It is this formula which will be used to analyze the HCl vibration-rotation band. Note that, if all the parameters listed above are significant, the line frequencies may be represented by a cubic equation in the variable ("index number") \( m \).

**Data treatment:**
The data obtained in the experiment are frequencies for a number of R- and P-branch lines for both the \(^{35}\text{Cl} \) and \(^{37}\text{Cl} \) isotopic varieties of HCl. (Also for DCl.) For each isotope, it is necessary to assign to each line its value of \( m \). Then the line frequencies must be fitted to a polynomial in \( m \). You must decide what maximum power of \( m \) is appropriate for the precision of your data, but Eq. 7 suggests that you should use no higher than \( m^3 \). A spreadsheet program may be used here, or some other data-processing program such as Origin. Any such program must be able to give you not only the parameters of the fit, but also their standard deviations in order that you may assess the precision of the results.

Since HCl has been extensively studied, accurate values of the vibration-rotation parameters in Eqs. 1 and 2 are available with which you may compare your results. Of particular interest is the bond length of HCl, which may be obtained from the rotational constant \( B \); you should calculate a value for this length and note how accurately it is obtained in a relatively simple experiment. The vibrational force constant \( k \) is obtained from the vibrational frequency; assuming that the force constant is the same for both isotopic frequencies, try to predict the pure vibrational frequency of the \(^{37}\text{Cl} \) isotope from that of the \(^{35}\text{Cl} \). For DCl, compare the parameters and see whether they follow your expectations.

Note: Data for one species (say H\(^{35}\text{Cl} \)) alone cannot give the values of \( \omega_e \) and \( \omega_x\chi_e \) separately. However, \( \omega_e \) should scale as \( \mu^{-1/2} \) and \( \omega_x\chi_e \) as \( \mu^{-1} \), so, if you also have data for D\(^{35}\text{Cl} \), you can get both the parameters. Here \( \mu \) is the reduced mass of the molecule, given by

\[ \mu = m_H m_{\text{Cl}} / (m_H + m_{\text{Cl}}) \quad (8) \]

The best reference for molecular parameters is Huber and Herzberg (Ref. 3). Many other references such as textbooks exist, but their values may not be as accurate, and they sometimes
confuse the band center frequency and $\omega_e$ or the rotational constant for the ground state (B_0) with the vibrationless value (B_e).

**Preliminary questions:**

1. Assuming the $^1$H$^{35}$Cl vibration frequency is 2900 cm$^{-1}$, what do you predict for the $^1$H$^{37}$Cl frequency? for the $^2$H$^{35}$Cl frequency?

2. Assuming the $^1$H$^{35}$Cl rotational constant B_0 is 10 cm$^{-1}$, what do you predict for the $^1$H$^{37}$Cl constant? for the $^2$H$^{35}$Cl constant?

3. How precisely do you need to know the rotational constant B_0 in order to determine the bond length with a precision of 0.005Å?
CONDUCTANCE OF SOLUTIONS

References:
1. Silbey & Alberty "Physical Chemistry" Ch 20.3
2. Atkins "Physical Chemistry", Ch 24.7-9
   "Conductance of Solutions".

Summary:
The electrical conductance of aqueous solutions of acetic acid, potassium acetate, potassium chloride, and hydrochloric acid are measured as a function of concentration. Equivalent conductances are determined by extrapolation to zero concentration. The dissociation constant of acetic acid is determined.

Introduction:
Electrolytic solutions obey Ohm's law

\[ V = I \cdot R \]  \hspace{1cm} (1)

where \( V \) is the applied voltage, \( I \) is the current, and \( R \) the resistance. The conductance, \( L \), is the reciprocal of the resistance and for a homogeneous body is given by

\[ L = \frac{1}{R} = \frac{\kappa}{A/l} \]  \hspace{1cm} (2)

where \( A \) is the cross sectional area of the sample and \( l \) the length. The ability of a solution to conduct electricity is characterized by a specific conductance, \( \kappa \). Solution conductivities are measured in a conductance cell. However, it is generally not possible to construct a cell with an exactly known value of \( A \) and \( l \), so in practice a cell constant \( K \) is obtained by measuring the resistance of the cell when it contains a solution of known \( \kappa \). Thus

\[ \kappa = \frac{K}{R} \]  \hspace{1cm} (3)

If one mole of electrolyte dissociates into \( n^+ \) moles of positive and \( n^- \) moles of negative ions, then \( n = n^+ z^+ = n^- z^- \) is the number of equivalents of positive and negative ions per mole. The concentration in equivalents per liter of positive or negative ions in a \( c \) molar solution of the solute is equal to the product \( n^*c \). Note that if the solute does not ionize completely, this equivalent concentration is \( \alpha n^*c \), where \( \alpha \) is the degree of ionization.

We now define the equivalent conductance, \( \Lambda \), by

\[ \Lambda = \frac{\kappa}{1000 n\cdot c} \]  \hspace{1cm} (4)

where the factor of 1000 is necessary to convert to standard units of \( \Omega^{-1} m^2\text{equiv}^{-1} \). If the ions have unit charge, the equivalent conductance is the same as the molar conductance.
The equivalent conductance is dependent on the concentration, and in dilute solutions it roughly follows the law

\[ \Lambda = \Lambda_0 (1 - b \cdot c^{1/2}) \] (5)

Measurement of the conductance (and thus the equivalent conductance) as a function of concentration can be extrapolated to infinite dilution to obtain \( \Lambda_0 \).

At infinite dilution the ions are independent, and it is possible to write

\[ \Lambda_0 = \lambda_0^+ + \lambda_0^- \] (6)

for the sum of the ionic conductances.

In this experiment the ionic conductances for strong electrolytes are combined to obtain \( \Lambda_0 \) for the weak electrolyte acetic acid (HAc).

\[ \Lambda_0 (\text{HAc}) = \Lambda_0 (\text{HCl}) + \Lambda_0 (\text{KAc}) - \Lambda_0 (\text{KCl}) \] (7)

Then, having measured the equivalent conductance for acetic acid at various concentrations, and remembering that acetic acid is not completely dissociated, we can find the degree of dissociation as

\[ \alpha = \frac{\Lambda}{\Lambda_0} \] (8)

The equilibrium constant for acetic acid dissociation is

\[ K_c = \frac{[H^+] [Ac^-]}{[\text{HAc}]} = c\alpha^2/(1 - \alpha) \] (9)

So the apparent dissociation constant can be obtained for each concentration measured, and extrapolation to infinite dilution will yield the thermodynamic value of \( K_c \).

**Equipment:**
VWR model 21800-012 conductance meter, thermostat, volumetric glassware. The meter measures conductance in Siemens (S) over the range 0.1 \( \mu \)S to 200 mS. It has been calibrated at the factory, but should be re-calibrated periodically. You will do this by measuring the conductance of a known solution of potassium chloride and establishing a correction factor if necessary for your use of the meter.

**Procedure:**
The cell constant is obtained by a conductance measurement on a solution of 0.02000 M KCl. Be aware of the precision of the concentration! Prepare and measure this solution carefully, as everything else depends on it. The specific conductivity of this solution is \( \kappa = 0.27653 \Omega^{-1} \text{ m}^{-1} \) at 25 °C.
Chem 332L

Solutions should be prepared using “conductivity water”; this may be deionized water which has been boiled to remove CO₂ gas and stored in a screw-cap plastic bottle. It should be possible to prepare water with conductivity \( \kappa < 2 \times 10^{-4} \, \Omega^{-1} \text{m}^{-1} \). Be sure to test this assumption.

Prepare solutions of each of the four substances with concentrations of about 0.04, 0.03, 0.02, and 0.01 M. Measure the conductance of each solution. It is best to measure (e.g. for the KCl) the 0.01 M solution followed by increasing concentrations, rinsing the cell with each solution. It is advisable to make a duplicate run through all solutions to check your precision.

For each solution except HAc, calculate the equivalent conductance and extrapolate to determine \( \Lambda_0 \). With the results obtained, process the HAc data to obtain \( K_c \).

**Preliminary Questions:**

1. How precisely can you measure conductance with the equipment available?

2. Compared to the precision of measuring conductance (above), how closely must you know the concentrations of your solutions? (Be sure you make them up at least this accurately!)

