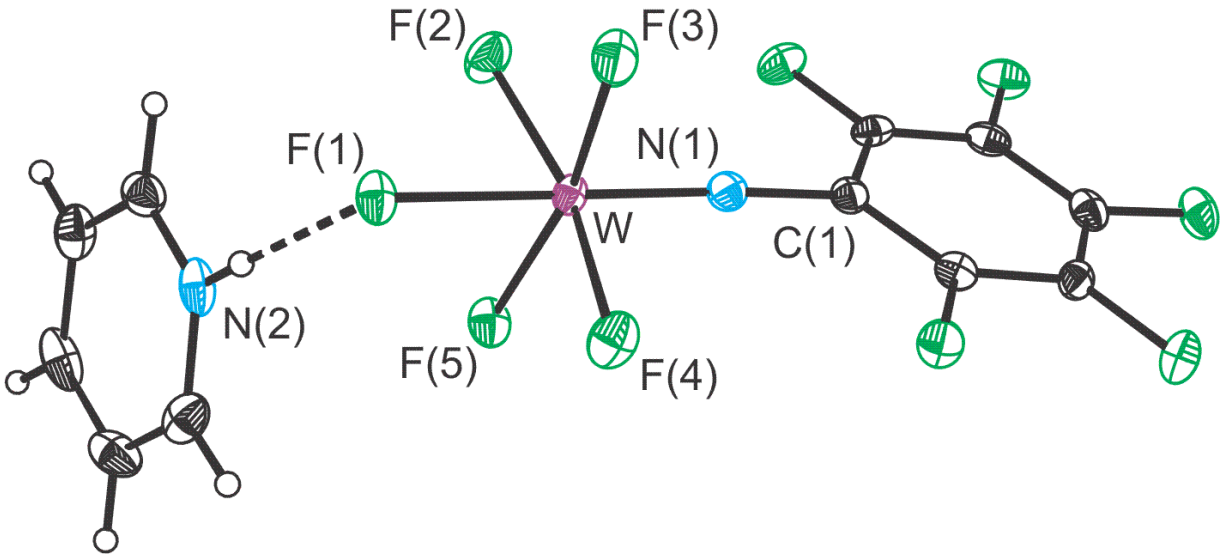
The University of Lethbridge

CHEMISTRY 3830 LABORATORY MANUAL

TRANSITION METAL CHEMISTRY



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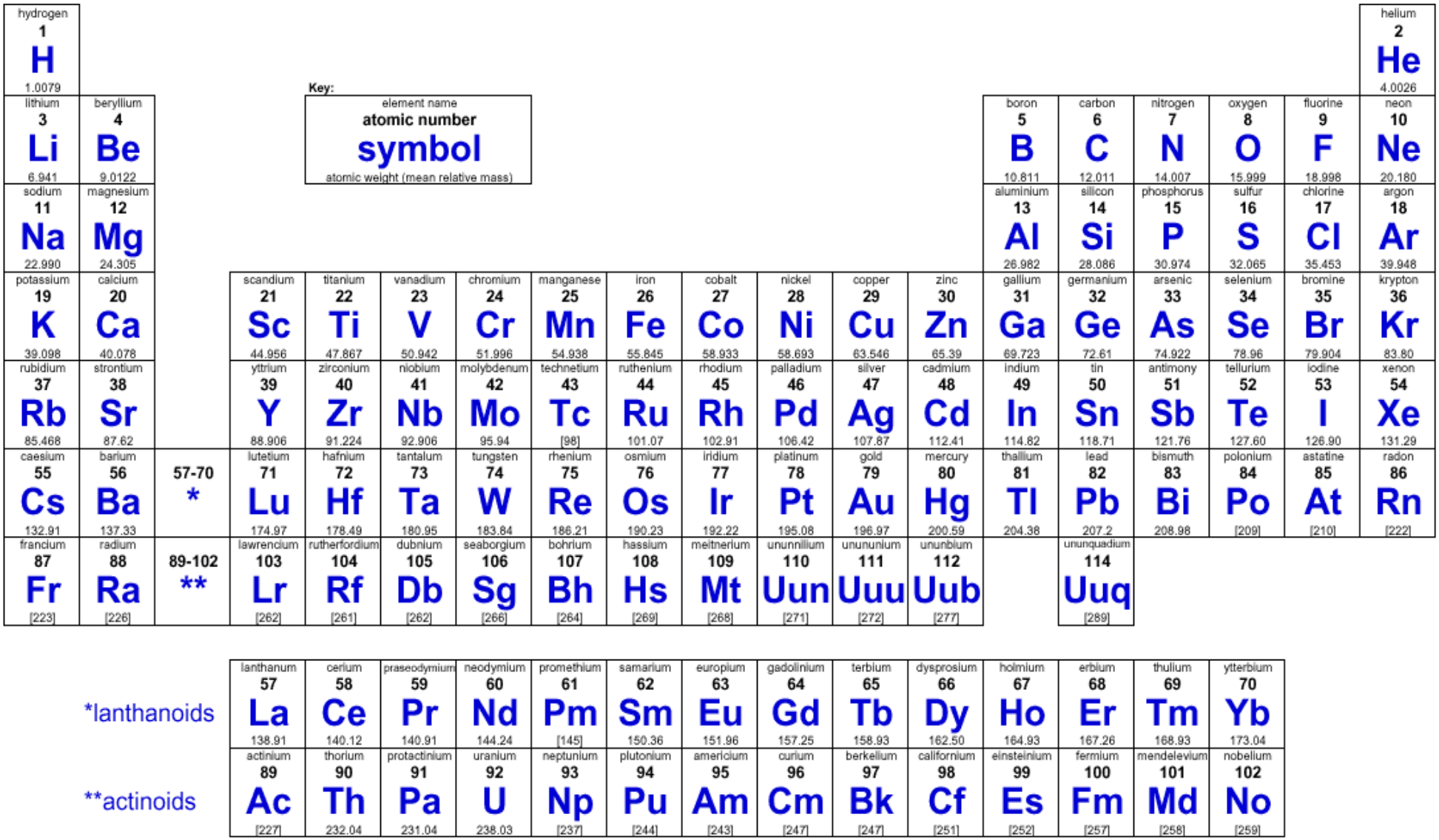
Department of Chemistry and Biochemistry


Key:
element name
atomic number
symbol
atomic weight (mean relative mass)
hydrogen 1 H 1.0079
helium 2 He 4.0026
lithium 3 Li 6.941
beryllium 4 Be 9.0122
boron 5 B 10.811
carbon 6 C 12.011
nitrogen 7 N 14.007
oxygen 8 O 15.999
fluorine 9 F 18.998
neon 10 Ne 20.180
sodium 11 Na 22.990
magnesium 12 Mg 24.305
aluminium 13 Al 26.982
silicon 14 Si 28.086
phosphorus 15 P 30.974
sulfur 16 S 32.065
chlorine 17 Cl 35.453
argon 18 Ar 39.948
potassium 19 K 39.098
calcium 20 Ca 40.078
scandium 21 Sc 44.956
titanium 22 Ti 47.867
vanadium 23 V 50.942
chromium 24 Cr 51.996
manganese 25 Mn 54.938
iron 26 Fe 55.845
cobalt 27 Co 58.933
nickel 28 Ni 58.693
copper 29 Cu 63.546
zinc 30 Zn 65.39
gallium 31 Ga 69.723
germanium 32 Ge 72.61
arsenic 33 As 74.922
selenium 34 Se 78.96
bromine 35 Br 79.904
krypton 36 Kr 83.80
rubidium 37 Rb 85.468
strontium 38 Sr 87.62
yttrium 39 Y 88.906
zirconium 40 Zr 91.224
niobium 41 Nb 92.906
molybdenum 42 Mo 95.94
technetium 43 Tc [98]
ruthenium 44 Ru 101.07
rhodium 45 Rh 102.91
palladium 46 Pd 106.42
silver 47 Ag 107.87
cadmium 48 Cd 112.41
indium 49 In 114.82
tin 50 Sn 118.71
antimony 51 Sb 121.76
tellurium 52 Te 127.60
iodine 53 I 126.90
xenon 54 Xe 131.29
caesium 55 Cs 132.91
barium 56 Ba 137.33
57-70 *
lutetium 71 Lu 174.97
hafnium 72 Hf 178.49
tantalum 73 Ta 180.95
tungsten 74 W 183.84
rhenium 75 Re 186.21
osmium 76 Os 190.23
iridium 77 Ir 192.22
platinum 78 Pt 195.08
gold 79 Au 196.97
mercury 80 Hg 200.59
thallium 81 Tl 204.38
lead 82 Pb 207.2
bismuth 83 Bi 208.98
polonium 84 Po [209]
astatine 85 At [210]
radon 86 Rn [222]
francium 87 Fr [223]
radium 88 Ra [226]
89-102 **
lawrencium 103 Lr [262]
rutherfordium 104 Rf [261]
dubnium 105 Db [262]
seaborgium 106 Sg [266]
bohrium 107 Bh [264]
hassium 108 Hs [269]
meitnerium 109 Mt [268]
ununnilium 110 Uun [271]
unununium 111 Uuu [272]
ununbium 112 Uub [277]
ununquadium 114 Uuq [289]
*lanthanoids
lanthanum 57 La 138.91
cerium 58 Ce 140.12
praseodymium 59 Pr 140.91
neodymium 60 Nd 144.24
promethium 61 Pm [145]
samarium 62 Sm 150.36
europium 63 Eu 151.96
gadolinium 64 Gd 157.25
terbium 65 Tb 158.93
dysprosium 66 Dy 162.50
holmium 67 Ho 164.93
erbium 68 Er 167.26
thulium 69 Tm 168.93
ytterbium 70 Yb 173.04
**actinoids
actinium 89 Ac [227]
thorium 90 Th 232.04
protactinium 91 Pa 231.04
uranium 92 U 238.03
neptunium 93 Np [237]
plutonium 94 Pu [244]
americium 95 Am [243]
curium 96 Cm [247]
berkelium 97 Bk [247]
californium 98 Cf [251]
einsteinium 99 Es [252]
fermium 100 Fm [257]
mendelevium 101 Md [258]
nobelium 102 No [259]

Acknowledgments

Most of the experiments in this laboratory are derived from existing procedures at other Canadian universities. In particular, the following colleagues are acknowledged for providing details of experiments:

Prof. R.T. Oakley,	University of Guelph
Dr. D. Berry,	University of Victoria
Prof. N. Burford,	Dalhousie University
Prof. A. Hunter,	University of Alberta

Mr. Ben Ireland has done a great deal of work preparing high quality instrument user manuals.

To all Chem 3830 students: *This manual was prepared to aid you in learning the "how to" of inorganic chemistry, and to do so SAFELY and EFFICIENTLY. Please read this manual from cover to cover!*

