CHMC41H3

APPENDIX TO THE LAB MANUAL

LABORATORY NOTEBOOKS

Unless an accurate and current record or "diary" is kept of all your lab work, the results or products produced may be of little use. Dated, witnessed, complete records of work are required in any "outside" work-place to authenticate any claims made against competitors, for example. A court case is was waged in Fall 1998 by Emory University, Atlanta and a Biotechnology company in Canada over who has first rights to a potentially lucrative chemical, which rested on the lab notebook entries. Many companies now keep microfilm copies of all their employees' notebooks in locked vaults. So, the habit of keeping a "good" lab notebook should become routine to all chemistry students. Even if an experiment is unsuccessful, a review of several different attempted procedures may lead to positive results on another attempt. All references can also be entered into the notebook, so that it becomes a main source of information (e.g. for studying for lab tests!).

Some preparatory notes should be entered into the notebook before the lab, such as an Introduction, Equation, Table of Reactants - including physical properties of reactants and products, toxicities of reagents and products, Theoretical Yield calculations etc. However, the majority of entries into the notebook should be made, **in permanent ink**, at the lab bench, as you perform the experiment. Memories are notoriously wrong or incomplete! A suggested format is as follows:

1. Leave several pages at the beginning of the book for an index.
2. **Begin each new experiment on a new, blank right hand page** to make finding any experiment easier. The notebook pages should be numbered.
3. Give each experiment a number. Then any products from the experiment may be given the same number (e.g. for storage in your locker). So, if experiment six makes two products, then the products may be labelled, e.g.: your initials; expt. number; letter, e.g. JP-6a and JP-6b.
4. Each experiment should be dated, each time work is performed on it.
5. A **reaction scheme**, equation etc. outlining the work to be carried out should be given first. Later, if the reaction did not work, the product may be slashed with a single red line. If another product was formed, it may be added in red or another colour.

6. List any **references** for the experiment, if known.
7. The following quantities should be listed, **in tabular form if possible**, under the equation: Molecular weights, number of moles, and grams or mL to be used, melting points and boiling points of reactants and products, and the theoretical yield.
8. Toxicities for all reactants and products must be given. Obtain this information either from the Merck Index or the Manufacturers Safety Data Sheets available in the labs **or** on the Internet.
9. A short introduction to the reaction may be given.
10. The procedure should then give an **exact** account of the practical method, including **all** observations, errors, spillages, incorrect additions etc. It can be fairly brief and in point form, if required for clarity.
11. Details of any reaction monitoring e.g. titrations, GC, TLC must be included in your notebook, with full size representation of the results.
12. Any details of product work-up or purification should be clear and concise. For example, a recrystallization should record the **solvent** used, the **amount** of **crude product** taken and the **quantity of solvent** , as well as the **final melting point range**. Distillations should record the boiling point range and pressure. Number your products.
13. Any spectroscopic information should be included - a list of **the literature values or expectations** should be stated, and a copy of your **actual spectrum** given with appropriate remarks.
14. Finally, make **concluding remarks** about the experiment.

SUGGESTIONS FOR WRITING FORMAL LAB REPORTS

Effective communication is essential in any aspect of organized society, and nowhere is it more so than in the sciences. Whether or not a discovery or theory is put to rapid use often depends upon how easily the original report can be read and understood by the scientific community. For this reason, a more or less standard format has evolved for journal publications, and this format should generally be followed in writing your lab report. Assume that you are writing for your peers, that is, that the person reading your report has approximately the same knowledge and experience as yourself.

The format of the report should be as follows:

8. **Abstract** - The ideal abstract briefly states the problem, or purpose of the work, indicates the theoretical or experimental plan used, accurately summarizes the principal findings, and points out major conclusions. It is generally no longer than one paragraph.

9. **Introduction** - A good introduction states the problem, or aim of the experiment, clearly. Relevant background theory should be introduced and any assumptions or approximations should be discussed, in your own words.

3 ocedure used, such that your peers would be able to repeat your work. Apparatus need only be described if a new technique was used. All background data, such as equations, and formulas should be included. Any unexpected changes or hazards encountered must be noted and emphasized.

4 **Results, Discussion and Conclusions** - Results may be tabulated, in a section by themselves, if several repetitions were done (e.g. titrations), otherwise they should be included here. Whichever, care should be taken to use correct units of measurement where necessary. The discussion section of the report is the **most important** part. Results should be interpreted and explained and any special features or limitations of the work should be pointed out. Any comparisons or contrasts with previously reported results (i.e. found in the literature) should also be discussed. A summary may clarify your presentation. If the problem has not been completely solved, further studies may be suggested.

5. **References** - **All** references used for your report should be mentioned, including chapters of pages used. It is often helpful if you mark your report with reference numbers that refer to this list.