3. If the concentration of the standard KCl solution is 0.02050 M rather than 0.02000 M, how would you find the cell constant from the cell resistance?
MAGNETIC SUSCEPTIBILITY

References:
1. Alberty & Silbey "Physical Chemistry" Ch 22.5-6 ;
2. Atkins "Physical Chemistry Ch 22.6-7;

Summary:
Magnetic susceptibility measurements are made, using a magnetic susceptibility balance, on a number of transition metal ions: Mn(VII), Mn(II), Fe(II)(H₂O)₆, Fe(II)(CN)₆⁻⁴, Fe(III)(CN)₆⁻³. The results are correlated with the electronic structures of the complex ions. A Ni(II) solution (NiCl₂) is used to calibrate the magnetic field.

Theory:
A magnetic moment can be induced when an object is placed in a magnetic field. Magnetic polarization is similar to electric polarization. In a magnetic field, \( H \), the polarization, \( M \), is given by

\[
M = \chi H
\]

(1)

where the dimensionless \( \chi \) (the volume susceptibility) is positive for paramagnetic substances and negative for diamagnetic. Mass susceptibility, \( \chi_{\text{mass}} \), is related to \( \chi \) by

\[
\chi_{\text{mass}} = \frac{\chi}{\rho}
\]

(2)

where \( \rho \) is the density. \( \chi_{\text{mass}} \) has units (S.I.) m³/Kg. The molar susceptibility \( \chi_M \) is

\[
\chi_M = M \chi_{\text{mass}} = \frac{M \chi}{\rho}
\]

(3)

where \( M \) is the molecular weight and \( \chi_M \) has units m³/mol.

All materials have a diamagnetic susceptibility, resulting from the orbital precession of electrons in atoms. It is generally quite small compared to the paramagnetic susceptibility which arises from the spin of unpaired electrons. An example of paramagnetism is oxygen, with two unpaired electrons. As a result, it is very desirable to use samples which do not contain dissolved oxygen because of its undesirable interaction with the results. Other examples include iron (III), nickel (II), and many other metal ions, as well as many metal complex ions such as those studied here.

An atom or molecule containing unpaired spins has a permanent magnetic dipole moment, \( \mu \), related to the number of unpaired spins

\[
\mu \text{ (spin)} = (n(n+2))^{1/2} \mu_B
\]

(4)
where $\mu_B$ is the Bohr Magneton equal to $9.274 \times 10^{-24}$ J T$^{-1}$. The molar susceptibility is related to the magnetic dipole by

$$\chi_M = A + N_a \mu_0 \mu^2 / 3kT$$  \hspace{1cm} (5)

where $A$ is the diamagnetic (small) contribution, $N_a$ is Avogadro's number, $k$ is the Boltzmann constant and $\mu_0$ is the permeability of vacuum. Expressing this equation as

$$\chi_M = A + C/T$$  \hspace{1cm} (6)

we find that

$$\mu = (3kC/N_a\mu_0)^{1/2}$$  \hspace{1cm} (7)

or

$$\mu = 798 \, C^{1/2} \, \mu_B$$  \hspace{1cm} (8)

where $C$ is a constant expressed in SI units m$^3$ mol$^{-1}$ K.

Magnetic susceptibility balance (Gouy Method): A sample of susceptibility $\chi$ is placed so that it extends from a zero field region into a magnetic field. It experiences a force (downward if it is paramagnetic)

$$F = 1/2 \chi \mu_0 H^2 A$$  \hspace{1cm} (9)

where $H$ is the field strength and $A$ the cross sectional area of the sample. The force is zero if $H$ is zero, so the difference in weight with and without the field is

$$\Delta W = 1/2 \chi \mu_0 H^2 A$$  \hspace{1cm} (10)

Equipment:

Technological advances have recently replaced the traditional Gouy balance method of measuring susceptibility; however, the theory has not changed. The Gouy balance is based on measuring the force which a magnet exerts on a sample. The mass susceptibility balance, which we will be using, works on the idea of a stationary sample and pairs of moving magnets in which the equal and opposite force which the sample exerts on a suspended permanent magnet is observed.

Based on the guidelines of the balance, the mass susceptibility is calculated using:

$$\chi_{\text{mass}} = C_{\text{Bal}} \cdot L \cdot (R-R_0)/10^9 \, m$$  \hspace{1cm} (11)

Where $C_{\text{Bal}}$ is the balance calibration constant for the instrument, $L$ is the length of the sample in the test tube (cm), $R$ is the reading for the tube plus sample, $R_0$ is the empty tube reading, and $m$ is the mass of the sample (grams). $C_{\text{Bal}}$ is determined using a sample of known susceptibility. **Note that the readings from the balance are in cgs units and must be converted to SI units.** Using the recommended test tubes, $R_0$ will vary only slightly and for most purposes a constant
value can be assumed. However, a series of runs of R₀ should be determined to obtain an accurate value. Since glass is diamagnetic, R₀ will be negative. For some samples readings can vary with ambient temperature. In such cases, the samples and balance should be allowed to come to temperature equilibrium before measurement and the temperature of the room should be recorded with the reading. Remember that your whole experiment depends on the care with which you make up and measure the Ni(II) calibration sample.

Samples:
The samples to be studied are NiCl₂, KMn(VII)O₄, Mn(II)SO₄, Fe(H₂O)₆][NH₄]₂(SO₄)₂, K₄[Fe(II)(CN)₆], and K₃[Fe(III)(CN)₆]. A 30% by weight sample of NiCl₂ sample is used to calibrate the system. For the rest of the samples, approximately 0.4 - 0.5 M concentrations should be used; the concentrations must be known precisely. It is helpful to prepare the samples in advance, since the solids may dissolve very slowly. Use good weighing technique and proper volumetric flasks.

Note that the solid samples may contain waters of hydration. Read the reagent bottle label to see what sample you are actually taking and calculate solution concentrations correctly.

Operation of the balance:
1. Turn the RANGE knob to the x1 scale and allow a 10 minute warm-up period before use.
2. After warm-up, adjust knob until the display reads 000.
3. Place an empty sample tube of known weight into the tube guide and take the reading, R₀.
4. Pack the sample as described and note the sample mass, m, in grams and the sample length, L, in cm.
5. Place the packed sample into the tube guide and take the reading, R.

If the display goes off scale turn the RANGE knob to the x10 scale, re-zero and multiply the reading by 10.

When using solid samples: The mass susceptibility balance has the ability to work with either solid or liquid samples. With solid samples, considerable care should be taken in packing the powder into the sample tube since the majority of error arises from inhomogeneous packing. The sample should be in the form of a reasonably fine and uniform powder. Large crystals will not pack sufficiently. Be sure to crush samples if not very fine.

A small amount of solid is introduced into the previously weighed sample tube, and the bottom of the tube gently tapped on the bench a number of times to settle the particulates. This procedure is repeated until a sufficient amount of sample is added, corresponding to the sample length, L, in the range of 2.5 – 3.5 cm. Even packing can be ensured by taking readings in between tapping the sample tube until the balance readings become constant. Further proof of the sample being homogeneous and well-packed can be obtained by taking readings while rotating the tube containing the sample and noting the readings in different positions.

After the first measurement, it is advisable to empty out the sample, repack the tube and repeat the procedure to ensure measurement reproducibility.
When using liquid samples: Liquid samples can be treated the same way as solids. However, the full expression for determining the mass susceptibility of the sample must include the susceptibility of the displaced air and a correction applied for the volume of the meniscus. However, if the density (gm/cc) of the solution is known, a convenient expression for the mass susceptibility $\chi_s$ of the solution is:

$$\chi_{mass} = C_{Bal} \cdot L \cdot (R - R_0)/10^9 \cdot A \cdot ds + \chi_{v\_air}/ds$$

(12)

where $A$ is the cross-sectional area of the tube (cm$^2$), $d_s$ is the density of the solution, and $\chi_{v\_air}$ is the volume susceptibility of the displaced air, which is approximately $0.029 \times 10^{-6}$ cgs at 20°C for oxygen which other constituents being two orders of magnitude less.

The dimensions of the standard sample tubes are:

<p>| | |</p>
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>Outside diameter</td>
<td>0.400 cm ± 0.0013 cm</td>
</tr>
<tr>
<td>Inside diameter</td>
<td>0.324 cm ± 0.0013 cm</td>
</tr>
<tr>
<td>Cross-sectional area</td>
<td>0.08245 cm ± 0.00066 cm$^2$</td>
</tr>
</tbody>
</table>

Procedure:
In order to determine $C_{Bal}$ of the equipment, which includes the geometry of the cell and the magnetic field strength, a 30% wt. sample of NiCl$_2$ is used. Prepare this solution carefully, as all further results depend on this calibration. You will need about 100mL of each solution. Using the best value of the observed reading for the NiCl$_2$ solution as well as Eqs. 12 and 13, find the instrument constant $C_{Bal}$.

