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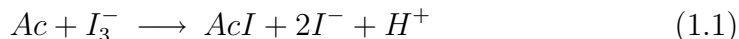MEADOW ANDERSON

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Contents

Part I
Kinetics and Thermodynamics

1 Reaction Kinetics of Iodine with Ketone

Introduction: In this experiment we investigate the kinetics of the iodination of acetone. The overall reaction is as follows, with Ac representing acetone

$$Ac + I_3^- \longrightarrow AcI + 2I^- + H^+ \tag{1.1}$$

Some general information about reaction 1.1 is known. The reaction of acetone with iodine in dilute aqueous solution is very slow in neutral solutions, but becomes appreciably faster in the presence of a strong acid. Neutral salts of strong acids do not increase the rate of reaction. A weak acid (such as acetic) increases the rate of iodination less than does a strong mineral acid such as HCl. This suggests that H^+ is involved in the kinetics; hence we propose a rate law of the form

$$-\frac{d}{dt}[I_3^-] = k[H^+]^a[Ac]^b[I_3^-]^c \tag{1.2}$$

where $k(T)$, a, b, and c are to be determined experimentally.

1.1 Theory

The kinetic technique of "swamping" or "isolation" can be used to simplify interpretation of the data. Suppose a reaction solution is prepared in which the initial concentration of I_3^- is much smaller than the initial concentrations of H^+ and Ac. During the course of the reaction, I_3^- and Ac are consumed, and H^+ is formed according to equation 1.1. Because of the large initial concentrations of H^+ and Ac, their concentrations do not change appreciably, while the concentration of I_3^- does change considerably. In other words, $[H^+]$ and $[Ac]$ are effectively constant during the reaction. In this case, equation 1.2 can be simplified to

$$-\frac{d}{dt}[I_3^-] = k'[I_3^-]^c \tag{1.3}$$

where

$$k' = k[H^+]_0^a[Ac]_0^b \tag{1.4}$$

This equation can then be integrated directly for a particular choice of c, giving the following possibilities:

$$\boxed{c=0} \qquad [I_3^-]_0 - [I_3^-] = k't \qquad (1.5)$$

$$\boxed{c=1} \qquad \ln[I_3^-]_0 - \ln[I_3^-] = k't \qquad (1.6)$$

$$\boxed{c=2} \qquad \frac{1}{[I_3^-]} - \frac{1}{[I_3^-]_0} = k't \qquad (1.7)$$

Plots of various functions of $[I_3^-]$ vs. t will indicate which of the above equations is valid, thus establishing c.

Suppose that the reaction is now carried out with a different initial concentration of H^+ (still large enough to satisfy the swamping requirements) and the same concentration of Ac. The data from this kinetics run will confirm the evaluation of c from the first results, but a different value for the apparent rate constant will be obtained. The values for the rate constant for the two different initial solutions are denoted by k_1' and k_2'. They are related by

$$\frac{k_1'}{k_2'} = \frac{k[H^+]_{0,1}^a[Ac]_0^b}{k[H^+]_{0,2}^a[Ac]_0^b} = \left(\frac{[H^+]_{0,1}}{[H^+]_{0,2}}\right)^a \qquad (1.8)$$

Here $[H^+]_{0,1}$ is the initial concentration of H^+ in solution 1, etc. Hence, the two values k_1' and k_2' plus the known initial concentrations of H^+ allow the determination of a. Similarly, variation of $[Ac]_0$ allows the determination of b. It is necessary to vary the initial concentrations by at least a factor of two to adequately characterize the exponents.

Of the species mentioned thus far, only I_3^-(aq) absorbs visible light, so it is convenient to follow reaction progress by using a spectrophotometer to monitor the disappearance of I_3^-. There is, however, a minor complication: I_3^- is involved in the following equilibrium:

$$I_3^- \rightleftharpoons I^- + I_2 \qquad (1.9)$$

with $K_{eq} \sim 1.4 \times 10^{-3}$ (Ref. 2). I_2 both absorbs visible light an acts as an effective iodinating agent. Hence reaction rate and the amount of light

absorbed by a given solution of I_3^- depend not only on the concentration of I_3^-, but on the concentration of I_2 as well. Using Beer's Law ($A = \epsilon \ell c$), the total absorbance of a solution containing both I_3^- and I_2 may be expressed as the sum of the individual absorbances.:

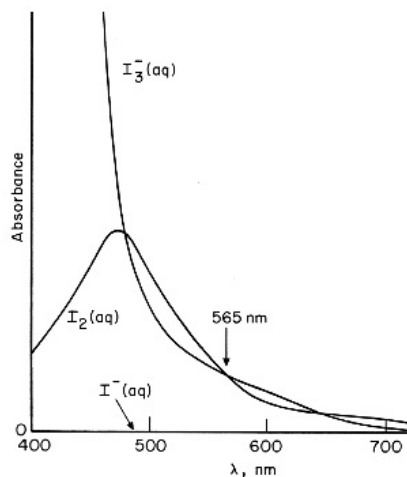$$A = \epsilon_{I_2} \ell [I_2] + \epsilon_{I_3^-} \ell [I_3^-] \tag{1.10}$$

Figure 1: Visible absorption spectrum of I_2 and I_3^-

The molar absorptivities, ϵI_2 and ϵI_3^-, are functions of the wavelength of light being absorbed, as indicated in Figure 1. While in general there is no relation between ϵI_2 and ϵI_3^-, note in particular the relationship which exists at $\lambda = 565$ nm. This is called an *isosbestic point*. Since the two molar absorptivites are equal at 565 nm, the absorbance of a solution of I_2 and I_3^- is

$$A = \epsilon_{I_3^-} \ell [I_2] + \epsilon_{I_3^-} \ell [I_3^-] = \epsilon_{I_3^-} \ell ([I_2] + [I_3^-]) \tag{1.11}$$

That is, the absorbance at this particular wavelength is proportional to the sum of the concentrations of I_2 and I_3^-. Consequently, we can monitor the total concentration of the iodinating agents (assumed to be I_3^- for simplicity of notation) in a solution by following the absorption at 565 nm, provided ϵ has been determined for this wavelength.

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The rates constants in the above analysis are constant with respect to concentration, but they vary with temperature, as indicated by the *Arrhenius equation*"

$$k = Ae^{-E_a/RT} \tag{1.12}$$

where A is constant related to the geometry of the molecules involved in the reaction and E_a is the activation energy. Both values can be determined if k is measured at several temperatures. Data analysis typically includes plotting $\ln(k)$ vs. $1/T$, so that the slope and intercept readily provide the desired values.

1.2   Experimental

The following solutions should be <u>carefully prepared using volumetric glassware</u>:

1. 25 mL of 0.047 M I_3^- (0.047 M in I_2 and 0.47 M in KI) **note 10-fold excess of KI**

2. 100 mL containing 7.0 mL of reagent grade acetone (calculate resulting molarity)

3. 100 mL of 1.0 M HCl

Keep solutions stoppered to avoid evaporation. All waste should go in the marked container in the hood.

A minimum of five kinetic runs is necessary for determination of the rate law and the temperature dependence. The rate law is typically determined at 25^oC. Select the set of reaction conditions with the smallest absorbance change for the additional kinetic runs at 30^oC and 35^oC.

Possible reaction mixture:

1. 10.0 mL acetone solution,

2. 5.0 mL 1.0 M HCl,

3. 8.0 mL water,

to which 2.0 mL of I_3^- solution will be added at $t = 0$ Record the delay before the initial spectrometer reading using a timer. (Note the initial concentrations; to what extent is the swamping satisfied?)

Possible procedure:

1. Carefully make up a reaction solution of the appropriate amounts of H^+ and Ac in a 25 mL volumetric flask, and add any water necessary. Equilibrate this solution and the stoppered I_3^- solution in a water bath maintained at the desired temperature.

2. Use the instructions given in the appendix at the end of this lab to prepare the spectrometer for data collection.

   When everything is ready, transfer the appropriate amount of the I_3^- solution to the reaction tube, and start a timer. Mix the solution vigorously. Transfer a small amount of the reaction mixture to the cuvette to rinse it out, then fill the cuvette with a fresh sample of the reaction mixture, and immediately begin data acquisition with the "Execute" button. Stop the timer when data acquisition begins.

3. To determine the molar absortivity ϵ of the iodine solution, use absorbance values for at least *three* solutions of known concentration. Standard solutions should have A_{565nm} between 0.1 and 1.5. Data collection is accomplished using the same general procedure as for the kinetic measurements but the delay time, integration time and end time can be adjusted.

1.3 Data Analysis

1. Determine the molar absortivity of the I_3^-/I_2 mixture by constructing a Beers Law plot with the data from your standards.

2. Use your ϵ to convert A to $[I_3^-]$ for each run.

3. Determine the reaction order with respect to $[I_3^-]$ using your best data set and plotting integrated equations for $c = 0, 1$, or 2. Running regression analysis and plotting residuals may help.

4. Obtain k' for each run.

5. Determine k, a, b, and c for the reaction.

6. Obtain the Arrhenius parameters by plotting $\ln(k)$ vs. $1/T$.

1.4 Discussion

1. There are two other isosbestic points in Figure 1. Why is 565 nm chosen for analysis?

2. A proposed mechanism for this reaction is given in figure 2. Using the notation presented there, derive an expression for the overall rate law. What assumptions must be made for it to match your experimentally determined rate law?
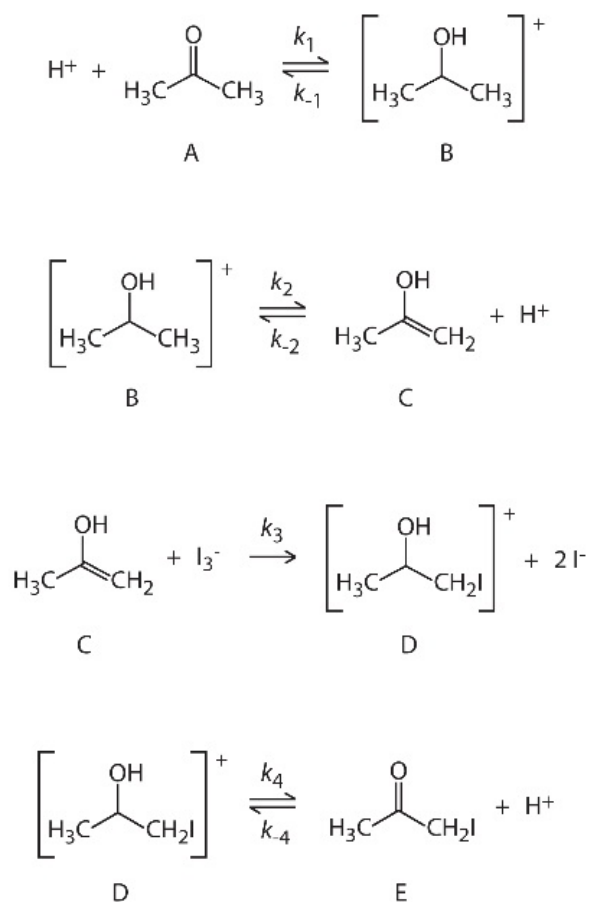

Figure 2: Proposed mechanism for acid-catalyzed iodination of acetone

3. Does the activation energy seem consistent with the proposed mecha-

nism?

4. How do your data compare with literature values?

5. In this experiment, we have made the assumption that I_3^- and I_2 have equal reactivity for ketone iodination. Is this valid?

6. Is the disappearance of I_3^- a good indicator of the overall reaction rate?

References

1. Birke, and Walters, *J. Chem. Ed.* 69, 585, July 1992

2. Jones and Koplan, *J. Am. Chem. Soc.* 50, 1845, 1928

3. Rice and Kilpatrick, *J. Am. Chem. Soc.* 45, 1401, 1923

4. McQuarrie and Simon. "Physical Chemistry," University Science Books (1997)

1.5   Appendix

HP-8450 Kinetics Measurement: **Bold** refers to keys on spectrometer. There is no space bar. Skipping steps is not recommended.

1. Turn on spectrometer and plotter.
   Put paper in plotter and select pen (left or right).

2. Wait until screen displays:
   ready

3. Turn on temperature controller.
   Select sample A, then dial in the desired temperature.

4. Initialize Printer: (press following buttons)
   Device 2 "IP1200,1300,10000,7000"
   Execute

5. Background absorbance correction:
   Fill both cells with distilled water and place in positions 3 and 4
   Measure 3 Balance Execute

6. Place sample cell in position 3, reference cell in position 4.

7. Kinetics measurement:
   Measure 3 Absorbance λ 564 Time <u>30,2,0</u> To <u>1000</u>
   Execute
   (Note: underlined values should be adjusted as necessary. The first
   set are: delay between measurements, integration time, and start time.
   The last number is the end time. All times are in seconds.)

8. Wait for scan to finish. Rescale display as needed:
   Y-scale 0 To 0.4 Execute
   (again, underlined values should be adjusted as necessary.)

9. Save and Recall spectra:
   Display To Standard 10 Execute
   (any number 1-99 can be useduse a unique number for each scan)
   Standard 10 To Display Execute
   (recalls your spectrum saved as 10)

10. Plotting:
    Plot Display Execute
    Plot "Title" Execute

11. Print. Place pen inside the plotting frame using the arrow keys on the
    printer
    Print Time 0 to 1000 Execute
    (prints out the data collected between "0" seconds and "1000" seconds)

12. Turn off temperature controller, plotter, spectrometer, and water bath.

1 Fluorescence Quenching in Gaseous I$_2$

1.1 Theory

When a molecule absorbs radiation it is promoted to a state of higher energy. Depending on the excitation energy, different energy levels of an excited electronic state are populated. This energy can be lost either through radiation or degraded into heat by radiationless transitions. The light which is given off is called fluorescence, and some systems produce a great deal of fluorescence and others produce none at all. Fluorescence is very useful and in the common fluorescence light bulb a specially prepared solid on the inside of the bulb is irradiated with ultraviolet light from a mercury discharge and this solid fluoresces giving a nearly white light. In this case, the fluorescence is at a longer wavelength than is the exciting radiation. This is also observed in most simple molecular systems. It can be easily explained from the Franck Condon principle when the excited and ground electronic states have different equilibrium bond distances as is true for the gaseous I$_2$ which we will study

A second type of light is sometimes observed to come from irradiated materials. This light can sometimes be seen to persist for a while even after the radiation is turned off or when the sample is quickly removed from the source of irradiation. This light comes from electronic states which are very different from the ones first populated and they can trap the energy and only slowly give off light. These electronic states are lower in energy than the ones giving fluorescence and have the ability to store energy for perhaps several seconds. The light that they give off is called phosphorescence, in honor of phosphorous which can give off light as it reacts with oxygen. Any phosphorescence is at an even longer wavelength than is fluorescence and must involve rather special excited electronic states such as those with unpaired electrons. It is common in mineral exhibits to irradiate the minerals with ultraviolet, or "black" light, to show fluorescence and then to turn off this light to show the longer lived phosphorescence which some minerals can produce. Both fluorescence and phosphorescence are used in biological work and most physical and biophysical texts discuss this field and have figures which show fluorescence spectra and typical energy level patterns.

In the early studies of fluorescence it was discovered that the fluorescence intensity could be decreased or quenched by the presence of certain foreign molecules. This quenching of fluorescence intensity is expressed by the Stern Volmer equation which has a term linear in the concentration of the quencher. In most cases the quencher could be visualized as stealing the excited state energy from the fluorescing molecules and losing this energy in radiationless transitions. In self quenching, collisions between ground state and excited state molecules accomplish this same loss of fluorescence intensity. These early studies involved continuous radiation and they measured the loss in the intensity of the fluorescence. With pulsed lasers it is possible to follow the time decay of the fluorescence after the excited states are produced. This is particularly convenient in studies of self quenching for one does not need to measure the amount of radiation absorbed by the fluorescing molecules as its concentration is changed.

After absorption of a photon takes place in our apparatus the excited iodine molecules (I_2^*) will lose energy and return to the electronic ground state. One of the processes by which the energy can be lost is re radiation of light either at the same wavelength as the original exciting radiation or more probably at longer wavelengths. Another way in which the excited iodine can lose energy is through collisions with other I_2 molecules. This nonradiative energy loss is referred to as collisional self quenching. Self quenching cross sections can be calculated to determine the effectiveness of collisions in the depopulation of the excited states. While both fluorescence and quenching contribute to the depopulation of excited states, collisional self quenching is strongly pressure dependent since the likelihood of a collision of I_2 with I_2^* is directly proportional to the iodine pressure. Thus the pressure dependence of the fluorescence decay times can be used to distinguish between the natural and pressure induced depopulations.

The spectral bandwidth of the monochromatic source determines whether one or more levels of the excited electronic states are preferentially excited. In the case of a heavy molecule like I_2 it is unlikely that the light is sufficiently monochromatic to distinguish between rotational states, but it is not too difficult to distinguish between vibrational states. If a laser is used as the source of monochromatic radiation the technique is known as laser induced fluorescence.

The absorption spectrum of iodine is discussed in Shoemaker and Garland, and it can be seen that discrete absorption occurs 640 and 495 nm. This absorption corresponds to transitions between the ground state ($^1\Sigma_g^+$) and the first excited state ($^3\Pi_u^+$). Fluorescence from selected vibrationally excited states can be obtained by exciting iodine with monochromatic light of different wavelengths in the 640 to 495 nm. range. The lifetime of the fluorescence process will depend both on the excitation wavelength and the pressure of iodine in the cell. The wavelength dependence is due to the different transition probabilities between the various excited and ground vibrational states, and the pressure dependence is a consequence of the collisional self quenching. Since the depopulation rate of the excited state is due to both a radiative decay rate and a self quenching decay rate, the kinetic theory form of the Stern Volmer equation

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \alpha P \tag{1.1}$$

where

$$\alpha = 4\sigma^2 \sqrt{\frac{\pi}{mk_BT}} \tag{1.2}$$

can be used to calculate both the natural lifetime and the self quenching cross section. The effective lifetime τ, is the time it takes the fluorescence intensity to drop by a factor of $1/e$. A plot of the inverse of the effective lifetime versus iodine pressure can be fitted to a straight line. The natural lifetime, τ_0 can be obtained by extrapolating the line to zero pressure. This lifetime, in the absence of molecular collisions, is a measure of the transition probabilities between vibrational states. The self quenching, impact distance σ can be related to the slope of the Stern Volmer plot (see figure 3). The self quenching impact distance is the apparent sum of the radii of I_2 and I_2^* in collisions depopulating the excited state.

1.2 Experimental

The experimental set up for the determination of the radiative lifetime in electronically excited I_2 by laser induced fluorescence consists of the following parts:
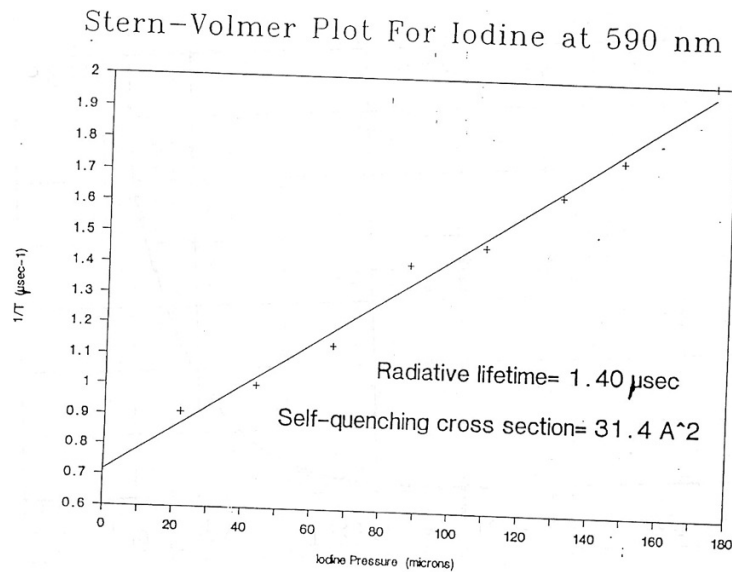
1. pulsed tunable laser source,

Figure 3: Stern-Volmer plot

2. high vacuum line,

3. evacuated fluorescence cell,

4. photomultiplier tube,

5. digital storage oscilloscope.