In summary, reports should be concise. They should be written in prose (i.e. **not** point form), generally in the **past tense** and **passive voice**. Visit the

library for problems with chemistry; problems with English should be solved by visiting the writing lab.

TECHNICAL WRITING: <u>GENERAL</u> REFERENCES

1. Anderson, John A. T11.A5

2. Day, Robert A., "How To Write and Publish a Scientific Paper" 1979 T11.D33

3. Morris, J.E. "Principles of Scientific and Technical Writing" 1966 T11.M58

4. Reisman, S.J, ed. "A Style Manual for Technical Writers and Editors" 1963 T11.R42

5. Trelease, S.F. "How to Write Scientific and Technical Papers" 1960 PE1475.T67

Other references, specific to a particular subject, e.g. anthropology, psychology, may be found by looking in the library catalogue in the subject index under "Technical Writing".

An example of a paper from the literature on a synthesis problem follows. Read it and use it when setting the format for your own Formal Report.

DRYING AGENTS

Water is a common and generally unwelcome impurity in liquid organic reagents, products and reaction mixtures. Water can suppress crystallization of hygroscopic compounds, depress melting points, form minimum boiling azeotropes with alcohols and can slowly react with many classes of organic compounds. It is therefore important that water be removed. Drying may be accomplished by physical means (e.g. fractional distillation, molecular sieves) or chemical means. Drying agents are an example of the latter type.

In most cases drying agents are anhydrous inorganic salts which are insoluble in organic solvents and which form hydrates upon contact with water, thus removing the water from solution. After drying, the hydrate salt can be removed by gravity filtration.

Drying agents vary in their capacity for water (weight of water taken up per gram of agent) and drying intensity (the percentage of water remaining in the liquid when in equilibrium with the product formed by reaction of the agent with water). They also vary in their rate of reaction with water, but this often depends on particle size and porosity of the solid rather than an intrinsic reaction rate. In general, the lower the solubility of water in the liquid, the easier it is to dry.

It is usually sufficient to add just enough drying agent to the liquid to cover the bottom of the stoppered flask containing it. After swirling, some of the granules of solid should still appear loose and not caked. A large excess of drying agent, however, results in loss of product due to adsorption on the solid agent. After allowing the mixture to stand for a short time, the drying process should be completed, and the spent agent should be removed before further work-up. (This is especially important if the next step of the reaction is a distillation because most hydrates break down at moderate temperatures and water would then distil over with the product). Removal of the drying agent is usually accomplished by gravity filtration because water would be "pulled off" the drying agent if vacuum filtration was used, defeating the whole exercise. Care should be taken not to expose the dried liquid to water or moist air for long periods of time.

Some of the commonly used drying agents are shown following:

Drying Agent	Products with H2O	Comments
$CaCl_2$ $CaCl_2 \cdot 2H_20$ $CaCl_2 \cdot 6H_2O$	$CaCl_2 \cdot H_2O$ $CaCl_2 \cdot 4H_2O$ $Ca(OH)_2$	Cheap. Moderate capacity, intensity and speed. Cannot be used for alcohols ketones, amines (reacts); $CaCl_2$ contains some $Ca(OH)_2$, so cannot be used with acids, phenols or esters.
$MgSO_4$	$MgSO_4 \cdot H_2O$ $MgSO_4 \cdot 2H_2O$ $MgSO_4 \cdot 4H_2O$ $MgSO_4 \cdot 5H_2O$ $MgSO_4 \cdot 6H_2O$ $MgSO_4 \cdot 7H_2O$	An excellent drying agent. Quite rapid. Used as a powder, needs careful filtration.
K_2CO_3	$K_2CO_3 \cdot 1.5\ H_2O$	Rather slow. Basic, so cannot be used with acidic substances.
Na_2SO_4	$Na_2SO_4 \cdot 7H_2O$ $Na_2SO_4 \cdot 10H_2O$	Rather slow. Poor intensity, high capacity, neutral. Used as powder.

Refractive Index

Refractive indices of many substances are measured with refractometer, of which there are several types. The most widely used is the Abbe refractometer, one of which you will be using here.

$$\textbf{Refractive index, } n_D^t = \frac{\textbf{speed of light in vacuum}}{\textbf{speed of light in the medium}}$$

where t = temp°C.

D = wavelength of light used.

and of course, light travels more slowly through any medium than it does in a vacuum.

As a physical measurement, the refractive index of a medium is useful to the chemist in a number of ways. It can serve as a means of identification of a substance, or as an estimate of its purity, or even as a means of qualitative analysis, since pure samples should have refractive indices almost the same as literature values. A knowledge of the refractive index of a substance is often necessary to calculate dipole moments of that substance. Molar refractions R, can also be calculated and are characteristic of a given molecule as well as indicative of its structure.

It is a simple and quick procedure to measure a refractive index for transparent or coloured solutions, turbid suspensions, emulsions, fine powders, etc. Measurements are made at a wavelength where the sample will not absorb, and may be estimated to four decimal places on the refractometers we have. Procedures for using both instruments follow.