For the calibrating solution, make several independent measurements of the NiCl$_2$ sample. During this process, make careful note of the precision of (a) the result comparing different samples, and (b) the precision of multiple measurements on the same sample. The latter will indicate your limiting precision.

For each of the other samples, again, make several measurements of the readings. For each one, determine the mass susceptibility using Eq. 12 and $C_{Bal}$, which is now known. In addition, once the calibration constant is known, Eq. 11 can be used for solid sample measurements.

For all liquid samples you will need the sample density. To measure this, fill the sample tube to the fiducial mark with water and weigh it; also weigh it empty. From the mass of the water and the density of the water (remember to measure the water temperature), determine the volume of the tube, and use this to determine the sample densities.

Results:
The magnetic susceptibility of aqueous nickel chloride is given by

$$\chi_{mass} = [10,030 p/T - 0.720 (1 - p)] \times 4\pi \times 10^{-9} \text{ m}^3/\text{Kg}$$

(13)

where $p$ is the mass fraction of NiCl$_2$ and $T$ the temperature. The first term is the paramagnetic effect of NiCl$_2$ and the second the diamagnetic effect of the water.
We can write the volume susceptibility, $\chi$, for each of the samples studied if the concentration of the sample is known as shown:

$$\chi = 1000 c \chi_M - 0.720 \times 4\pi \times 10^{-9} (\rho - 1000 c M) = \chi_{mass} \rho$$  \hspace{1cm} (14)$$

where $\chi_M$, $\rho$, and $M$ are in S.I. units ($m^3$ mol$^{-1}$, kg m$^{-3}$, kg mol$^{-1}$) and $c$ is the molarity of the solution.

From $\chi$ the molar susceptibility, $\chi_M$, can be obtained.

If the sample is paramagnetic (positive R reading), the small diamagnetic term $A$ in the theoretical equation for $\chi_M$ in Eq. 5 and 6 may be neglected, and thus the magnetic moment determined. In addition, the apparent number of unpaired electrons can be determined using equation 4.

Since the procedure is relatively simple, we shall consider the question of precision and reproducibility of the work as a very important part of this experiment. You should present the results with a good analysis of precision and errors. Qualitative statements such as "solutions were possibly made with error, etc." are inadequate; quantitative or semi-quantitative statements based on multiple measurements are necessary. Treatment in terms of the analysis of errors discussed in the text is appropriate.

**Analysis:**
The number of unpaired electrons is related to the electronic structure of the metal complex ions (particularly the $d$-electrons). Comparison of your results with those expected from these structures is expected.

**Comment:**
The magnetic moments measured in this experiment are the same ones which are measured in the N.M.R. experiment on quenching of spin polarization by transition metal ions. Comparison of the results of these two experiments (if you do both, or collaborate with another student) would be interesting and beneficial to you. Also, experiments performed on solid samples compared to those on aqueous solutions are also an important point to address.

**Preliminary Questions:**
1. Which of the transition metal ions should be paramagnetic? and which diamagnetic?
2. Which of the ions should be “more paramagnetic” than Ni(II)? less?
3. When you start the experiment, examine the analytical balance, estimate how precisely you can read it, and decide how precisely you should make up the standard NiCl$_2$ solution.
ELECTROMOTIVE FORCE AND ACTIVITY COEFFICIENTS

References:
1. Silbey & Alberty "Physical Chemistry" Ch 7.1-6
2. Atkins "Physical Chemistry" Ch 10.3-5

Summary:
Electromotive force (EMF) measurements are made on the cell

$$\text{Ag(s)} | \text{AgCl(s)} || \text{HCl(aq,m)} | \text{H}_2(\text{g,p}) | \text{Pt(s)}$$

under reversible conditions at a number of concentrations of aqueous HCl. By extrapolation to zero concentration, the standard EMF, $E^\circ$, for the cell is obtained, and activity coefficients are derived for the HCl concentrations used.

Equipment:
The Ag/AgCl and Pt electrodes are provided. Except when in use, the electrodes should be left immersed in distilled water, or the surfaces (particularly the platinum one) will become deactivated, resulting in little chance of reaching equilibrium in the measurements.

Ask a TA to check out your system before beginning to use the hydrogen gas. Use a slow gas flow and turn it off after the experiments. Large amounts of hydrogen escaping into the laboratory can be a fire hazard. Moreover, a slow flow gives more precision.

The EMF of the cell is measured using a digital multimeter capable of reading to 0.1 mV. Get a TA's help to make sure you know how to use it. Be sure you know which electrode is the positive one, and understand why. Use of this multimeter allows you to watch the cell coming to equilibrium. (Can you say what requirement is placed on this multimeter in order that it measure the cell under equilibrium conditions? Could you use just any multimeter?)

Procedure:
Make sure the constant temperature bath is working, and regulated to 25 °C. Check that the hydrogen cylinder is properly connected and that the hydrogen flows smoothly through the bubbler, which saturates the gas with water vapor at room temperature. A slow flow of hydrogen is all that's needed: at equilibrium the voltage shouldn't jump up and down much as the hydrogen bubbles form. You may stop the flow almost entirely when you are actually taking a reading if you wish. Note that the pressure of hydrogen delivered to the cell is atmospheric pressure minus the vapor pressure of water.

The EMF of the cell is to be determined for HCl concentrations of 0.1, 0.05, 0.025, 0.0125 and 0.00625 M. Solutions are prepared by dilution from a standard commercially-supplied 0.1 M HCl M stock. Prepare 200 mL of each solution.
A first step in the work is to study the EMF of one sample (e.g. the 0.1 M solution) to gain confidence in the method and to see that the cell comes to equilibrium in a reasonable time. When the cell is filled and put in the constant temperature bath, the voltage will drift with time as the cell comes to temperature and chemical equilibrium. Watch the voltage on the meter, and take data when the cell has stabilized. A plot of voltage versus time before and during data-taking is instructive. In order to reduce equilibration time, prepare the next solution to be used and store it in the constant temperature bath to bring it to temperature.

The key to this experiment is care in preparing the cell and patience in taking the data. The condition of the electrodes is crucial, so take care of them. Before you make any measurements, calculate the approximate voltages you expect, using an estimated E° of 0.2 V, and how they will change with concentration. If your voltages aren't reasonable, you are doing something wrong.

The experimental program should include at least two determinations of the cell voltage for each solution concentration. If the two don't agree, further work will be necessary. Run a series making one determination for each concentration, and then repeat the series; making two determinations does not simply mean reading the voltage twice. For each concentration, rinse the cell with water, then with the solution to be studied. This is particularly important if you are moving to a smaller concentration. It is perhaps best to work from low to high concentration, as the danger from left-over sample is less in this direction. For each concentration, be sure the cell has reached equilibrium, and think carefully about how you will decide on a single final value for the voltage at each concentration.

A preliminary rough graph of E°" (see below), prepared point-by-point as the data are obtained for each concentration, is a valuable indicator of whether the experiment is going well, and makes simple errors (e.g. wrong solution) obvious. Make such a plot in your notebook as your experiment proceeds.

Results:
The Nernst equation relates the EMF of a cell to the activities of its component chemical entities

$$E = E^\circ - \frac{RT}{nF} \ln (Q)$$  \hspace{1cm} (1)

In this cell, \(Q = \frac{p^{1/2}}{(a(H^+) a(Cl^-))}\), and \(a(H^+) = m \gamma\), etc. So \(Q = p^{1/2} / m^2 \gamma^2\), where \(\gamma\) is the activity coefficient and \(m\) is the concentration.