Lethbridge, September 2021

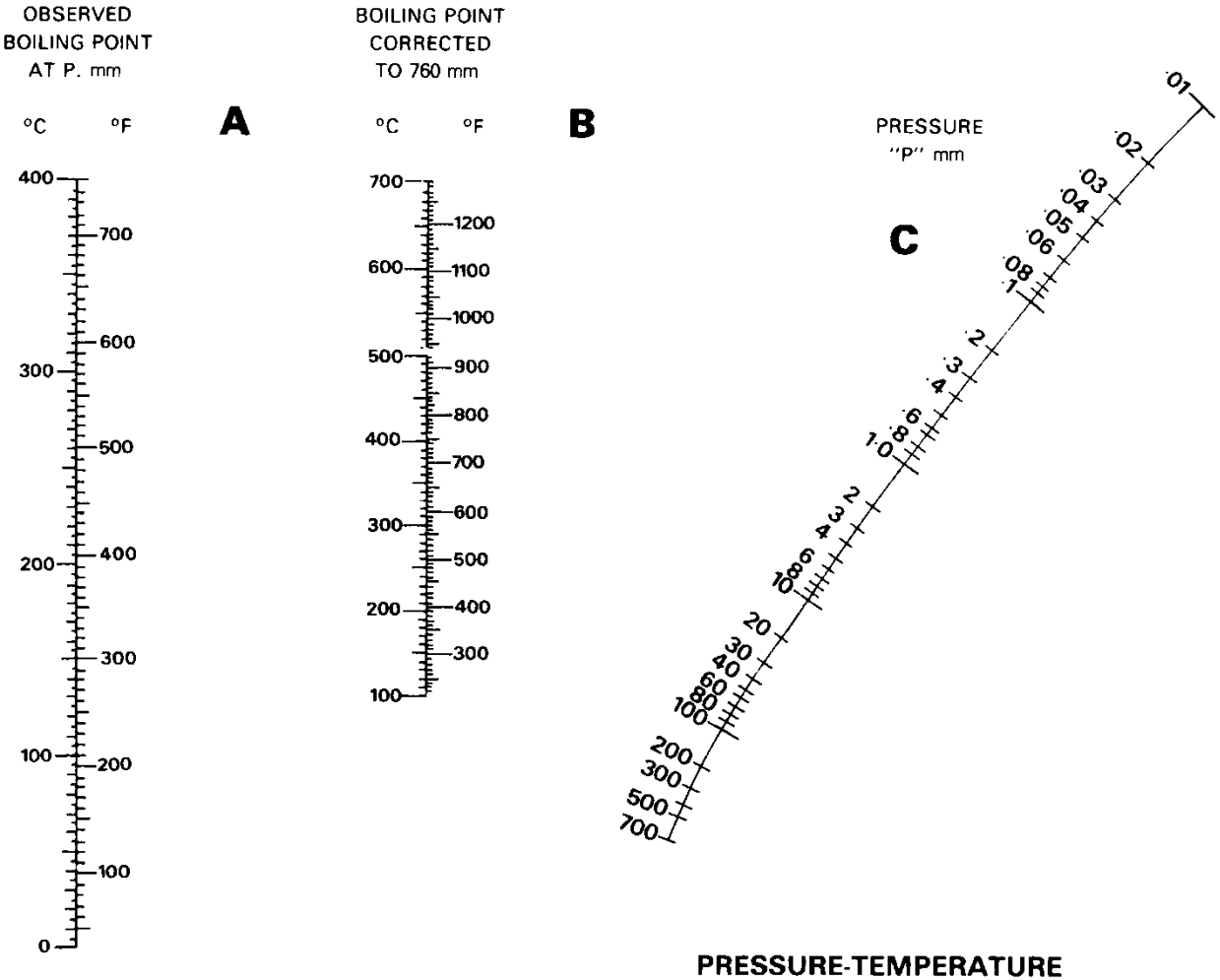
Fall 2021 Chemistry 3830 Schedule

Monday	Wednesday	Friday	Lab
Sept. 6	Sept. 8 **First day of classes**	Sept. 10	**No Labs**
Sept. 13 **Last class before add/drop deadline (Sept. 14)**	Sept. 15	Sept. 17	**Lab Introduction & Check-in**
Sept. 20	Sept. 22	Sept. 24	**Lab 1a**
Sept. 27	Sept. 29	Oct. 1 **Assignment #1 Due**	**No Labs**
Oct. 4	Oct. 6	Oct. 8 **Midterm Exam #1**	**Lab 1b**
Oct. 11 **Thanksgiving No Class**	Oct. 13	Oct. 15	**Lab 2a**
Oct. 18	Oct. 20	Oct. 22	**Lab 2b**
Oct. 25	Oct. 27	Oct. 29 **Assignment #2 Due**	**Lab 3a**
Nov. 1	Nov. 3	Nov. 5 **Midterm Exam #2**	**Lab 3b**
Reading Week: No Classes or Labs.			
Nov. 15	Nov. 17	Nov. 19	**Lab 4a**
Nov. 22	Nov. 24	Nov. 26	**Lab 4b**
Nov. 29	Dec. 1	Dec. 3 **Assignment #3 Due**	**Lab cleanup & checkout**
Dec. 6	Dec. 8 **Midterm Exam #3** **Last day of classes**	Dec.10	

Table of Contents

USEFUL DATA ON CONCENTRATED REAGENTS					
Reagent	%	Molar Mass (g/mol)	Molarity (M)	ρ (g/mL)	Aliquot*
Hydrofluoric acid HF	48.8	20.0	29.0	1.19	34.5
Hydrochloric acid HCl	37.2	36.5	12.1	1.19	82.5
Hydrobromic acid HBr	48.0	80.9	8.90	1.50	120
Hydroiodic acid HI	47	127.9	5.51	1.50	180
Perchloric acid $HClO_4$	70.5	100.5	11.7	1.67	86
Sulfuric acid H_2SO_4	98	98.1	18.0	1.84	55.5
Nitric acid HNO_3	70	63.0	15.9	1.42	63.5
Phosphoric acid H_3PO_4	85.5	98.0	14.7	1.70	69
Acetic acid CH_3COOH	99.8	60.0	17.4	1.05	57.5
Ammonia $NH_{3(aq)}$	29	17.0	14.8	0.9	67.5

* aliquot = mL of reagent which dilutes to 1L of 1M solution



PRESSURE-TEMPERATURE ALIGNMENT CHART

If literature b.p./pressure given; line up the 2 values in A & C. The theoretical b.p. @ 760 mm is read off in B. Line up this figure in B with another pressure in C and the approximate corresponding b.p. can be read off in A.

Laboratory operation and evaluation

Dress code:

In a chemistry laboratory, firm footwear and long pants that cover the entire leg must be worn at all times. Shorts, skirts, and sandals are not permitted, since they do not provide protection from spills. In addition, a lab coat and safety glasses (contact lenses are not permitted) must always be worn in the lab. You will not be allowed to proceed with the experiment if you are not following these safety guidelines (and the ones listed in section C). The dress code will be strictly enforced. You are responsible if you lose precious time and cannot complete experiments because of inappropriate attire.

Assignment

- Complete a total of 4 experiments (2 weeks each) as follows (Please note that Experiments 7 and 8 must be performed as a pair (1 week each), and together constitute 1 of the 4 experiments which must be conducted. In addition, if you elect to perform experiments 7 and 8 you must submit a lab report for each experiment):
  - One experiment from each of Parts II, III and IV, and an additional one from any section
- (Optional) Complete the glassblowing course (Part I).

Students will work **in groups**, but must submit independent reports and completed pre-lab questions. ***Any evidence of passing-on portions of reports (including those from previous years), either between partners or to others, will be treated as plagiarism and individuals will be prosecuted according to the rules of the University. There is a zero tolerance policy for any kind of plagiarism, duplication or cheating.***

Evaluation

The lab is worth 30% of the total grade for Chem 3830. These 30 points are broken down as follows:

Laboratory reports and results	200 pts
Laboratory performance and safety	20 pts
Pre-lab exercises and pre-lab discussion	40 pts
Laboratory notebook	40 pts
Total	300 pts

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Note: *All experiments must be performed (and submitted before the end of the course) in order to pass*. A grade of 50% constitutes a pass.

The pre-lab exercise must be completed in writing no later than the agreed-upon pre-lab meeting time before the laboratory period. In the pre-lab discussion each group will be asked about

specific safety issues, the experimental procedure, anticipated time management and the theoretical background of the experiment.

The instructor's evaluation of your performance in the laboratory will be based on an assessment of the student's advance preparation and understanding of the experiment, laboratory technique, safety consciousness, consideration of others, and cleanliness and tidiness.

Laboratory Notebook

A complete and accurate record is an essential part of chemical research. Although your Chemistry 3830 notebook is not a record of original research, an important objective of this laboratory is to provide training in keeping a research notebook. The record of any experiment should be sufficiently clear that another chemist reading it could understand **exactly** what was done, what results were obtained and, if necessary, repeat the work exactly as it was done. Your notebook will be judged primarily on how well it meets these criteria. Clarity and completeness are more important than neatness (although it must still be legible). It is not necessary to adhere to any particular format or organization as long as sufficient detail is provided. **It is very important to write down what you do as you do it.** Likewise, any observations should be recorded immediately – it is not acceptable to fill in your lab book after completing the entire experiment! It should also be noted that while the pre-lab exercises are both beneficial and mandatory, it is not acceptable to pre-record your *intended* experimental protocol. Changes in method are frequent, and readily forgotten when one has filled in a lab book prior to actually performing the experiment. In addition, this is very bad practice for those who will someday partake in original research where it is essential to write things down as they are done.

A bound, hard cover, lined notebook is required. Spiral or loose-leaf notebooks are unacceptable. The pages should be numbered consecutively and some blank pages left at the beginning for a table of contents. Begin each experiment on a new page and **write only in blue or black ink**. If you have read the entire procedure in advance you will have some idea how much information is to be recorded. Leave sufficient space to record the experiment on consecutive pages. Each experiment should be dated. When the experiment extends over more than one laboratory period, a date should be entered at the beginning of the entries for each separate day's work or observations. (See Figure I-1.)

Include a short tabulation of the physical and chemical data of the compounds you are using, *i.e.* b.p. (remember to correct for altitude), m.p. (remember this is always a range), solubility, etc. (consult the CRC Handbook or the Merck Index for this information). Important equations (*e.g.* those developed for the pre-labs) should be included as well. All data are to be recorded directly into the laboratory notebook at the time they are obtained. Do not write data on a loose piece of paper for later copying. Nothing should ever be erased or removed from the notebook. If you make an incorrect entry, draw a line through the mistake and add a correction.

The laboratory notebook is also a good place to write down your thoughts and speculations as to the progress of your experiments. You may wish to include alternate methods

and techniques in order to better achieve the end result. Finally, include any notes that may aid you in understanding and writing up the experiment (e.g. structures, references, equations, etc.). When writing scientifically (*e.g.* in your notebook) it is important to avoid first and second person (I, you, we, us, our). Also, your lab notebook should be written in **past tense** (unlike Figure I-1).

In summary, always include (as a minimum):

1) Date
2) A reference for the experiment, if one exists
3) A balanced equation with expected product
4) Weights, volumes and moles of reagents used
5) Estimated volumes used for solvents for all steps of a reaction (including recrystallizations)
6) Time between each manipulation or observation. Time of day works well.
7) Detailed observations, including, but not limited to, colour change, precipitate formation, gas evolution, exothermicity, etc.
8) Yield (Total and for each crop (when applicable))
9) A table of contents in the front of your book (reserve 1 – 2 pages for this) – keep it up to date
10) Key data collected (elemental analysis, IR peaks, NMR interpretation)

p. 9

September 20th 1990

Preparation of potassium trioxolatochromate(III)

$K_2Cr_2O_7$ + $C_2O_4H_2$ + $K_2C_2O_4 \cdot H_2O$
294.19 90.04 184.24
$\longrightarrow$ $K_4[Cr(C_2O_4)_3]$ + CO_2

9.01 g of oxallic acid (100 mmol) is dissolved in 20 mL of d. H_2O, warming to 50°C

2.02 g of potassium dichromate (6.87 mmol) is added as a solid to the above solution in portions; vigorous effervescence occurs.

As the orange crystals of $K_2Cr_2O_7$ are added to the oxallic acid solution an instantaneous reaction occurs, leaving a very dark brown or black solution

After boiling this solution for about 2 min, 3.50 g (19.0 mmol) of potassium oxalate is added as a solid, rapidly. The solution soon turns a deep blue colour

After cooling the solution to R.T.

Figure I-1 Sample of notebook page

Laboratory Reports

You will be required to provide a **typed** report on every experiment you perform. These reports should not be a regurgitation of the information provided in the laboratory manual, but rather a concise summary of the results obtained. Two or three pages will usually be sufficient. These reports must be formatted in the American Chemical Society (ACS) format (a Word-document template can be found on the ACS website, though an abstract is not required).

A lab report should start with a **title** and a brief **introduction**, giving a short description of the background that is necessary to understand the goal of the experiment. A concise description of the **experimental procedure** (reference to the lab manual is not enough), including simple observations, such as times, colour changes, clarity, yield, melting points (remember clear and colourless are not the same concepts) is crucial. Always specify the number of moles of reactants, reaction conditions. A simple sketch of the apparatus is frequently useful. In the **results and discussion** section, discuss yields of products, melting points, and present and discuss (analyze) spectral results. References to background information, mechanisms, spectral or structural interpretation or any physical data, etc. should be included. The **references** should be listed under a separate heading at the end of the report, in the order in which they were cited. The format for such references varies from journal to journal; use the ACS style (*i.e. J. Am. Chem. Soc.*).