Temperature Correction: An increase in temperature causes a liquid to become less dense, usually causing a decrease in refractive index. For each degree celsius of temperature change, the average temperature correction has been found to be 0.00045 units for a wide range of compounds. So, if the reading was 1.4370 at 18°C, this would be corrected to 1.4370 - 0.0009 = 1.4361 at 20°C.

Procedure

1. Open prism assembly and remove lens tissue. Inspect the prism for cleanliness. If necessary, clean with water, methanol, or acetone.

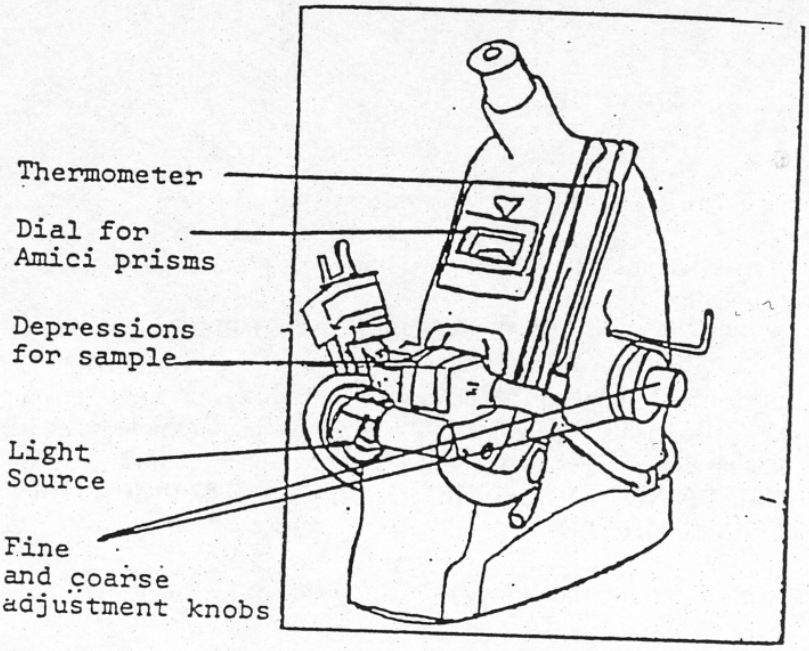
N.B. DO NOT WIPE DRY PRISMS WITH TISSUE.

2. Place liquid sample on the depression in the lower prism, using a pipette, and close the prisms. Experience will show how much sample is necessary. Too much sample is messy, whilst too little gives poor contrast for reading.

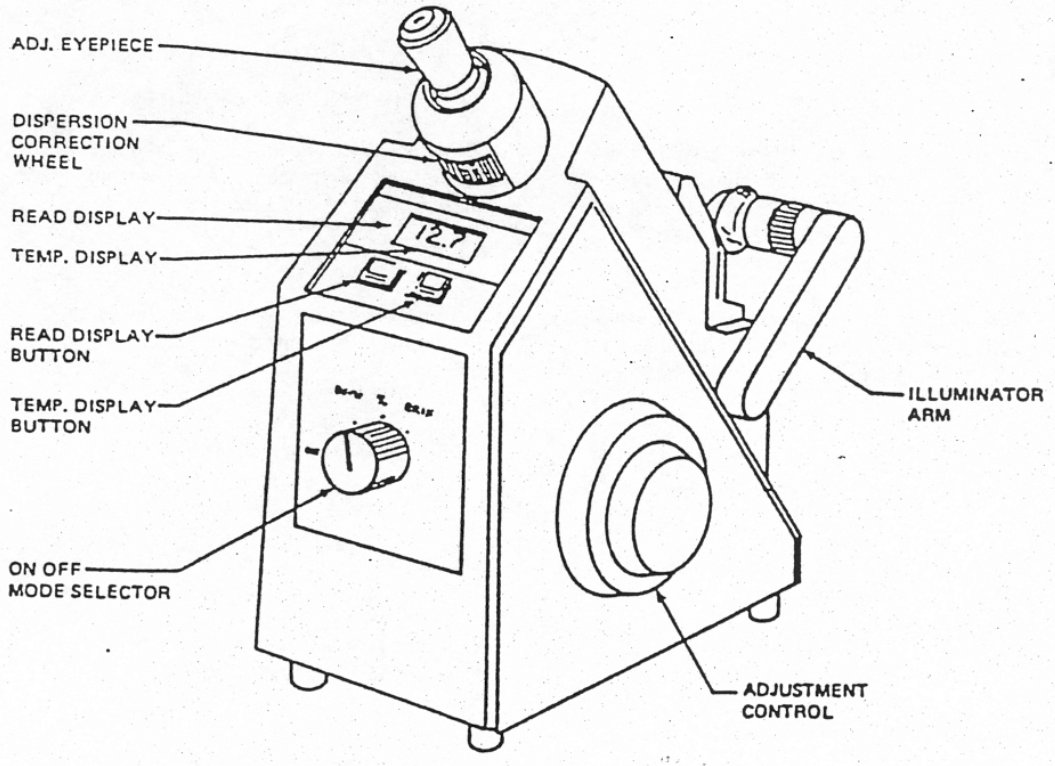
N.B. DO NOT ALLOW METAL OR GLASS APPLICATORS TO TOUCH THE PRISMS.