The vacuum line consists of a mechanical pump and a diffusion pump separated from the fluorescence cell by a liquid nitrogen cooled trap and its purpose is to evacuate the fluorescence cell. A capacitance diaphragm gauge (CDG) measures the pressure in the cell. The iodine trapped within the cell is excited by a single pass of the laser light. The fluorescence is passed through an optical filter and amplified by the photomultiplier tube. The fluorescence signal can be directly recorded using the digital oscilloscope and from this signal the effective fluorescence lifetime determined.

Figure 4 shows a diagram of the laser induced fluorescence experimental set up. It is important that you become acquainted with the different components, especially with the vacuum line and the different valves.
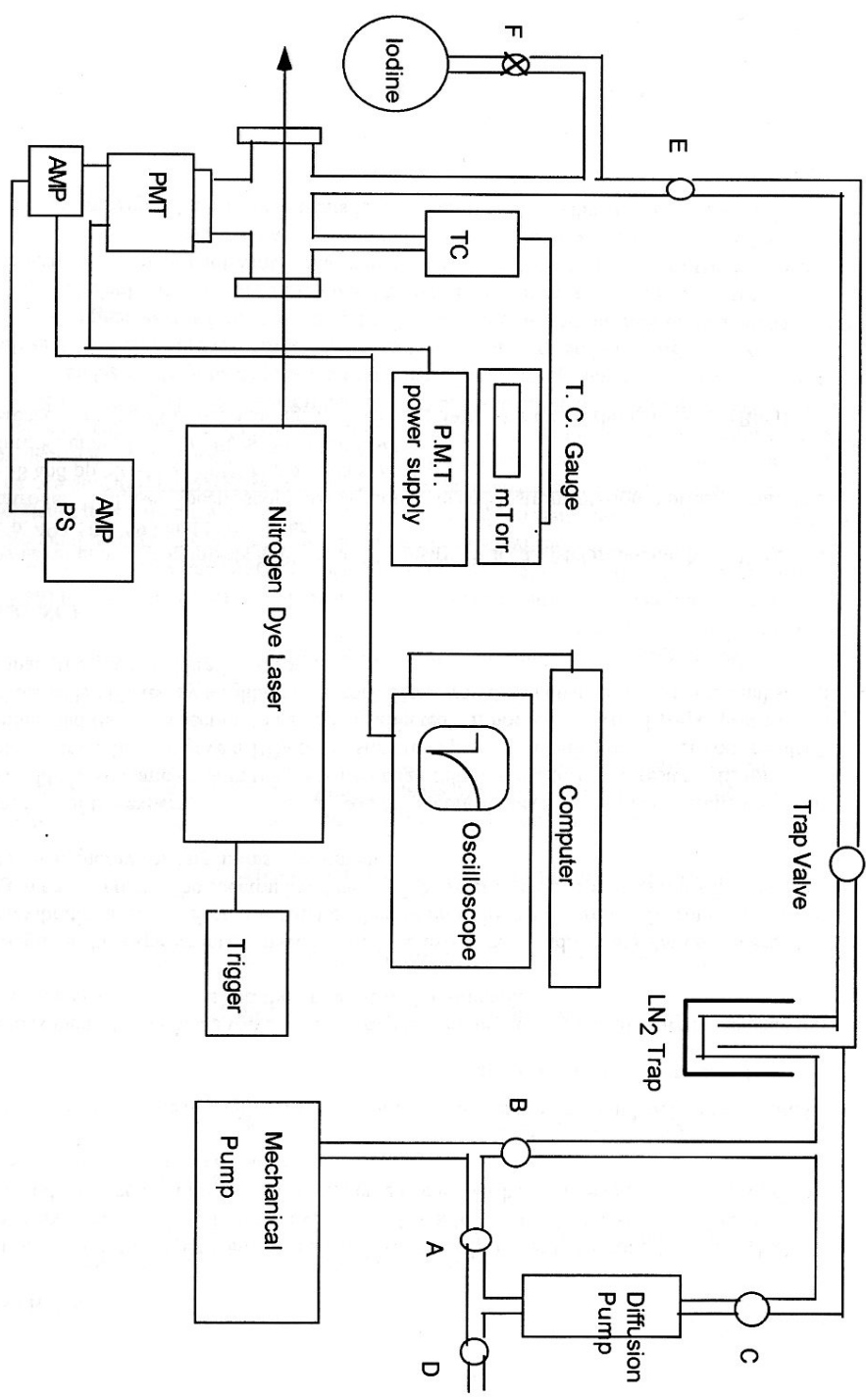
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Figure 4: Experimental layout

The "backing" valve (A) connects the mechanical pump to the diffusion pump (DP) foreline. This valve must remain open as long as the DP is being used to pump out any part of the system. The "roughing" valve (B) is used to bypass the diffusion pump until the pressure in the vacuum line is low enough for the DP to operate. Note that roughing and backing are two operations which cannot be carried out simultaneously. That is valve B must be closed before opening valve A. The "DP Isolation" valve (C) connects the throat of the DP to the vacuum line. If the DP is hot valve C should only be opened once the pressure in the vacuum line has dropped below 100 microns. The "vent" valve (D) is used to vent the liquid nitrogen trap at the end of the experiment. Before opening valve D make sure that valve C is closed to avoid venting the hot diffusion pump. The "pumping" valve (E) connects the vacuum pumps to the fluorescence cell. Finally the "reservoir" valve (F) connects the iodine reservoir to the cell.

Pump Down Procedure: SAFETY: if you have not had experience handling liquid nitrogen please seek help from a GSI before handling it. A cloth handling glove is provided, make sure you are farmiliar with harzards of cryogenic liquids.

1. With all valves closed, turn the mechanical pump on (skip steps 1 and 2 if the mechanical pump is already running).

2. Open valves B, C, E and the LN2 trap valve. Wait for quiet mechanical pump operation. If the pump doesn't quiet, or emits a lot of vapor, call the storeroom or the GSI.

3. Place a Dewar on the trap and fill slowly with liquid nitrogen.

4. Plug in the pressure gauge (power bar).

5. With the LN_2 valve and valve E open, the cell will pump out to about 100 mTorr, or less, in a few minutes.

6. Open the "reservoir" valve (F) to ensure that air has not been trapped in it, and then quickly close it again.

7. Turn "on" the diffusion pump switch box. Note that the diffusion pump cannot be turned "on" until the water valve and drain are open. This is to insure that the diffusion pump is never run without cooling

water. You may also need to flick the latch on the switch box if the red light(switch box) does not come on. Then close valve B and open valve A so the diffusion pump can operate.

8. The DP should warm up in 10 min and reach its full pumping speed. Within 30 minutes of turning on the DP the pressure gauge should read < 30 mTorr.

9. After the pressure has stabilized, briefly open valve F again to remove residual air. Close it and wait to return to the original pressure. Repeat this process twice.

TABLE III

HEAT OF SUBLIMATION AND VAPOR PRESSURE OF IODINE

T, °K.	Inter. mm.		ΔH_s from	Cal. mole⁻¹ ΔH_{T}	Ref.
	$P_{expt.}$	$P_{calc.}$	$P_{expt.}$	calcd.	
273.15	0.030	0.03051	15667	15025	7
288.15	.131	.1286	15647	14964	7
298.15	.305	.3080	15664	14922	7
303.15	.469	.4669	15655	14901	7
308.15	.699	.6971	15656	14880	7
313.15	1.025	1.028	15659	14858	7
318.15	1.498	1.494	15657	14836	7
323.15	2.154	2.147	15656	14814	7
323.15	2.154	2.147	15656	14814	8
328.15	3.084	3.052	15651	14791	7
328.15	3.069	3.052	15654	14791	8
333.15	4.285	4.293	15659	14768	8
338.15	5.962	5.969	15658	14744	8
343.15	8.196	8.216	15659	14720	8
348.15	11.21	11.22	15656	14696	8
353.15	15.09	15.15	15659	14672	8
358.15	20.21	20.28	15660	14647	8
363.15	26.78	26.95	15663	14619	8
368.15	35.24	35.52	15663	14575	8

Av. 15658 ± 3

Figure 5: Table for determination of iodine vapor pressure

Thermocouple Gauge Calibration: The thermocouple gauge measures pressure by measuring thermal conductivity through a gas. A small current is run through a wire which is placed near a thermocouple junction. The current heats up the wire and heat is transferred to the thermocouple through collisions between gas molecules. The higher the pressure of the gas present, the more effective the heat transfer to the thermocouple. The thermocouple

gauge, however, is calibrated to read air pressure. Heat transfer through molecular collisions is inversely proportional to the square root of the masses of the colliding molecules. Iodine (MW=254) is considerably heavier than air (MW=28) and is therefore less efficient in transferring heat from the wire to the thermocouple. A thermocouple gauge calibrated for air will therefore give a low iodine pressure reading. We therefore have to recalibrate the thermocouple gauge to compensate for this effect.

The calibration procedure is as follows:

1. Evacuate the fluorescence cell by opening the pumping valve (E) maintaining the iodine reservoir valve (F) closed.

2. It might be necessary to warm up the cell walls with a heat gun to remove any iodine condensed on cold Spots.

3. Immerse the Iodine reservoir in a Dewar full of ice, allow the temperature of the iodine in the reservoir to equilibrate, record the temperature, open the reservoir valve (F) and close the pumping valve (E) to trap iodine vapor in the cell. Wait a few minutes for the pressure to stabilize.

4. The pressure in the cell should be the normal vapor pressure of iodine at the equilibrium temperature. Record the pressure gauge reading and determine the iodine vapor pressure at that temperature using the table in figure 5.

5. Close the reservoir and evacuate the cell.

6. Empty out the Dewar and refill it with cold tap water (18-20°C), immerse the reservoir in the Dewar and allow the temperature to equilibrate, allow iodine into the cell and take a new pressure gauge and vapor pressure reading.

7. Repeat the measurement at three or four intermediate temperatures by adding small amounts of ice to the Dewar and mixing until a stable temperature is obtained.

8. Make a plot of Thermocouple Gauge reading vs. Iodine Pressure, fit it to a straight line, and determine the slope. Figure 6 shows such a calibration curve.
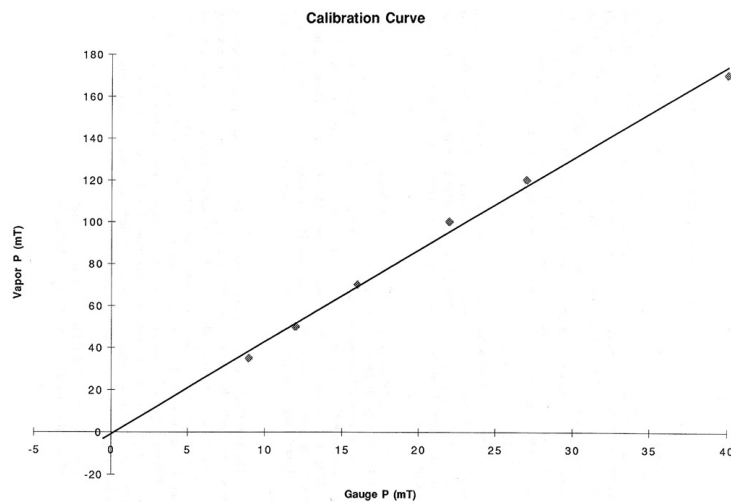
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Figure 6: Calibration curve

Starting up the laser: In this experiment we will use a pulsed nitrogen pumped dye laser to induce fluorescence in gaseous iodine. The nitrogen laser produces monochromatic ultraviolet radiation at 337 nm. This UV radiation is used to excite an organic dye which in turn produces visible laser radiation. The dye lases in the direction perpendicular to the excitation beam in a cavity formed by a partially reflecting mirror on one end and a reflection grating on the other. The reflection grating reflects a given wavelength giving selective feedback to the cavity so that rotation of the grating tunes the dye over its wavelength range (Ref. 4).

To start up the laser follow these steps:

1. Set the wavelength by adjusting the micrometer to 0.591 0.592. The laser wavelength can be changed over a small range by adjusting the micrometer dial which moves the reflection grating. Maximum intensity for Rhodamine 6 G dye is around 590 nm. The micrometer setting equals the laser wavelength in micrometers.

2. Turn the key to the "on" position and wait 10 seconds.

3. Turn on the laser trigger signal on the gray box marked amplifier and push the 256 "start"' button on the new pulse box (the laser should be

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set for external triggering).

4. Open the beam shutter. You should see bright flashes of orange laser light in the dye cell if either of the trigger sources is activated.

5. Lasing can be interrupted by either turning off the trigger or switching off the laser. NOTE: This laser has a finite life. To extend its lifetime trigger only while taking data. Do not pulse needlessly, the new 256 trigger box should solve this problem.

Collecting Fluorescence: The tuned laser radiation is passed through an evacuated cell containing gaseous iodine. Fluorescence is detected through a window on the cell perpendicular to the light path. Behind this window is a Wood's horn blackened to absorb scattered laser light. The window is coupled to a photomultiplier tube which detects and amplifies the fluorescence. The window is also covered with a Corning 2-60 optical filter which filters out wavelengths below 600 nm. Since the maximum in the fluorescence is at longer wavelengths than the excitation, this filter prevents most of the scattered laser light or background room light from reaching the photomultiplier tube, but you still see a sharp signal corresponding to the laser pulse.

The fluorescence signal from the photomultiplier tube passes through an amplifier to drive the coaxial cable so that it can be displayed on the oscilloscope without significantly distorting its pulse width (see Appendix). The signal recorded on the scope can then be stored on a floppy disk to later calculate the effective lifetime of the fluorescence event.

1. Turn on the PMT power supply to deliver about 800V (negative) to the photomultiplier.

2. Turn on the digital oscilloscope. Check that the 50mV sensitivity is shown on its screen.

3. Close the "pumping" valve (E) and open the iodine reservoir (valve F) until a stable gauge reading between 20-50 mTorr is obtained. Close the reservoir again, and wait for about 3min to see how much this pressure might drop. If it goes below 20 mTorr open valve F again and wait another 2-3 min. This should trap enough iodine in the cell to obtain a good fluorescence signal.

4. Turn on some trigger pulses and observe the signal on the oscilloscope. Next clear the scope by pushing "save/cont" twice and change the micrometer about 0.5 unit in the last place or 0.5 nm. Pulse again and see if the signal has gotten larger or smaller. Try to tune the micrometer to a near maximum in the signal. This will be near the top of the saw toothed feature called a band head. They are only about 3 nm apart. Record the micrometer reading, but it is accurate in wavelength to only about 1nm.
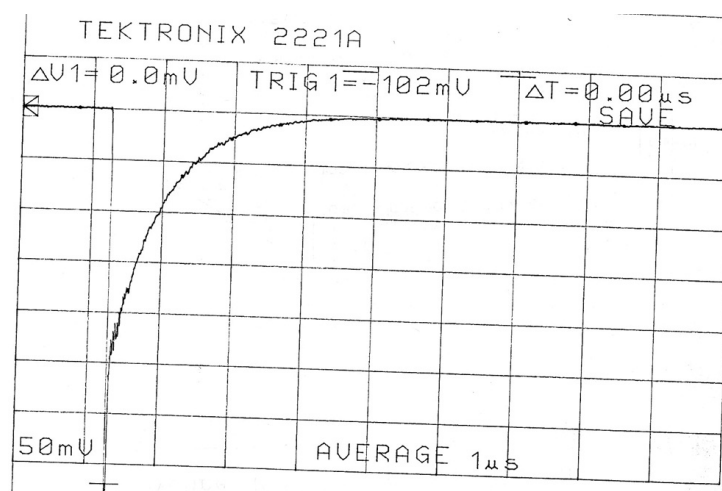

Figure 7: Oscilloscope trace

5. When the desired exponential rise, see figure 7, occupies about one half of the scope screen then the PMT voltage is all right. If the signal is too small raise the PMT voltage by 25-50 V and if it is too small lower it. Clear the signal from the screen and pulse again. The final PMT voltage should be between 700 and 1000 V. The appendix gives some useful hints of how to go about running the oscilloscope and finally storing the data.

Collecting the Data: The laser output power fluctuates some from shot to shot so that not every laser shot gives the same intensity of fluorescence. In addition the signal to noise ratio from a single pulse is only fair. The digital oscilloscope allows us to average the signal from a large number of

shots thus providing a stable display as well as reducing random noise. After the digitized data is collected it will be transferred to a PC for converting into X-Y data and saving on a floppy disk. This transformed data can then be used to calculate the characteristic decay time.

Once you have calibrated the pressure gauge and become familiar with the oscilloscope (Appendix) you should try to collect all the data in one session.

1. Record the laser wavelength by reading it directly from the micrometer dial on the grating. Set the scope to Average for 256 shots with a weight of 1/256 for each shot.

2. To start the data transfer program, after the PC boots up, type: TEKDIG. If everything is set up properly, the words "on line" should appear at the bottom right of the Main Menu box. Select the following options in the Main Menu:

Select Waveform Memory Location	A
F1	Select Driver: 2200 DSO
F2	Select Data Source: CH1

3. With valve E closed, open the reservoir and allow the cell to fill. Close the reservoir and allow the pressure to stabilize.

4. Once the pressure is stabilized, press the "save/cont." button on the scope to start averaging. You should be able to see the shot number on the scope; after 256 shots the display will freeze and the word "Limit" will appear on the top right of the display. Press "save/cont." to store the waveform in the oscilloscope memory buffer.

5. To transfer the data to the PC, from theTEKDIG Main Menu select:

F3	Acquire Waveform
F8	Save Spreadsheet Data to Disk
From Save Spreadsheet menu:	
F5	Change Waveform Directory : TXTDAT
	(The data will be saved in this location,
	unless otherwise specified.)
F2	Scaled X-Y Pairs
	Enter Filename: ABC50mT
	(your initials and cell pressure)
F10	Return to Main
F4	Graph Waveform
	(Displays the waveform with a great deal of
	random noise, a peculiarity of
	this data transfer program.
F10	Return to Main

6. Partially pump out the cell, or open the reservoir to increase the pressure (it may be necessary to warm up the reservoir), and repeat steps 4 and 5 .

7. Repeat 6 until you have collected and saved data for five or six different pressures between 5 and 50 mTorr gauge reading.

   Since every other line in the data contains garbage this is difficult to clean up if you use an ordinary spreadsheet program. So if you want data which can be used in an ordinary spreadsheet you should send it through our special program stored as waveform.bat as follows:

8. When all the data has been collected, exit the TEKDIG program.

9. Remove the noise incorporated in the data. The data was saved in the TXTDAT directory, to change directory type: `cd TXTDAT`

   To clean up the .txt file, at the DOS prompt, type:

(prompt)	waveform.bat
"enter filename:"	abc50mT.txt
"enter new filename:"	abc50mT.out

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This new file will also be saved in TXTDAT, unless you specify where it should go. (It is good practice to save your data on your own disk; it also may avoid a great deal of aggravation later on.)

Important notes: Although the cell is completely leak tight the pressure fluctuates when iodine is trapped inside it. This is because some iodine inevitably condenses at "cold spots" inside the cell establishing an adsorption/desorption equilibrium. When iodine is first put in the cell the pressure tends to creep downward as iodine condenses onto the wall. At the lowest pressures it may even creep up as some of the condensed iodine desorbs from the walls. It is, therefore, important to collect the data quickly to insure a stable pressure during the averaging process. If the fluctuations over the averaging time are large it is a good practice to record the pressure both at the beginning and end of the averaging process, and use the average of the two in the calculations.