Now we define \(E^\circ'\) and \(E^\circ"\) as

$$E^\circ" = E + 2.303 \frac{RT}{F} \log(p^{1/2} / m^2)$$  \hspace{1cm} (2)

$$E^\circ' = E + 2.303 \frac{RT}{F} \log(p^{1/2} / m^2) - 2 (2.303) \frac{RT}{F} (0.509) m^{1/2}$$  \hspace{1cm} (3)

Note that these would be the true E° values if (a) activities equal m, or (b) activity coefficients follow the Debye-Huckel law.
Plotting $E^{\circ}$ (which takes into account an approximate value of the activity coefficients) versus $m$ is the best way to obtain $E^\circ$. Why do you suppose this way is better than plotting $E^{\circ\prime}$? Make a least squares fit for the plot ($E^{\circ\prime}$ vs $m$), and show the experimental data as symbols and the fitting equation as a line. The least squares fitting procedure should give the standard error of the intercept $E^\circ$. A second plot of $E^{\circ\prime\prime}$ vs $m^{1/2}$ should give closely the same final $E^\circ$. (Why should the plot be against the square root of $m$? What slope should this plot have?)

Once $E^\circ$ is obtained, it is possible to calculate the activity coefficients from the cell voltage at each concentration.

Your results should show tabulated values of the best value of $E$ for each concentration, plots resulting in $E^\circ$, and calculated activity coefficients for the experimental conditions.

Plot the activity coefficients appropriately to compare them with theory. Notice the relationship of $E^{\circ\prime\prime} - E^\circ$ to the activity coefficients; you've already calculated $E^{\circ\prime\prime}$. In this plot, show the experimental values of the activity coefficients as symbols and show a line (or curve) for the theoretical values from the Debye-Hückel law.

**Preliminary Questions:**

1. Write the chemical reaction which occurs in the cell, remembering that the left hand side of the conventional cell diagram is where oxidation takes place.

2. Make preliminary estimates of the voltage to be expected from your cell with solutions of concentration 0.1, 0.01 and 0.001 M. Use the figure 0.2 V for the standard reduction potential of the Ag/AgCl electrode as a rough guess for this estimate.

3. Which electrode will be positive and which negative (assuming $E^\circ=0.2$ V)? Be sure you agree with the experiment on this!

4. Estimate how much the cell voltage will change for a small change in solution concentration. Use this estimate to decide how accurately you must know the concentrations of the solutions you make, taking into consideration the precision of the multimeter (and be sure to prepare the solutions carefully enough!).


PULSED NMR DETERMINATION OF ION MAGNETIC MOMENTS

References:
3. Alberty & Silbey "Physical Chemistry" Ch 15.1, 15.6

Summary:
The nuclear polarization of the protons in water is studied using pulsed NMR. In the presence of paramagnetic complex ions, the polarization is rapidly quenched. Study of the polarization as a function of pulse delay allows determination of the rate constants for quenching and thus the magnetic moments of the ions.

Theory:
When a nucleus with non-zero nuclear spin is placed in a magnetic field, the magnetic moment may take up specific, quantized alignments relative to the field. The spectroscopy involving the resultant energy levels is nuclear magnetic resonance (NMR) spectroscopy. There is a preference for alignment parallel to the field (lower energy), and in a system of a large number of nuclei there is a net magnetic moment parallel to the field. Distribution of the nuclear moments among the various quantum states is controlled by the Boltzmann distribution at the temperature of the system.

If the system of nuclei is subjected to a pulse of electromagnetic radiation at the NMR frequency, the thermal distribution among the quantum states may be perturbed; but after a time the system will relax back to the thermal distribution. The relaxation process obeys unimolecular kinetics, and is characterized by a relaxation time, $\tau_1$. The pulsed NMR phenomenon, and the meaning of its characteristic times, is discussed clearly by Smith and Prouix².

There are many mechanisms contributing to the relaxation process, but when the solution containing the NMR nuclei also contains paramagnetic ions such as transition metal complex ions, it is the influence of these ions which dominates the relaxation. Conger and Selwood² have shown that for an aqueous solution of certain paramagnetic ions the relaxation time of the protons of the water is given by

$$\frac{1}{\tau_1} = KN\mu_m^2 \quad (1)$$

where, $K$ is a proportionality constant, $N$ is the concentration of the paramagnetic ion (in ions/cc), and $\mu_m$ is the magnetic moment of the metal ion. The proportionality constant can be expressed as:

$$K = 12\pi^2 G_p^2 \eta N\mu_m^2/5k_B T \quad (2)$$

where $G_p$ is the gyromagnetic ratio of the protons, $\eta$ is the viscosity of the solution, $k_B$ is the Boltzmann constant and $T$ is the temperature (in K). Thus a determination of $\tau_1$ allows calculation of the magnetic moment of the metal ion. The constant, $K$, is to be determined by a
series of calibration measurements. For this purpose quenching by Cu(II), for which the magnetic momentum is known, is used as a reference.

In this experiment, $\tau_1$ is measured for aqueous solutions of several metal ions (such as Fe(III), Cr(III), Cu(II), Mn(II) and Ni(II)), and magnetic moments of the ions are determined.

**Experiment:**
The instrument used is the Praxis pulsed NMR monitor, in conjunction with an oscilloscope to display the NMR signal as a function of time. The Praxis instrument provides pulse sequences of the 90-t-90 type which are most useful in determining $\tau_1$ (1). It contains a display circuit which allows for monitoring the pulse intensities and for summing the results of a number of pulses. The pulse intensities are obtained by a boxcar integrator, which determines the integral over the pulses. Multiple-pulse data may also be taken on the digital storage oscilloscope. Record at least one oscillogram for the report. The article by Smith and Prouix (2) should be consulted for a discussion of the use of this instrument to determine $\tau_1$.

Figures 1 and 2 from Ref. (2) show the schematic of the experiment and the effect of the 90° and 180° pulses.

![Diagram of NMR experiment](image)

The magnetic field in the Praxis instrument is not particularly homogeneous, and it is necessary to calibrate the system using a perturbing ion with known magnetic moment; this may be done using a series of $\tau_1$ measurements on Cu(II), whose magnetic moment is 2.0 in a 0.100 M solution. Using $\tau_1$ determined for this solution, it is possible to find K, which can be used in Eq. 1 for the study of the other ions.

For each of the metal ions to be studied, prepare solutions of known concentration in the 1.0 to 0.01 M range. Determine $\tau_1$ using the methods of (2) and from this obtain the magnetic moment.
Sample measurement:
A student made measurements on a Cu(II) sample which are illustrative. He made a stock solution of 12.6 g CuSO₄ in 100 mL of solution, and studied samples prepared by dilution.

The results, obtained using the integrator feature of the Praxis instrument, are given in Table 1, where t is the time delay in the 90-t-90 pulse sequence (in ms). A₀ and A₁ are the first and second peak intensities. The "boxcar" integrator must be used in order to obtain intensities, since they are rather small in the aqueous solutions. For the 4:1 diluted sample the clock rate for the Praxis was 50 ms, for the 8:1 it was 200 ms. Since the A₀ amplitude remained essentially constant during each experiment, these clock rates were slow enough to allow complete relaxation between sequences.

The column labeled "y" is the function “-ln[(A₀-A₁)/A₀]" discussed by Smith and Prouix. A plot of y against t should be a straight line with slope 1/τ₁. Figure 3 shows such plots. From the slopes of the two lines, τ₁ is found to be 5.88 and 11.56 ms, respectively, for the 4:1 and 8:1 dilutions. The ratio of the τ₁ values is essentially the same as the dilution ratio, which it should be.

Table 1. Results of the measurements on Cu(II) for 4:1 and 8:1 samples.

<table>
<thead>
<tr>
<th></th>
<th>4:1 dilution</th>
<th></th>
<th>8:1 dilution</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>t</td>
<td>A₀</td>
<td>A₁</td>
<td>y</td>
</tr>
<tr>
<td>4:1</td>
<td>5</td>
<td>91.2</td>
<td>55.3</td>
<td>0.932</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>91.1</td>
<td>66.0</td>
<td>1.289</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>91.2</td>
<td>76.0</td>
<td>1.792</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>91.1</td>
<td>80.5</td>
<td>2.151</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>91.1</td>
<td>84.8</td>
<td>2.657</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>91.2</td>
<td>86.8</td>
<td>3.031</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>91.1</td>
<td>88.4</td>
<td>3.519</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>91.1</td>
<td>89.3</td>
<td>3.924</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>99.2</td>
<td>87.9</td>
<td>2.172</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>99.0</td>
<td>89.8</td>
<td>2.376</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>99.4</td>
<td>94.3</td>
<td>2.970</td>
</tr>
</tbody>
</table>

- 35 -
Results and discussion:
The primary results of this work are the $\tau_1$ values at various concentrations and magnetic moments of the various metal ions involved in the relaxation of the proton resonance polarization. From your knowledge of the electronic structures of these ions, you may discuss the correspondence of the results obtained to the values expected for the ions.