	Abbe 3L (Bausch and Lomb)	**AO Abbe Refractometer**
3.	Move the illuminator arm upwards.	Move the illuminator arm upwards.
4.	Turn the adjustment control until the lower field appears dark, and the field bright.	Turn the adjustment control until the lower field appears dark, and the upper upper Field bright.
5.	Focus on the cross hairs by moving the eyepiece.	Turn the mode selector to n_D. Focus on the cross hairs by moving the eyepiece.
6.	Rotate the dial for the Amici prisms until a sharp dividing line can be seen. There may be a tinge of red at one end of the line and a tinge of blue at the other.	Turn the Dispersion Correction Wheel until minimum colour is seen. Adjust the lamp for maximum contrast, if necessary.
7.	Turn the adjustment controls to adjust the sharp dividing lines to precisely intersect with the cross hairs.	Turn adjustment controls to adjust the sharp line to precisely intersect with the cross hairs.
8.	Press contact switch at left side of instrument. Reading the top scale, estimating the 4th decimal place.	Depress **READ** button and record reading.
9.	Take a temperature reading from the attached thermometer.	Depress **TEMP** botton and record reading.
10.	Clean the prisms by wiping off the sample with a lens tissue, followed by cleaning with methanol, water, or acetone.	Clean the prisms by blotting off the bulk of sample with a lens tissue, followed by cleaning with water, methanol or acetone. ,

11. If you are the last student to use the instrument: make sure the prisms are clean and <u>close</u> them. <u>Turn the instrument off.</u>



Abbé refractometer. (Courtesy Bausch and Lomb Incorporated, Rochester.)



A0 Abbe refractometer

Infrared Spectroscopy

Refer to a textbook for the theory of infrared spectroscopy.

Infrared spectra will be run on a Nicolet 5DX FTIR, kept in room S-164. This is a modern, single beam, fully computerized instrument with which you should familiarize yourself early in the year.

Spectra can be taken in the solid, liquid or solution, or in the gas phase; however, only solids and liquids will be run in this course. For most organic compounds solution (or neat liquid) spectra are preferable. If a solid compound is not soluble in suitable solvents, then that compound may be run as a mull. Rarely, in this course, a KBr disc must be prepared.

READ CAREFULLY THE INSTRUCTIONS WHICH FOLLOW

1. Care of Cells and Discs

Since cells and discs are made from either NaCl or KBr, great care must be taken in the handling of them. They are sensitive to **any** moisture, whether from your hands, in your sample or from the tap. **Water will dissolve and destroy cells and discs** so **samples <u>must</u> be dry.** [**Cheap** discs cost about $60 US, cheap cells around $400) Water absorbs strongly in the IR (at 3710 cm^{-1} and ~1630 cm^{-1}) and may therefore also mask the peaks you are seeking.

Protect expensive IR cells and discs by:

1. Never handling on the faces through which the IR beam passes;
2. Handling either on the edges or by the cell holder;
3. Using **dry** samples and **dry**, spectroquality solvents;
4. Cleaning cells and discs immediately after use by flushing with fresh, dry, spectroquality solvent.

Samples will be prepared in prep. room fumehoods only - usually S-164 where the FTIR is located. Cell caps (stoppers) should be used with all solution cells to minimize odours.