Shut down procedure:

1. Distill I_2 back to the reservoir by placing a dewar of LN_2 under it. Remove LN_2 from trap, close valve C and open F. Wait until the trap is clean of I_2.

2. Meanwhile turn "off" the power supplies, oscilloscope and computer.

3. Turn "off" the external laser trigger and the laser. Close the beam shutter.

4. Turn "off" the diffusion pump. Power "off the pressure gauge.

5. Allow pump to cool for 15-20 minutes before turning the cooling water "off". If all I_2 has been distilled to the reservoir, close F then open B (to let the mechanical pump operate). You can now remove the LN_2 from the reservoir.

6. Leave the mechanical pump "on," and the system under pressure (make certain F is closed).

7. Make sure you copy your files to a floppy (3.5") disk. (after you've "cleaned" them with waveform.bat). You will need to use a DOS copy

command like *copy c:\TEKDIG\TXTDAT*.out a:* at the command prompt (copies all files with a .out extention is the list directory to the 3.5" disk drive).

1.3   Data Analysis

1. Use the gauge calibration plot to convert the pressure readings into true iodine pressures.

2. Use the saved X-Y formatted curves to calculate the decay time for each of the plots. Ideally the oscilloscope signal should be a sharp step function followed by a purely exponential rise, but it is a little difficult to tell where the step function ends and the exponential begins to any better than a few tenths of a microsecond. Fortunately, an exponential fit does not depend upon the zero in time. You can use a spreadsheet program, but to use its fitting routine you must change the signal to a log or ln function. You must also see that the baseline has been subtracted away. The data over 8 microseconds passed the pulse gives no information other than providing the baseline.

3. Make a Stern Volmer plot and from it calculate the radiative lifetime as well as the self quenching cross section for laser induced iodine fluorescence at that wavelength.

4. Estimate your experimental error in both the pressure and lifetime. Include both vertical and horizontal error bars in your Stern Volmer plot. Draw the two extreme straight line fits through the error bars to estimate the error in both slope and intercept.

5. Compare your results with literature values and comment on the agreement.

1.4   Discussion

1. You carried out the experiment with a fixed wavelength (hopefully around 600 nm) which was determined by the maximum wavelength of the dye curve. Look for a published absorption spectrum of iodine and determine the upward transition being excited at this wavelength. Give appropriate spectroscopic notation for that transition.

2. What is the energy (wavelength) of the transition to the next vibrational level on the excited manifold?

3. While looking at the fluorescence signal with the oscilloscope in the SAMPLE mode you might have noticed that the fluorescence decay seems to follow a bi-exponential decay. that is, two different decay constants can be observed. Since the intensity of one of the components is very small this effect tends to be "averaged out" and therefore does not show up in the averaged scope traces. Can you give an explanations for this biexponential behavior? Is your answer consistent with your answer to questions 1 and 2?

4. Is the fluorescence wavelength longer or shorter than the excitation wavelength? Why? Is this consistent with the use of the corning 2-60 filter in front of the PMT?

5. Throughout this experiment we have ignored the existence of rotational energy levels for each vibrational state. From the rotational constant of iodine determine the rotational energy spacing in manometers. The spectral bandwidth of the laser is between 1 and 3 nm. Is it justified to ignore the rotational energy spacing in this experiment?

6. What part of the experimental set up do you think contributes most to the experimental error? How would a systematic error in thepressure gauge calibration affect your results. If, for example, your calibration gave a 10% over estimate in pressure would you expect your results for the lifetime and the cross section to be equally affected? If not, which would you expect to be more drastically affected by a calibration error? How would you change the experimental set up to eliminate the gauge calibration errors?

References

1. Shoemaker et al., *Experiments in Physical Chemistry*, fifth ed. (Mc-Graw Hill, New York 1989), p. 497 502, 593 and front cover.

2. Demtroder, W, *Laser Spectroscopy,*: Basic Concepts and Instrumentation, Spring Verlag 1982, pp 35 38 and pp 591 593. Note: His σ equals our $\pi\sigma^2$.

3. Sakuri, K. et al., *J. Chem. Phys.* 54, 1220 (1971).

4. Reference 2, pages 338-343, and Fig. 7.22 on page 349. Our dye is rhodamine 6G (R6G).

1.5   Appendix

GETTING A SIGNAL ON THE DIGITAL OSCILLOSCOPE: The photomultiplier tube amplifies each fluorescence photon by giving a cascade of electrons which constitute a short current pulse the duration of which represents the lifetime of the fluorescence event. This negative current pulse can be dropped across a 200 ohm resistor and monitored on the oscilloscope as a voltage pulse. Since we are interested on the duration of the pulse we must be careful not to distort its shape in converting it from a current into a voltage. So we have a wide band line drive amplifier to drive the 50 ohm coaxial cable which is terminated by 50 ohms at the scope input. We set the oscilloscope gain at 50 mV because a signal greater than the full screen display or 0.5 V is near the maximum current which the PMT can produce. The light signals from the fluorescence are quite large. The lifetime for iodine fluorescence is in the order of 1 μsec.

The digital oscilloscope has the ability to store the waveforms which greatly aids in their display. The oscilloscope can act as either a normal or digital oscilloscope. The "store/non store" button on the upper right of the panel changes the scope from digital to analog function. The best way to get acquainted with the oscilloscope operation is to read the short reference manual provided by the manufacturer.

Within the digital storage operation, the scope can acquire data in one of four modes (SAMPLE, AVERAGE, PEKDET, ACCPEK). The later two are of no interest in this experiment. The SAMPLE mode digitizes the analog trace and actualizes the display on the screen every time the scope triggers. The intensity of the trace in this mode is brighter than in the non storage (analog) mode making it easier to see the displayed waveform. The signal, however, tends to jump around due to its fluctuating amplitude. The sample mode is recommended to get a feel for how the signal changes from shot to shot and how the pressure in the cell affects the pulse duration.

The AVERAGE mode allows to average the digitized trace over a given number of shots. This is recommended during the actual data taking since it reduces both signal fluctuation and noise. Within the AVERAGE mode you can chose the number of shots to be averaged as well as the weight of the most recent shot. These parameters can be changed from the "acquisition" menu which can be reached by pressing the "Acq" button on the upper left on the panel. Use the four small keys on the edge of the display to move through the menu choices and the "Cursor" knob to change numerical parameters within the menu. Pressing "Acq" exits the menu. The "Mode" key can be used to toggle between the four modes without having to go into the menu. The following is a list of the typical scope settings:

Storage mode:	STORE (use the "store/non store" key)
Channel 1	selected with 50 mV/div and DC coupling
Time base:	1 μsec/div
Trigger source	CH1 (or possibly also VERT)
Trigger Couple:	Normal
Trigger Slope:	Negative
Mode	(either SAMPLE or AVERAGE)

The menu parameters for the AVERAGE mode have been stored in memory so that they will be preset by default at power up. They can, however, be changed from within the acquisition menu. Check that you have the following setting in your "acq" menu:

Trig. Pos	128/1K
Avg. Wgt.	1/256
Swp. Lim.	250

In the AVERAGE mode the shot number appears on the screen until the limit (256) is reached; the display is then frozen and can be saved by pressing "save/cont." Pressing "save/cont" one more time restarts the averaging process. Pressing the "save/cont" button twice is the simplest method for seeing how a changed wavelength or PMT voltage affects the signal during continuous triggering.

Exponential Fit using Excel: Excel can be used to read the iodine fluorescence data which has been transferred from the Tektronix scope to a floppy as scaled X-Y pairs, but first these files must be manipulated before they can be matched to an exponential decay with a least squares fit. The floppy files should contain a two column ASCII file showing a time scale and the vertical signal display of the scope. Together they can form an x-y plot. If your file was saved directly without cleaning it up using the second program called "waveform.bat," it will have 2050 rows of data and the extension ".txt." However its x-y pairs will contain 50% garbage and half the pairs have to be discarded. Only Tektronix knows why they contain meaningless values. These "txt" files can be cleaned up using Excel. If you did run "waveform.bat" your files have whatever extension you gave them and now have only about 1024 rows. In the next few pages we will go through the procedure to fit the iodine fluorescence emission to an exponential change, and plot out the data points and the least-squares fit line. The procedure may appear complicated at first, but once learned it goes very fast.

Load the data to an Excel spreadsheet: Open the file using "general" Column Data Format, and "comma" as the Column Delimiter. The first four rows of the file contain non-data file information; the data should be in two columns, the first containing time, and the second the signal intensity. Expand the number range (in Format menu) so that the data is not truncated.

Saving the files: With the scope horizontal scale on 1 microsecond per division, data are indicated as being taken every 0.01 microseconds, but half of these are garbage so the real data appears spaced every 0.02 microseconds. If one keeps 1000 points there is more than enough data for our observed exponentials. Also, the first 128 data points show a negative time and appeared in the scope before the laser pulse. (See previous section about the oscilloscope, Trigger Position.)

The files cleaned using "wavefrom.bat" program have 1024 data points, with the alternate noise entries already removed. Delete the first four non-data rows and continue with the next section.

Use the following procedure with the ".txt" files:

1. Delete the first four non-data rows.

2. Insert an "x" (or any other symbol of your choosing,) in cell C1.

3. Highlight cells C1 and C2.

4. Move the mouse prompt to the bottom of the right hand corner of the highlighted area, until it turns into a "+", and drag to fill down to the end of the data. This should put a x on every other row entry.

5. On cell D1 enter: = IF(C1 = "x", A1, " ")

6. On cell E1 enter: = IF(C1 = "x", B1, " ")

7. Highlight D1 and E1, move the mouse to the bottom of the right hand corner, and fill down.

8. Remove the blank rows by copying columns D and E into a new sheet, using "Paste Special" and "Values Only."

Viewing the Spreadsheet: The spreadsheets should now be identical. Write down the average value of the baseline before the laser pulse. Later, this will be subtracted from the data. These values do not represent millivolts, they seem to be scope division numbers starting from just below the screen. The time values are in seconds, and are spaced as even numbers every 0.02 seconds. Scroll down and find the start of the laser pulse, sending the B values down towards zero. The laser pulse appears to last 0.06 seconds. Lastly scroll down to the rows around 400, or A = 9 microseconds and check that the B values have returned to the selected baseline.

Editing the Data: Now produce a spreadsheet with only the exponential part of the data, to use in the exponential fitting routine. First, remove the rows which contain the early baseline plus a few more with the laser pulse. Scroll down the spreadsheet and look for the time the laser pulse sends the signal down, go a little past where the data are most negative and find a point where the values are heading back up. On the recommended settings for the Tektronix scope this is near row 66, but at other settings it will be different. Remove all data above this value. Next go down the spreadsheet and delete all data below 10 microseconds (about 500 data points.)

Preparing the data for exponential fit: Excel has a model for fitting data which is a simple exponential function as part of the Trendline Tool. It is of the form

$$A = A_0 e^{-kt}$$

However, the baseline must be subtracted from the data for this two parameter function. The time scale does not have to be adjusted, but the floating point notation is not particularly convenient, shifting the zero in time makes the plots easier to scale, and we should throw out the factor of one-half.

Rescaling Time: In cell C1 enter "=(A1*1000000-t0)*0.5". The t_0 value is time in microseconds shown in cell A1. The 0.5 factor was discovered by calibration, for the times indicated in the spreadsheet are too large by a factor of two. Only Tektronix knows why this is, but clearly it has to do with the garbage data. Fill Down the rest of the column.

Adjusting the baseline: As mentioned before, the data for least squares should go to near zero at longer times, such as 5 microseconds. As we zero the baseline, we'll change the sign of the data to have it decay to zero from above. In cell D1 enter " = (your baseline) - B1". Fill Down the rest of the column. The baseline choice is quite important, because Trendline does not fit to an exponential data that decays down to zero. The D values at the bottom of the spreadsheet should be around 10^{-4}.

Exponential Fit and Graph: Charts in Excel are created with the Chart Wizard tool. The following procedure was developed for Excel 98; for other versions the particular commands may be slightly different:

Time	Intensity	Adjusted Time	Int. - Baseline
0.000005	0.00984375	0	0.00935625
0.00000502	0.00890625	0.01	0.01029375
0.00000504	0.0078125	0.02	0.01138750
0.00000506	0.0096875	0.03	0.00951250
0.00000508	0.0110937	0.04	0.00810630
0.0000051	0.011875	0.05	0.00732500
0.00000512	0.011875	0.06	0.00732500
0.00000514	0.0114062	0.07	0.00779380
0.00000516	0.0114062	0.08	0.00779380
0.00000518	0.01125	0.09	0.00795000
0.0000052	0.0115625	0.1	0.00763750
0.00000522	0.0121875	0.11	0.00701250
0.00000524	0.0115625	0.12	0.00763750
0.00000526	0.0120312	0.13	0.00716880
0.00000528	0.0126562	0.14	0.00654380
0.0000053	0.0123437	0.15	0.00685630
0.00000532	0.0125	0.16	0.00670000
0.00000534	0.0125	0.17	0.00670000
0.00000536	0.0126562	0.18	0.00654380
0.00000538	0.013125	0.19	0.00607500
0.0000054	0.013125	0.2	0.00607500
0.00000542	0.0132812	0.21	0.00591880
0.00000544	0.0134375	0.22	0.00576250
0.00000546	0.0132812	0.23	0.00591880
0.00000548	0.0132812	0.24	0.00591880
0.00000992	0.0190625	2.46	0.00013750
0.00000994	0.0190625	2.47	0.00013750
0.00000996	0.0190625	2.48	0.00013750
0.00000998	0.0190625	2.49	0.00013750
0.00001	0.0190625	2.5	0.00013750
0.00001002	0.0190625	2.51	0.00013750
0.00001004	0.0190625	2.52	0.00013750
0.00001006	0.0190625	2.53	0.00013750

Figure 8: Excel data

1. Select columns to be graphed, C and D in this case, by clicking on their headings to highlight the entire column.

2. Click on the Chart Wizard icon to launch the graphing program, and

in

(a) Under Standard Types, select "X-Y Scatter" for Chart Type, and, "Points Only" for Chart Sub-Type.

(b) Under Data Range, select "Columns" in "Data Series in" entry. At this point the sample graph appears as an inset.

(c) Enter chart and axes titles, labels, etc.

(d) Finish the graph. Rescale the graph if needed.

Activate the graph by clicking on any point within it.
Next from the top menu, select "Add Trendline", and

1. Under Type, select "Exponential,"

2. from Options, select "Dispaly Equation on Chart" and "Dispaly R-Squared Value."

The graph will now show the fit line superimposing the data points, as well as the equation for the exponential and r-squared value.
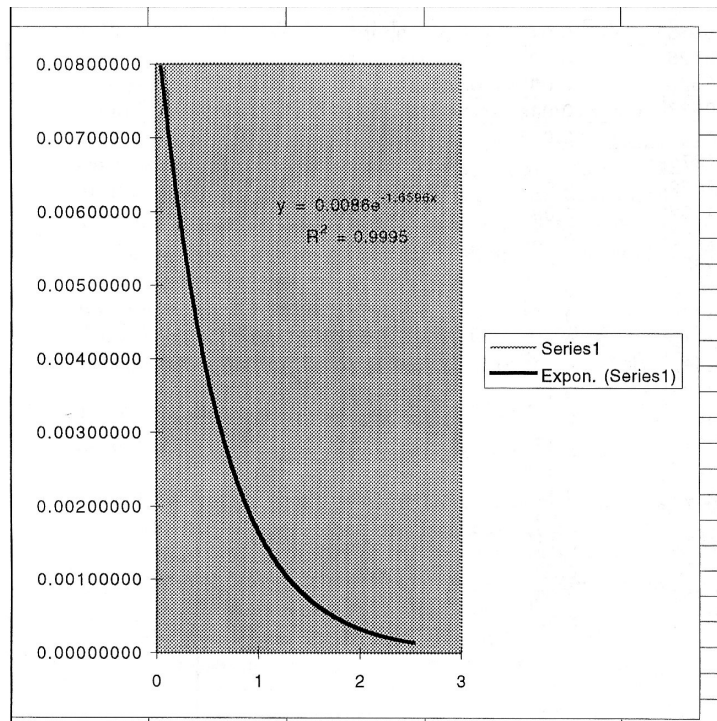
Figure 9: Excel exponential fit

2 Physical Adsorption of Gases

Introduction: [1] This experiment[2] is concerned with the multilayer physical adsorption of a gas (the *adsorbate*) on a high-area solid (the *adsorbent*). Since such adsorption is caused by forces very similar to those that cause the condensation of a gas to a bulk liquid, appreciable adsorption occurs only at temperatures near the boiling point of the adsorbate. The adsorption of N_2 gas on a high-area solid will be studied at 77.4 K (the boiling point of liquid nitrogen), and the surface area of the solid will be obtained.

2.1 Theory

We shall be concerned with the adsorption isotherm, i.e., the amount adsorbed as a function of the equilibrium gas pressure at a constant temperature (Ref 1). For physical adsorption (sometimes referred to as van der Waals adsorption), five distinct types of isotherms have been observed; we shall discuss the theory for the most common type, a typical example of which is shown in figure 10.
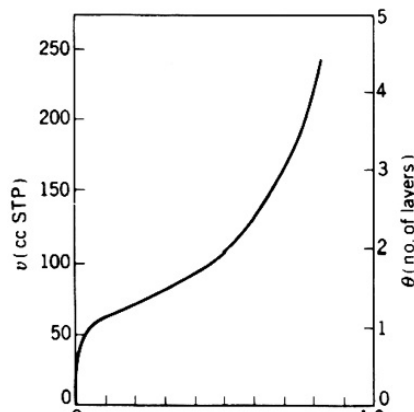
Figure 10: A typical isotherm for the physical adsorption of nitrogen on a high-area solid at 77 K.

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[1] revised by Allison Caster, Spring 2007

[2] This lab is taken from Garland, Nibler, and Shoemaker. "Experiments in Physical Chemistry," Ed. 7. McGraw-Hill. N.Y. (2003) p. 301-310.

It has unfortunately become standard practice to express the amount adsorbed by ν, the volume of gas in cubic centimeters at STP (standard pressure and temperature: P = 1 atm, $T = 273.15K$) rather than in moles. If the adsorbed volume required to cover the entire surface with a complete monolayer is denoted by ν_m one can describe the isotherm in terms of the coverage θ:

$$\theta = \frac{\nu}{\nu_m} \tag{2.1}$$

As shown in figure 10, adsorption increases rapidly at high pressures, and several layers of adsorbate are present even at a relative pressure $p/p_0 = 0.8$. The pressure p_0 is the saturation pressure of the gas (i.e., the vapor pressure of the liquid at that temperature). When $p/p_0 = 1.0$, bulk condensation will occur to form a liquid film on the surface ($\theta \to \infty$). One can also see from figure 10 that there is no clear, sharp indication of the formation of a first layer; indeed, the second and higher layers usually begin to form before the first layer complete. Clearly, we cannot obtain a good value of ν_m from the adsorption isotherm without the aid of a theory that will explain the shape of the isotherm.

Brunauer, Emmett, and Teller (Ref. 2) were the first to propose a theory for multilayer adsorption (BET theory). Since the behavior of adsorbed molecules is even more difficult to describe in detail than that of molecules in the liquid state, the BET theory contains some rather drastic assumptions. In spite of this, it is still a generally useful theory of physical adsorption. The BET theory gives a correct semi-quantitative description of the shape of the isotherm and provides a good means of evaluating ν_m (which is then used to estimate the surface area of the solid).