A key part of your write-up is your response to the points raised at the end of each experiment. The ideal case is to include them in your discussion, but do not forget to answer all of them. If you so choose, you can address each question separately after the general results and discussion section. These questions are designed to probe your understanding of the chemistry involved; you may well have to consult the literature cited in the manual in order to find an answer. *One or more questions on the final exam will probably be lifted from the material covered in the laboratory, so you are advised to study these points carefully.*

Each report will be due at the beginning of the lab (1:00 p.m. sharp) following the completion of each experiment – late reports will be docked 20% per 24 hours to a maximum of 48 hours. After 48 hours, late reports will not be graded (a mark of zero will be awarded). *Electronic copies of lab reports must be submitted to the lab coordinator prior to the start of the lab*. It is important to remember that you must pass the laboratory component of Chem 3830 in order to receive credit for the course, regardless of your overall average. Likewise, all lab reports must be submitted (even if late) to pass the laboratory component (and thus, the entire course). The reports will not be returned to you until the last week of classes (feedback and your grade will be provided prior to this point). Your lab notebooks will be examined throughout the semester, at your instructor's discretion.

General Tips for Lab Reports

Experimental:

- Use scientific units of time (minutes, hours, days, etc.). "Overnight" is not an acceptable period of time.
- Use appropriate American Chemical Society (ACS) style abbreviations: mg, g, mL, L, etc.
- Use significant figures.
- Report yields in both g and %.
- Melting points should always be reported as a range (mp xx-yy ºC) or (mp xx-yy ºC, dec).
- NMR data should be reported as such: NMR ^{1}H (C_6D_6, -35 ºC): δ 2.08 (s, 9H, $SiMe_3$), 1.16 (d, $^{4}J_{PH}$ = 2.5 Hz, 9H, $SiMe_3$), 0.32 (d, J = 7.2 Hz, 9H, $CHMe_2$).

Results:

- Avoid vague comments – give specific details, such as temperature, colour change, time, etc. whenever possible.
- If equations are inserted into the text, place them at the end of the first paragraph which mentions them.
- Number compounds, figures, schemes, etc. in the order they first appear in the text.

Discussion:

- Make a list of all remarkable or noteworthy results. Then go back and discuss each, trying to put it into perspective with known chemistry.
- Reserve broad, sweeping statements for the conclusions (or omit them completely).

Conclusions:

- This should be an analysis of the content of the experiment, focusing on implications and putting the work into perspective.

Tenses:

- Pay close attention to tenses. Use past tense for results which pertain to experiments and descriptions of results obtained. When describing spectral data, use present tense ("the spectrum reveals").

Pronouns:

- Do not use first and second person (I, you, we, us, our).

Miscellaneous Writing Tips:

- Formulas are not nouns. ("A resonance for the Me group" rather than "A resonance for Me").
- Use "exhibits" or "displays" rather than "shows".
- Within the text of the report, use numbers with units of times or measure (4 h, 8 g). For all else, use word for numbers less than 10 and numbers for 10 and above.
- Use a semicolon between independent clauses joined by conjunctive adverbs such as "that is", "however", "thus" and "therefore" (the intermediate is not easily observed; therefore, the final product is observed initially).
- Always begin a sentence with a word. Do not begin a sentence with a number or chemical formula.
- Always use complete sentences, even in the experimental section.

Common Abbreviations (as per the ACS format, unless noted, no periods are used):

min – minutes
mL – milliliters
ca. – approximately
s – seconds
dec. – decomposition
equiv. – equivalent(s)
eq. – equation
vs. – versus
mmol – millimoles
m.p. – melting point
h – hours
THF – tetrahydrofuran
g – grams

Suggestions

Your instructor appreciates feed-back and constructive criticism regarding the operation of the laboratory and the design and effectiveness of the experiments. Suggestions are welcome.

"The boss sort of keeps an open mind."

General Laboratory Procedures

Safety Equipment

The safe operation of any chemical laboratory is dependent upon the extent to which adequate safety measures are observed and practiced. As such, always be safety minded. This means that every student must do all they can to prevent accidents in their own work and they must be prepared for accidents by knowing in advance what emergency aids are available and how to use these aids.

The laboratory is equipped with several types of safety and first aid equipment. It is essential that you become familiar with the location and operation of these tools.

Shower There is an emergency deluge shower located in each laboratory. These are for use when corrosive liquids have spilled over large areas of clothes and skin, or when clothing is on fire.

Eye Wash Station Each laboratory is equipped with an eye wash station. These stations dispense tempered (luke-warm) water and provide thorough irrigation of the eyes and face in the event a person is splashed with an irritating chemical. The contaminated body part should be rinsed for a minimum of 15 minutes.

Fire Extinguisher Carbon dioxide fire extinguishers are in each laboratory. Know the location of these and how to operate them. They are very effective for fires involving organic liquids and electrical fires. Sand pails should be utilized for metal (*e.g.* sodium or potassium) fires. If a fire extinguisher is used even momentarily it must be given to the laboratory coordinator for recharging. Small fires in test tubes, beakers, etc. can usually be smothered by covering with a watch glass.

Use of Time

The efficient use of time is an asset not only to a student, but especially to a researcher. Plan your experiments so that you will profitably use time which would otherwise be spent watching, *e.g.* a distillation, a sublimation or a non-hazardous reaction that need not be attended. This course allows some latitude in the planning of experiments and you should be constantly looking for opportunities to use the available time effectively. Remember, if you manage to finish an experiment early you are free to leave.

Cleanliness

.....is next to Godliness. Since most of the experiments will involve the use of equipment which other students will use during the course, it is absolutely essential that all equipment be left in good condition at the end of each period. Any equipment which is broken should be reported to the instructor immediately so that a replacement may be found in time for the next class. Wash bottles of detergent, alcohol and acetone are provided, as well as scrubbers, sponges and rubber gloves. If you have particular difficulty cleaning a dirty piece of glassware, notify the lab supervisor. ***Since there are a variety of communal areas which make it difficult for the instructor to establish who is responsible for a given mess, the entire class will lose 10% of the value of their lab report if the laboratory is not left in satisfactory condition!***

Balances and weighing

A great many experiments in chemistry involve weighing at some stage. Much time can be wasted during weighing procedures, and one of the biggest time wasters is the habit of weighing to a degree of accuracy in excess of the requirements of the experiment.

For synthetic work, including parts of most of the experiments in this course, weighing to 0.1 g or 0.01 g is quite sufficient. Only for analytical work, such as in the characterization of some of the compounds prepared in this course, is greater accuracy required, on the order of 0.001 g or 0.0001 g.

Even if weighing is only carried out to the required degree of accuracy, time can be wasted in the actual process, and unless some method is used whereby weighing is carried out rapidly, many experiments cannot be done in the time normally available.

At no time are chemicals to be weighed directly onto the pans of the ANALYTICAL BALANCES. *All of these balances will be irreparably damaged by exposure to the kinds of chemicals you will be handling in this laboratory.* For synthetic work, you will use only the top-loading balances located in the lab (D776). *Please do not disturb other classes by queuing up at the balances located in their labs.* Should you require a more accurate measurement than allowed by the top-loaders, follow the method of weighing by difference described in the following paragraphs. *Although they are more robust, even the top-loading balances are susceptible to corrosion. Make it a practice to clean up any spilled chemicals <u>on</u> or <u>around</u> the balances i<u>mmediately!</u> Balances used in these laboratories (all types) cost between $2000 and $4000, and must be treated with utmost respect. The balances in the balance room (D745) are not to be used under any circumstances.*

Accurate weighing technique: weighing by difference

To weigh an accurate amount of solid (*i.e.* to the nearest 0.001 g or better), place a **weighing bottle** (and cap) on a balance, tare it, remove the bottle from the balance, and place an estimated amount of material into the bottle. If the solid contains large crystals or lumps it should be lightly ground in a mortar before weighing.

The weighing bottle (with contents) is now capped, wiped clean and weighed using the correct procedure on the analytical balance (if the weight is significantly different from desired, remove the bottle from the balance and repeat the above procedure until close (but there is no need to be exact)). *Immediately* record the weight in your notebook.

Return to the lab, and tip the solid into your flask, vessel or whatever is suitable, no attempt being made to remove the traces of solid which will cling to the weighing bottle. *Return to the balance room* and re-weigh the nearly empty bottle accurately. The loss in weight is the accurate weight of solid taken. This avoids the rather awkward process of washing all of the solid from the bottle and is quicker and more accurate.

This method is often used, as it is rarely necessary to weigh out an exact amount. It is bad practice to weigh out, for example, 1.25 g of a solid to make an exact 0.10 M solution. It is better to use the above method, finish up with a weight of 1.32 g and express the solution as:

$$(1.32 \text{ g}/12.6 \text{ L})\ M = 0.105\ M$$

This avoids the very messy practice of adding and removing odd crystals to try to get an exact weight.

By using the above method it is *never necessary* to have any loose chemicals near a balance, as only a closed bottle is used on the balance.

Setting up apparatus

When ground-glass joints are used, it is not necessary to lubricate them except when high temperatures or vacuum are involved or an inert atmosphere is required. If a joint becomes seized, notify your instructor. A common cause of seizure is a caustic alkali. Try to keep alkalis off the ground-glass, and if they do get on it, wash thoroughly as soon as possible. Seizures can usually be avoided by dismantling the apparatus immediately after use. Where required, the procedures call for lubricating the joints with silicone grease ("high vacuum grease"). *CAUTION: silicone grease may cause corneal damage. In order to avoid accidental transfer of grease to your eyes, be sure to thoroughly wash with soap and water to remove residual silicone grease from your skin.*

Care should always be taken, when glass apparatus is set up, to avoid **strain**. It is best to start with one piece, and build from there. Take a distillation apparatus as an example:

(a) Lightly clamp the flask at a height convenient for heating,

(b) Attach the still-head, screw-cap adapter and thermometer (no more clamps are needed for these),

(c) Attach the rubber tubing to the condenser, then position a clamp and stand so that the condenser will rest on the lower, fixed, side of the clamp. Attach the condenser to the still-head, and clamp lightly,

(d) Attach and support the receiver adapter and the receiver.

A similar procedure should be followed for the other assemblies.

Notes on individual assemblies

Reflux Clamp the flask and the condenser. If an air condenser is used, clamp it at the top.

Distillation Use a vented receiver adapter in the following circumstances:

(a) if a noxious gas or vapour is given off, and must be led off by rubber tubing to an absorption apparatus or a sink,

(b) if an inflammable vapour is given off (for example in ether distillation), and must be led off by rubber tubing to below bench level.

Where an air condenser is specified, it is frequently adequate to attach the receiver adapter directly to the still-head.

Fractional distillation Clamp the fractionating column only at the top. If a column is not available, a vertical air condenser or an ordinary condenser with an empty jacket can be used instead, though it will be less efficient.

Gas evolution A 250 mL flask, with a B24 joint, and a 100 mL dropping funnel are satisfactory for most purposes. If these are not available, it is convenient to prepare a number of standard rubber stoppers, each carrying a dropping funnel and a delivery tube, which will fit 250 mL wide-necked flasks.

Gas drying If ground-glass jointed apparatus is not available, a 250 mL conical flask with a rubber stopper is perfectly adequate.

Gas absorption If it is necessary to dissolve a gas in a liquid, the best method is to use a Büchner flask fitted with a wide glass tube in a rubber stopper. This overcomes the 'suck-back' problem by equalizing the internal pressure with that of the atmosphere.

Use of corks Even when apparatus with ground-glass joints is normally used, there are still occasions when corks are required. For efficiency corks must be rolled before use, and bored with care. A cork of the correct size should only just go into the neck of the flask. Soften it by rolling between the fingers, or between sheets of paper on the bench. Never try to roll a cork which already has a hole in it; it will almost certainly split.

To bore a cork, or a rubber stopper, choose a sharp borer slightly smaller than the tube or thermometer which is to go into the hole. Hold the cork in the hand, and push and rotate the borer until the hole is approximately half way through it. Now reverse the cork, and continue boring from the other end until the holes meet in the middle. Now use a rat-tailed file to increase the size of the hole until the tube or thermometer fits it with gentle pushing, but with no strain. Place the cork on the file, and rotate it with the hand or

on the bench; do not use a sawing action as this will cause an eccentric hole which is likely to leak.

When inserting tubes or thermometers into holes in corks, it is an advantage to moisten them with a little ethanol as a temporary lubricant. If a cork becomes stuck to a tube or a thermometer during use, it is best to cut it off, rather than risk breakage.

Reflux and distillation

Unlike ionic reactions, which are frequently extremely rapid, reactions between covalent substances tend to be slow. Particularly in main-group and organometallic reactions, it may be necessary to keep a reaction mixture hot for a matter of hours. This, coupled with the fact that volatile and inflammable solvents must be employed, makes it necessary for special equipment to be used.