Preparation of Samples

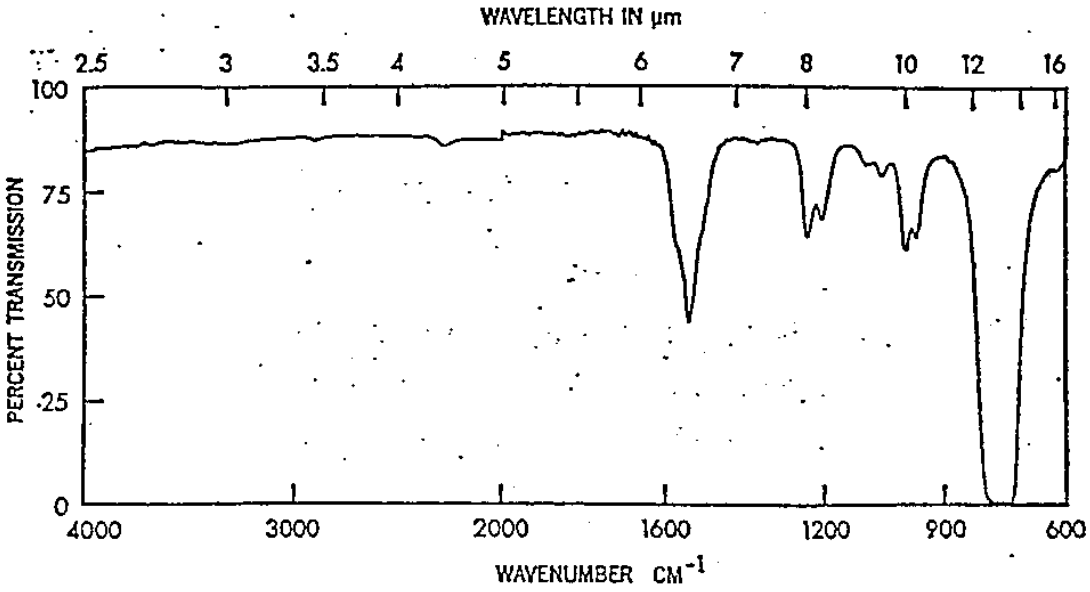
1. Neat Liquids:

Pure liquids are examined between salt plates. Pressing a liquid sample between flat plates produces a thin film. Small amounts of liquid are required (1-10 mg). Thick samples (≥0.1 mm) generally absorb too strongly for satisfactory results.

2. Solutions:

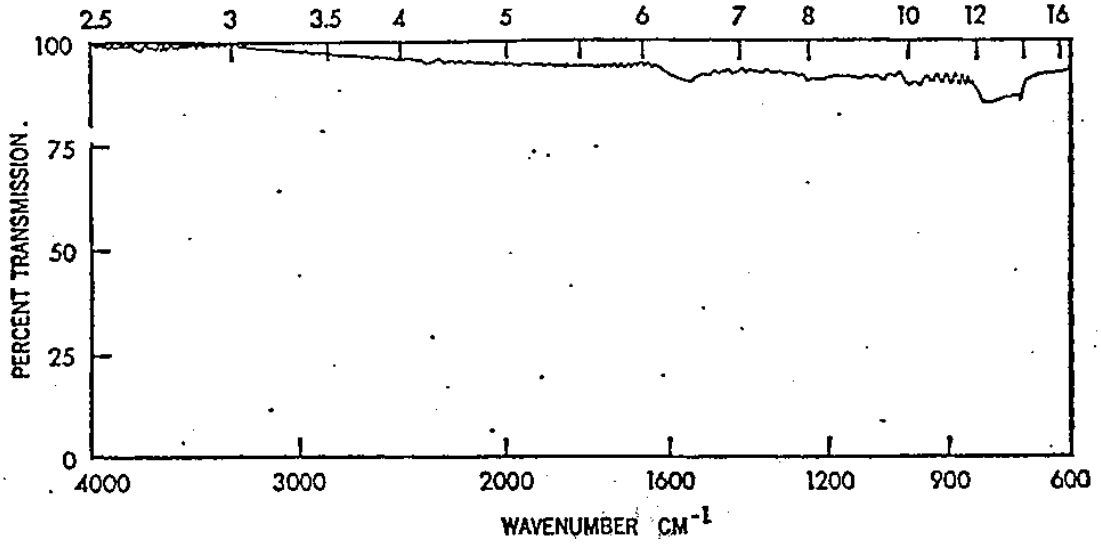
Less than 1 mL of a 0.05-10% solution is required. Most solvents show some absorption in parts of the infrared spectrum, as seen in spectrum 1 of carbon tetrachloride. Solvents should be transparent in the region(s) of interest, or several solvents should be used. An alternative method is to use pure solvent as a **background** reference, which will be subtracted from the solution spectrum thereby cancelling the peaks due to pure solvent, as in spectrum 2.