The usual form of the BET isotherm is derived for the case of a free (exposed) surface, where there is no limit on the number of adsorbed layers that may form. Such an assumption is clearly not good for a very porous adsorbent, such as one with deep cracks having a width of a few monolayer thicknesses, since the surface of these cracks can hold only a few layers even when the cracks are filled. Fortunately, the BET theory is most reliable at low relative pressures (0.05 to 0.3), at which only a few complete layers have formed, and it can be applied successfully to the calculation of ν_m even for porous solid. The original derivation of the BET equation (Ref. 1 and 2)

was an extension and generalization of Langmuir's treatment of monolayer adsorption. This derivation is based on kinetic considerations - in particular on the fact that at equilibrium the rate of condensation of gas molecules to form each adsorbed layer is equal to the rate of evaporation of molecules from that layer. In order to obtain an expression for θ as a function of p (the isotherm), it is necessary to make several simplifying assumptions. The physical nature of these assumptions in the BET theory can be seen most clearly from a different derivation based on statistical mechanics (Ref. 3). Neither derivation will be presented here, but we shall discuss the physical model on which the BET equation is based. A detailed review of this model has been given by Hill (Ref. 4); the important assumptions are as follows:

- The surface of the solid adsorbent is uniform; i.e., all "sites" for adsorption of a gas molecule in the first layer are equivalent.

- Adsorbed molecules in the first layer are localized; i.e., they are confined to sites and cannot move freely over the surface.

- Each adsorbed molecule in the first layer provides a site for adsorption of a gas molecule in a second layer, each one in the second layer provides a site for adsorption in a third, with no limitation on the number of layers.

- There is no interaction between molecules in a given layer. Thus the adsorbed gas is viewed as many independent stacks of molecules built up on the surface sites.

- All molecules in the second and higher layers are assumed to be like those in the bulk liquid. In particular the energy of these molecules is taken to be the same as the energy of a molecule in the liquid. Molecules in the first layer have a different energy owing to the direct interaction with the surface.

In brief, the statistical derivation is based on equilibrium considerations – in particular on finding the distribution of the heights of the stacks that will make the free energy a minimum. The BET isotherm obtained from either derivation is

$$\theta = \frac{N}{S} = \frac{cx}{(1-x)[1+(c-1)x]} \qquad (2.2)$$

where S is the number of sites, N is the number of adsorbed molecules, x is the relative pressure (p/p_0), and c is a dimensionless constant greater than unity and dependent on the temperature. Note that θ equals zero when $x = 0$ and approaches infinity as x approaches unity, in agreement with figure 10. Making use of 2.1, we can rearrange 2.2 to the usual form of the BET equation:

$$\frac{x}{\nu(1-x)} = \frac{1}{\nu_m c} + \frac{(c-1)x}{\nu_m c} \tag{2.3}$$

Thus a new plot of $[x/\nu(1-x)]$ versus x should be a straight line; in practice, deviations from a linear plot are often observed below $x = 0.05$ or above $x = 0.3$. From the slope s and the intercept I, both ν_m and c can be evaluated:

$$\nu_m = \frac{1}{s+I} \qquad c = 1 + \frac{s}{I} \tag{2.4}$$

The volume adsorbed (in cm^3 at STP) is related to n, the number of moles adsorbed, by

$$\nu = \frac{nRT}{P} \tag{2.5}$$

where $T = 273.15$ K, $P = 1$ and $R = 82.06$ cm$^3 \cdot$atm/K$\cdot$mol. The total area of the solid is

$$A = N_0 n_m \sigma \tag{2.6}$$

where N_0 is Avogadro's number and σ is the cross-sectional area of an adsorbed molecule.

Although we shall not be concerned experimentally with measuring heats of adsorption, it is appropriate to comment that since the process of adsorption results in a decrease in entropy, ΔH for the physical adsorption of a gas is always negative. The *isosteric heat of adsorption* (the heat of adsorption at constant coverage θ) can be obtained by application of the Clausius-Clapeyron equation if isotherms are determined at several different temperatures; the thermodynamics of adsorption have been fully discussed by Hill (5).

2.2   Experimental

Adsorption from the gas phase can be measured by either gravimetric or volumetric techniques. In the gravimetric method, the weight of adsorbed gas is measured by observing the stretching of a helical spring from which the adsorbent is hung (see figure 11).
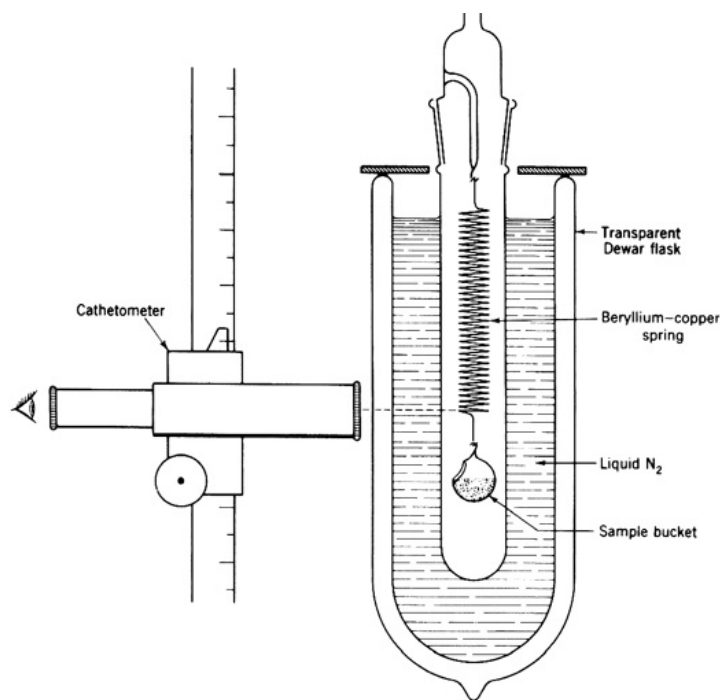

Figure 11: Gravimetric adsorption apparatus

Alternatively, an electrostatic balance may be used. In the volumetric method, the amount of adsorption is inferred from pV measurements that are made on the gas before and after adsorption takes place. An excellent review of the many apparatus designs in common use has been given by Joy (Ref. 6); we shall consider only a conventional volumetric apparatus similar to one that has been very completely described by Barr and Anhorn (Ref. 7). This apparatus is shown in figure 12. The central feature in this design as a gas burette connected to a manometer that can be adjusted to maintain a constant volume in the arm containing the gas.
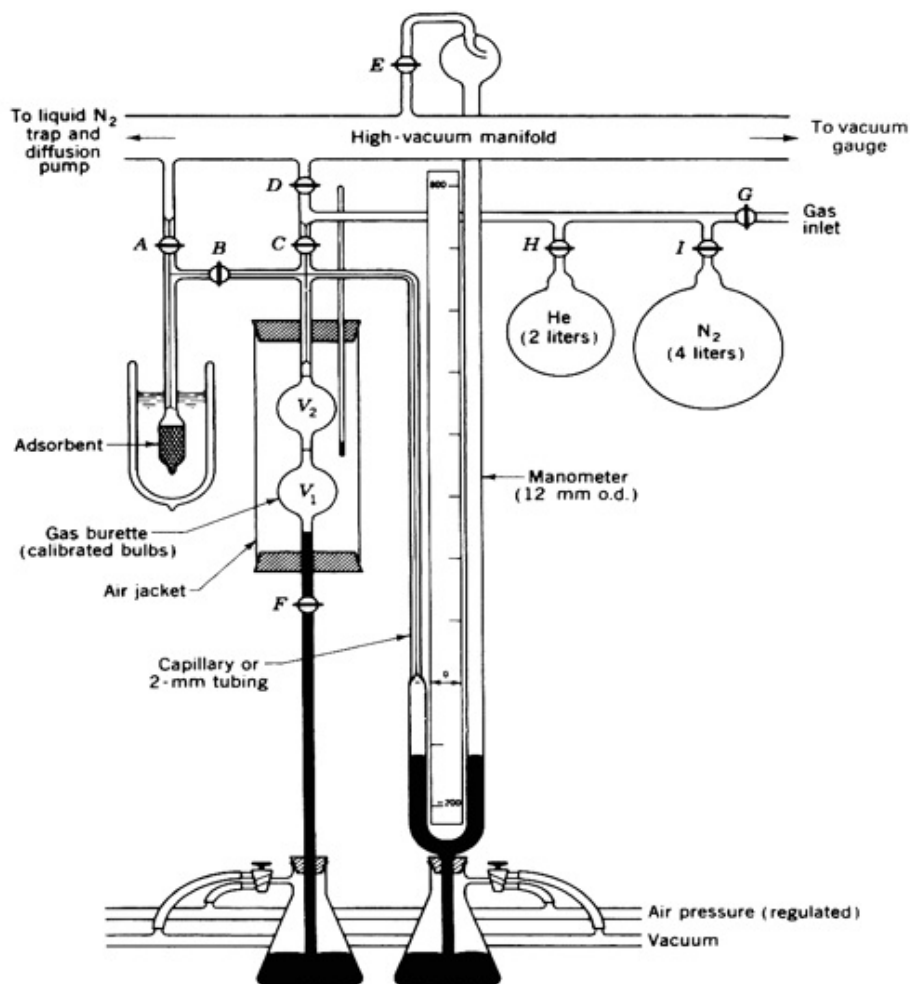
Figure 12: Gravimetric adsorption apparatus

The gas burette shown in figure 12 is constructed from two 50-mL bulbs, large-bore capillary tubing, and a stopcock (F). Fiducial marks (white lines) are engraved above the top bulb, between the bulbs, and below the bottom bulb. Before the burette is attached to the vacuum system, the volume between fiducial marks (V_1 and V_2) can be measured accurately by weighing the mercury required to fill each bulb. More elegant designs (Ref. 6) achieve greater flexibility in operation by using five or six bulbs, but two are sufficient for the purpose of evaluating V_3, the volume of the tubing between the top

of the gas burette and the zero level in the manometer. This is accomplished by measuring the pressure p of gas with both bulbs in use, then filling the lower bulb with mercury and determining the new pressure value p From the perfect-gas law,

$$V_3 = \frac{pV_1 - (p' - p)V_2}{p' - p} \tag{2.7}$$

When an isotherm is being determined, the temperature of the gas in the burette system must be known and should remain constant. Although a water jacket is often used, an air jacket is sufficient for the present experiment.

Adsorbent: For the apparatus described in figure 12, a sample of a high-area solid adsorbent that has a total surface area of 150 to 250 m^2 should be used. Of the adsorbent most commonly used (charcoal, silica, alumina), silica is recommended as an excellent choice. The sample bulb should be small enough that it is almost completely filled with the powder. Figure 13 shows a type of bulb that can easily be filled; a loose plug of Pyrex wool in the capillary will prevent loss of powder during filling and later during degassing.
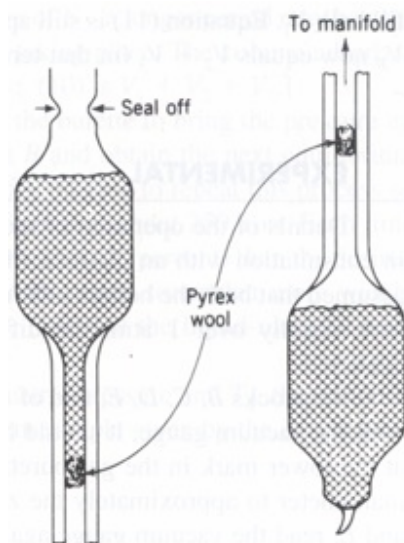
Figure 13: Detail drawing of the sample bulb, showing method of filling.

The exact weight of the sample should be determined before the bulb is attached to the system. After it is attached to the vacuum line, the sample must be degassed (i.e., pumped on to remove any physically adsorbed substances, principally water). This can be done by mounting a small electrical tube furnace around the sample bulb and heating to 200 to 250°C for several hours. Before heating, stopcock A should be opened to pump out all the air (stopcock B remains closed); this must be done cautiously to avoid forming a tight plug of powder in the capillary tube (gentle tapping will help also). After this initial degassing, a shorter degassing period will suffice between adsorption runs.

Adsorbate Gas: For physical adsorption, any pure gas that does not react with the solid adsorbent can be used. However, for quantitative area measurements, a molecule known adsorption area is required. Nitrogen gas is a very common choice and will be used in this experiment. Liquid nitrogen is the most convenient constant-temperature bath for isotherm measurements with N_2 gas. For high-precision work, the temperature of this bath should be measured with a thermocouple so that an accurate value of p_0 can be obtained, or p_0 should be measured directly with a separate nitrogen vapor-pressure manometer (Ref. 6 and 7). For this experiment it is adequate to assume that p_0 is equal to the atmospheric pressure in the room.

We can now develop the necessary equations for calculating the amount adsorbed from the p_V data obtained during a run. Let us denote the known volume of the gas burette by $V_B (= V_1 + V_2 + V_3$ or $V_2 + V_3$ as the case may be) and its temperature by T_B. Since the sample bulb is not completely filled by the solid adsorbent, we must also consider the so-called dead-space volume occupied by gas. Let us denote this volume by V_s and consider it to be at a single temperature T_s. If the burette is filled with gas at an initial pressure p_1^0 and then stopcock B is opened, the pressure will drop to a new equilibrium p_1. The number of moles adsorbed is

$$n_1 = \frac{p_1^0 V_B}{RT_B} - \left(\frac{p_1 V_B}{RT_B} + \frac{p_1 V_s}{RT_s} \right) \tag{2.8}$$

where typically the V_s are expressed in cm^3, the p's in atm, and R = 82.06 cm^3·atm/K·mol. Equation 2.8 can be rewritten in terms of ν_1 (the amount

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adsorbed in cm^3 at STP) by using equation 2.5:

$$\nu_1 = p_1^0 V_B^* - p_1(V_B^* + V_s^*) \tag{2.9}$$

where the p's are now in Torr and

$$V_B^* = \frac{273.15}{760 T_B} V_B \qquad V_s^* = \frac{273.15}{760 T_s} V_s \tag{2.10}$$

The value of V_B^* can be calculated from V_B and T_B, which are known. V_s^* is constant but unknown; however, it can be determined if a run is made using helium gas. Since He is not significantly adsorbed at liquid-nitrogen temperature, $\nu_1 = 0$ and V_s^* can be calculated from equation 2.9.

If N$_2$ gas is admitted to the bulb, adsorption does occur and equation 2.9 yields a value of ν_1, the "volume" adsorbed at the equilibrium pressure p_1. Now stopcock B is closed and more N$_2$ gas is added to the burette to achieve a new initial pressure p_1. When B is opened, more adsorption will occur and the pressure will change to an equilibrium value p_2. The final volume adsorbed at p_2 is

$$\nu_2 = [p_1^0 V_B^* + (p_2^0 - p_1)V_B^*] - p_2(V_B^* + V_s^*) \tag{2.11}$$

Equation 2.11 can be generalized for ν_j, the volume adsorbed at p_j after j additions of gas to the burette; for example

$$\nu_3 = [p_1^0 V_B^* + (p_2^0 - p_1)V_B^* + (p_3^0 - p_2)V_B^*] - p_3(V_B^* + V_s^*) \tag{2.12}$$

Note that the brackets contain an expression for the *total* amount of gas added to the system and the second term represents the amount remaining in the gas phase at equilibrium. Since the effect of errors is cumulative in this method, care should be exercised in measuring all pressures.

Normally the entire gas burette is used ($V_B = V_1 + V_2 + V_3$), but on occasion it may be convenient to obtain two points on the isotherm from a single filling of the burette; this can be accomplished after the first point is obtained by raising the mercury level so as to fill bulb V_1, equation 2.11 is still applicable, but the value of the last term is changed, since V_B now equals $V_2 + V_3$ (in that term only) and a new equilibrium pressure must be used.

2.3   Data Analysis

The sample is 1.0 g of silica gel. $V_1 = 54.55$ cm^3 and $V_2 = 53.17$ cm^3. The cross-sectional area for an adsorbed N_2 molecule may be taken as 15.8 $\mathring{A}^2$.

1. From your helium data and the known values of V_1 and V_2, calculate V_3 from equation 2.7. If the temperature at the gas burette has been fairly constant throughout the experiment, use the average value as T_B in equation 2.10 and calculate values of V_B^* when $V_B = V_1 + V_2 + V_3$ and when $V_B = V_2 + V_3$. These values can then be used in all further calculations. If TB has varied by more than $\pm 0.5^oC$, appropriate changes in should be made where necessary. Now use equation 2.9 to calculate V_s^*.

2. For each equilibrium point on the isotherm, calculate a value of ν, the volume adsorbed at pressure p. If the barometric pressure has been almost constant, its average value may be taken as p_0, the vapor pressure of nitrogen at the bath temperature. For each isotherm point, calculate $x = p/p_0$.

3. Plot the isotherm (ν versus x) at 77 K and compare it qualitatively with the one shown in 10. Finally, calculate $x/\nu(1-x)$ for each point and plot that quantity versus x; see equation 2.3. Draw the best straight line through the points between $x = 0.05$ and 0.3, and determine the slope and intercept of this line. This evaluation can be made graphically or by a linear least squares fit of the data with 2.3 (see Chapter XXII). From equation 2.4, calculate ν_m and c for the sample studied.

4. Using equations 2.5 and 2.6 and the known mass m of the adsorbent sample, calculate the specific area A in square meters per gram of solid. The cross-sectional area for an adsorbed N_2 molecule may be taken as 15.8 $\mathring{A}^2$.

5. To a good approximation the constant c is related to the heat of adsorption, q_{ads}, through the relationship

$$c = e^{(q_{ads} - q_l)/RT} \tag{2.13}$$

where q_l is the heat of liquefaction ($q_l^{N_2} = 1334$ cal/mol N_2), R = 1.987 cal/mol·K and T is the temperature at which the adsorption takes place ($\sim$77K). From the evaluated c, calculate q_{ads}.

2.4   Discussion

1. What factors can you think of that would tend to make the BET theory less reliable above $x = 0.3$ or below $x = 0.05$?

2. Derive the Langmuir isotherm from the following chemical equation:

$$A(g) + S \; \rightarrow \; A(ads) \tag{2.14}$$

   where A is the adsorbate and S is the surface.

3. What is the Langmuir isotherm for dissociative adsorption? (Hint: the molecule produces two adsorbed species when it adsorbs on a surface)?

4. How is adsorption affected by temperature?

5. What is c (qualitatively) and what does it affect?

References

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2.5 Appendix

ALWAYS WEAR SAFETY GLASSES WHEN WORKING WITH VACUUM SYSTEMS

Before starting, review the operating principles of the McLeod, Pirani and capacitance gauges, and of the mechanical and oil diffusion pumps.

SAFETY ISSUES: Work on a vacuum system requires preliminary review of procedures and careful execution in order to avoid damage to the apparatus and possible injury from broken glass; in addition, the liquid nitrogen used for cold traps must be handled properly (see Appendix C of Garland et. al.). Safety glasses must be worn. In the event of breakage, any mercury spill must be cleaned up promptly and carefully as described in Appendix C.

APPARATUS Adsorption apparatus (figure 12), containing high-area sample, attached to high-vacuum line equipped with McLeod gauge or other vacuum gauge, diffusion pump, and liquid nitrogen trap (see Chapter XIX); high-purity helium and nitrogen gas; small electrical tube furnace; narrow-mouth taped Dewar flask and clamp for mounting; glass wool or clean towel; 0 to 30°C thermometer; stopcock grease; Liquid nitrogen.

Preparing the System: The mechanical pump should be on; if it is not, contact the GSI or the stockroom.

1. Turn on the water to the diffusion pump-cooling jacket. The flow meter should be spinning rapidly enough that you cannot see the spokes.

2. Open the two stopcocks that connect the diffusion pump to the system, and close the stopcock that bypasses the diffusion pump. Make sure you review the proper techniques for opening and closing stopcocks.

3. Stopcock H should be closed and the McLeod gauge isolated from the system. Make sure other parts of the system, such as the sample and the burette, are open to the pumps (stopcocks A, C, D, and C1).