Preliminary Questions:
Consider the following questions in addition to the usual comparison with other known data and analysis of the errors of the experiment:

1. Draw a schematic of the experiment and the time dependence of the excitation and free induction decay pulses.

2. Draw the orientation of the magnetic moments of the H-atoms during the various stages of the experiment.

3. Explain the origin of the signal after the second 90° pulse, as well as the cause of the third pulse which appears in the oscilloscope.

4. Why does the signal decay so fast even though the polarization of the protons remains for a much longer time?

5. Why is the rest polarization proportional to $-\ln[(A_0-A_1)/A_0]$ ?
6. What frequency of the oscillating field is required for NMR experiments on protons in a magnetic field of 5000 G?

7. This experiment may be described as a quenching experiment, in which quenching rate constants are obtained. Explain. Why does there seem to be a problem at low metal ion concentrations?

8. The results from this experiment should be directly comparable to those obtained by the Gouy balance method used in another experiment available in this laboratory. Are they? If you wish, you may carry out both these experiments and compare the results.
MONTE CARLO SIMULATION OF LENNARD-JONES FLUID

Statistical mechanics allows one to calculate the properties of a macroscopic amount of a substance in various ways. The most direct requires knowledge of the energy levels of the macroscopic sample, clearly not possible except for the simplest of substances (e.g. an ideal gas). Approximate methods have, however, been developed which yield quite good properties. They are based on "computer simulations" of two general types, referred to as "Monte Carlo" and "Molecular Dynamics" simulations.

In each method some assumed intermolecular potential energy must be postulated, and the atoms/molecules of the sample interact under control of this assumed function.

Molecular Dynamics

Here a sample consisting of a number (hundreds to thousands) of atoms is constructed in a possible initial state (sample size, atom positions, atom velocities). Then the atoms are allowed to move, one step at a time, following Newton's laws of motion. The time steps are very short (typically some femtoseconds). After some time it is supposed that the sample has come to equilibrium. Then such properties as the radial distribution function, diffusion coefficient, pressure and various dynamic properties may be calculated from the equilibrium distribution and its time development.

Monte Carlo

Here a sample is constructed as for the MD method. The total energy of the sample is calculated using the postulated potential energy function. Then one (or more) molecule is moved slightly to a new position, and the energy calculated again. If the new energy is less than the old one, the move is accepted, giving a modified sample. On the other hand, if the new energy is greater than the old, acceptance is based on two factors: the Boltzmann factor \( \exp(-\Delta E/kT) \), and a random number (thus the name Monte Carlo). Note that the temperature is specified.

Each atom is moved in sequence, and the resulting change in structure of the sample accepted or rejected, to complete one cycle of movement. The simulation run consists of many (thousands) of such cycles. At the end of the run it is supposed that the sample has reached thermal equilibrium. Then the static properties (e.g. radial distribution function, diffusion coefficient and pressure) may be calculated. The MC method is not suited to determining dynamic properties (since no mention of time appears in the calculation).

Study of a fluid using the Monte Carlo method

Objectives:

To predict the behavior, specifically the equation of state, of a fluid of atoms which interact with one another according to the "Lennard-Jones 6-12" potential.
To compare these predictions with the actual behavior of a real gas (e.g. Ar, Kr).

These predictions are to include regions where the fluid is dense as well as where the fluid is (almost) an ideal gas.

**Method:**

A computer program, F11FGNNN.EXE, will be used. This program employs the Monte Carlo concept, under conditions of constant Number of molecules, Volume and Temperature. In using it, one specifies the density and temperature of the fluid and the program yields values for the pressure and energy of the fluid sample. A radial distribution function is also produced.

The program applies to any Lennard-Jones gas. In fact, within the program reduced units are used such that energy is expressed in terms of a unit e and distance in terms of a unit \( \sigma \). These are simply the parameters of the Lennard-Jones potential

\[
V(R) = 4 e \left[ \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^6 \right]
\]

The number of atoms in the sample, NATOM is specified in the program code, and several values (108, 256, 500 and 864) are compiled into the executable programs furnished here. Input to the program are the density \( r = N/\sigma^3 \) and the temperature \( t = kT/e \). (Typical input might be \( r = 0.01 \) and \( t = 2.0 \), corresponding to 1 atom per 100 \( \sigma^3 \) and \( T = 2.0 \ e/k \). Note that \( k \) is the Boltzmann constant, and that the Lennard-Jones \( e \) parameter is usually tabulated as \( e/k \). A suitable file of atom positions is produced prior to the actual run using the furnished executables MAKENNN.EXE.

To compare the output to a real gas (or to plan the program runs to compare to a real gas) These inputs are calculated using 6-12 parameters for the real gas.
Monte Carlo Simulation of a Lennard-Jones Fluid

This document describes the actual use of the program \texttt{f11fgNNN} to carry out a simulation of a monatomic fluid in which the atoms interact with a Lennard-Jones 6-12 potential. The algorithm is a conventional Monte Carlo simulation under conditions of constant N (number of atoms), V (volume) and T (temperature). An auxiliary program \texttt{make.exe} constructs a box in which the atoms are positioned on a face-centered cubic (close-packed) lattice; the atom positions are contained in a file \texttt{cnfile}.

The following is extracted from the source file \texttt{f11.for}, explaining the units used in the program.

\begin{verbatim}
C ** UNITS:
C ** THE PROGRAM USES LENNARD-JONES UNITS FOR USER INPUT AND
C ** OUTPUT BUT CONDUCTS THE SIMULATION IN A BOX OF UNIT LENGTH
C ** FOR EXAMPLE, FOR A BOXLENGTH L, AND LENNARD-JONES PARAMETERS
C ** EPSILON AND SIGMA, THE UNITS ARE:
C **
C ** PROPERTY     LJ UNITS         PROGRAM UNITS
C **
C ** TEMP          EPSILON/K        EPSILON/K
C ** PRES          EPSILON/SIGMA**3  EPSILON/L**3
C ** V             EPSILON          EPSILON
C ** DENS          1/SIGMA**3        1/L**3
\end{verbatim}

The current program takes input from a file \texttt{f11f.in}. The control parameters include (this is not an exhaustive list) the number NSTEP of steps taken, the temperature TEMP, the density DENS and the cutoff distance RCUT, beyond which the potential is calculated analytically. The temperature and density are input in reduced variables, such that the temperature is in units of epsilon/k, the density in atoms per sigma-cubed.

The simulation results in the energy per atom (in units of epsilon) and the pressure (in units of epsilon/sigma-cubed), plus their standard deviations, for the simulated system.

The program includes the production of a radial distribution function of atomic positions (output to file GR.OUT). Finally, there are several modifications
of the programs, with compiled executables, reflecting the possibility of using various numbers of atoms: 108, 256, 500, 864 (Note that these numbers are the numbers of atoms in 3x3x3, 4x4x4, etc, blocks of face centered cubic unit cells). Of course, the larger the number of atoms the better are the statistics but the longer the execution time. The execution time scales roughly as the square of the number. It is suggested that a reasonable compromise for student use would be the 256-atom version. In this case the maximum density allowed (with a typical 5.00 value of RCUT) is about 0.25. This limitation results from insisting that the value of RCUT is no more than ½ the box size.

The use of reduced Lennard-Jones variables means that any given run of the program applies to any Lennard-Jones fluid, but to a different real volume and temperature for each different fluid. For example, input of TEMP = 1.1 and density = 0.01 corresponds to a real temperature of 1.1 epsilon/k and a density of 0.01 atoms per sigma-cubed volume. For Argon, eps/k = 124 K and sigma = 342 pm, while for Xenon the values are 229 K and 406 pm. Thus the conditions specified correspond to

\[ 1.1 \times 124 = 136 \text{ K and } 0.01 \times \left(\frac{1}{342 \times 10^{-12}}\right)^3 = 2.500 \times 10^{26} \text{ atoms/m}^3 \]

for Argon.