Spectrum 1



Carbon Tetrachloride at 0.1 mm Path Length

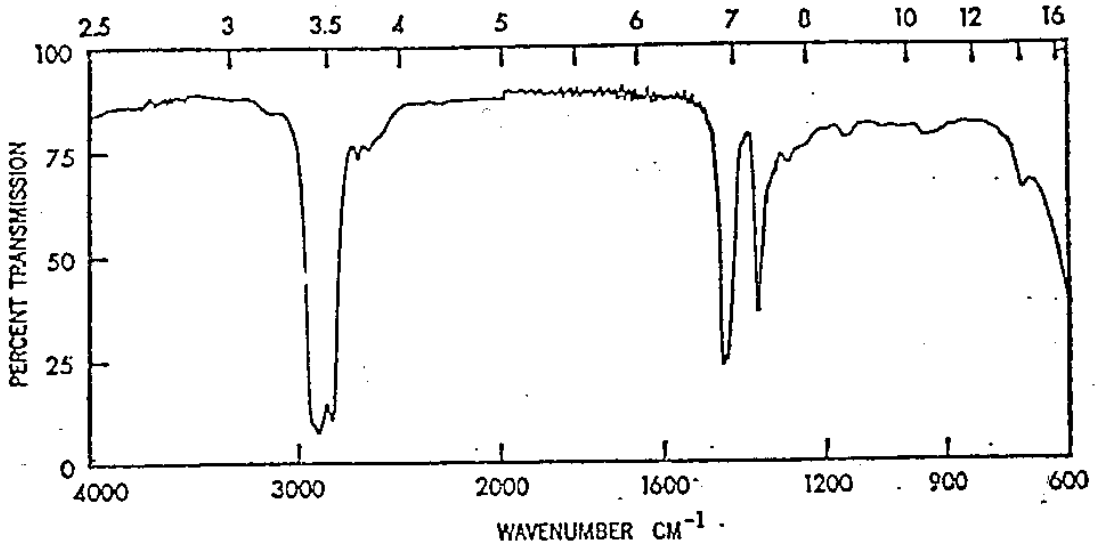
Spectrum 2



Carbon Tetrachloride vs. Carbon Tetrachloride

3. Mulls:

Mulls are prepared by grinding 2-5 mg of solid in a smooth agate motar. Drops of mulling oil (e.g. nujol = mineral oil) are added and grinding continued until a homogeneous, toothpaste like mull is obtained. The suspended particles must be very small so that the radiation is not scattered. The mull is then spread as a thin film between two salt plates. Nujol absorbs in the region shown below:



IR Spectrum of Nujol

4. KBr Discs:

Powdered KBr (or other alkali metals) can be intimately mixed and ground to small particle size with a small amount of dry solid sample. (1 mg sample = 100 mg KBr). After grinding in an agate mortar, the mixture is transferred to special dies and placed under a pressure of 10,000-15,000 pounds per square inch, in vacuo. A transparent disc should result. The quality of the spectrum depends upon the efficiency of mixing and small particle size.

In general, a dilute solution in a non-polar solvent leads to the best spectra for organic samples. Polar compounds are often insoluble in non-polar solvents, and often shown hydrogen bonding effects as a neat liquid, mull, disc or film. KBr discs often show strong water absorption.

Instructions for using the Nicolet FTIR are given in the IRpract experiment

Characteristic Group Stretching Frequencies

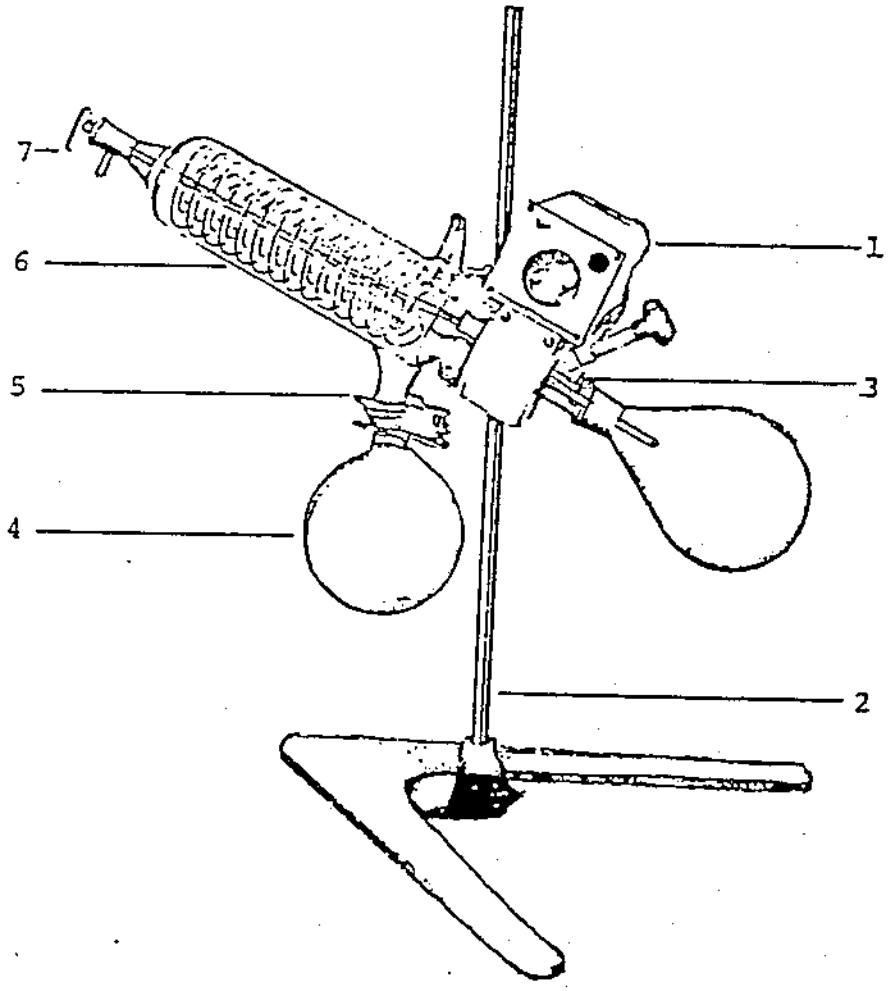
Bond	**Type of Compound**	**Frequency,cm^{-1}**	**Intensity**
-C-H	Alkanes	2850-2960	strong
=C	Alkenes & arenes	3010-3100	medium
–C-H	Alkynes	3300	strong,sharp
-C-C-	Alkanes	600-1500	weak, of no diagnostic use
C=C	Alkenes	1620-1680	variable
-C≡C-	Alkynes	2100-2260	variable
-C≡N	Nitriles	2200-2300	variable
-C-0-	in Alcohols, Ethers, Acids, Esters	1000-1300	strong
C=0	Aldehydes	1720-1740	strong
C=0	Ketones	1705-1725	strong
C=0	Acids, Esters	1700-1750	strong
C=0	Amides	1600-1700	strong
-0-H	Phenols, Alcohols	3590-3650	variable,sharp
-0-H	H-bonded alcohols and Phenols	3200-3400	strong,broad
-0-H	H-bonded acids	2500-3000	variable,broad
$-NH_2$	Amines, Amides	3300-3500	medium
$-NO_2$	Nitro compounds	~1560,1350	two bands, strong