4. Turn on power to the Pirani and capacitance gauges, and open stopcocks X and XI.

5. If the pressure on the Pirani gauge is below 1 Torr, fill the dewar for the mechanical pump trap with liquid nitrogen. Cover the top of the dewar with a cloth to reduce the heat transferred from the room to the liquid nitrogen. (This step should not be done if the pressure is higher than 1 Torr, lest you condense liquid air, which is explosive!!!)

6. Turn on the diffusion pump by turning on the Variac and the interlock box.

7. Wait 1/2 hour, then note the pressure with the Pirani gauge; if the pressure is below 1×10^{-4} Torr (i.e. in the 10^{-5} Torr range), you may begin. If not, see Edmundo. While you are waiting, go to Step 8.

8. Record the barometric pressure (the barometer is in the stockroom) and the burette temperature.

9. Turn on the capacitance manometer. It should read 0.2 Torr or less.

10. Now that you have a low pressure, you can clean the surface of the silica. Heat the sample with the heat gun for at least 20 minutes. Don't shortcut this step! It is by far the most critical for the success of your experiment. If you don't heat the sample long enough, you will end up needing to repeat the experiment because of poor data, which will cost you extra hours of time. Have patience and do it right the first time!

11. **Wait for the sample to cool down**. THEN, clamp the small dewar around the sample and fill it with liquid nitrogen. Cover the top of the dewar with a cloth; this is to reduce the amount of water and oxygen which dissolves into the liquid nitrogen from the air, thus raising the boiling point above 77.4 K, which you will assume in your calculations is the correct sample temperature.

In the following steps, never have any of these stopcocks open at the same time:
H or I (these open to the He and N_2 bulbs)
C or D (C opens to the burette and D opens to the pumps)
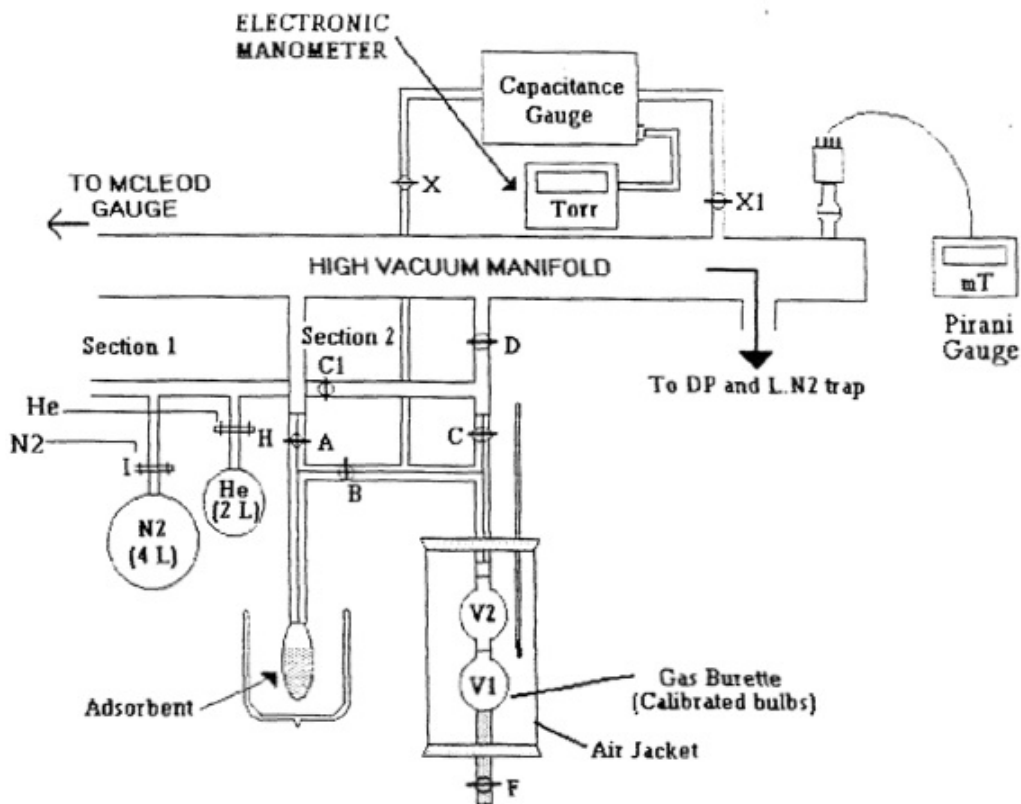
Calibration

Figure 14: Apparatus for measuring adsorption by the volumetric method located in Room 301.

12. Move the mercury level in the burette to the white line below the lower bulb. Close the stopcock that connects the burette with the flask of mercury beneath it (stopcock F).

13. Isolate the sample and the burette from the pumps and from the gas bulbs (close stopcocks A, B, C and D, but keep C1 open.)

14. Open the He stopcock (stopcock H). This immediately fills the volume between stopcock H and stopcocks C and D with He gas.

15. Close stopcock H. Now you have created a new source of He between stopcocks H, C, and D.

16. Close stopcock C1. Now you have two separate sources of He: one between stopcocks H and C1 (we will call this "Sect. 1"), and a second between stopcocks C1, C, and D (we will call this "Sect. 2").

17. Fill the burette with about 100 Torr of He from Section 2 by doing the following:

    (a) **Slowly** open stopcock C to let He into the burette, watching the manometer digital readout. Close the stopcock when the pressure is almost at 100 Torr.

    (b) Wait for the pressure to stabilize, then open stopcock C again very slowly until you reach 100 Torr. Close stopcock C. If you are a little under or a little over 100 Torr, that is fine; make sure to record the pressure reading in your notebook.

18. If you added more than 200 Torr, evacuate some of it with the mechanical pump by doing the following (**WARNING: DO NOT USE THIS STEP FOR NITROGEN, SEE STEP 29.**):

    (a) Open the stopcock that bypasses the diffusion pump. Close the two stopcocks that connect the diffusion pump with the rest of the system, because the diffusion pump is not meant for pumping high pressures of gases.

    (b) Do not open stopcock D, because this will evacuate the He in Section 2. Instead, open stopcock A.

    (c) **Slowly** open stopcock B and evacuate whatever excess He you added.

    (d) When the pressure is back down to about 100 Torr, close stopcock B, wait a few minutes, and then close stopcock A. The He will not adsorb on the sample at 77 K.

    (e) Open the two stopcocks that connect the diffusion pump with the rest of the system. Close the stopcock that bypasses the diffusion pump. (MAKE SURE to do steps 18(a) and l8(e) every time you pump off high pressures of gases, even when it is not explicitly stated in the procedure.

19. If there was not enough He in Section 2 to give a pressure of 100 Torr in the burette, do the following:

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(a) Close stopcock C.

(b) Open stopcock C1. Because the pressure of He in Section 1 is greater than the pressure of He in Section 2, He will flow into Section 2 until the pressure in Sections 1 and 2 is equal.

(c) Close stopcock C1. This again isolates Section 2 from Section 1.

(d) Repeat step 15.

(e) If there is still not enough He to give 100 Torr, slowly open C1.

(f) If there is still not enough He to give l00 Torr, repeat steps 11-15, to refill sects. 1 and 2

20. Now that you have about 100 Torr of He in the burette, open stopcock F and carefully raise the mercury level in the burette up to the white line between the two bulbs. Wait until the pressure stabilizes, then record the new pressure. You will use this data to calculate V_3, the volume between the white line above the upper bulb and the capacitance manometer.

21. Close stopcock F. This is to keep the mercury level from rising when the He pressure decreases in Step 19.

22. Carefully open stopcock B to let He into the sample. Wait for the pressure to stabilize and record the new pressure. You will use this data to calculate V_s the volume between stopcocks A, B, and the sample (including its dead space).

23. Do Step 18(a), then slowly open stopcock A to pump off the He from the sample.

24. Lower the liquid nitrogen Dewar from around the sample and allow the sample to warm up to room temperature; this will allow any gas that might have adsorbed to be pumped off.

25. Open stopcocks C, D, and C1, so that the burette and Sections 1 and 2 will all be evacuated. After a few minutes, do Step 18(e). Then allow everything to evacuate for at least another 10 minutes.

26. Clamp the small liquid nitrogen Dewar around the sample.

27. Close stopcocks A, B, C, and D. Wait a few minutes for the sample to cool to 77.4 K.

Adsorbing Nitrogen Gas onto Silica:

28. Fill the burette with 100 Torr of N_2 using the techniques from Steps 14-17 and Step 19, using stopcock I instead of stopcock H. DO NOT USE STEP 18 FOR NITROGEN; INSTEAD, SEE STEP 29.

29. If you fill the burette with more than 125 Torr nitrogen for this first data point, evacuate the excess by doing the following:

    (a) Open the stopcock that bypasses the diffusion pump. Close the two stopcocks that connect the diffusion pump with the rest of the system.

    (b) Stopcocks C and C1 should be closed.

    (c) Slowly open stopcock D. Allow Section 2 to evacuate.

    (d) Now slowly open stopcock C until the pressure starts to decrease. Continue until the pressure is about 100 Torr, then close stopcock C.

    (e) Close stopcock D.

    (f) Open the two stopcocks that connect the diffusion pump with the rest of the system. Close the stopcock that bypasses the diffusion pump.

30. Record the pressure in the burette; this is the initial pressure, p_1^0 . Now open stopcock B to allow the nitrogen to come into contact with the sample.

31. Wait at least 10 minutes for the pressure to stabilize (although it will still be slowly drifting downward). Record the pressure; this is the final pressure, p_1. It should be very small (less than 10 Torr). If it is less than 10 Torr, go on to Step 32. If it is greater than 10 Torr, you should not continue because your sample is not clean enough. Do the following (otherwise, go to step 30):

    (a) Close stopcock B. This isolates the sample from the burette.

(b) Do Step 18(a), then slowly open stopcock A to evacuate the sample. After 5 minutes, do Step 18(e), and then wait about 10 more minutes.

(c) Remove the small liquid nitrogen Dewar from the sample. Wait another 15 minutes. While you are waiting, go to step 29(d)

(d) Note the pressure with the Pirani gauge. By this time, the diffusion pump should have pumped the system down well into the 10^{-5} Torr range. If not, see Edmundo. This may be your problem. If the pressure is fine, go to Step 29(e).

(e) Heat the sample with the heat gun for 20 minutes. This is crucial.

(f) Wait for the sample to cool. Replace the small liquid nitrogen Dewar around the sample. Wait a few minutes for the sample to cool to 77.4 K.

(g) Close stopcock A.

(h) Repeat Step 28, adding nitrogen to the burette as needed to increase the pressure to 100 Torr.

(i) Repeat steps 30-31.

32. Close stopcock B.

33. You need to obtain seven to ten more data points for values of the final pressure, p_i $(i = 2 - 10)$, ranging from p_1 to 250 Torr.

34. If you have time, obtain some widely spaced points over the range 250-650 Torr. In any case, you should obtain a total of at least 10 points.

Shutdown:

35. When you have taken all of your data, evacuate the whole system by doing the following:

(a) Stopcocks A, B, C, D, and C1 should be closed.

(b) Open the stopcock that bypasses the diffusion pump. Close the two stopcocks that connect the diffusion pump with the rest of the system.

(c) Slowly open stopcock A. This pumps the sample down.

(d) Open stopcock C1.

(e) Slowly open stopcock D. This pumps Sections 1 and 2 down.

(f) Slowly open stopcock C. This pumps the burette down. Wait about 5 minutes.

(g) Open the two stopcocks that connect the diffusion pump with the rest of the system. Close the stopcock that bypasses the diffusion pump.

36. Now let the system pump down for a total of 30 minutes before you remove the small liquid nitrogen Dewar (Step 34(a)). If you do not let it pump down that long, then when you remove the Dewar, so much nitrogen will 'desorb' from the silica that the glass could explode! Be careful!

37. After the sample has pumped down for 30 minutes:

(a) Remove the small liquid nitrogen Dewar from the sample. This nitrogen will evaporate with time.

(b) Turn off the diffusion pump, but leave the water on for 15 more minutes. Otherwise, oil vapor will enter the rest of the system!

38. Open the stopcock that bypasses the diffusion pump and close the two stopcocks that connect the diffusion pump with the rest of the system.

39. When the diffusion pump has been off for at least 15 minutes, turn off the water.

40. Turn off the capacitance manometer.

41. Leave all parts of the system (except the diffusion pump) open to the mechanical pump.

3 Heat of Combustion (LabVIEW)

Introduction: In this experiment the standard enthalpy of combustion for an organic compound will be measured by means of a bomb calorimeter. As will be shown below, the enthalpy of combustion can be calculated from the temperature rise, which results when the combustion reaction occurs under in a calorimeter. If is important that the reaction in the calorimeter take place rapidly and completely. To this end, the material is burned in a steel bomb with $O_2(g)$ under a pressure of about 25 atm. Combustion of a molecule with a known standard enthalpy of combustion, benzoic acid in this experiment, leads to a measurable temperature rise in the calorimeter. Knowledge of the heat input in conjunction with the measured temperature rise yields the heat capacity for the calorimeter. Once the heat capacity of the calorimeter has been determined, it can be used to determine the energy/enthalpy of combustion for other combustible compounds (benzil, sucrose, or another molecule of choice).

3.1 Theory

From the first law of thermodynamics, the change in internal energy for a process is

$$\Delta U = q + w_{PV} + w_{non-PV} \tag{3.1}$$

where ΔU is the internal energy change for system, q is energy transfer into system by heat flow, w_{PV} is pressure-volume work, and w_{non-PV} is all other forms of work. For a constant volume process, where no other form of work is allowed,

$$\Delta U = q_V \tag{3.2}$$

The subscript V indicates a constant volume process. Equation 3.2 implies that a measurement of the heat added to, or removed from, a constant-volume system, as it moves from products to reactants, is really a measure of the internal energy change. As it is often more practical to conduct experiments at constant pressure as opposed to constant volume, we will define enthalpy, H, to be

$$H \equiv U + PV \tag{3.3}$$

For a constant pressure process where no other forms of work are allowed, the change in enthalpy is

$$\Delta H = q_P \qquad (3.4)$$

where the subscript P indicates a constant pressure process.

Whether the determination of the change in energy is carried out at constant pressure or at constant volume is largely a matter of convenience. Generally, it is easier to work at constant pressure; however, the determination of the heat of combustion is more easily carried out in a bomb calorimeter. In either case, switching between internal energy and enthalpy is straightforward as the definition of H leads directly to

$$\Delta H = \Delta U + \Delta(PV) \qquad (3.5)$$

Since the standard enthalpy and energy for a real gas are so defined as to be the same, respectively, as the enthalpy and energy of the gas in the zero-pressure limit, the ideal-gas equation may be used to evaluate the contribution of gases to $\Delta(PV)$ in Equation 3.5. The result is

$$\Delta(PV) = (n_2 - n_1)RT \qquad (3.6)$$

where n_2 is the number of moles of gaseous products and n_1 is the number of moles of gaseous reactants. The contribution to $\Delta(PV)$ from the net change in PV of solids and liquids in going from reactants to products is generally negligible.

The standard enthalpy of combustion for a substance is defined as the enthalpy change $\Delta_c H^o$ which accompanies the complete oxidation (reaction with O_2) of an organic compound to form specified combustion products: $CO_2(g)$, $H_2O(l)$, $N_2(g)$ $SO_2(g)$. Standard enthalpy of combustion at the given temperature implies that the reactants are pure, unmixed, and in their standard states and that products are pure, separated, and in their standard states. Thus the standard enthalpy of combustion of benzoic acid at 298.15 K is given by

$$C_6H_5CO_2H\,(s) + \frac{15}{2}O_2\,(g) \quad \rightarrow \quad 7CO_2\,(g) + 3H_2O\,(l) \qquad (3.7)$$
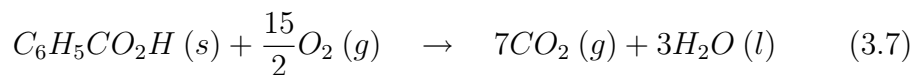
$$\Delta_c H^0_{298.15} = 3228.2 \; \frac{kJ}{mole} = 26.43 \frac{kJ}{g} \tag{3.8}$$

More generically, the reaction of the form

$$A(T_0, P_0) + B(T_0, P_0) \quad \rightarrow \quad C(T_0, P_0) + D(T_0, P_0) \qquad \Delta_c H^0 \tag{3.9}$$
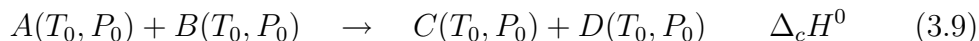
It should be recognized that the process that actually takes place in the bomb calorimeter does not correspond exactly to one of the type of Equation 3.9. It should be easily noted that this is a constant volume process, i.e. we are measuring energy rather than enthalpy. In addition, for the actual calorimeter process the reactants and products are not in their standard states.
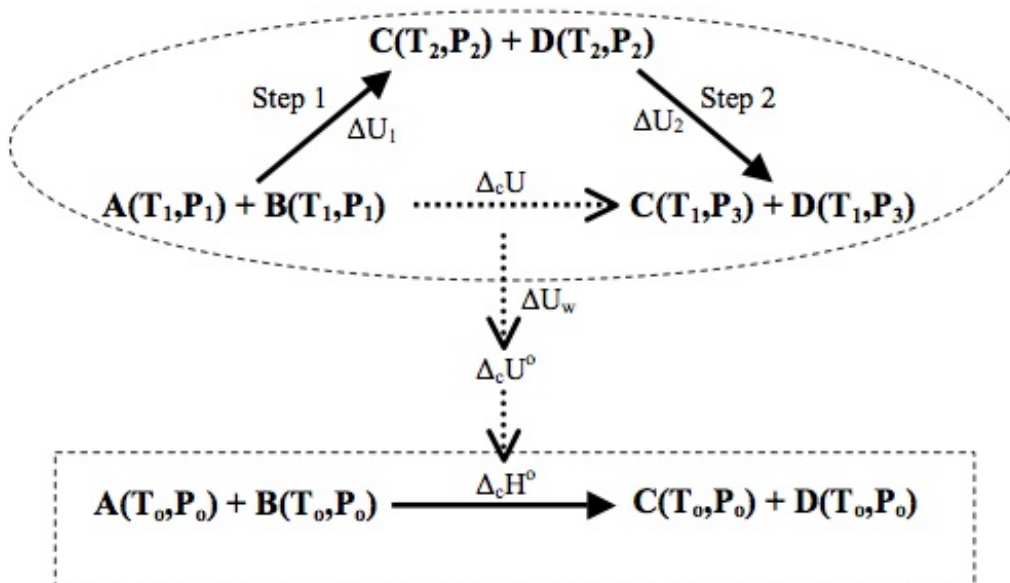
Figure 15: Relationship between pertinent states of the calorimeter system. Isothermal standard state process is boxed and the calorimeter process is circled.

The constant volume combustion process within the bomb is more accu-

rately given by

$$A(T_1, P_1) + B(T_1, P_1) \quad \rightarrow \quad C(T_1, P_3) + D(T_1, P_3) \qquad \Delta_c U \qquad (3.10)$$
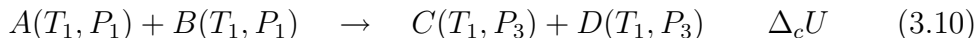
Considering that energy/enthalpy changes are state functions and path independent, in calorimetry it is usually more convenient to consider the reaction as the sum of two steps:

1. Adiabatic reaction ($q = 0$):

$$A(T_1, P_1) + B(T_1, P_1) \quad \rightarrow \quad C(T_1, P_3) + D(T_1, P_3) \qquad \Delta_c U_1 \quad (3.11)$$
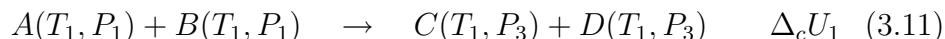
2. Products are returned to the initial temperature by either adding heat to the system or removing heat from the system.

$$C(T_2, P_2) + D(T_2, P_2) \quad \rightarrow \quad C(T_1, P_3) + D(T_1, P_3) \qquad \Delta_c U_2 \quad (3.12)$$
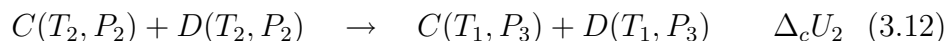
Since the change in energy is independent of path the energy of combustion, $\Delta_c U$ (dashed arrow in Figure 15) is the sum of step 1 and step 2. Once the energy of combustion is known, $\Delta_c U_0$ and then ΔH_0 can be calculated.