Argon: 136 K and 0.415 moles/liter
Xenon: 252 K and 0.248 moles/liter

**Use of the program:**

a) select the number of atoms desired and run the appropriate make program (e.g. for 256 atoms, run make256) resulting in a cnfile.

b) edit the f11f.in file to select the desired run length (e.g. 5000 steps), temperature (e.g. 1.1) and density (e.g. 0.01). Edit the parameters which control printing frequency and cutoff distance if desired.

c) execute f11fg.exe (e.g. f11fg256.exe). If desired, the output (normally to the terminal) can be redirected to a file (e.g. f11fg256 > outfile).

d) when complete, examine the output for V/N (the energy per atom) and the pressure, both in Lennard-Jones units.
NOTE: If only small changes are made in density/temperature for a new run it is not necessary to create a new cnfile (step a).

Sample results of running fl1fg

**Objective:** To investigate the Virial equation of state

\[ \frac{pV}{RT} = 1 + Bp + Cp^2 \ldots \]

Method: Runs were carried out for several densities (0.001, 0.01, 0.02, 0.03 and 0.04, and at two temperatures, 1.3 and 1.5) for 5000 steps with $RCUT = 5.0$. The resulting values of PRESS were combined with TEMP and DENS

\[ Z = \frac{PRESS}{TEMP \times DENS} \]

and the results plotted versus PRESS. Note that this value of $Z$, just as the value $Z = \frac{pV}{RT}$ for an actual gas, approaches unity at zero pressure.

Results: The following values resulted from the runs

<table>
<thead>
<tr>
<th>DENS</th>
<th>$p$ (T=1.3)</th>
<th>$p$ (T=1.5)</th>
<th>$Z$(T=1.3)</th>
<th>$Z$(T=1.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>0.0013</td>
<td></td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>0.0126</td>
<td>0.0147</td>
<td>0.969</td>
<td>0.980</td>
</tr>
<tr>
<td>0.02</td>
<td>0.0243</td>
<td>0.0286</td>
<td>0.935</td>
<td>0.953</td>
</tr>
<tr>
<td>0.03</td>
<td>0.0352</td>
<td>0.0417</td>
<td>0.903</td>
<td>0.927</td>
</tr>
<tr>
<td>0.04</td>
<td>0.0452</td>
<td>0.0544</td>
<td>0.869</td>
<td>0.907</td>
</tr>
</tbody>
</table>

Plot $Z$ versus $p$. and fit to a linear equation $Z = 1 + Bp$.

For the data above this yields $B(T=1.3) = -2.62 (0.45)$ and $B(T=1.5) = -2.29 (0.08)$. These values must, of course, be converted from Lennard-Jones to standard units for the particular fluid being studied.
Calculations for “Crystals”

It would be possible to approximate crystal calculations by setting the density appropriate to that of the crystal and the temperature in the range of crystallinity. Several calculations over a range of densities should give a value for the energy of the stable crystal (the energy minimum), and the runs will give the radial distribution function for the crystal in the file GR.OUT. However, such a large density requires a larger value of the number of atoms in order to use a reasonable RCUT.

Study of a rather dense fluid can result in an interesting radial distribution plot. An example of the calculation follows. The structure of crystalline Argon at 40 K is face-centered cubic with unit cell edge 543 pm. The Lennard-Jones 6-12 parameters for Argon are 124 K and 342 pm. Note that the nearest neighbor distance in the crystal is 384 pm, while the 6-12 minimum distance is also calculated to be 384 pm. From the crystal data the Lennard-Jones density is calculated to be 1.00. For this particular study, however, the density was varied from 0.5 to 0.1 (RCUT = 5.5), using the 864 atom executables. The temperature was 1.0, certainly in the fluid range, not the crystal range.

The radial distribution function is shown in the plot for density = 0.2. Several neighbor distances are clearly indicated, showing that the fluid does have meaningful “neighbors”.

PLOT OF GR.OUT for density 0.2, temperature 1.0
STOPPED-FLOW KINETICS

References:
1. Atkins, 'Physical Chemistry', p 864 (brief mention only)

Summary:
Two solutions, potassium dichromate and potassium hydroxide, are mixed rapidly in the stopped-flow apparatus by injection from two syringes. Recording the intensity of transmitted light as a function of time after mixing allows determination of the rate law and rate constant of the conversion of dichromate to chromate.

Experiment and Objectives:
The measurement of rapid reaction rates is difficult or impossible using laboratory techniques which involve mixing samples followed by withdrawing and analyzing portions or reading analytical instruments, such as a spectrometer. For chemical reactions with characteristic times to completion on the order of milliseconds to seconds, the method of stopped-flow kinetics may be used.

The stopped-flow technique consists of rapidly mixing the initial reagents and recording the spectrophotometric absorption (or perhaps some other property) of one of the species during the time of the reaction. The mixing is accomplished using a special apparatus designed to accomplish the task in a very short time, and typically only a few milliliters of sample are required for each experimental run. The recording is done by following the intensity of light passing through the spectrometer and the sample. The light is detected by a photomultiplier, after which the signal is passed to a digital storage oscilloscope. After the run (total time usually less than one second) the resulting data may be presented visually and written to a file for further analysis by computer.

In this laboratory, you will study the kinetics of the following reaction:

\[ \text{Cr}_2\text{O}_7^{2-} + 2 \text{OH}^- \rightarrow 2 \text{CrO}_4^{2-} + \text{H}_2\text{O} \]  

*(1)*

*Your objective is to obtain the rate law for the reaction:*

\[ \text{Rate} = k \left[ \text{Cr}_2\text{O}_7^{2-} \right] \left[ \text{OH}^- \right]^n \]  

*(2)*

Assume first-order dependence on Cr₂O₇²⁻ (which can be checked).

Apparatus:
You will use the Applied Photophysics, Ltd. Rapid Kinetics Spectrometer Accessory. This device provides the mixing of the sample in a small spectrometer cell. A digital storage oscilloscope records the light intensity transmitted through the cell and a spectrometer. In a
separate spectrophotometer experiment, you select the appropriate wavelength for study of the reaction mixture using a Varian 50-Bio VIS-UV spectrometer.

Some discussion of these reactions appears in the Instruction Manual referenced below.

**Preparation:**
Read the Instruction Manual and examine the equipment carefully. Important modules include:

- The Rapid Kinetics Accessory. Read the Instruction manual.
- The spectrometer setup: understand the optical arrangement, the light source, the photomultiplier, and the wavelength-setting mechanism.
- The digital oscilloscope: understand its operation and the settings needed for this experiment, specifically the timescale.
- The pneumatic driver: The pneumatic driver is an optional addition to the experimental setup that provides controlled injection of the two samples. Check with the TA on its operation.

Prepare an 8mM dichromate (Cr₂O₇²⁻) solution (~0.234 g/100 mL) containing 2 mM KNO₃ so that the ionic strength of the dichromate and hydroxide solutions is the same. In general, the dichromate will be present in small amount, while the other species are in excess and remain constant during the reaction. You will have to prepare solutions of various concentrations of potassium hydroxide, ~0.2 M KOH and lower. The ideal dichromate concentration, assuming you are working at a wavelength where dichromate is the only strong absorber, would result in perhaps 50% initial absorption of the light.

All solutions should be made using de-ionized or distilled water. The injection apparatus and spectrometer cell must be rinsed carefully and thoroughly with de-ionized water prior to and after each of your finished runs to ensure proper conditions. When you have finished for the day, be sure to rinse the apparatus again with water. Do this by flowing two or three syringes of pure water through the apparatus. The equipment will be inspected for cleanliness at the end of each day, and must be clean and free of all but water.

**Preliminary testing:**
Use the UV-VIS spectrometer to measure the absorption spectrum in the 400-700nm range for the reaction mixture prior to and after reaction. To do this you create two solutions: one which simulates the reaction mixture just after it has been mixed but right before any reaction has occurred, the other simulating the mixture after the reaction has gone to completion. For dichromate measure a sample obtained by diluting your dichromate 1:1 with pure water (adjusted to proper ionic strength in the same way the original sample was). For the second solution measure a sample of dichromate plus the KOH solution (to get a comparable chromate spectrum). Determine a good wavelength for the experiment (where there is a large change between reactant and product spectra). Why is this important? Verify that the proper wavelength observed here is set on the stop-flow device. Find the molar absorptivity (ε) values at this wavelength.
Using your planned concentrations of reactants, make several runs. The purpose of this is to gain familiarity with the equipment and to ensure that you are doing the runs properly. You should be able to get two or three runs to agree with each other. If using the pneumatic device, use rather high (~4 psi) pressures on the pneumatic driver to decrease noise and improve reproducibility. If you observe a lot of noise in your signal, ask the TA for help in removing bubbles from the sample line. **DO NOT try to do this yourself as you may damage the device.**

The kinetics of the absorption is recorded using a digital oscilloscope. Be sure that the time scale and triggering are set properly in order to record the entire range of the signal change. Save the results of each run using a USB flash drive. Each "run" consists of two parts: (i) the main run observing the time-dependence of the reaction, and (ii) a second run, done immediately after (i) without pushing new samples into the cell. The second run determines the infinite-time spectral transmission of the sample, and is needed in the analysis. For the second run you need only include about 100 points. To do this run, simply activate the “single trace” mode on the storage scope and press the “force trigger” button. At this time, analyze the data obtained as far as possible in order to see what is involved in the analysis. Pay attention to the precision with which you can get results. We suggest you do the experiment up to here in one laboratory session, and then analyze the data before coming in for the next session and performing the "real" experiment.