Reflux The use of a reflux condenser is often necessary. It is used whenever a reaction mixture has to be kept boiling for an appreciable time and the solvent is volatile. A water condenser may be used for solvents boiling up to approximately 130 °C, and for higher boiling-point solvents an air condenser is adequate. The flask must never be filled more than half way; the size of flask should therefore be chosen by consideration of the total volume of the reaction mixture. A boiling stone or similar substance should be used to promote even boiling for all reflux procedures which do not employ magnetic stirring. The object of the apparatus is to keep the solution hot without loss of solvent. It is pointless to boil violently; the heating should be controlled so that the solution is merely simmering. The flask may be heated by an **electric heating mantle** controlled by a Variac **(NEVER plug a heating mantle directly into an electrical outlet!)**, or by using an oil bath on an electric hot plate.

Distillation The purpose of distillation is to purify a liquid, or to remove a solvent from a solution. The flask must never be more than half full, a boiling stone or magnetic stirring must always be used, and the choice of condenser is the same as for reflux work. The heating of the flask may be accomplished using any of the usual means. Purification of a liquid by distillation is best performed at a rate not exceeding 2 drops of distillate per second. Alternatively, removing a large quantity of solvent may be done much more rapidly.

Fractional distillation The purpose of fractional distillation is to separate two liquids of different boiling-point. As with other forms of distillation, the flask must never be more than half full, and a boiling stone or magnetic stirring must always be used. In order to get good separation of the liquids, it is essential that the distillation be carried out very slowly. The slower the distillation, the better the separation. A rate of 1 drop of distillate per second should be the aim.

Since the efficiency of the process depends on the fractionating column reaching thermal equilibrium (there should be a gradual increase in temperature from the top to the bottom of the column), best results are obtained if drafts are excluded. In addition, the source of heat should be steady.

Use of the separatory funnel

The separatory funnel is used for several important processes. Unless care is taken, its use can be one of the major causes of mechanical loss. The choice of size is particularly important and, as with flasks in distillation, the smallest which will properly do the job, is best.

Separating two immiscible liquids The liquid mixture is poured into the funnel, and the funnel is gently agitated to assist in the separation into layers. The funnel should always be stoppered, but if a particularly volatile substance, such as ether, is present, the funnel should be vented occasionally through the stopcock *(hold it slightly inverted while doing this)* to avoid the possible buildup of pressure.

When separation into layers has occurred, the stopper is removed and the lower layer drained into a small flask. Swirling the funnel and omce again allowing separation to occur frequently provides a further small sample of the lower layer.

The top layer is poured from the top of the funnel into a second flask. It is a wise precaution to always keep both liquids, even if one of them is to be discarded. It is surprising how often the wrong layer is thrown away!

Washing a crude liquid One of the most common procedures consists of shaking a crude liquid product with an aqueous solution to remove some of the impurities. The reagents should always be used in small quantities, and the process repeated if necessary. Mechanical loss is always greater when large volumes of washing solutions are used.

Gases are often formed in considerable quantities during the cleaning process, thus, it is essential to release the pressure frequently. This is best done by inverting the well-stoppered funnel and opening the tap.

If the required substance is the top layer, then allowing the bottom layer to run off is quite simple. The entire bottom layer of waste should not be run off each time. It is better to leave a small quantity of the aqueous solution, and add further fresh reagent. Careful separation is completed only when running off the last of the various washing solutions. This avoids the risk of inadvertently losing a few drops of the treated product.

When the required substance happens to be the bottom layer, avoiding mechanical loss becomes more difficult. If the product is run off between each wash and then returned to the funnel for the next, the loss can become very great. The best compromise is obtained by using rather large volumes of washing solutions, and decanting the spent solution from the top of the funnel. In this way the product never leaves the funnel until

the final wash is over. It is then run out into its receiver, leaving the final washing solution in the funnel.

Liquid extractions The separatory funnel is often used to extract a solute from one solvent by means of a second solvent immiscible with the first. The removal of a solute from water by means of ether is one of the most common examples of this application.

The size of the funnel is chosen to accommodate the whole of the aqueous solution. This saves time which would otherwise be spent in repetition. A series of extractions with a small quantity of ether is much more effective than one with a large amount of ether. In practice the volume used is that which gives the smallest manageable top layer, bearing in mind that the ether solution must be decanted from the top of the funnel. If the layer is too small, decantation becomes difficult. The solution is usually extracted about three times with fresh quantities of ether, and all of the ether extracts are decanted into one flask. After the final extraction the aqueous layer is run off and the last ether layer decanted completely into the flask. The ether solution is then dried, and the solute obtained by distillation of the ether.

Filtration methods

There are a variety of techniques used for the separation of a liquid or solution from a solid.

Simple filtration The use of a filter funnel and a piece of filter paper folded into four is usually reserved for ionic substances (*e.g.* NaCl) precipitated from aqueous solution. Precipitates obtained in qualitative analysis and inorganic problem work are often rather fine, and cannot be efficiently filtered using a pump. Covalent solids, however, are usually separated from a volatile solvent, and the comparative slowness of simple filtration brings in complications caused by evaporation.

It is essential in simple filtration to ensure that the paper is carefully folded. The paper must be fitted carefully into the funnel and wetted thoroughly with water, or the appropriate solvent, prior to the start of the filtration.

The contents of the filter paper should remain at least 1.5 cm from the top of the paper. These simple precautions can make a dramatic difference in the time required for a filtration to reach completion, and should never be neglected.

Filtering of organic liquids This is usually done to remove solid impurities which are not in a very fine state of subdivision. A normally folded filter paper will work for this purpose, but the 'fluted' filter paper gives a faster rate of filtration. A fluted filter paper is essentially one that is folded to give a corrugated effect which allows the whole of the paper to be active rather than only half, as is the case with simple filtration.

There are a variety of ways of folding such a paper; one of the easiest is as follows:

The paper is carefully folded in half, opened out, and then folded in the same direction at right angles to the original fold. The paper is then folded twice more, the folds being all in the same direction and mutually at 45°. Each section is now individually folded in the opposite direction. The result is a fluted paper with sixteen faces. The paper is then placed in a suitable sized funnel and pushed down so that all of the ridges touch the side of the funnel. Since all of the paper is being used, only one layer thick, filtration is appreciably faster.

When filtering a small amount of liquid to free it from a drying agent it is best to use a very small piece of cotton wool, pushed lightly into the top of a funnel stem, or even into the narrow part of a disposable Pasteur pipette. The mechanical loss entailed by absorption on a filter paper is thus obviated, and much higher yields of product are obtained.

The Büchner funnel and filter pump This system of filtration is the most widely used when dealing with recrystallized substances. The Büchner funnel may be attached to the flask by means of a cork, but a much more useful device consists of a flat piece of rubber with a hole in the center capable of receiving the funnel stem and making a good seal.

The disc of rubber allows, within reason, any size funnel to be fitted to any size flask. If this method is adopted, then the size of the funnel chosen is the smallest that will hold the solid, and the flask is similarly chosen to be the smallest that will hold the liquid, if both solid and liquid are required. If the solid is to be discarded, than a large funnel can be used to increase the rate of filtration. Alternatively, if the liquid is to be discarded, then the flask may be large enough to hold all of the liquid as well as the washings. The choice of size is very important, as mechanical loss during filtration can be significant.

The filter-paper disc is placed in the funnel, and wetted with the solvent present in the solution to be filtered. It is essential that the funnel and flask be perfectly dry. If the solvent concerned is ethanol, then the paper may be wetted with water. If available, connect the suction flask to a Woulff bottle (ask the instructor how to use a Woulff bottle). The pump is then turned on and the paper pressed into place. During filtration the pump must never be turned off, as this may cause water from the pump to be drawn back into the filtrate. When all of the material has been filtered, open the stopcock of the Woulff bottle to ambient pressure (or disconnect the pump from the flask) while the pump is still running. If some of the solid has not been transferred to the funnel, a portion of filtrate can be retrieved and used for swilling the residue into the funnel. The solid is washed free of filtrate by pouring a small portion of chilled fresh solvent into the funnel while the pump is disconnected. Finally, the solid is drained as dry as possible using suction from the pump while applying pressure with a clean glass stopper.

Gravimetric filtration In quantitative work it is essential that all of the solid be transferred and retained in the filter funnel. A **filtering crucible** with a porous sintered-glass bottom is

the most convenient apparatus to use. Porosities from 0 (coarse) to 5 (very fine) are available, although for most purposes a porosity of 3 is best; a few fine precipitates will require a porosity of 4.

The sintered-glass crucible is dried in an oven, cooled, and accurately weighed before use. To collect the solid the pre-weighed crucible is set in the mouth of the Büchner flask by means of a firm rubber cone. The pump is turned on, and as much supernatant as possible is decanted off through the crucible. The liquid should be directed into the crucible via a glass rod.

The solid is then transferred, using a gentle jet of the appropriate solvent to swill out all particles. If solid clings to the apparatus, it can be collected using a glass rod protected with a **rubber 'policeman'**. The pump suction at this stage should be as gentle as possible; otherwise the porous glass may clog. Finally, the solid and crucible are washed repeatedly to remove all soluble materials, and dried to constant weight.

Drying methods

The drying of liquids In the majority of cases with organic liquids extreme drying is not necessary and drying agents such as *anhydrous calcium chloride* or *anhydrous sodium sulfate* are adequate. Of the two, calcium chloride is the more efficient, but also the more messy.

As calcium chloride will remove water and ethanol, it is employed when both need removing. If, however, the drying only needs to remove water; anhydrous sodium sulfate is generally employed. Sodium sulfate will only work at temperatures below 30 °C and should generally be used at room temperature. It is capable of removing its own weight of water, but the use of too much drying agent should be avoided at all times as this will cause the drying agent to become 'wetted' with the product and a large mechanical loss will be entailed.

In order to dry an organic liquid, whether a product or a solution containing the product, the liquid should be placed in a suitable sized conical flask, fitted with a good stopper or cork, and the drying agent added. The corked flask should be shaken at intervals, and left for at least five minutes, preferably longer.

If sufficient drying agent has been used some should remain unchanged in appearance: i.e. a fine opaque powder of sodium sulfate or firm granules of calcium chloride.

The drying of solids Various methods exist for drying solid materials. When deciding which method to use it is important to know something about the physical properties of the material. For example, if dehydration of a hydrate or melting of an organic solid occurs, recrystallization will have to be repeated resulting in further loss of time and material.

Although the method of air drying takes longer than the others, it is one of the most safe for non-deliquescent solids. The damp solid, drained as dry as possible on the filter, is transferred to a watch-glass and spread out evenly. The solid can then be left to

dry overnight in a location free of dust and drafts. As an added precaution against dust, a second, larger watch-glass should be placed over the product in such a fashion that free evaporation remains possible.

Though the desiccator is ideal for drying many solids, care must be taken when drying hydrates. It is quite possible to lose some water of crystallization if the dehydrating agent is too effective. Thus, samples to be dried should be spread out on a watch-glass and labeled with their name and date.

The desiccator must be regularly recharged with fresh desiccant, and the ground-glass seal kept greased with a minimum quantity of silicone grease, so it appears transparent. Several desiccants are listed in Table I-1 with comments on their relative usefulness.

Table I-1 Common drying agents

Desiccant	**Remarks**
P_4O_{10}	Expensive, fast and efficient.
Conc. H_2SO_4	Cheap, hazardous, fast and efficient. If $BaSO_4$ is dissolved in the acid, it precipitates when the drying capacity is exhausted.
$CaCl_2$	Cheap, moderate effectiveness. Use if ethanol was the solvent.
Soda-lime	Use if acidic vapours need to be absorbed.
Silica gel	Readily regenerated, but limited effectiveness. Changes colour when exhausted if stained with $CoCl_2$.
Drierite	(Anhydrous sodium sulfate) Commonly stained with $CoCl_2$; Blue when fresh, red when exhausted. Very inert; use for most applications.
$MgSO_4$	Ensure it is anhydrous! Used to dry organic liquids, especially ethers.

It is important to remember that after opening, a desiccator takes at least two hours to re-establish a dry atmosphere.

A vacuum desiccator is used to speed the drying of a sample. The sample must be covered with a second watch-glass and the desiccator evacuated and filled slowly to avoid blowing the sample about. In order to guard against implosion, a vacuum desiccator must be covered with strong adhesive tape, or be enclosed in a special cage when being evacuated and de-evacuated.