Figure 15 is a diagram of the relationship of the calorimeter process (circled) to the isothermal standard-state process (boxed). Calorimetry is typically done at or near 298 K and in most cases it is reasonable to assume that $T_0 \approx T_1$. In addition to this simplification, the reactants and products need to be corrected to the standard state (convert $\Delta_c U$ to $\Delta_c U_0$); this step is marked with ΔU_w in Figure 15. The correction to standard states, called the *Washburn correction*, may amount to several tenths of 1 percent and is important in work of high accuracy; consequently, we will neglect it for this experiment. The principal Washburn correction terms allow for the changes in U associated with (a) changes in pressure, (b) mixing of reactant gases and separating product gases, and (c) dissolving reactant gases in, and extracting product gases from, the water in the bomb.

To find $\Delta_c U$ we simply need to sum ΔU_1 and ΔU_2. Since step 1 was carried out adiabatically, $\Delta U_1 = 0$ and, consequently, $\Delta_c U = \Delta U_2$. To find ΔU_2, we need to measure the heat required to bring the combustion products

back to the starting temperature. In practice, it is often unnecessary to actually complete this step. (Although you should think about how this might be done.) If we know, or can calculate, the heat capacity of the system, the change in temperature associated with step 1 can provide the requisite information to find ΔU_2. From the first law, we know that

$$dq = dU = \left(\frac{\partial U}{\partial T}\right)_V dT = C_V dT \tag{3.13}$$

After integration, the energy change in going from T_2 to T_1 (step 2) is given by

$$\Delta U = \int_{T_2}^{T_1} C_V dT \tag{3.14}$$

Note that the heat capacity we are interested in is for the system and does not include the heat capacity contribution from the products. For small temperature changes, the heat capacity is nearly constant and Equation 3.14 can be simplified to

$$\Delta = C_V(T_1 - T_2) \tag{3.15}$$

In the first part of this experiment, we calculate C_V with a known ΔU and a measured temperature change. In the second part, we use the calculated heat capacity to find an unknown ΔU with a measured temperature change.

3.2   Experimental

About the calorimeter: A bomb calorimeter has the metal bomb inside of a metal bucket containing water. That metal bucket sits loosely inside an insulated jacket. There is a stirrer that sticks into the water in the bucket and is driven by a motor outside of the calorimeter. A thermometer also sticks into the water in the bucket and is the device that will be used to determine the change in temperature during the reaction. Two electrical leads connect to the top of the bomb from outside and they will deliver the current that initiates the reaction.

The Parr 1108 O_2 bomb is a 342 mL pressure vessel with a removable head and a closure that can be sealed by simply turning a knurled cap until it is hand tight. Sealing forces develop internally when the bomb is pressurized,
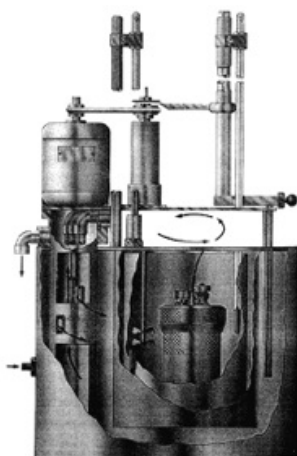
Figure 16: Calorimeter cross-section

but after the pressure has been released the cap can be unscrewed and the head lifted from the cylinder. Two valves with replaceable stainless bodies are installed in the bomb head. On the inlet side there is a check valve, which opens when pressure is applied and closes automatically when the supply is shut off. On the outlet side gases are released through an adjustable needle valve, passing through a longitudinal hole in the valve stem and discharging from a short hose nipple at the top. Turning a knurled adjusting knob controls gas flow through the outlet valve. A deflector nut on the inlet passage diverts the incoming gas so that it will not disturb the sample. A similar nut on the outlet side reduces liquid entrainment when gases are released. A special acid-resistant alloy is used for the construction of the bomb because water and acids are produced in the reaction.

Under normal usage Parr O2 bombs will give long service if handled with reasonable care. However, the user must remember that theses bombs are continually subjected to high temperatures and pressures that apply heavy stresses to the sealing mechanism. The mechanical condition of the bomb must therefore be watched carefully and any parts that show signs of weakness or deterioration should be replaced before they fail. Otherwise, a serious accident may occur.

The head gasket and the electrode seals are the parts that will require most frequent replacement. Check the head gasket frequently and replace it if there is any uncertainty as to its age or condition. Also check and replace the sealing rings in the valves and insulated electrode if there is any evidence of leakage at these points. **Do not fire a bomb if gas bubbles are observed.** Disassemble the bomb and install new seals immediately. Also, do not use extreme force when closing a bomb valve. A moderate but firm turn on the valve knob should be sufficient to stop all gas flow. Excessive pressure will deform the valve seat and possibly close the gas passage. If this happens in the 1108 bomb, unscrew the valve body and replace the 20VB valve seat. Always keep the 397A-packing nut in this bomb tightened firmly in order to maintain a tight seal between the 20VB valve seat and the valve body.

Never under any circumstances use oil on valve or fittings that handle compressed O_2. This precaution applies to all of the O_2 bomb parts as well as to the O_2 filling connection.

Although Parr O_2 bombs are made from alloys that will withstand most corrosive gases, these bombs will not resist chlorine, fluorine, or bromine in the presence of moisture. If samples yielding appreciable amounts of these elements are burned in a Parr bomb, the interior surfaces may become etched or corroded. In such cases, the bomb should be emptied and washed as quickly as possible after each combustion.

The metal bomb provides a constant-volume system in which the combustion reaction will take place. The sample pellet is placed in the ignition cup and the fuse wire is carefully arranged to touch the pellet but not the cup. The bomb is sealed by screwing the cap on and then filled with a high pressure of pure into the water bucket.

Precautions which must be followed to avoid explosion of Parr bomb

1. The amount of sample must not exceed 1 g.

2. The oxygen pressure must not exceed 30 atm.

3. The bomb must not be fired if gas bubbles are leaking from it when submerged in water.
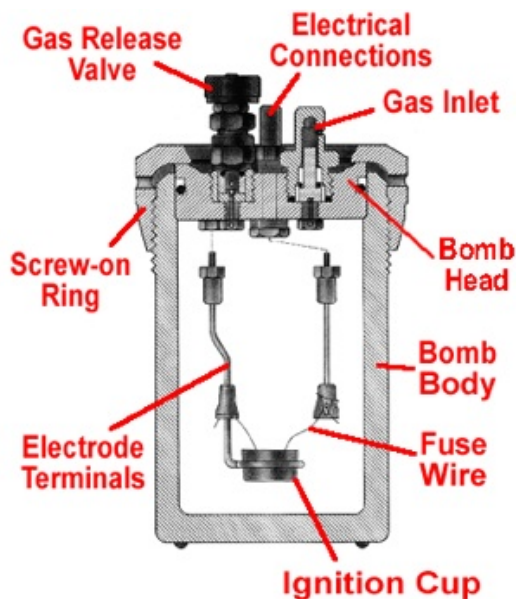
Figure 17: Parr bomb cross-section

4. The operator should stand back for at least 15 seconds after igniting the sample and should keep clear of the top of the calorimeter. An explosion would be most likely to drive the top upward.

5. Much less than 1 g sample should be used for testing materials of unknown combustion characteristics.

6. The use of high-voltage ignition systems is to be avoided. Arcing between electrodes may cause the electrode seals to fail and permit the escape of hot gases with explosive force.

Standardizing the calorimeter

Standardization procedure: The term "standardization" as used here denotes the operation of the calorimeter on a standard sample from which the energy equivalent or effective heat capacity of the system can be determined. The energy equivalent, W, of the calorimeter is the energy required to raise the temperature one degree, expressed as calories per degree Celsius. The

procedure for a standardization test is exactly the same as for testing a fuel sample. Use a pellet of calorific grade benzoic acid weighing not less than 0.9 or more than 1.25 g. Determine the corrected temperature rise, t, from the observed test data, also titrate the bomb washings to determine the nitric acid correction and measure the unburned fuse wire. Compute the energy equivalent by substituting in the following equation:

$$W = \frac{Hm + e_1 + e_3}{t} \tag{3.16}$$

W = energy equivalent of the calorimeter in $cal/{}^oC$
H = heat of combustion of the standard benzoic acid sample in cal/g
m = mass of the standard benzoic acid sample in g
t = net corrected temperature rise in ${}^oC$
e_1 = correction for heat of formation of nitric acid in cal
e_3 = correction for heat of combustion of the firing wire in cal

Example: Standardization with a 1.11651 g benzoic acid sample (6318 cal/g) produces a net corrected temperature rise of 3.077${}^oC$. The acid titration required 11.9 ml of standard alkali and 8 cm of fuse wire were consumed in the firing. Substituting in the standardization equation,

H = 6318 cal/g
m = 1.1651 g
e_1 = (11.9 ml) (1 cal/ml) = 11.9 cal
e_3 = (8 cm) (2.3 cal/cm) = 18.4 cal
t = 3.077 ${}^oC$
    Therefore,

$$W = \frac{(6318)(1.1651) + 11.9 + 18.4}{3.077} = 2402.1 \; cal/{}^oC \tag{3.17}$$

Poor Combustion: The difference in combustion characteristics of the wide variety of materials which may be burned in an O_2 bomb make it difficult to give specific which will assure complete combustions for all samples. However, two fundamental conditions may be stated. First, some part of the sample must be heated to its ignition temperature to start the combustion

and, in burning, it must liberate sufficient heat to support its own combustion regardless of the chilling effect of the adjacent metal parts. Second, the combustion must produce sufficient turbulence within the bomb to bring O_2 into the fuel cup for burning the last traces of the sample.

An incomplete combustion in an O_2 bomb is nearly always due to one or more of the following causes:

1. Excessively rapid admission of gas to the bomb during charging, causing part of the sample to be blown out of the cup.

2. Loose or powdery condition of the sample that will permit unburned particles to be ejected during a violent combustion.

3. The use of a sample containing coarse particles that will not burn readily.

4. The use of a sample pellet that has been made too hard or too soft. Either condition sometimes causes spilling and the ejection of unburned fragments.

5. The use of an ignition current too low to ignite the charge, or too high, causing the fuse to break before combustion is under way.

6. Insertion of the fuse wire loop below the surface of a loose sample. Best results are obtained by barely touching the surface or by having the wire slightly above the sample.

7. The use of insufficient O_2 to burn the charge, or conversely, the use of a very high initial gas pressure that may retard the development of sufficient gas turbulence within the bomb.

8. Insufficient space between the combustion cup and the bottom of the bomb. The bottom of the cup should always be at least one-half inch above the bottom of the bomb, or above the liquid level in the bomb, to prevent thermal quenching.

Magnitude of Errors: The following examples illustrate the magnitude of errors that may result from faulty calorimeter operations. They are based upon an assumed test in which a 1.0000 g sample produced a 2.800^oC temperature rise in a calorimeter having an energy equivalent of 2400 cal/^{o}C.

- An error of 1 ml in making the acid titration will change the thermal value 1.0 cal.

- An error of 1 cm in measuring the amount of fuse wire burned will change the thermal value 2.3 cal.

- An error of 1 g in measuring the 2 kg of water will change the thermal value 2.8 cal.

- An error of 1 mg in weighing the sample will change the thermal value 6.7 cal.

- An error of 0.002^oC in measuring the temperature rise will change the thermal value 4.8 cal.

If all of these errors were in the same direction, the total error would be 17.6 cal.

3.3 LabVIEW

Temperature Measurement Using Computer Data Acquisition System and LabVIEW Program

In the tradition of calorimetry experiments, at least the one described in your lab write-up, temperature is measured by a thermometer and a series of readings are taken to follow the temperature change over the entire combustion and heat transfer process. In this experiment, besides the conventional calorime6try method, you will learn how to take advantage of the modern computerized data acquisition technique. Instead of a thermometer, you will be using a thermocouple to measure the temperature and letting the computer read and record the data. At the same time, you will also have the opportunity to program the analog-to-digital converter board using LabVIEW software.

Before the lab: Read "Getting Started with LabVIEW" and attend one of the prelabs.

Procedure:

1. **Practice programming in LabVIEW**

   (a) After attending the prelab, get a floppy disk from the stockroom. You are allowed to use this disk on the PC designated for this lab experiment **ONLY** during the lab period you are doing the lab. This means after the lab, take it home and use whatever software you are comfortable with to do the data analysis. **NEVER** bring it back.

   (b) Turn on the computer and start Windows XP. Insert you floppy disk to the drive and format it.

   Using the mouse, double click on "My Computer," then right click the floppy drive icon to bring down the menu. Select "Format" to format the disk.

On the Desktop background of Windows XP, you should see a file "TCE.vi" (the suffix "vi" is not visible). Copy this file to your floppy disk.

Right click the file to open the drop-down menu, then choose "copy." Double click "My Computer" on the desktop background, then double click the floppy drive icon. On top of the new window choose the "edit" drop-down menu and choose "paste."

Close all opened windows on the desktop. From now on, you are allowed to operate files ONLY on this floppy disk.

(c) Following the "Getting Started with LabVIEW" build your own Random Number Generator and test it. When you succeed in Step 8 save your data file into your own floppy disk as "data1.txt." Also save your VI program file. In the next step, use "Notepad" to open that data file.

Click "Start" at the bottom left corner of the computer screen. Move the mouse pointer through "program" → "accessories" and click "Notepad."

In Notepad, you should see your data is organized in a long row, separated by a space as follows:

$$0.8750.5780.2340.4780.211\ldots$$

It is not convenient to use this format of data. Common spreadsheet software prefers all data listed in a column, which looks like

$$0.875$$
$$0.578$$
$$0.234$$
$$0.478$$
$$0.211$$
$$\ldots$$

(d) To *transpose* the above data array, do the following: Right below the picture of the "Write to Spreadsheet File.vi" (figure 18), create a Boolean constant (figure 19):

Put the mouse pointer in an empty place, right click, and choose "Boolean" and place it right below the "Write to Spreadsheet File.vi" icon.

Figure 18: Write to Spreadsheet File.vi

(e) Change your mouse pointer to "operation" (little hand with index finger pointed out) if you are not yet using it. Left click the "T" letter in the box. Using the "Wiring" tool to connect this constant box with the Boolean constant (figure 19) icon. Make sure you find the correct terminal on the icon to make the connection.

Figure 19: Boolean constant

(f) The correct terminal is a tiny green square at the bottom side of the icon, right under the lower left corner of the small disk picture. When the mouse is pointed at it, a yellow box will pop out and show "transpose? (no:F)." When you finish, you should see the picture in figure 20.

(g) Save your program under a different name. Execute it and save the new generated file to "data2.txt." Use Notepad to check if your data array is transposed. Close the program and all windows in LabVIEW and go back to the "LabVIEW" dialog page.

2. **Build your own data acquisition Virtual Instrument**
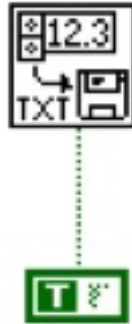
Figure 20: Correct wiring to transpose data array

(a) Open "TCE.vi" from your disk by selecting "Open VI" in the LabVIEW dialog page. It will be open as a panel. Click "Windows" on the top menu bar and choose "Show Diagram." In a new window, you should see the diagram in figure 21.

This is a subroutine for sampling thermocouple output by an Analog-to-Digital converter board installed on the PC and converting voltage signal to temperature (in degrees C). You should build a complete program based on it, without changing it too much:

- The whole program is inside a "For loop," which controls everything inside to repeat 100 times (preset by the number on the upper left corner). The whole loop takes about 1 second to finish. When the loop is running, data can be obtained from outside through tunnels (black marks on the right side of the loop box in this handout, orange boxes on the computer screen).

- Inside the Loop on the left there are two analog input readout boxes using channels 0 and 1 on the A-to-D board. Channel 0 reads the thermocouple output and channel 1 reads the board zero offset.

- After the subtraction of the readouts, the board offset is eliminated (the A-to-D card offset is compensated).

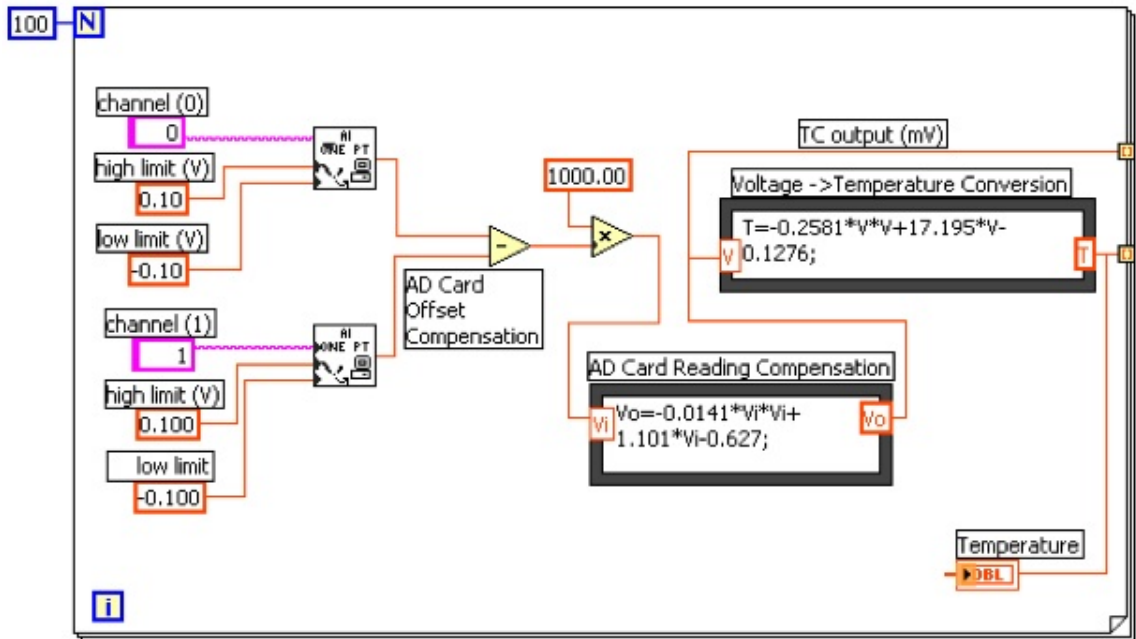- Multiplying by 1000 converts the signal unit from volts to millivolts.

Figure 21: Subroutine for sampling thermocouple output by an A-to-D converter board.

- The signal then flows into the first equation box "AD card reading compensation" to correct the nonlinear readout behavior of the voltage readout. The equation box is obtained by calibrating the board with a high precision digital voltmeter.

- The corrected signal is then split. One way goes directly out of the box, labeled as "TC output (mV)."

  You do not really need to use this signal in the experiment, but it helps to check how accurate out data acquisition board is, by hooking the output to an indicator and comparing the reading with the digital voltmeter reading. See 2h

  The other goes to the second equation box labeled as "Voltage → Temperature Conversion," in which the equation is obtained by fitting data in the 20 to 30 degree C region in the

standard type E thermocouple output chart. Between 17 and 32 degrees C, the accuracy of the equation is better than 0.01 C. A digital indicator labeled as "T sample" and also directed out of the "For Loop," ready to use, then displays the output of this equation.