**Production runs:**
Decide which concentrations of the solutions will work best for you, prepare the solutions, and run the experiments. For each pair of solutions, you should obtain at least two runs which agree with each other closely. Don't forget the "infinite time" sub-runs (ii) above. It is possible to see a display of the run's data immediately, so you can decide if the run is okay. Sometimes there is noise which makes the run unacceptable.

You will need to make runs with several concentrations of KOH in order to determine the dependence of the reaction rate law on [OH⁻]. It is assumed that the dependence on dichromate is first order. (Where, in your data analysis, are you able to confirm this?)

When you are done with the equipment for the day, rinse out the flow system thoroughly with deionized water by pushing a number of syringes of water through the cell, and leave the area clean.

**Analysis of the results:**
The detection method in this apparatus is by absorption of light at a single wavelength. The absorbance (A) is related to the observed light signal by

\[ A = \log_{10}(I_0/I) \]  

where \( I_0 \) is the light signal in the absence of the sample and \( I \) is with the sample present. The cell length is 1 cm.

With a single absorbing sample present, \( A = \varepsilon \cdot C \), where \( \varepsilon \) is the absorption coefficient and \( C \) the concentration (typically moles/L). When two colored materials are present, the sample
absorbance is $A = \varepsilon_1 C_1 + \varepsilon_2 C_2$. The absorption coefficients are wavelength-dependent. In this experiment, we choose a wavelength where the difference between $\varepsilon_1$ and $\varepsilon_2$ is large in order to observe changes in concentration with time via changes in the total absorbance, $A$.

**Preliminary questions:**
You should answer these questions before you do the production runs. There is no reason in fact why you shouldn't be able to answer them before even the preparation work.

1. Sketch a plot of how the concentrations of dichromate and chromate should change with time, first order in dichromate with an effective first order rate constant of 10 s$^{-1}$.

2. Based on the previous question, sketch a hypothetical absorbance versus time plot assuming the spectrometer "sees" only absorbance due to chromate ion. As during the experiments, both the chromium species are present, with $\varepsilon$ for dichromate significantly larger than for chromate.

3. Based on the previous question, sketch a hypothetical yet realistic plot of light intensity versus time.

**Details of data and processing:**
Based on Eq. 3 and Beer’s law for the present reaction involving two absorbing species, absorption can be related to the concentration as a function of time. Assuming a cell path length of 1cm, Eq. 3 can be rewritten as follows:

$$A = \log_{10}(I_0/I) = \varepsilon_2 c(t) + 2 \varepsilon_1 (c_0 - c(t))$$

where at time $t = \infty$,

$$A = \log_{10}[I_0/I(t=\infty)] = 2 \varepsilon_1 c_0$$

(5)

Taking the difference between $\log_{10}[I_0/I(t)]$ at $t$ and $\log_{10}[I_0/I(t=\infty)]$ at infinite time we obtain

$$\log_{10}[I(t=\infty)/I(t)] = c(t)[\varepsilon_2 - 2 \varepsilon_1]$$

(6)

and thus,

$$c(t) = \log_{10}[I(t=\infty)/I(t)] / (\varepsilon_2 - 2 \varepsilon_1)$$

(7)

Therefore, the log of $I(t=\infty)/I(t)$ is proportional to $c(t)$. Assuming the reaction is pseudo first order (i.e. first order in dichromate at constant hydroxide),

$$c(t) = c_0 e^{k t}$$

(8)

Thus, a plot of the natural log of $c(t)$ as a function of $t$ should be a straight line whose slope is related to the pseudo first order rate constant. However, it should be noted that in order to obtain the rate constant using Eq. 8, care must be taken with evaluating log of data points. Therefore, a suggested and more appropriate method of determining the rate constant can be achieved by a
non-linear fit of the data itself using equation 8 in Origin. Compare the differences between
these methods.
LASER-INDUCED FLUORESCENCE QUENCHING

References:
1. Albery & Silbey "Physical Chemistry" Ch 14.8, 19.7
3. Halpern "Experimental Physical Chemistry"

Summary:
Laser light pulses from a nitrogen laser are used to excite fluorescence from the uranyl ion. The fluorescence decay is recorded using a digital storage oscilloscope. The fluorescence lifetime is measured as is the rate constant for quenching of the fluorescence by chloride ion.

Equipment:
A nitrogen laser produces pulses of 337 nm light lasting a few nanoseconds at a rate of roughly 10Hz. These pulses of light are passed into a cell containing the uranyl ion (uranyl nitrate) in phosphoric acid. The uranyl ion absorbs the light, is excited, and subsequently re-emits the light as blue-green fluorescence. A photodiode detector, oriented at right angles to the incident light beam, detects the fluorescence, which decays over a time on the order of tens of microseconds.

The signal from the photodiode is connected so as to display it on the digital storage oscilloscope. The signal from a single pulse of the nitrogen laser is observed and stored in a file. The fluorescence from several laser pulses should be accumulated using the digital oscilloscope to increase the signal-to-noise ratio (S/N). The data may be transferred via a USB flash memory to a computer and processed when convenient for the lifetime of the decay.

Additional samples of the uranyl ion, containing different concentrations of chloride ion, are also studied, and a change in the fluorescence lifetime is observed. Application of Stern-Vollmer theory to the results yields the rate constant for fluorescence quenching by chloride ion.

Precautions:
Laser light can damage your eyes! The laser system is meant to be covered when in use. The laser beam, which is NOT visible, can reflect off surfaces and enter your eyes leading to tissue damage and blindness.

The uranyl ion is radioactive. Normal use and exposure to this material in the context of this experiment poses no hazard. However, be cautious when pipeting, handling and disposing of the uranium salt and solutions. Wash your hands after handling this material!

Procedure:
Prepare a stock solution which is 40 mM uranyl nitrate hexahydrate (UO₂(NO₃)₂·6H₂O) and 1 M H₃PO₄. About 25 mL is required. Also prepare a stock solution of 40 mM hydrochloric acid with 1 M H₃PO₄. Use deionized water to be sure there is no chloride ion (or other quencher) in the solvent. Prepare five solutions (about 5 mL of each) which are 20 mM in uranyl ion and 0, 2, 5, 10 and 20 mM in chloride ion. Flush the solutions with a stream of nitrogen gas bubbles to remove oxygen, which is a very efficient quencher, just before filling the cell.
Three or four milliliters of each solution are put in a clean UV-transmitting fluorescence cell. Start with the 0 M Cl\(^-\) solution (so there is less chance of leftover Cl\(^-\) in the following experiment), and work up in concentration. Adjust the cell and/or detector position for maximum fluorescence by observing the oscilloscope trace. Once the signal is adequate, record the fluorescence. Each trace is transferred from the storage scope to a file on a USB memory. Be sure to record all the experimental conditions in your notebook for each stored trace.

The sequence of measurements should be repeated at least once to obtain an idea of the reproducibility of the measurements.

**Analysis and Results:**

In order to analyze the data, import it into a spreadsheet. One column can represent the time and another column can be used for each concentration of chloride.

The signal will in general consist of an exponentially-decaying fluorescence plus a constant background (zero light) signal, B:

\[
S(t) = I_0 \exp(-kt) + B
\]

The parameters: \(I_0\), \(k_f\), and \(B\) can be obtained by a nonlinear fitting of the results to Eq. 1 using, for example, Origin. Benefits from this approach are: (a) there is no problem with points going negative (and thus destroying the log calculation), (b) the noise inherent in the process is not falsely presented (as it is in a log plot), and (c) there is a certain satisfaction in seeing the fit to the actual data, rather than to a log plot of modified data. However, it is easier to see the confirmation of a single exponential decay in the log plot (which should give a straight line).