Recrystallization and purification of solids

Inorganic solids, when first prepared, are rarely pure. The original solid must be recrystallized from an appropriate solvent. If the solvent is a flammable liquid, as it often is, it is better to carry out a recrystallization under reflux, until more experience has been gained. With ethanol, a very common solvent, it is quicker and neater to use a conical flask, but this does entail a risk of fire.

Reflux method The solid is placed in a suitable sized flask, preferably a conical flask as it can be easily put aside to cook, and a condenser attached. A small volume of solvent is poured down the condenser and the mixture is raised to its boiling point. If all of the solid has not dissolved, a bit more solvent should be added after removing the mixture from the hot plate. Repeat this process until the solid just dissolves at the boiling-point. If there are no insoluble solid impurities, the solution will be clear. The mixture should then be removed from the hot plate and slowly allowed to cool to room temperature. Once the solution reaches room temperature, it may be necessary to gently swirl the flask in order to initialize crystallization. The solid usually crystallizes upon cooling, but, if crystallization is slow to start, scratching the inside of the flask with a glass rod frequently helps crystals to form. The flask should be cooled to at least room temperature, or preferably lower, by placing it in either iced water or a refrigerator.

The pure product is filtered off at the pump. It is essential for both the filter flask and funnel to be clean and dry, except for the solvent concerned. The mixture to be filtered is poured on to the filter paper and the solid remaining in the flask is washed out with the filtrate. This is important. The filtrate is, of course, a saturated solution of the required solid, and so the filtrate cannot reduce the yield by dissolving some of the crystals. The filtrate should be used for washing out the flask several times, until all of the solid has been transferred to the filter. On no account should fresh solvent be used for transferring the solid to the filter. The recrystallized solid is then dried in a suitable manner, bottled and labeled.

Open flask method This is essentially the same as the previous method, but is carried out directly on the hot plate with an open conical flask. The solvent is only just allowed to come to a boil and then the flask is removed from the heat. At this point, it should be possible to see the vapour condensing inside the flask, and there should not be a risk of fire if care is taken. The obvious advantage of this method is speed. This approach is not suitable for low-boiling solvents such as ether or pentane.

Recrystallization requiring hot filtration If, during a recrystallization, there is an insoluble solid impurity, it becomes necessary to filter the hot solution. Care must be taken that no crystallization occurs during the process as this would block up the filter funnel and cause great difficulty. To avoid this, the following procedure is used:

The crude solid is dissolved in the solvent in the normal way, and when all of the solute has just dissolved at the boiling-point, a further small quantity of solvent is added. This ensures that the solution is not quite saturated. This solution is kept hot while a separate sample of solvent is heated to boiling and then poured through the prepared Büchner funnel. This procedure heats up the funnel and flask. The filter paper, which must be in position, is held in place by a glass rod. The selected funnel should be reasonably large as this will retain the heat better and the filtration will be faster.

The hot solution is rapidly filtered with the pump on full. As soon as all of the solution is through the funnel, the pump is disconnected and the funnel removed.

At this stage the solute will almost always have begun to crystallize in the receiving flask. To save mechanical loss, the solution should be kept in the flask and cooled in the normal way. The final filtration to collect the crystals therefore requires another flask.

The use of activated charcoal

Sometimes there are coloured impurities present in the crude material to be recrystallized. These are removed from the solution while hot by adsorption onto activated charcoal.

The recrystallization is carried out normally until the crude material is dissolved. At this point, a little extra solvent is added, and the mixture cooled slightly. A small amount of activated charcoal is added to the cooled solution. It is important to cool the solution before adding the charcoal, as this material tends to promote boiling. If the solution is not sufficiently cooled prior to the addition of the characoal, the entire mixture will usually boil over violently.

The mixture with the charcoal is allowed to boil gently for a few minutes, and is then filtered hot, using the method described above. It is important to ensure that the paper is well fitted or charcoal may get around the edges and contaminate the product. As in hot filtration, the funnel should be large so that the filtration is as rapid as possible. The flask should be of a suitable size for the volume of purified solution obtained.

Column chromatography

Chromatography using columns of adsorbent material is useful for separations on the preparative scale because gram quantities of material are readily purified. Many adsorbents are available, but these experiments all use aluminum oxide (alumina) or silica gel.

Packing the column Clamp the glass tube upright and check that the tap is closed. Wash the walls of the column by pouring ~20 mL of solvent down the inside walls. Half fill the column with the chosen eluting solvent. Push a pad of non-adsorbent cotton-wool or glass-wool to the bottom of the tube; be careful not to ram it down too hard and make sure that there are no air bubbles trapped in the glass or cotton-wool.

Method 1: Dry Packing:

Now slowly pour in roughly 25 g of chromatographic aluminum oxide or fine silica gel. Use a filter funnel to guide in the powder and, if a blockage occurs (*e.g.* just above the solvent level), rock the tube gently. You can also tap the tube gently with your fingers to settle the powder uniformly and release any trapped air bubbles.

Push a second pad of cotton-wool down the tube to protect the upper surface of the column from disturbance. Drain off the excess solvent until the level falls to the upper cotton-wool pad; never let the solvent level fall lower, otherwise the uniformity of the column will be ruined by trapped air bubbles. The column is now ready for use.

Method 2: Slurry Method:

Add a sufficient quantity of solvent to the weighed out chromatographic aluminum oxide or fine silica gel so that when you swirl the flask, the contents move freely (make sure that no air bubbles are trapped in the slurry). Pour the slurry into the top of the column while you drain solvent out the bottom (save this solvent to use when running the column). Be sure to close the stopcock when the solvent is approximately 0.5 cm above the absorbant. Finally, push a second pad of cotton or glass-wool down the tube onto the top of the column. The column is now ready for use.

Loading the column Dissolve your sample in the minimum volume of solvent required to make a homogeneous solution. Using a pipette, place the sample directly on top of the column. Allow the column to drain slowly and wash in the sample by adding small portions of fresh solvent. The sample should now be adsorbed as a narrow band at the top of the column.

Developing the column Develop the column by running solvent through it. Fill up the tube with solvent being careful to pour the solvent down the wall of the tube. This is important to ensure the top of the column is not disturbed. Allow the solvent to pass through the column at a rate of approximately 5 mL per minute. Keep the tube topped up, as the liquid pressure will encourage a good flow rate and there will be less danger of letting the column run dry (which will make it virtually impossible to achieve proper separation). If the flow rate is too slow, pressure can be applied by attaching a small hand bellows to the top of the tube (flash chromatography).

Collect equivolume fractions of solvent draining from the column. Coloured materials are readily seen as they are eluted from the column, but colourless substances must be found by evaporating the fractions to dryness, or by running t.l.c. on each fraction.

Thin-layer chromatography

In thin-layer chromatography (t.l.c.) a suitable adsorbent is spread on a glass plate. After activation of the adsorbent by heat, the plate is spotted with a dilute solution of the material under study and then developed with a suitable solvent. When the solvent has risen a convenient distance up the thin film, the plate is dried and treated with a detecting agent. Commercial plates with plastic or foil backing are also available, and are extremely convenient.

Silica gel is the preferred adsorbent for t.l.c., although cellulose and alumina thin films can also be readily prepared. In all cases the adsorbent must be specially manufactured for t.l.c. work, and it is simpler to use materials free of special additives or binders. T.l.c. is generally faster than other techniques and sharper separations are possible, but to master the method you will have to work with care and ensure your apparatus is properly cleaned.

Preparing the plates

(a) Silica Gel A slurry of roughly 30% w/v of silica gel in chloroform is kept in a well-sealed wide-mouthed bottle, and microscope slides are coated by dipping them into the slurry. The slurry bottle should be placed on a large sheet of blotting paper in a fume cupboard. Shake the slurry bottle and then dip in two well-cleaned microscope slides, held together at the top by crucible tongs. Dip in and lift out the slides in a continuous movement; do not coat the top 1 cm of the slides. Allow to drain briefly. Handling the edges only, ease the slides apart and lay them, thin film uppermost, on the blotting paper for five minutes to dry. Activation is not necessary. If the film is not uniform, the microscope slide was not clean.

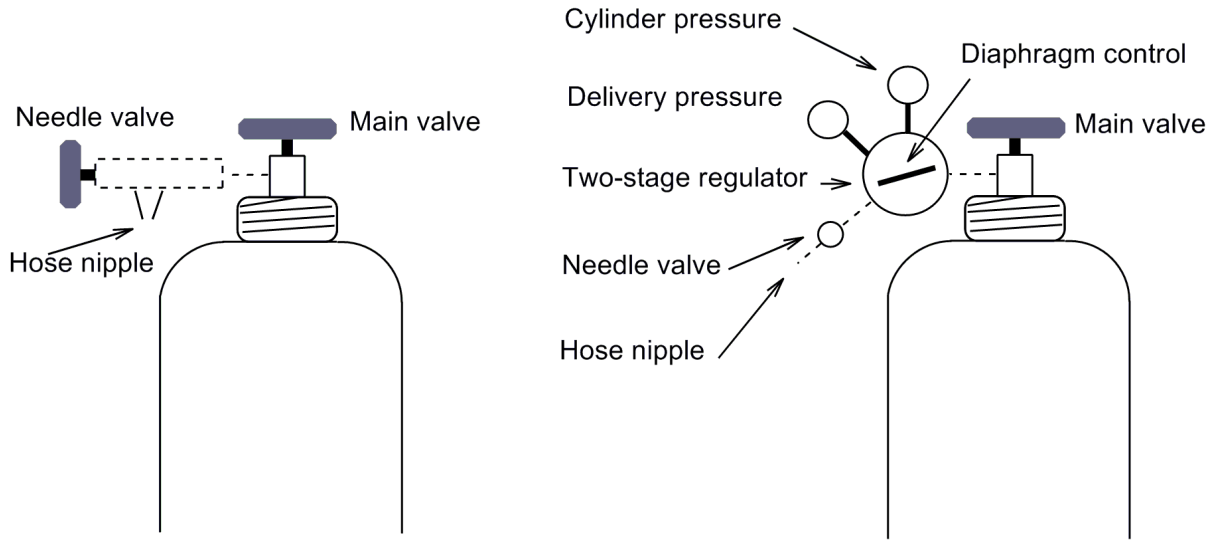
(b) Prepare a slurry of 1 g of cellulose in 5 mL of acetone by mixing well in a small glass mortar. Hold a 15 cm x 5 cm glass plate over a sheet of blotting paper and pour the slurry on to one end of the plate. By gently rocking the plate, spread the thin film uniformly over the plate, and then lay it down for five minutes to dry. Activation is not necessary. By use of the same technique it is possible to spread on 15 cm x 5 cm plates slurries of alumina or silica gel (1 g in 2.5 mL of 85% aqueous ethanol; if the slurry proves too thick or too thin, slightly vary the volume of solvent). Allow to dry at room temperature, then activate in an oven at about 120 °C for thirty minutes.

Spotting the plates Thin films must be handled and spotted with extra care because of their fragile nature. Spot the plates with a maximium of 0.002 mL of 0.01-0.1 M solutions from a capillary or fine wire loop. If possible, solutions should be prepared in the same solvent that will be used for development of the chromatogram.

As many as three separate spots can be placed on a microscope slide, if channels are scratched in the thick film with the edge of a spatula and surplus material is cleaned from the edges of the slide.

Compressed Gas Cylinders

Several experiments make use of gases which are commercially available in compressed gas cylinders. They come in a variety of sizes with several valves and regulators. The metallic content of the values is dictated by corrosive properties of the gas. The facile reaction of N_2O_4 with copper, for example, requires that the cylinder and valve contain very little copper. Many cylinders contain a safety valve or nut which is designed to rupture if the pressure inside exceeds the specifications of the cylinder. Under no circumstances should anyone tamper with the safety nut.



(a) Gas requiring only a needle valve

(b) Gas requiring a two-stage diaphragm regulator

Figure I-2 Details of the two main types of compressed gas cylinders used in the lab

The main valve (Figure I-2) on a cylinder is simply an on-off valve which allows no control of the gas flow; it should always be used with some type of control valve. A needle valve permits such control but if the cylinder contains a compressed gas, the cylinder pressure will decrease as the cylinder is used and the gas flow will likewise decrease. Thus, for compounds which exist as gases (e.g. CO, N_2, BF_3) in a cylinder, a given flow rate cannot be maintained without continuous adjustment. Compounds which condense to form liquids under pressure exert their natural vapour pressure so long as any liquid remains in the cylinder. For these gases (e.g. MeBr, NH_3) a continuous flow rate can be obtained with a needle valve.