N.B.: Refer to the Aldrich Library of Infrared Spectra kept in room S-140 for spectra of specific products and general functional group peaks.

THE ROTARY EVAPORATOR

The rotary evaporator is an expensive, but convenient apparatus to use when concentrating a solution which has a **low boiling solvent.** Essentially, it performs a vacuum distillation without having to go to the trouble of setting up the usual apparatus. Solvents which boil below 65°C are “stripped” (distilled off) best; water cannot be removed successfully by this method.

A diagram of the apparatus is shown below:



1. Motor unit
2. Stand
3. Centre tube
4. Receiving flask
5. Ball joint clamp
6. Condenser
7. Stopcock

Normally, the apparatus will be already set up for use. Your flask should be roughly half to two-thirds full at the start of the concentration procedure. Choose the correct ground glass adapter size to fit from the centre tube to your flask joint. Make sure all joints are **clean** and **lightly greased** before using the apparatus, otherwise your sample may become contaminated or the flask may become frozen onto the apparatus. When ready to begin:

1. Turn on the condenser water flow to obtain a "trickle" output. Turn on the vacuum aspirator tap **fully**.

2. Place any adapter and then your flask onto the centre tube (3) and hold the bottom of the flask with your hand.

3. Close the stopcock (7). You will hear the sound of the water change as vacuum is obtained and usually bubbles will start to form at the edges of the solution.Continue when this happens.

4. Turn on the motor until the flask is rotating at medium speed. Evaporation has a cooling effect, so fill up the water bath with warm water and elevate until the flask is submerged in the warm water. You may not see the removed solvent collecting in the receiving flask, but the volume should decrease in your rotating flask.

5. When evaporation is complete, judged by a "stable" volume, turn off the motor and lower the water bath. Then, holding the bottom of the flask, open the stopcock at the top of the condenser.

6. Remove your flask and store safely. Then clean the centre tube (e.g. rinse with acetone into a beaker) and, if necessary, empty the receiving flask, clean and reclamp into position.

CHEMICAL KINETICS

The kinetics of a chemical reaction can often provide decisive information as to the mechanism of that reaction. In general the kinetics deal with the rate at which a reaction occurs; that is the number of molecules reacting in unit time. The rate law for a reaction expresses the rate in terms of rate constants, time units, and the concentration of molecules.

Chemical reactions may involve many steps and many reacting species. The kinetics deal only with those species that affect the rate. If a single step determines the rate of a reaction that is referred to as the rate-determining or rate-limiting step. Only a few simple cases are considered here.

First-Order Reaction

$$A \xrightarrow{k} B \qquad (1)$$

In this reaction a single species is converted to another (eq. 1) and there is a negligible tendency for B to reform A. In this case the rate of reaction is equal to the rate of disappearance of A and is determined solely by the concentration of A and a rate constant k which is a function of the temperature and solvent. This may be expressed by the differential equation 2 for the rate of change of concentration of A as a function of time:

$$\frac{d(A)}{dt} = -k(A) \qquad (2)$$

This may be rearranged and directly integrated between the limits t_o (time zero) and t (any time after the reaction commences) as in eq. 3 and 4.

$$\frac{d(A)}{(A)} = -kdt \qquad (3)$$

$$\ln\frac{(A)}{(A_o)} = -k(t-t_o) \qquad (4)$$

The rate constant k can then be determined from the concentration of A remaining at any time t (eq. 5).

$$k = \frac{\ln(A)/(A_o)}{(t - t_o)} \qquad (5)$$

In order to test if a reaction actually follows first-order kinetics ln $(A)/(A)_o$ should be measured at various intervals and plotted versus $(t-t_o)$. A good straight line confirms first order behaviour, and the slope of the line allows accurate determination of the rate constant. The concentration of A may be measured in any convenient way. The calculation may be carried out using a quantity proportional to the concentration, as the proportionality constants will be divided out of eq. 5.