Therefore, the linear regression technique can also be used. In this case you should first determine \(B\) by looking at the pre-laser pulse value of \(S(t)\). Then take the logarithm of \([S(t) - B]\) and obtain \(k_f\) and \(I_0\) using a fit to a linear equation. You will have to be careful that the \([S(t) - B]\) data column does not contain any negative numbers, which will cause an error when you take the logarithm. Two procedures are useful:

(a) **Smoothing the data:** Each point is made to be the average of a number (say 9) of points; i.e. point \(N\) is the average of points from \(N - 4\) to \(N + 4\). The spreadsheet will do this easily. Note that this smoothing makes the first four points and the last four points of the data meaningless. However, since you have a large number of points this loss is not significant.

(b) **Truncating the data set:** After a certain time the signal has decayed down into the noise. Simply cut off the data just before you run into trouble, i.e. before the first negative \([S(t) - B]\) point. You may also wish to discard a number of data points at the beginning of the run, due to noise associated with the laser pulse; similarly truncate the data before \(t = 0\).

When \(k_f\) for each of the experiments has been obtained, a Stern-Volmer plot

\[
k_f = k_i + k_0 [\text{Cl}^-]
\]
will yield the value of the quenching rate constant $k_Q$. The value of $k_i$ should be the value of the fluorescence decay rate constant in the absence of Cl$^-$. Your report should include a table of results of $k_f$ versus [Cl$^-$] and values of $k_i$ and $k_Q$. Each result should be shown with a standard deviation (or some other measure of the precision obtained). Compare these with literature values.

**Preliminary Questions and Exercises:**

1. Draw schematic of the energy levels of the uranyl ion involved in the experiment and indicate excitation, fluorescence, and quenching processes.

2. The digital scope allows accumulation of a number of fluorescence events (laser shots) to give a bigger signal than is available from a single shot. How does this affect the signal-to-noise ratio?

3. What sort of signal would you observe if you tracked the fluorescence from some material which had a very short lifetime? (Note: this signal depends on the capabilities of the detector and storage scope as well as the electronics of the system.) You might try exposing the detector to fluorescence from a piece of high-quality paper (stationery), whitened with agents which have such short fluorescence lifetimes.

4. Bromide and iodide ions also quench uranyl fluorescence. Try to measure the rate constant for quenching by Br$^-$ ion if you have time. If you do this, use Br$^-$ concentrations about one tenth those used for Cl$^-$. 
GAS ADSORPTION ON SURFACES

References:
1. Albery & Silbey "Physical Chemistry" Ch 24.1-3;
2. Atkins "Physical Chemistry" Ch 28.10-11

Summary:
The adsorption of N₂ gas on powdered silica or charcoal is studied at liquid nitrogen temperature, and the results obtained are used in connection with BET theory to determine the surface area of the solid sample.

Vacuum Apparatus:
The vacuum system should be designed and assembled out of standard stainless steel KF (Klein flange, also called Quick flange) pieces and valves. The system is pumped using a mechanical vacuum pump. A thermocouple pressure gauge is used to test for good (less than one millitorr residual pressure) vacuum in the system to ensure the absence of leaks. In the absence of leaks, after the system is pumped for about 10 minutes, the pressure should not rise above one millitorr when closed off from the pump.

The same vacuum system is also used to apply known amounts of N₂ gas onto the solid. When nitrogen gas is introduced into the system, its pressure is measured using a Barytron pressure sensor and digital readout. The amount of gas adsorbed on the sample is determined using the ideal gas law, knowing the changes in pressure observed at a known volume. The Barytron is very sensitive and expensive; it is imperative that all changes in pressure occur gently, so as to prevent undue shock to the pressure sensors. Use pressures below atmospheric, since overpressure can damage the Barytron manometer as well as vacuum valves.

NOTE: Show the assembled apparatus to the TA before pumping.

Procedure:
(1) Startup: Turn the floor pump on. The thermocouple gauge should soon show a pressure on the order of a few millitorr. Open the valve to the Barytron pressure sensor gradually, and watch the Barytron readout to see that the pressure drops to zero. Actually, the gauge will probably read a small value (either above or below zero, depending on the temperature of the room) which you should record as a zero-point for your measurements. This check should be repeated often during your work, as room temperature can change. If you accidentally change the temperature of the sensor (by touching it or via hot air from the heat-gun) it may change its base reading.

Admit some N₂ gas from the inert gas line (talk with a TA about how to do this!). Using the Barytron for pressure measurement, and a known standard volume, determine the volumes of other portions of the vacuum system by expanding gas samples from one volume to another in conjunction with the ideal gas law. Repeat this measurement until you're sure you have good values for pertinent volumes in the apparatus you have constructed. At this point you should be familiar with the vacuum system, including handling N₂ gas samples and measuring pressures. Ask yourself, 'How accurately do I know the volumes I've measured?'
(2) Sample: Powdered silica is available in the desiccators (charcoal may also be used); return the main sample to the desiccators after you have taken some. About 0.5-1.0 gram is the appropriate amount. The sample may be weighed directly in the sample tube. Be sure to clean the sample tube standard joint before putting the sample in the tube.

Attach the sample tube with sample to your vacuum system. Evacuate the sample tube and heat gently with the hot-air blower to allow the sample to de-gas. Be careful not to heat too much or you will lose powder in the vacuum line, affecting your results. In addition, excessive heating may damage the rubber O-rings and metal gaskets, so be careful. This heating under vacuum is continued until no more gas comes off the sample (as evidenced by no pressure rise in the system when it is cut off from the vacuum line). Next, the volume of the sample tube is measured, again by expanding known pressures of nitrogen gas from the main bulb, measuring the pressure changes, and using the ideal gas law. This is all done at room temperature, because it is assumed that no nitrogen adsorbs on the sample at room temperature.

(3) Measurements: The evacuated sample tube is now cooled to liquid nitrogen temperature by immersion into a small Dewar vessel containing N₂ liquid. Use the laboratory barometer to measure the atmospheric pressure, as this controls the temperature of the boiling nitrogen and thus is the same as the vapor pressure of liquid nitrogen, p₀, needed in the calculations.

You are now ready to do the measurements. A run consists of a series of steps. For each step, the basic idea is that a volume, Vₐ, contains nitrogen at some pressure with the sample tube, Vₛ, closed off. Then the sample tube is opened to Vₐ and the system is allowed to equilibrate. When the final equilibrium pressure has been reached, it is recorded. The amount of gas adsorbed in this step is determined by the pressure drop and the volume of Vₐ, while the equilibrium pressure is the one recorded. For the first step the pressure in Vₐ before opening Vₛ is low. For the next step it is higher. Nitrogen gas is added to Vₐ at each step.

Note that the total amount of gas actually adsorbed on the sample after each step includes that from all previous steps since the beginning of the run. Remember that you are using the ideal gas law to determine the amount (number of moles) of nitrogen moved around the system, so you must also know room temperature in order to do any calculations (the temperature of all but the sample tube). Measure the temperature occasionally and record it as you record the other data.

It is important to understand the method of accounting for the aliquots of N₂ gas added and for the amounts adsorbed in order to perform the final calculations correctly. In particular, remember that the pressure drop measured in each step is partially due to adsorption and partially due to expansion from Vₐ into the combined volume Vₐ+Vₛ.

When starting, try an initial pressure in Vₐ of about 20 Torr, and then make decisions about additions which will give you a good spacing of equilibrium pressures. Your decisions here will strongly affect your results! Remember that the theory is useful only for a region of equilibration pressure from about 5% to 35% of the vapor pressure of N₂, p₀.
You should make two runs, starting with de-gassed samples, in order to obtain adequate data and to judge the reproducibility of the measurements.

**Calculations:**
Calculate the volumes adsorbed (at STP) at each equilibrium pressure (p), and plot against x (= p/p₀) (where p₀ is the vapor pressure of liquid nitrogen, equal to atmospheric pressure). Subsequent calculations, plots and so forth, are described in the references for use of BET theory.

**Preliminary Questions:**
1. What shape do you expect the curve of adsorbed volume versus pressure to have?
2. What is the order of magnitude of the surface area per gram of solid silica?
3. Suppose that atmospheric pressure is 750 Torr. What is the temperature of the liquid nitrogen in the little Dewar vessel and what is the vapor pressure of nitrogen at that temperature?