(b) Outside the "For Loop," build a mean function and indicator. Using the "Wiring" tool, wire the Temperature output (the lower tunnel) to the X input terminal of the "Mean VI." Now you can average the 100 temperature readouts generated by the "For Loop" and display the mean value on a digital indicator.

(c) Outside the "For Loop," create a waveform chart and connect it to the "Mean VI" output. Change the Y scale range to 10-40 temporarily for test purposes. Later, during the experiment, change it to 15-30 or whatever you feel better).

(d) Make a "While Loop" to enclose everything. Change to the "Panel" window. Make a vertical toggle switch. Find the switch terminal in the "Diagram" window and make sure it is outside the "For Loop," but inside the "While Loop." Then wire the switch terminal to the conditional terminal.

(e) Select "Write to Spreadsheet File.vi" and place it outside the "While Loop." Transpose the data array, as described above in 1c. Wire the 1D data input terminal of this VI to the "Mean VI" inside the "While Loop" (See Guide 2-16 Steps 8-9). Make sure you enable indexing for the new tunnel on the wall of the "While Loop."

Now you have built the whole program, your own VI to do the temperature measurement and data acquisition.

(f) The thermocouple wires should already be connected to a Hewlett-Packard Digital Multimeter and to the National Instruments AD board. Make sure that throughout the entire lab the cold reference junction of the thermocouple is immersed in an ice water bath.

(g) Test your program by changing the temperature of the thermocouple sensor (using water with different temperatures or by touching it with your hand) and see if the digital indicator and wave graph

give you the correct response. Do not forget to turn on the toggle switch to keep the "While Loop" running. When you turn off the toggle switch, a file saving window will pop out. If you like, save the data file, then open it by Notepad, and check if the data are correctly recorded.

(h) You can also test your program by checking the data from "TC output" (the upper tunnel on the wall of the "For Loop"). Wire it to a "Mean VI" and an indicator, just like what you have done in 2b. When the VI is running, compare the reading on the indicator with the reading on the digital voltmeter and see how close the compensating equation works.

(i) Your VI will take a measurement about every second. The whole combustion and heat transfer process takes about 25 minutes and you will end up taking 1500 data points for each trial. If you do not want to process this amount of data, you can change the size of the "For Loop" from 100 to a bigger number. In doing this, you are averaging the reading for a longer time, thus getting less data points in a certain period of time.

(j) Print the Diagram of your VI program. In the diagram window press Ctrl-P, or click File >> Print window.

Now you are ready for the combustion experiment!

3. **Pellet making with a Parr pellet press**

(a) Making a pellet is done to prevent scattering of material during combustion, with consequent incompleteness of reaction. The die and its holder are located on the base of the press. Set the die in its holder with the beveled edge of the die cavity facing upward and with the bottom of the die resting on the flat surface in the reversible holder. The die should be filled with a little less than 1 g of benzoic acid or naphthalene.

(b) Place the die and die holder filled with your sample on the press and push the lever down to compress your sample into a pellet. The lever should require a firm push as you swing the handle. If you cannot swing the lever completely, lower the anvil

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The anvil what the die holder is sitting on. To lower the anvil, turn to the left. You should be able to turn the anvil easily so if you are exerting force, it is probably as low as it can go and you should reweigh your sample.

until you can swing the lever completely. Conversely, if the lever swings freely, the anvil needs to be raised.

(c) Next you need to remove the pellet from the die. To do this, you first need to reverse the die holder to bring the deep cavity under the die and return the die holder and die on the press. You should take care to hold the die and swing the lever carefully so as not to destroy the pellet. If the pellet is not ejected, raise the anvil and swing the lever again. Remove the pellet with forceps.

(d) You are now ready to begin assembling the Parr Bomb.

4. **Assembling the Parr bomb**

(a) Weigh the pellet and place it in the sample pan.

(b) A fuse wire should be made to be 10 cm. The fuse wire is found in the drawer below the calorimeter. There are two terminals on the lid of the Parr bomb with holes for the wire to be inserted. Once the wire is attached to the terminals the covers for the terminals should be lowered to insure that the wire does not slip out one the bomb is assembled. The wire should make contact with the top of the pellet without shorting.

If there is a short in the wire, you will not be able to ignite the system and will have to reassemble the bomb. It is also important to avoid getting kinks in the fuse wire since fusion may occur at such points before the portion of wire in contact with the pellet becomes hot enough to initiate combustion.

(c) The surfaces inside the bomb must be kept very clean and dry. It is also important to keep the O-ring of the bombs lid dry. If the O-ring is not dry, leaks may occur and you will have to dry the O-ring and reassemble the bomb.

(d) The cover of the bomb should be carefully assembled with the bomb and tightened. You are now ready to pressurize the bomb.
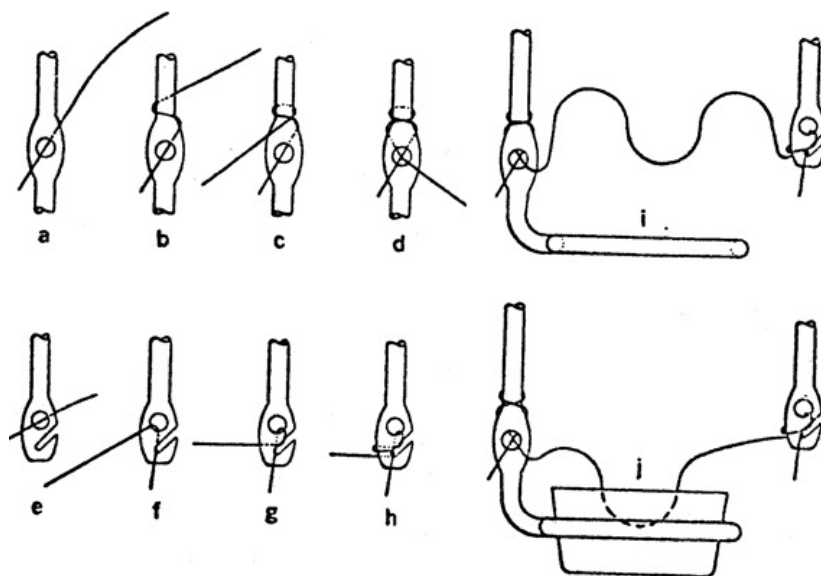
Figure 22: Steps in binding fuse wires to electrodes

5. **Filling the Parr bomb with O_2**

   (a) The O_2 tank is located next to the door. Place the loaded bomb on the cart next to the tank and connect the fill line. On the end of the fill line there is a square metal piece with a hole that fits over one of the connections on the bomb (the connection has a small hole on its side that allows the bomb to be pressurized). The connection has two O-rings that are important in pressurizing the bomb. Care should be taken to insure that these O-rings remain in the connection.

   (b) Close the valve on the gas regulator along with the toggle switch.

   (c) Open the main valve on the O_2 cylinder

   (d) Be sure the vent valve on the Parr bomb is close. You will hear the gas leaving the bomb if this valve is not close.

   (e) Slowly open the filling valve on the regulator until the pressure gauge reads 10 atm.

   (f) Close the filling valve on the regulator and open the toggle switch to relieve the line pressure.

(g) Open the vent valve on the Parr bomb slowly and slowly vent the gas to purge the bomb of N_2.

(h) Repeat steps 5d to 5g.

(i) Repeat steps 5d to 5f filling with 25 atm instead of 10 atm.

6. **Measurement procedure**

(a) Place the filled bomb in the calorimeter WITHOUT TIPPING and attach the ignition leads. Tipping the bomb can cause the pellet to come out of the sample pan and/or the fuse wire to detach from the sample.

(b) The calorimeter must be filled with 2000 ml of water. There is a volumetric flask next to the calorimeter that can be used. The temperature of the water should be near room temperature. The calorimeter is placed within an adiabatic jacket. The water must cover the bomb. If gas bubbles escape, the assemble may require tightening or the gasket may need to be dry or replaced.

(c) Lower the bakelite cover by loosening the screws. Make sure the ignition wires are attached before you lower the cover. Also, check to see that the wires are not caught on the lip of the calorimeter since they can be pinched and broken when the lid is in place. The lid should rest on the top of the calorimeter. You may want to tighten the screws to ensure that heat does not escape the calorimeter.

(d) Make sure that the thermocouple junction is in an ice bath.

(e) Lower the stirrer as far as it can go and tighten the screw on the top of the stirrer. Turn on the stirrer.

(f) Start running your LabVIEW program and monitor the temperature for five minutes. Do not forget to turn on the toggle switch to keep the While Loop running. When you are finished collecting data, stop the run by turning off the toggle switch so that you can save your data.

(g) Turn on the variac and power supply for the ignition device. Noting the time, press the ignition button and hold down until the red light goes out. **DO NOT HOLD YOUR FACE OVER THE**

CALORIMETER WHILE FIRING OFF FOR SOME 60 SECONDS THEREAFTER.

(h) If the sample has ignited, the temperature should start to increase in about 30 seconds. If you do not see and increase in temperature, press the button once more.

(i) The temperature will continue to increase for about 10 minutes. You should continue to record data for 5 minutes after a steady state is reached. Stop the LabVIEW program by turning the toggle switch off. If you hit the red stop button, your data will not be stored and you will have to redo the experiment.

(j) Remove the bomb from the calorimeter and carefully vent the gas before opening.

(k) Clean and dry the calorimeter, bomb, and parts. Handle the bomb carefully so as not to damage precision machined parts.

(l) You should do two trials of benzoic acid and two trials of naphthalene.

3.4 Data Analysis

Finding ΔT:

1. Plot Temperature vs. time for both foredrifts and afterdrifts

2. Extrapolate forward and backward in time to midpoint of temperature rise. The vertical distance at the midpoint is ΔT for the run.

3. Using the $T_{initial}$ table find T_{final}, $T_{average}$, and ΔT for the run.

Note: The data file stored in the disk contains only a single column of temperature data array. To draw the temperature time plot, we still need the time series, which is not available in the data file. However, there is a way to get around this problem. We know the time spacing between two consecutive temperature data is a constant, which is determined by the size of the "For Loop." Besides, exact timing for the experiment is not necessary; because what we need are just the initial and final temperature of the water bath. Therefore, we can generate our own X coordinate series as long as it has evenly space number. For convenience, we can use the numeric order of each temperature data point as the "time" coordinate. If is just a linear

transform of the X coordinate, you can time the experiment and then convert the above number series to a real time series.

Calculations:

$$C = mC_{H_2O} + C_o \qquad (3.18)$$

where m is the mass of water in can and C_{H_2O} = the heat capacity of water per gram = 0.999 cal deg^{-1} g^{-1}, at room temperature. Here C$_o$ represents the heat capacity of the calorimeter (bomb and contents, can immersed portion of thermometer, etc.). The value of C$_o$ may be assumed to be the same for all four runs.

For the benzoic acid runs, ΔU is considered to be known, and C$_o$ may be calculated from the temperature rise. The value of ΔU is calculated by allowing (see Ref. 1) -6318 cal/g of benzoic acid burned and the value specified by the manufacture [4] for the wire burned. The contribution from nitric acid formed may be calculated when necessary as 13,800 cal/mol of HNO$_3$ produced.

The data for the naphthalene runs are used to calculate $\Delta_c U^0$ and the standard heat of combustion $\Delta_c H^0$; for student work, the difference between $\Delta_c U(T)$ and $\Delta_c U^0(T)$ may be considered negligible. The values of $\Delta_c U^0$ and $\Delta_c H^0$ should be reported for 1 mole of sample.

The standard enthalpy of formation of naphthalene is then calculated from the values -94.05 and -68.32 kcal/mole for the standard enthalpies of formation of CO_2 (g) and H_2O (l), respectively, at 25°C. If the experimental values of T$_1$ are within a few degrees of 25°C, the correction of the enthalpy of combustion from T$_1$ to 25°C may be omitted.

3.5 Discussion

1. How does the order of magnitude of the error introduced into the experimental result by the assumption of the perfect-gas law in equation 3.6 compare with the uncertainties inherent in the measurements in this experiment?

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[4]For example, -2.3 cal/cm for Parr 45C10 (No. 34 B & S gauge Chromel C).

2. What is the magnitude of the uncertainty introduced by lack of knowledge of the specific heat of the sample?

3. Does your $\Delta H^0_{T_1}$ value pertain to the initial or the final temperature?

4. Why doesnt the temperature display in your LabVIEW program read 23^oC before ignition of the bomb?

References

1. Garland, C. W.; Nibler, J. W.; Shoemaker, D. P. *Experiments in Physical Chemistry*, 7 ed.; McGraw-Hill: Boston, 2003.
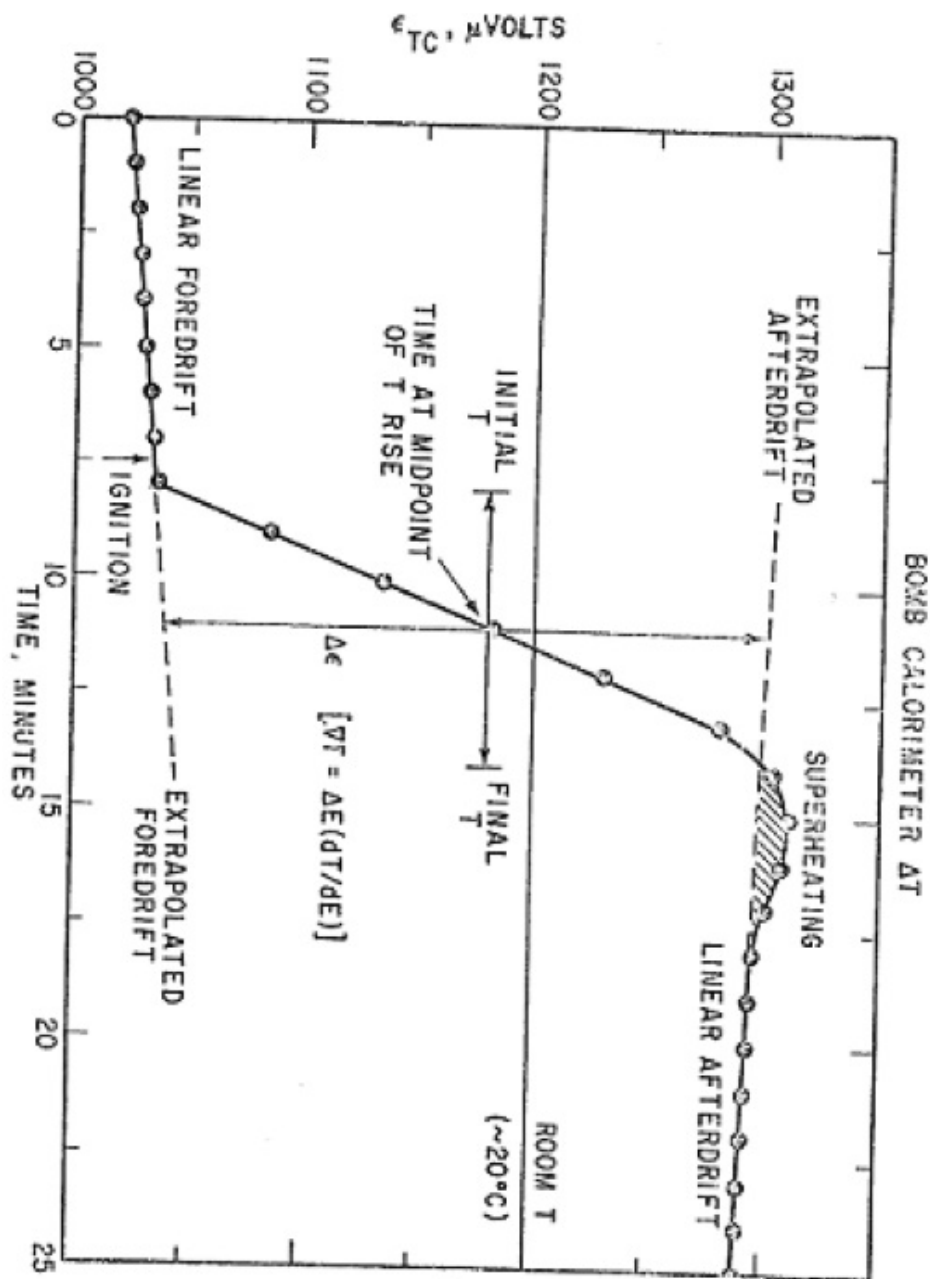
2. Atkins, P. W.; De Paula, J. 2002.

Figure 23: R.S. Jessup, Precise Measurement of Heat Combustion with a Bomb Calorimeter, *Natl. Bur. Std. U.S. Monograph* 7, 1960

4 Knudsen Effusion

Introduction: [5] Knudsen effusion can be used as a dynamic method of vapor pressure determination provided that it is restricted to the measurement of very low pressures. Effusion simply means that a <u>small</u> hole (with area, A) of the wall is empty, allowing molecules to escape (see figure the following figure). There is emphasis on *small* because this allows the consideration of the container of gas molecules as having a defined pressure and temperature, and permitting the use of the equations from the kinetic theory of gases.
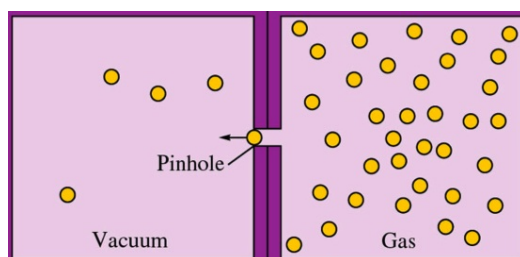
Figure 24: Effusion process

The maximum pressure that can be measured by this method lies between 10^{-2} and 10^{-3} mm Hg (torr). In present day research the technique is usually used for the determination of vapor pressures at high temperatures. However, the high temperature is not an essential feature of the method. The only requirement is that the pressure be low. The material whose vapor pressure is to be determined is placed in a container with a small hole. *The vapor pressure is nothing more than the amount of material that escapes through this hole in a given length of time.*

4.1 Theory

In order to determine the amount of material escaping (effusing) through the hole, the first task is to calculate how many molecules collide with the wall. That is,

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[5]revised by Paul Peng, Spring 2007

molecules that collide with wall = molecules escaping through area A

Implicit to this is a duration of *time* that this is happening. Define the variable, $\dot{G}$, to be the mass lost per time (grams/sec):

$$\dot{G} \equiv \frac{G}{t} = \frac{\text{\# collisions}}{\text{time area}} \times m \times A \tag{4.1}$$

The "# collisions/time·area" term turns out to be

$$\frac{\text{\# collisions}}{\text{time area}} = \frac{1}{4}\frac{N}{V}\langle v \rangle \tag{4.2}$$

where m is the mass of one molecule and N/V is the number density of molecules. Its simplicity can be misleading; there are crucial assumptions and a number of steps that are required to arrive at this result. Most importantly, the entire basis of the experiment rests on the applicability of the *kinetic theory of gases* to the system. Kinetic theory assumes the following:

1. Size of the molecules are much smaller than the average distance *between* other molecules and the container

2. Molecules *do not interact* with one another

3. Motion is *random* such that the gas can be considered *isotropic*

Kinetic theory predicts the number of molecules that hit a given area in a given period of time. The problem is then to relate the number of molecules which pass through the opening with those that enter the opening. If the mean free path of the molecules is large compared to the diameter and length of the opening, practically all of the molecules which hit the orifice will pass through to the other side. If, on the other hand, this condition is not fulfilled, a number of molecules, due to collisions, will be reflected back to the space from which they originated. It is not always possible to make this correction. Thus, a necessary condition is that the mean free path be large compared to the dimensions of the hole. It is this condition which restricts the method to low vapor pressures.

Two other conditions must be satisfied if this method is used:

1. the rate of effusion through the hole must be slow compared to the rate of vaporization, and

2. the result of the effusion in the vicinity of the hole must be such that the velocity distribution of the molecules is essentially unchanged. These two requirements also make it necessary to have a small hole.