For example, if acid is generated in eq. 1, it is convenient to titrate the product acid with standard base. The data then consists of a series of volumes V_o, V_1, ... V_∞ of base required for titration at zero time, various intervals, and at the end of the reaction (V_∞, commonly taken as at least 99.9% reaction). Then (A) is proportional to $(V_\infty-V)$ and (A_o) is proportional to $(V_\infty-V_o)$ and eq. 5 may be expressed as eq. 6.

$$k = \frac{\ln(V_\infty-V)/(V_\infty-Vo)}{(t - t_o)} \qquad (6)$$

First-Order Reaction Tending Toward Equilibrium

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \qquad (7)$$

In this case an equilibrium is established between A and B. The rate equation for the change in concentration A is as in eq. 8.

$$\frac{d(A)}{dt} = -k_1(A) + k_2(B) \qquad (8)$$

If the reaction begins (as in an experiment on the mutarotation of glucose) with (A) = $(A)_o$ and no B present, then at any later time eq. 9 holds, which can be combined with 8 as in eq. 10 and 11.

$$(B) = (A_o) - (A) \qquad (9)$$

$$\frac{d(A)}{dt} = -k_1(A) + k_2(A)_o - k_2(A) \qquad (10)$$

$$\frac{d(A)}{dt} = k_2(A_o) - (k_1 + k_2)(A) \qquad (11)$$

At equilibrium the concentration of A and B no longer change, that is d(A)/dt = 0, so 11 is rewritten:

$$k_2(A)_o = (k_1+k_2)(A)_{eq} \text{ or } A_o = \frac{(k_1+k_2)}{k_2} (A)_{eq} \qquad (12)$$

Substitute 12 into 11

$$\frac{d(A)}{dt} = (k_1+k_2)(A_{eq}) - (k_1+k_2)(A) \qquad (13)$$

It may be seen that 14 is a solution to 13 by differentiating 14

$$(A) = (A)_{eq} + [(A)_o-(A)_{eq}]e^{-(k1+k2)t} \qquad (14)$$

$$\frac{d(A)}{dt} = -(k_1+k_2)[(A)_o-(A)_{eq}]e^{-(k1+k2)t} \qquad (15)$$

Substituting 14 into 15 gives 16, which is the same as 13.

$$\frac{d(A)}{dt} = -(k_1+k_2)[(A)-(A)_{eq}] \qquad (16)$$

Rearrange 14

$$\frac{(A)_{eq}-(A)_o}{(A)_{eq}-(A)} = e^{(k_1+k_2)t} \qquad (17)$$

$$\ln \frac{(A)_{eq}-(A)_o}{(A)_{eq}-(A)} = (k_1+k_2)t \qquad (18)$$

From eq. 18 the sum k_1+k_2 can be calculated from measured values of (A). If k_{eq} - k_1/k_2 is also known then the individual value of k_1 and k_2 may be determined.

Second-Order Kinetics

$$A + B \xrightarrow{k_2} C \qquad (19)$$

In this case the rate of reaction depends on both the concentration of A and B, or on the square of the concentration of one of the reagents.

$$\text{Rate of reaction} = -\frac{d[A]}{dt} - \frac{d[B]}{dt} = -k_2[A][B] \qquad (20)$$

$$= \frac{-d[A]}{dt} = k_2[A]^2$$

For the special case where $A_o = B_o$,

$$\frac{d(A)}{dt} = -k_2 (A)^2 \qquad (21)$$

$$\frac{d(A)}{(A)^2} = -k_2 dt \qquad (22)$$

$$1/(A) - 1(A)_o = k_2(t-t_o) \qquad (23)$$

$$[(A)_o-(A)]/(A)(A)_o = k_2(t-t_o) \qquad (24)$$

Where A_o does not equal B_o : Let the initial concentration of A = a and B = b. If x represents the amount of reaction, then after time t the amount of A and B present is (a-x) and (b-x), respectively. Then,

$$\frac{dx}{dt} = k_2[(a-x)][(b-x)] \qquad (25)$$

$$\frac{dx}{[(a-x)][(b-x)]} = k_2 dt \qquad (26)$$

This expression can be integrated by the method of partial fractions, and the limits from 0 to x substituted to give eq. 27.

$$\frac{1}{(a-b)} \ln \frac{b(a-x)}{a(b-x)} = k_2 t \qquad (27)$$