To achieve a constant flow rate for gases which do not condense under pressure in a cylinder, a pressure regulator is required. (Figure I-2b) First, open the main valve; the gas pressure in the cylinder is given on the right hand gauge. Next, open the regulator valve by turning the knob counterclockwise. Such regulators should not be operated with the valve

partially open; it is best to open it completely and then close it a quarter of a turn. Finally, adjust the flow rate to the desired level by opening the needle valve. The pressure between the needle valve and the regulator is given on the left-hand gauge. The regulator will maintain this pressure. During the experiment, the flow can be halted by closing the needle valve, but when you are finished with the cylinder for the day, close the main valve to prevent loss of the gas in case the regulator leaks slightly. Do not empty a cylinder completely; leave approximately 25 psi so that the cylinder does not become contaminated with air or other gases before it is returned to the supplier for refilling.

In several experiments, N_2 gas will be used to flush air from a reaction system, as shown below. Before the reaction is begun, the N_2 flow is sometimes turned off with the stop-cock. This normally produces a pressure build-up which could result in the rupture of the Tygon tubing connecting the apparatus to the nitrogen cylinder. To prevent this, it is convenient to connect an oil or mercury bubbler to the nitrogen line to act as a pressure release valve for the excess nitrogen (Figure I-3).

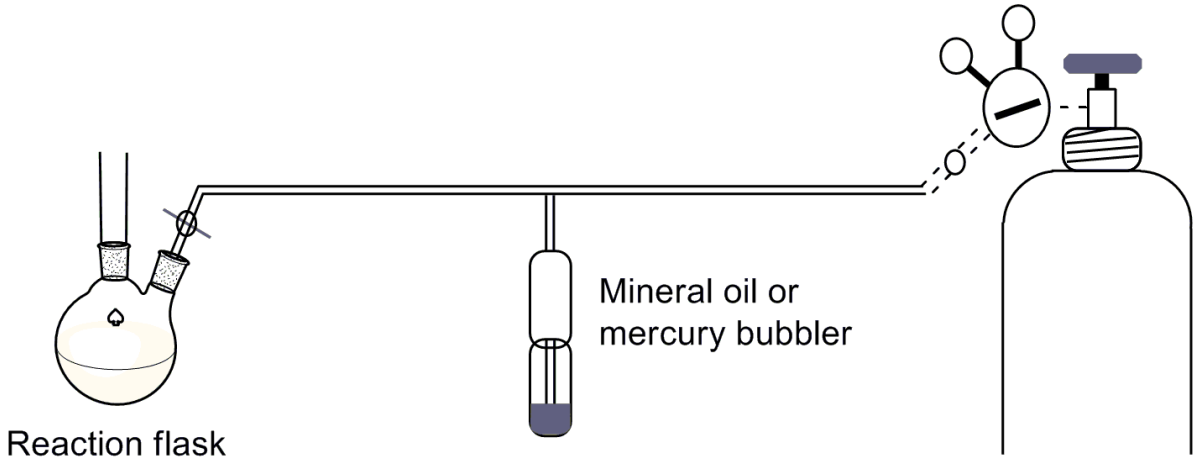


Figure I-3 In-line connection of a gas-bubbler

Handling Air-Sensitive Reagents

A large variety of air-sensitive reagents is available commercially. Specific examples include solutions of boron complexes, organoboranes, borohydrides, Grignard reagents, organoaluminums, organolithiums, and organozincs. Since all of these reagents react with water or oxygen or both (sometimes violently), they must never be exposed to the atmosphere.

Most modern synthetic chemists are familiar with the utility of these versatile organometallic reagents. However, because the compounds are air-sensitive or pyrophoric, some workers hesitate to make use of the remarkable chemistry of these reagents. Some chemists still believe that very specialized equipment and complicated techniques are required for handling these materials. This is often not the case.

Air-sensitive reagents available from Aldrich Chemicals are packaged in special bottles. The Aldrich Sure/Seal packaging system (Figure I-4) provides a convenient method for storing and dispensing research quantities of air-sensitive reagents. With this bottle, reactive materials can be handled and stored without exposure to atmospheric moisture or oxygen. The reagent comes into contact only with glass and Teflon, yet it can be readily transferred using standard syringe techniques.

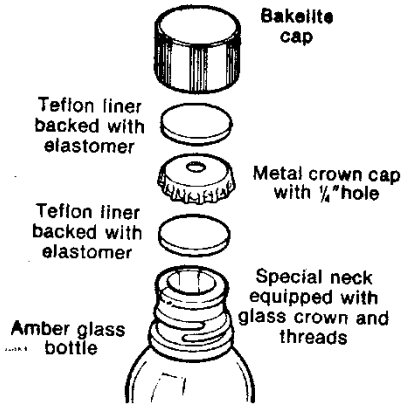


Figure I-4 The Aldrich Sure/Seal packaging system

The Bakelite cap on a Sure/Seal bottle can be removed because the crown cap, with its teflon-elastomer liner, is already crimped in place. The reagent can then be dispensed using a syringe or double-tipped needle (cannula) inserted through the hole in the metal crown cap. After the needle has been withdrawn from the bottle, a small hole will remain in the Teflon/elastomer liner. Under normal circumstances, the hole in the liner will self-seal and the reagent will not deteriorate. However, the possibility exists that once an elastomer is punctured, it may leak on long-term storage. This possibility is virtually eliminated with the Sure/Seal system because when the Bakelite cap is replaced, the Teflon/elastomer liner in the cap forms a seal against the top of the metal crown. Thus, the contents are effectively protected from moisture and oxygen in the atmosphere.

Laboratory glassware contains a thin film of adsorbed moisture which can be easily removed by heating in an oven (125 °C/12 hours or 140 °C/4 hours). The hot glassware should ideally be cooled in an inert atmosphere by assembling the glassware while still hot and then flushing with a stream of nitrogen or argon. Keck clips or rubber bands are required to secure all joints during the flushing process.

Small quantities (up to 50 mL) of air-sensitive reagents may be transferred with a syringe equipped with a long needle (8-16”). The long needles are used to avoid having to tip the reagent bottles. The reagent may be introduced into the reaction vessel via a rubber septum. These rubber septa slowly degrade upon contact with organic vapours, and therefore will only provide a positive seal for a limited number of punctures, depending on the needle size. The lifetime of the septum may be extended by always reinserting the needle through the same hole and by replacing the septum with a glass stopper immediately upon completing the addition. If a glass

syringe and plunger are utilized, they should be oven-dried before use. The syringe and plunger should not be assembled before being placed into the oven, and should be cooled afterwards before assembly. If a plastic disposable syringe is to be used, it should not be placed in the oven, as it will warp upon exposure to prolonged heat.

The syringe transfer of liquids can be readily accomplished by first pressurizing the Sure/Seal bottle with dry nitrogen. This can be achieved by inserting a hose attached to a nitrogen cylinder, as illustrated in Figure I-5. A much more safe, and thus, preferred method, however, is to inject a slightly greater volume of nitrogen gas into the Sure/Seal bottle as liquid that will be removed. This maintains a constant neutral pressure inside the bottle and can be carried out by flushing (withdraw a full syringe of nitrogen gas from an appropriate source and then expel it) the needle and syringe with nitrogen gas three times prior to injecting the desired quantity of nitrogen. The nitrogen pressure is used to slowly fill the syringe with the desired volume of the reagent. Note that the nitrogen pressure pushes the plunger back as the reagent enters the syringe. As such, the plunger should be pulled back only if needed, and in these cases only very slowly, since rapid movements tend to cause leaks and creates gas bubbles. Once the desired quantity of reagent is in the syringe (remember that a small amount is still in the needle!), reorient it such that the plunger is pointing downward toward the floor. Gently create a small "head space" by pulling the needle out of the solution (but keep it in the bottle) and withdrawing several milliliters of nitrogen gas into the syringe. The needle can now be pulled completely out of the bottle and the reagent quickly transferred to the desired vessel by puncturing the rubber septum on the reaction flask or addition funnel. Be sure to keep the syringe upside down until after the needle punctures the rubber septum. This process will ensure that absolutely none of the potentially dangerous reagent is lost during transfer.

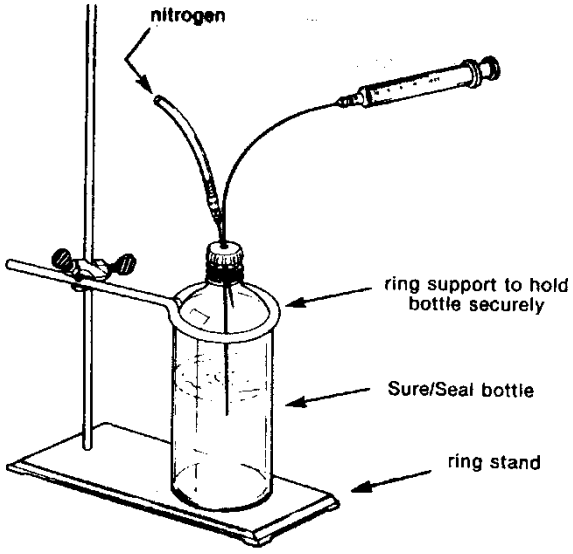


Figure I-5 Filling syringe using nitrogen pressure

When handling air-sensitive materials, it is important that the user be thoroughly familiar with the basic chemistry of the reagent. Also, the user should be prepared for unexpected problems. For example, at least one extra set of clean, dry syringes and needles should always be available in case the first set becomes plugged.

Chemistry Laboratory Rules and Safety Precautions

1. Wear appropriate clothing in the laboratory:
   (a) a lab coat and safety goggles has to be worn at all times
   (b) no sandals or open-toed shoes are allowed
   (c) no shorts or skirts are allowed inside the laboratory

2. If you have any possible conflicts between the lab environment and any acute and/or chronic medical conditions (epilepsy, diabetes, allergies, etc.) please consult your lab coordinator/instructor prior to any scheduled lab work. Likewise, if you are pregnant, or are trying to conceive you should consult your instructor to ensure that you are not unknowingly exposed to teratogenic materials.

3. Never work alone in the laboratory.

4. Smoking, eating, and drinking are not permitted.

5. Unauthorized experiments are strictly prohibited.

6. Know the location and use of the fire extinguisher, safety showers, and first aid kit.

7. Contact lenses are particularly dangerous and they **must not be worn** in the laboratory.

8. Report all injuries to your instructor at once.

9. Never taste chemicals or solutions. Use the wafting technique to smell things.

10. Use the fumehoods at the sides of the laboratory for all poisonous reactions or any reactions which produce noxious gases.

11. When diluting concentrated acid or base *always add the concentrated acid or base to water* (never the reverse), while stirring the solution.

12. Keep an orderly, clean laboratory bench or fumehood. Return glassware to the lab drawer or kit when finished using it to keep the work area from becoming cluttered.

13. Leave outside materials (backpacks, coats, etc.) at the back of the lab. Never block aisles with personal effects, or leave clothing, etc. on the benches.

14. Waste crocks are provided for the disposal of all solid chemicals and paper, etc. as well as:
   (1) Non-halogenated solvents
   (2) Halogenated solvents
   (3) Sulfur chlorides (when appropriate)

15. If stock reagent bottles are placed on the side bench or beside the balances, leave them at that position.

16. Always read the label twice before taking any chemical from a bottle. If you are not sure if you have the right chemical, ask!

17. Properly label and initial all chemicals or reagents, including newly prepared samples.

18. When pouring reagents, hold the bottle so the label points upwards facing the palm of the hand. The accumulation of reagent on bottle lip may be removed by touching the bottle lip to the rim of the receiving vessel.

19. Avoid using an excess of reagent. If you happen to have measured out too much, see if someone else can use the excess. If not, do not return it to the stock bottle.

20. We repeat, due to possible contamination of the contents of a whole stock bottle, never return unused chemical to the stock bottle.

21. Always check your glassware before you use it. If it is broken or cracked, exchange it for a new one.

22. There is one container reserved for broken glass. All broken glassware should be placed in the glass disposal bin and no other.

23. If corrosive chemicals or liquids come in contact with the skin or clothing, flood with copious amounts of water for an extended period of time.

24. Spilled chemicals should be wiped up immediately; spilled acid or base should be carefully neutralized with soda ash (for acids) or citric acid (for bases) along with plenty of water and then wiped up.

25. To insert glass tubing or thermometers through a rubber stopper, first lubricate the tube and stopper with glycerol, ethanol, or water, then while holding the tube near the end to be inserted, insert slowly while rotating the tube. BE VERY CAREFUL!