Deriving equation 4.2 requires:

1. Obtaining an expression for the *velocity* of the gas molecules, which leads to

2. a description of molecular *collisions* to the wall and a notion of *averaging*

Taking the entire gas as a whole, the average energy $\langle E \rangle$ is

$$\langle E \rangle = \left\langle \frac{1}{2}mv^2 \right\rangle \tag{4.3}$$

where $\langle E \rangle$ is merely the *internal energy* of the gas system with

$$\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle \tag{4.4}$$

The assumption that motion is random has an implication that there is no preferential direction for the gas molecules. Therefore,

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle \tag{4.5}$$

Substituting,

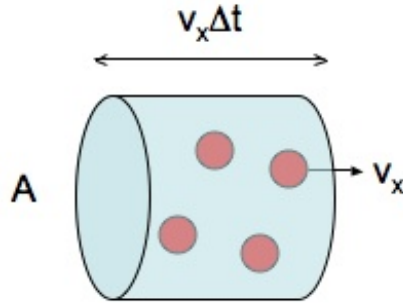$$\langle v^2 \rangle = 3\langle v_x^2 \rangle \tag{4.6}$$

Figure 25: Volume swept out by molecules

Consider the following picture of molecules traveling only in the x-direction with $v = v_x$. In a time frame of Δt before colliding with the wall, the molecules will travel a distance, $d = velocity \times time = v_x \Delta t$.

The *volume* swept out by these molecules upon colliding with the wall (of area, A) is nothing more than the volume of the cylinder,

$$A \cdot v_x \Delta t \tag{4.7}$$

How many molecules are contained in this cylindrical volume that's undergoing the collision? Since the number density, n is number of molecules divided by volume,

$$\text{number of molecules colliding} = \frac{N}{V} A v_x \Delta t \tag{4.8}$$

The molecules that have velocity v_x actually fall under a sliver of velocities, $f(v_x)dv_x$,

$$\text{number of molecules colliding with } v_x = \frac{N}{V} A v_x \left(f(v_x) dv_x \right) \Delta t \tag{4.9}$$

the total number of collisions requires integrating over a distribution of velocities of all the molecules:

$$\underline{\text{total}} \text{ \# molecules colliding with } v_x = \frac{N}{V} A \int_0^\infty v_x f(v_x) dv_x \Delta t \tag{4.10}$$

The integral term is related to the general equation for calculating the absolute value (since the molecule can move, symmetrically, with either positive or negative velocities) of the average of v_x:

$$\langle |v_x| \rangle = \int_{-\infty}^{\infty} |v_x| f(v_x) dv_x$$

$$= 2 \int_{0}^{\infty} |v_x| f(v_x) dv_x$$

It is possible to obtain an explicit value for this integral writing $f(v_x)$ as

$$f(v_x) = \sqrt{\frac{m}{2\pi k_B T}} e^{-\frac{mv_x^2}{2k_B T}} \qquad (4.11)$$

Therefore

$$\langle |v_x| \rangle = 2 \int_{0}^{\infty} v_x f(v_x) dv_x = 2 \int_{0}^{\infty} v_x \sqrt{\frac{m}{2\pi k_B T}} e^{-\frac{mv_x^2}{2k_B T}} dv_x \qquad (4.12)$$

With a change of variables, letting

$$a = \frac{mv_x^2}{2k_B T} \qquad (4.13)$$

meaning that

$$da = \frac{m}{k_B T} v_x dv_x \quad \text{or,} \quad v_x dv_x = \frac{k_B T}{m} da \qquad (4.14)$$

the integral is now

$$\langle |v_x| \rangle = 2\sqrt{\frac{m}{2\pi k_B T}} \int_{0}^{\infty} \frac{k_B T}{m} e^{-a} da$$

$$= 2\sqrt{\frac{m}{2\pi k_B T}} \frac{k_B T}{m} \int_{0}^{\infty} e^{-a} da$$

$$= \sqrt{\frac{2k_B T}{\pi m}}$$

Now that there is an expression for molecules that travel and collide along x (and hence effuse out of the cell), the next goal is to relate this velocity to

the average velocity $\langle v \rangle$ in three dimensions. The new velocity distribution is

$$
\begin{aligned}
F(v_x, v_y, v_z) &= f(v_x)f(v_y)f(v_z) \\
&= \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mv^2}{2k_B T}}
\end{aligned}
$$

Going to spherical coordinates, $F(v_x, v_y, v_z)$ becomes $F(v, \theta, \phi)v^2 \sin\theta d\theta d\phi dv$, and integrating over the isotropic angular components gives a factor of 4π,

$$
F(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mv^2}{2k_B T}} v^2 \tag{4.15}
$$

This distribution function $F(v)$ has just *one* variable, greatly simplifying the mathematics even though it is in three dimensions. The average velocity is thus

$$
\begin{aligned}
\langle v \rangle &= \int_0^\infty v F(v) dv \\
&= \int_0^\infty v \cdot 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mv^2}{2k_B T}} v^2 dv \\
&= 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_0^\infty v^3 e^{-\frac{mv^2}{2k_B T}} dv
\end{aligned}
$$

From an integral table,

$$
\int_0^\infty v^3 e^{-\frac{mv^2}{2k_B T}} dv = 2 \left(\frac{k_B T}{m} \right)^2 \tag{4.16}
$$

and simplifying yields the equation for *average velocity*:

$$
\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}} \tag{4.17}
$$

which, if written as

$$
\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}} = 2\sqrt{\frac{2k_B T}{\pi m}} \tag{4.18}
$$

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can be related to $\langle |v_x| \rangle$:

$$\langle v \rangle = 2\langle |v_x| \rangle \tag{4.19}$$

This is useful because the original goal was to derive an expression for the total number of collisions

$$\frac{N}{V} A \int_0^\infty v_x f(v_x) dv_x \Delta t = \frac{N}{V} m A \Delta t \frac{\langle |v_x| \rangle}{2} \tag{4.20}$$

in terms of $\langle v \rangle$. Substituting $\langle |v_x| \rangle = \langle v \rangle / 2$,

$$\# \text{ collisions} = \frac{N}{V} A \Delta t \frac{\langle v \rangle}{4} \tag{4.21}$$

Therefore,

$$\frac{\# \text{ collisions}}{\text{time area}} = \frac{1}{4} \frac{N}{V} \langle v \rangle \tag{4.22}$$

Finally, the equation for $\dot{G}$ can be written as

$$\dot{G} = \frac{1}{4} \frac{N}{V} m \langle v \rangle A \tag{4.23}$$

With the ideal gas law equation and the explicit form of $\langle v \rangle$,

$$P = \frac{G}{At} \sqrt{\frac{2\pi RT}{M}} \tag{4.24}$$

with G in grams, M the molar mass of the substance, and $R = 8.312 \times 10^2$ dynes· cm/mol· K.

This is the primary equation for the Knudsen effusion experiment. What it says is that if the *mass loss* is measured from a timed, t, trial at a particular temperature, T, then the *pressure* from the effusing material can be determined. It can be further simplified to a more useful form:

Clausius-Clapeyron Equation: If several experiments – each at a different temperature – are run, then the results can together reveal the *heat of vaporization* of the substance via the Clausius-Clapeyron equation:

$$\frac{dP}{dT} = \frac{P \Delta \overline{H}_{vap}}{RT^2} \tag{4.25}$$

the validity of which is guaranteed by *Trouton's Rule*: the heat of vaporization of a substance divided by the absolute temperature of the boiling point is constant. Integrating the above equation yields

$$\ln \frac{P_2}{P_1} = -\frac{\Delta \overline{H}_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{4.26}$$

Molecular collisions: If each molecule's diameter is given by d, then the dashed line in the following figure represents the region for which collisions will happen (i.e. the *collision cross section*). This dashed line has a *radius* of d, as illustrated, so the collision cross section σ is written as

$$\sigma = \pi d^2 \tag{4.27}$$
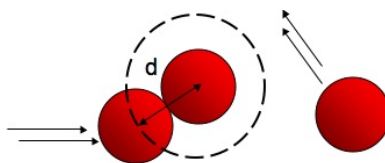
Figure 26: Molecule-molecule collision

Like in the analysis of the molecules sweeping out a cylindrical volume, consider one molecule with cross sectional area σ sweeping out a volume. Suppose the molecule is traveling with an average speed. Then to find the number of collisions per time it has with other molecules, rearrange the first equation's left-hand side:

$$\frac{\# \text{ collisions}}{\text{time area}} = \frac{N}{V}\langle v \rangle \tag{4.28}$$

turns into

$$\frac{\# \text{ collisions}}{\text{time}} = \frac{N}{V}\langle v \rangle \times \text{area} \tag{4.29}$$

But since area in our case is σ,

$$\frac{\# \text{ collisions}}{\text{time}} = \frac{N}{V}\langle v \rangle \pi d^2 \tag{4.30}$$

Recall that in the average speed equation, m is the mass of a gas molecule. During a collision, however, we need to treat the two particles colliding as one system that is moving and hence m is replaced by μ, the reduced mass of the two particles. If the two particles are the same, then

$$\mu = \frac{m}{2} \tag{4.31}$$

Substituting this into the average speed equation yields a *relative average speed*

$$\langle v_{rel} \rangle = \sqrt{\frac{8k_B T}{\pi \mu}} = \sqrt{\frac{8k_B T}{\pi \frac{m}{2}}} = \sqrt{2}\sqrt{\frac{8k_B T}{\pi m}} \tag{4.32}$$

Therefore,

$$\langle v_{rel} \rangle = \sqrt{2}\langle v \rangle \tag{4.33}$$

and it is $\langle v_{rel} \rangle$ that should be substituted in equation 4.30:

$$\begin{aligned}
\frac{\text{\# collisions}}{\text{time}} &= \frac{N}{V}\langle v_{rel} \rangle \pi d^2 \\
&= \frac{N}{V}\sqrt{2}\langle v \rangle \pi d^2
\end{aligned}$$

This equation can be used to calculate how far a molecule moves before it collides with another molecule; that is, the *mean free path, λ*.
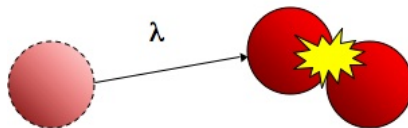

Figure 27: Mean free path λ

The mean free path is nothing more than a *length*, and we can use dimensional analysis to see that we need

$$\lambda = \frac{\text{length}}{\text{collision}} = \frac{\text{velocity}}{\frac{\text{\# collisions}}{\text{time}}} \tag{4.34}$$

because velocity is $length/time$. Therefore,

$$\lambda = \frac{\langle v \rangle}{\frac{N}{V}\sqrt{2}\langle v \rangle \pi d^2} = \frac{1}{\frac{N}{V}\sqrt{2}\pi d^2} \tag{4.35}$$

4.2   Experimental

Figure 28 depicts the layout of the vacuum line.

1. Review the instructions from the GSI on how to pump down the vacuum line using the mechanical pump and diffusion pump (see figure 29).

Always turn stopcocks using two hands. Never pull on the stopcock plugs.

2. The mechanical pump is left on at all times, producing a pressure of about 0.01 Torr or less. To reduce the pressure further, the oil diffusion pump is used in series with the mechanical pump, (see diagram for proper stopcock connections). This step may take 40 to 60 minutes. The liquid nitrogen traps must be filled and the condenser water turned on before powering the diffusion pump.

3. The diffusion pump should not be run isolated from the rest of the system. Do not let air into a hot diffusion pump. Make sure that the pressure gauge is displaying a sufficiently low pressure; check with your GSI.

4. Time permitting, check the pressure in your system using the McLeod gauge. Run the mercury up slowly, and lower the mercury to the reservoir after the pressure reading. When you are using the McLeod, do not use any other part of the system. Do not let air into the McLeod (What will happen?). Leave the McLeod turned off from the vacuum line after the pressure reading.

5. While the pressure is stabilizing obtain from the stockroom:
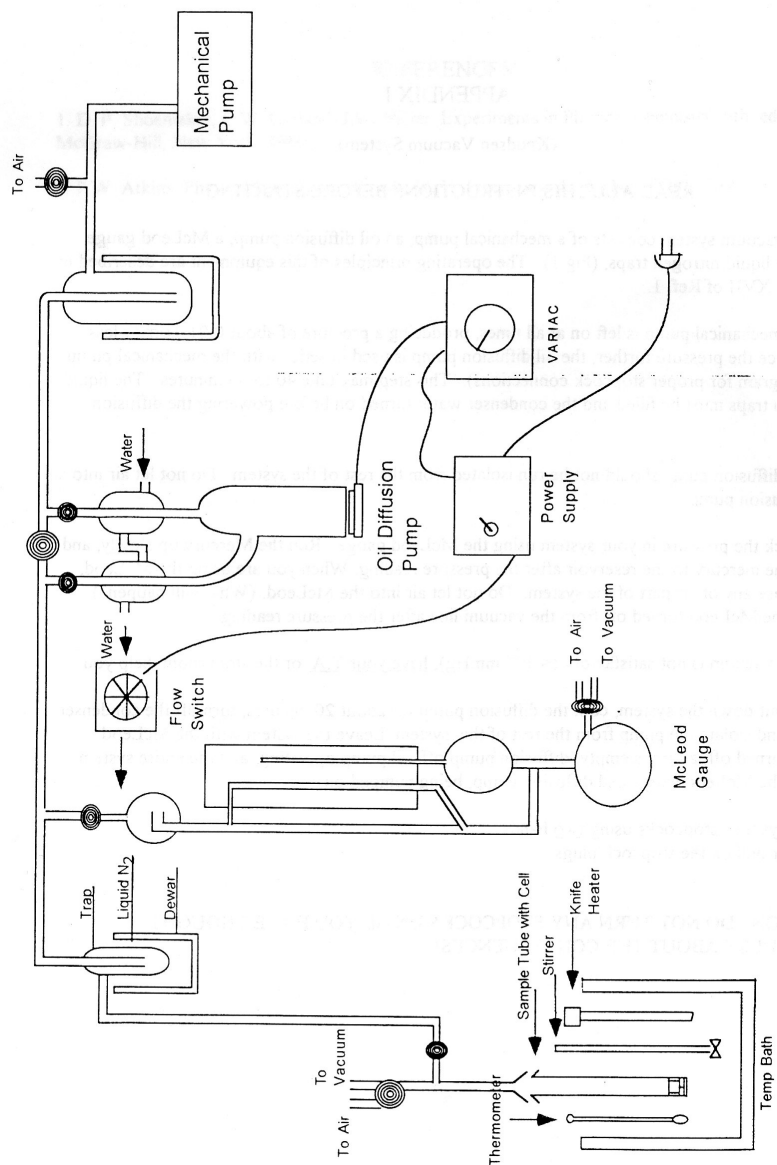
   (a) Approximately 200 mg of camphor

Figure 28: Vacuum line layout

(b) The Knudsen cell (shown in figure 30) and key (figure 31), along with the gold foil with pinhole

(c) Sample chamber with plunger

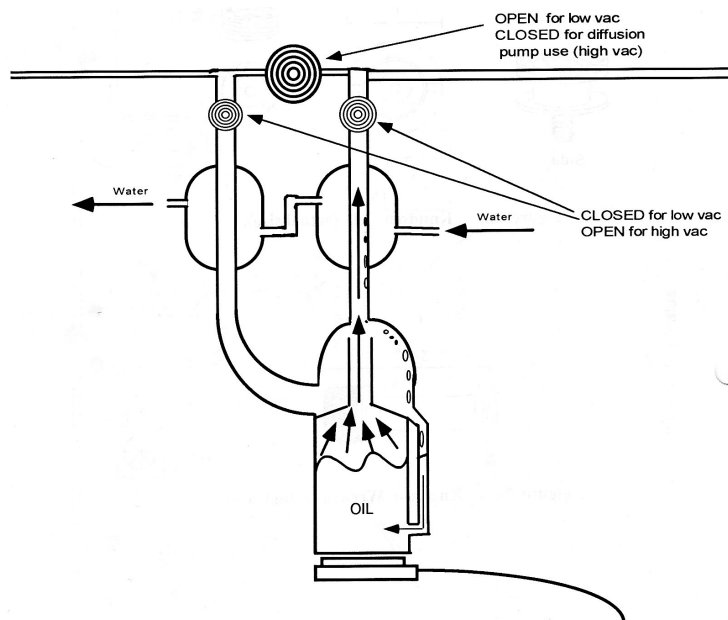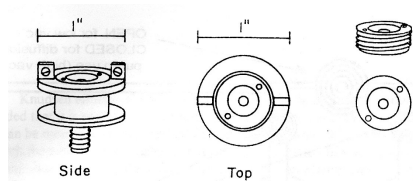Figure 29: Diffusion pump

Figure 30: Knudsen cell

Hole area, Sample preparation:

1. The hole diameter should be $\sim$0.3 mm. Place the foil under the microscope comparator to determine whether the hole is circular or not, and its diameter proper. (If it is not circular, or of an improper size,obtain a new piece of foil.) Measure the size of the hole carefully with the microscope comparator. The dimension should be measured in six different directions. The final diameter to be used in computing the hole area, A, should be taken as the average of all the measurements. Since the orifice tends to collect obstructing particles, wash it with acetone

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and blow it out carefully with filtered compressed air or nitrogen gas before using it.

2. Place about 200 mg of the substance whose vapor pressure is to be determined, and the foil, in the cleaned and dried Knudsen cell, screw on the cap and weight to 0.1 mg. Place the cell in the bottom of the metal sample tube.

3. Check once again that the vacuum pressure is $< 10^{-5}$ Torr, and prepare for the first temperature trial at 25°C: Attach the sample tube to the vacuum line by first holding it against the ground-glass ball joint and opening the three-way stopcock to the house vacuum, (the tube will stick to the joint if there is a good seal,) then clamping it. Rough pump the sample for about two minutes, close the stopcock to the house vacuum, and open the teflon stopcock to connect it to the high vacuum line. Start measuring the time from the moment that this stopcock is opened. Let the system stand for about **two hours**. At the end of the desired time, close the stopcock to the vacuum line, and remove the holder by opening the three-way stopcock to air. Reweigh the cell to 0.1 mg.
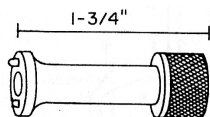

Figure 31: Key for the Knudsen cell

Other trials: While the first temperature trial is running, fill the temperature bath with enough water that will submerge the bottom of the sample tube. Set the dial of the heater for 50°C – check with a thermometer. After the cell is reweighed and mass lost recorded, run the experiment again at 50°C for **30 minutes**.

The last trial at 0°C is run **overnight**. Fill a bucket full of ice yet enough for the sample tube to fit inside. Cover the top with foil.

4.3 Data Analysis

1. Compute the vapor pressures P_{vap} at each of the three temperatures and compare to literature values.

2. Construct a P vs. $1/T$ plot such that the Clausius-Clapeyron equation

$$\ln P_{vap} = -\frac{\Delta H_{sub}}{R}\frac{1}{T} + \text{const.} \qquad (4.36)$$

can be used to extract the heat of sublimation/vaporization, assuming that ΔH_{sup} is temperature-independent. Also compare this to the literature value.

3. Estimate the collision diameter of camphor using its bond lengths and compute the mean free path at all temperatures.

4.4 Discussion

1. Explain how the diffusion pump works and how it is different from the mechanical pump. Why is the diffusion pump necessary in this experiment?

2. Why is metal used as the container in these experiments in preference to glass?

3. Use your data to discuss whether the experimental conditions for effusion are met. What are the possible errors? How valid is the application of the kinetic theory of gases to this experiment?

4. Review the derivation of $\langle v \rangle$ and its relationship to $\dot{G}$. Implicit to its calculation is the function $f(v_x)$ in equation 4.11. Where does this function come from, what does it look like (provide a simple sketch), and how does it change, qualitatively, as a function of temperature and molecular mass? That is, does $\langle v \rangle$ vary as well, consequently affecting $\dot{G}$?