26. When you are ready to leave the laboratory, your bench area should be rinsed off with a and the water, gas, and air valves shut off.

27. The chemistry store room is forbidden to students. If you require apparatus, ask your instructor for it.

28. Disposable nitrile gloves are provided. If required for certain experiments, polyethylene gloves will be made available.

29. Never pipette by mouth.

30. Safety Data Sheets (SDS) are available for all chemicals and reagents, and are easily accessed online by searching for the chemical on a manufacturer's website (Sigma-Aldrich, Strem, etc.).

Consent Form

This form must be completed, signed, and submitted to the laboratory instructor before any laboratory work is begun.

* * * * * * * *

I have read and understood both the general procedures and the safety rules within this manual that appear on pages B-1 – B-19 and C-1 – C-3 respectively, recognize that it is my responsibility to observe them, and agree to abide by them throughout this course.

Name (please print) _____

Date _____ Signature _____

Mel-Temp 3.0 for Melting Point Determination

Preparing Your Sample:

1.) Solid samples may be loaded directly into provided m.p. tubes by pressing the open end of the tube into the sample, inverting the tube then gently tapping it on a solid surface to move the sample to the bottom of the tube.

NOTE: If the tube is overloaded, the temperature of the sample will not be fully homogeneous during m.p. determination and the obtained m.p. range will be quite broad. In practice, the ideal amount of material to use for m.p. determination is the smallest practical amount that can be loaded into the m.p. tube while remaining clearly visible through the eyepiece of the m.p. unit.

ALSO NOTE: It is possible (with slight modification) to use a m.p. unit for b.p. determination (not discussed here). If this is required, ask your instructor for assistance in modifying your procedure to determine the boiling point of a liquid sample.

Setting Up:

1.) If the instrument is powered off, press the power switch. This will activate the light so your sample is visible through the eyepiece. The current temperature of the unit will be displayed on the digital readout on the front of the instrument.
2.) Check through the eyepiece to see if previous users have broken m.p. tubes off inside the instrument and notify your instructor if this is the case. Slide your sample into any open sample slot on the top of the instrument. Your sample should be well-lit and clearly visible as you will need to watch it closely. If necessary reposition the sample prior to heating.
3.) Set the temperature range that you wish to examine (low and high end) and the rate at which you would like the instrument to heat. This is done by pressing "Set" ("start" will be visible on the lower readout) and using the up/down arrows to set the low end of the temperature range that you wish to examine by pressing "Set" again. The "end" prompt should be visible on the lower readout. Increase the temperature using the up arrow until you reach the upper end of the range of interest and press "Set." "rate" should now be visible on the lower readout. Set the rate at which you wish to heat (in °C/min) using the up/down arrows. Pressing "Set" again will initiate the heating protocol (see "Recording a melting point", step 1).

NOTE: For any known materials, you should have an approximate idea of the melting point before you come arrive at the lab. Examining a temperature range of 5 to 10 °C about the expected value and heating at a rate of 1 °C/min is recommended.

If you have no idea what the m.p. is (*e.g.* a novel compound has been prepared), start at room temperature and end at the highest limit of the instrument (400 °C) scanning at the maximum rate (10.0 °C/min). Watch the sample and record an approximate m.p. value when it begins to

melt. At this point, a more accurate m.p. range may be determined by preparing a new sample and closely observing its behavior within 5 to 10 °C about the approximate value. For the more accurate m.p. range, set the instrument to heat at a rate of 1 °C/min.

Recording a Melting Point:

1.) Once you have set up the instrument, press "Set" one final time to begin heating the sample. The instrument should rapidly heat to a point below the set temperature range and continue heating at the set rate. If the instrument remains well below your temperature range of interest for an extended period of time, the "Ramp" button will allow the user to temporarily override the programmed rate and manually increase the temperature. The heating element will be active while the button is depressed. Note that holding the "Ramp" button down for extended periods of time will cause the instrument to heat rapidly, potentially overshooting the desired melting point.
2.) Watch your sample closely and record the temperature from the digital readout when you reach the melting point.

NOTE: Remember that all melting "points" should be recorded as ranges beginning when the sample shows visible signs of melting (appearing damp or "sweating") and ending when the sample is completely liquid. A narrow m.p. range (< 2 °C) is generally indicative of high purity, though exceptions do exist. Record your observed melting point in your lab book in ink. If you have recorded an approximate m.p. or have conducted multiple trials (recommended) please highlight the values you wish to submit in your lab report and briefly note a rationale if replicate trials are inconsistent with each other (poor precision often results from improper instrument usage or poor sample homogeneity) or with literature values (poor accuracy often results from low purity or differences in instrumentation used. If possible, use other characterization techniques to identify any impurities present).

ALSO NOTE: Some samples do not melt; but rather, decompose below their respective melting points. If your sample undergoes a clear transition without melting (often a colour change to black) record your "melting point" as "m.p. = ___°C (dec)." A single value, rather than a range, may be appropriate if the decomposition is abrupt.

FINALLY, NOTE: Some samples may neither melt nor decompose below the maximum limit of the Mel-Temp 3.0 (400.0 °C). If you observe a material to be stable up to 400.0 °C, simply record "m.p. > 400.0 °C."

Cleaning Up:

Dispose of any used m.p. tubes in the provided containers. If a m.p. tube breaks off in the instrument, please notify your instructor so the problem may be corrected.

Bruker Tensor 37 IR Spectrometer

Setting Up (ignore if you are not the first user of the day):

The main power switch for this instrument is located on the back. If the instrument is powered off prior to use, it will take about one minute to warm up before it is ready to use.

1.) Start the instrument control software (OPUS 6.5) using the desktop icon and log in using the following account:

    Username: ftiruser
    Password: user

    The software will take about one minute to initialize.
2.) Click "OK" on the "about OPUS" window if it opens.
3.) From the "measure" menu at the top of the screen, select "setup measurement parameters." From the new window, load the dataset "FIR.xpm" (for far IR) or "MIR.xpm" (for mid IR) which can be found in the C:\OPUS65\XPM directory.
4.) Click "Save and Exit" to apply your changes.

Preparing Your Sample:

A wide variety of techniques exist for preparing a sample for IR collection. By default, the instrument will be set up for neat solid samples. Some of these techniques will require reconfiguration of the spectrometer hardware – please ask your instructor for assistance if needed.

1.) Neat solid samples on crystal plates: A sample of a solid is pressed onto a reusable crystal plate. The IR spectrum is recorded directly. Conceptually, this is very similar to solid sample preparation for the Alpha FT-IR spectrometer.

2.) Neat liquid samples or solutions on salt (NaCl, KBr or CsI) plates: A (non polar) solution or liquid may be placed on an appropriate salt plate (CsI are recommended) and either allowed to dry (in the case of solutions), creating a film of the sample, or sandwiched between two plates, creating a thin uniform layer of the fluid. Please verify that your solvent or sample will NOT dissolve or corrode the plates (consult you instructor if necessary). * Requires installation of a special sample holder. Consult your instructor for any necessary hardware changes.

3.) Nujol mull on salt plates: Similar to above, but a solid sample is prepared in nujol (an inert mineral oil), which is then sandwiched between salt plates. * Requires installation of a special sample holder. Consult your instructor for any necessary hardware changes.

4.) KBr pellets: A small amount of a solid sample is ground into excess KBr (generally 1 mg of sample to 100 mg of KBr), which is then pressed into a plate or pellet using a sample press. KBr pellets are discarded after use. * Requires installation of a special sample holder. Consult your instructor for any necessary hardware changes.

5.) Neat gaseous samples: A gaseous sample is held in a specially-designed sample container. Crystal (or any non-IR-absorbing material) windows in either end are aligned such that the path of IR radiation proceeds unobscured through the sample. * Requires installation of a gaseous sample holder. Consult your instructor for any necessary hardware changes.

Using the Instrument:

Note: If OPUS 6.5 is not open when you arrive at the instrument, please start at setup step 1.

1.) BEFORE loading your sample, click on the "advanced data collection" icon. Give your sample a name in the appropriate field and click "start background measurement." This will collect a background spectrum (of air) that will be subtracted from your sample spectrum.

NOTE: Depending upon the nature in which the sample has been prepared it may be necessary to run a background spectrum of the medium which contains your sample (*e.g.* nujol or KBr).

2.) The exact nature of the instrument preparation will vary according to the method which you have used to prepare your sample. For the standard neat solid preparation, place a small amount of solid onto the crystal plate of the sample holder then lower the top anvil until it clicks into place. Place the holder into the sample chamber of the spectrometer. For alternate methods of sample preparation, consult your instructor for assistance.

3.) Click "start sample measurement." Wait a few moments until the collection is complete and your spectrum appears.

4.) If your spectrum appears too weak (peaks are of low intensity and not well separated from the baseline) or too strong (the detector is saturated and your peaks are not resolved) right click on the spectrum, select "remove from display," and restart at step 2, adjusting the amount of material used accordingly.

Preparing Your Spectrum:

1.) Once your spectrum has been collected, a number of tools are available. If your spectrum is poorly centered on the screen, the "spectrum adjustment" tool will allow you to correct it.

2.) You may need to adjust your baseline (using "baseline correction" tool) if it deviates substantially from level. Otherwise, proceed directly to "peak picking."

3.) The automatic peak picking tool (activated by clicking the "peak picking" icon) will label the major peaks in the spectrum.

4.) If you would like more or less detail, the minimum peak height may be set using the "interactive peak picking" tool (activated by clicking the drop-down arrow on the side of the icon, then selecting the "interactive peak picking" option). Click and drag on the arrow tool to set the desired peak height.

5.) Once you are satisfied with your spectrum, print it using the "Quick Print" tool (the "Print" tool should only be selected by advanced users).

Cleaning Up:

Cleanup will vary according to the experiment type. Neat samples on crystal plates must be wiped clean using *iso*propanol.

If NaCl, KBr or CsI plates have been used they will need to be removed from their holders and wiped clean using acetone. NEVER clean any salt plates with water or alcohol – they will dissolve! Please return salt plates to their respective containers/dessicators promptly to preserve them for future use.

KBr pellets should be removed from holders and discarded into an appropriate solid waste container. Residual KBr may be rinsed off of metal holders using water. If rinsed, dry holders thoroughly or rinse with acetone (non-plastic holders only) and allow to air dry before returning them for other users.

It is generally sufficient to allow neat gas chambers to ventilate in a fume hood to remove gaseous samples. The process may be expedited by flushing the chamber with nitrogen or air. Any corrosion or staining caused by the sample should be noted and cleaned if possible.

Bruker Alpha FT-IR Spectrometer

Setting Up (ignore if you are not the first user of the day):

If the indicator light in the top right corner is blinking green, the instrument is not on. Press the small green button on the rear left (near the power cord) to start the instrument. Warm-up takes approximately 8 minutes. When the indicator light is solid green, the instrument is ready to use.

1.) Start the instrument control software (OPUS 6.5) using the desktop icon and log in using the following account:

    Username: ftiruser
    Password: ftir

    The software will take about 1 minute to initialize.
2.) Click "OK" on the "about OPUS" window if it opens.
3.) From the "measure" menu at the top of the screen, select "setup measurement parameters." From the new window, load the dataset "basic ftir.xpm" which can be found in the C:\OPUS65\XPM directory.
4.) Click "Save and Exit" to apply your changes.

Preparing your sample:

This instrument will collect IR spectra of neat solid and liquid samples. Most samples will work provided that they are not air sensitive or highly corrosive – consult your instructor if you are uncertain. Samples are loaded directly onto the crystal plate and no specific preparation is required.

Using the instrument:

Note: If OPUS 6.5 is not open when you arrive at the instrument, please start at setup step 2.

1.) Check that there is no visible debris on the crystal plate or beneath the ATR arm. If there is, first complete cleanup step 2.
2.) BEFORE loading your sample, click on the "advanced data collection" icon. Give your sample a name in the appropriate field and click "start background measurement." This will collect a background spectrum (of air) that will be subtracted from your sample spectrum. If you wish to use a blank, load your blank material onto the crystal plate (see next step for loading instructions) before taking a background scan and clean it off before adding your sample (see cleanup step 2).
3.) Load the instrument by placing a very small amount (a few milligrams at most) of your sample on the crystal plate in the center of the instrument and lower the anvil by pressing down on the ATR arm until it clicks into place. A red dot should now be visible on the front of the arm – if not, consult your instructor.
4.) Click "start sample measurement." Wait a few moments until the collection is complete and your spectrum appears.

5.) If your spectrum appears too weak (peaks are of low intensity and not well separated from the baseline) or too strong (the detector is saturated and your peaks are not resolved) right click on the spectrum, select "remove from display," and restart at step 2, adjusting the amount of material used accordingly.

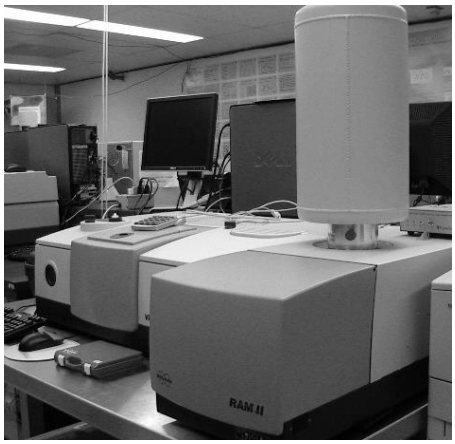
Preparing your Spectrum:

1.) Once your spectrum has been collected, a number of tools are available. If your spectrum is poorly centered on the screen, the "spectrum adjustment" tool will allow you to correct it.
2.) You may need to adjust your baseline (using "baseline correction" tool) if it deviates substantially from level. Otherwise, proceed directly to "peak picking."
3.) The automatic peak picking tool (activated by clicking the "peak picking" icon) will label the major peaks in the spectrum.
4.) If you would like more or less detail, the minimum peak height may be set using the "interactive peak picking" tool (activated by clicking the drop-down arrow on the side of the icon, then selecting the "interactive peak picking" option). Click and drag on the arrow tool to set the peak height.
5.) Once you are satisfied with your spectrum, print it using the "Quick Print" tool (the "Print" tool should only be selected by advanced users).

Cleaning Up:

1.) If you do not wish to save your work, right click on the spectrum and select "remove from display." If you wish to save your work, consult your instructor. You will likely be asked to place your work in a specific directory.
2.) Lift the ATR arm and clean the crystal plate and the bottom of the arm thoroughly using a kimwipe and *iso*propanol. Allow the instrument to air-dry for a few minutes before the next reading.

Bruker Ram II / Vertex 70 FT-IR/Raman Spectrometer



NOTE: The RamII/Vertex 70 is capable of functioning as either a Raman or standard IR spectrometer, though only one mode may be active at a given time. Explicit discussion of the IR mode will not be covered in this guide; however, note that operation of the Vertex 70 IR spectrometer is highly similar to operation of the Bruker Tensor 37, discussed previously.

ALSO NOTE: The Raman spectrometer is extremely sensitive to vibration. Do not place any items related to sample preparation directly on the instrument bench top (as with any instrument) and avoid using the instrument bench top as a writing surface. Be very cautious not to bump the instrument or do anything else which might cause nearby vibrations (*e.g.* stomping or dropping items on the floor) while spectra are being collected.

Setting Up:

1.) *To be done well in advance of instrument usage (3 to 4 hours)*: Ensure that the 4L liquid nitrogen storage tank contains at least 1L of liquid nitrogen (preferably, fill the tank – provided that subsequent users will need the instrument in the near future). Verify that the liquid nitrogen tank is capped to minimize loss of coolant or contamination of the storage tank. This step must be done well in advance to allow for temperature equilibration. A large plastic funnel is useful for filling.

NOTE: All remaining setup steps may be completed immediately prior to data collection.

2.) If the control computer is offline, turn it on and log in to the account using:

Username: ftiruser
Password: user

3.) Turn on the laser source (the small peripheral device located behind the liquid nitrogen storage tank) by first switching the power supply to "on" at the back of the device, then turning the key in the lock at the front of the device to the "on" position. At present (spring, 2009) the security key is simply kept in the instrument. If it has been removed for security reasons, consult your instructor or a department technician regarding its whereabouts.

4.) Open the beam splitter compartment (on the top of the Vertex 70 component, behind the sample compartment) and check that the CaF_2 beam splitter (labeled "SI") is in place in the central slot. The KBr beam splitter is used only for mid-IR collection and may be stored in the spare beam splitter slot on the far right of the compartment. Close the beam splitter compartment.

5.) Start the instrument control software (OPUS 6.5) using the desktop icon and log in to the account using:

Username: ftiruser
Password: user

The software will take approximately 1 minute to initialize.

6.) Click "OK" on the "about OPUS" window if it opens.
7.) Click the "advance data collection" tool on the main toolbar. You should start at the "basic" tab of the new window. In the "Experiment" field, load the dataset "raman.xpm" which can be found in the C:\ProgramFiles\OPUS65\XPM directory.

NOTE: Fields within this window are colour-coded according to the set parameters. All fields should appear white (normal), yellow (caution), or red (danger). The instrument will operate safely if all parameters are depicted with a white "normal" or yellow "caution" background but the obtained data may not be ideal if key fields are set to "caution" values. If, at any stage in the setup procedure, you observe a field with a red "danger" background, immediately notify your instructor as this may indicate a problem with the instrument.

8.) The laser power may also be set from the "basic" tab of this window. Set it to 100mW unless another power level is specifically noted in your experiment. Record the laser power and report it along with all other relevant instrument parameters.
9.) Under the "advanced" tab, set the desired number of scans for your spectrum collection (64 scans are generally sufficient).
10.) Set the desired resolution for your final spectrum. Note that higher resolution (lower values as measured in cm^{-1}) collection will take longer periods of time and necessitate a smaller aperture setting for the source radiation, which in turn reduces the intensity of the observable signal. Resolution at 4 cm^{-1} is generally sufficient for coursework; however, resolution to 2 cm^{-1} may be accomplished under normal conditions using this instrument. Once your desired resolution is set, navigate to the "optic" tab and check the background colour of the "aperture" field. If you have increased the resolution relative to the last user, this field will likely be yellow (caution). Increase or decrease the aperture size such that the value in the field is as large as possible without triggering the "caution" background (the background for your final value should be white). This will set the incident radiation to be as intense as possible (giving maximum signal) within the restraints of the set resolution level. Setting the aperture size too high will lower the resolution (the "caution" background warns you of this) so if more power is needed, as is the case with a weakly diffracting sample, first return to the "advanced" tab, lower the resolution, then increase the aperture size to the maximum allowable value from the "optic" tab.
11.) Under the "optic" tab, verify that the beam splitter is correctly set to "CaF_2." Also verify that the "accessory" field is set to "XYZstage."

NOTE: Some additional setup is required, and is specific to each sample. See "Using the Instrument" for sample-specific parameters.

Preparing your sample:
A number of sample preparation methods are available depending on the state of your sample. Regardless, sample holders are located in a small blue case generally kept on top of, or near the instrument. Raman spectroscopy requires only small quantities of material, so use of neat solid holders or capillary tubes will minimize waste. NMR tube and cuvette sample holders are available, but should only be used if these types of samples have already been prepared for other characterization purposes.

1.) Small quantities of solid may be directly pressed into solid sample holders using the press included with the sample case. Note that one such holder contains a standard sample, and may not be washed out or re-used (it is sealed to prevent this).
2.) Solid or liquid samples may be placed within a capillary tube (kept next to the melting point instruments) which may then be fitted into an appropriate holder (found in the sample case) which may in turn be placed into the instrument. Sealed capillary tubes are preferred to minimize the chance of spillage, but open tubes are acceptable if the user is cautious to properly orient the tube within the sample compartment of the instrument.
3.) Liquid or solution samples may be placed in an NMR tube for which a sample holder is provided (as is the case with capillary tubes). For solution samples, be aware the solvent may possess vibrational modes which may obscure those of the material of interest. In such cases the solvent should be carefully chosen.
4.) Larger quantities of liquids or solutions may be placed in the provided mirrored cuvette. For solution samples, be aware the solvent may possess vibrational modes which may obscure those of the material of interest. In such cases the solvent should be carefully chosen.

Using the instrument:
NOTE: The Raman spectrometer is extremely sensitive to vibration. Do not place any items related to sample preparation directly on the instrument bench top (as with any instrument) and avoid using the instrument bench top as a writing surface. Be very cautious not to bump the instrument or do anything else which might cause nearby vibrations (*e.g.* stomping or dropping items on the floor) while spectra are being collected.

ALSO NOTE: This section is a continuation from "Setting Up" (above). The previously outlined setup steps may be appropriate for sequential users with similar samples; however, it is important to note if any special settings have been made by the previous user. If you are the first group to use the instrument, consult your instructor to verify that setup has been completed. If you are following another group, verify that their instrumental settings are appropriate for your sample.

1.) Open the compartment at the front of the Ram II (below and in front of the liquid nitrogen tank). Open the sample holder by pulling back on the plunger, then set your sample into the sample holder. Solid sample holders should be oriented with the sample toward the detector. Liquid and solution samples in a cuvette should be placed such that the mirrored surface on the cuvette faces the detector (the darkened outer surface faces away from the detector). Any samples in unsealed capillary tubes should be oriented such that the tube is in an upright position to avoid spillage. Gently release the plunger to hold your sample in place. DO NOT allow the sample holder to snap shut as this will cause

certain sample holders (particularly solid sample holders) to eject sample toward the detector. This will necessitate cleaning of the instrument. Close the sample compartment.

2.) Open the "advanced" tab of the "advance data collection" window. Enter a file name for your spectrum in the appropriate field and verify that the designated path is within your class directory (C:\DocumentandSettings\CHEM3830).

3.) Return to the "basic" tab and enter a sample name, (including your initials to minimize confusion) and a brief description to help identify your sample, in the appropriate fields.

4.) Navigate to the "check signal" tab and select "spectrum" from the list of options on the left. The preview window should show a weak spectrum (see note below if not). Toggle "store mode" on. This will track changes to the spectrum and facilitate maximization of the signal. Any signals visible in the spectrum should be maximized by centering the sample physically using the XYZ stage. Buttons to adjust the alignment are found within the "check signal" tab, but the same procedure may be accomplished using either the keypad attached to the instrument, or the number pad of the keyboard. The keypad is preferable as it may be held in the hand above the instrument bench to minimize vibration, though all three methods are acceptable. Adjust X (left/right), Y (up/down), and Z (toward/away from the detector) parameters to maximize the intensity of the signal observed in the preview window. Clicking and dragging to select a region will adjust the view (by zooming in on the selected region) if certain peaks are of interest. To zoom out, right click on the preview window.

   Each directional parameter (X, Y, and Z) must be independently optimized. It is often useful to begin at the setting X = 100, Y = 100, Z = 100 to 130, independently optimizing X, Y, and Z in that order. Once each parameter has been independently optimized, vary each by a few increments to check that the sample is indeed centered (the signal should decrease if the location is changed in any direction from optimal).

   NOTE: If a spectrum is not observed in the preview window, the sample is likely badly out of alignment. Reset the physical location to X = Y = Z = 100. The "interferogram" setting may be used as a rough centering tool. In this mode, the amplitude of the observed signal should be maximized using the same procedure outlined above. Once a peak is clearly visible, final centering should be conducted using the "spectrum" setting.

5.) Click "Sample Raman Spectrum" to begin spectrum collection.

6.) Progress may be tracked along the lower portion of the spectrum screen. When the indicated number of scans has been completed, a spectrum will appear in the main window.

Preparing your Spectrum:

1.) Briefly inspect your spectrum to verify that the peaks are clearly distinguishable from the baseline. If your signal appears weak, your sample may be improperly centered (see "using the instrument," step 4) or weakly diffracting. In the former case, centre the sample and repeat the collection procedure. In the latter, either increase the number of scans collected to enhance the signal:noise ratio ("setting up" step 9) or decrease the resolution and increase the aperture size ("setting up" step 10). Repeat the spectrum collection.

2.) Once your spectrum has been collected, a number of tools are available. If your spectrum is poorly centered on the screen, the "spectrum adjustment" tool will allow you to correct it.
3.) You may need to adjust your baseline (using "baseline correction" tool) if it deviates substantially from level. Otherwise, proceed directly to "peak picking."
4.) The automatic peak picking tool (activated by clicking the "peak picking" icon) will label the major peaks in the spectrum.
5.) If you would like more or less detail, the minimum peak height may be set using the "interactive peak picking" tool (activated by clicking the drop-down arrow on the side of the icon, then selecting the "interactive peak picking" option). Click and drag on the arrow tool to set the desired peak height.
6.) Once you are satisfied with your spectrum, print it using the "Quick Print" tool (The "Print" tool should only be selected by advanced users).

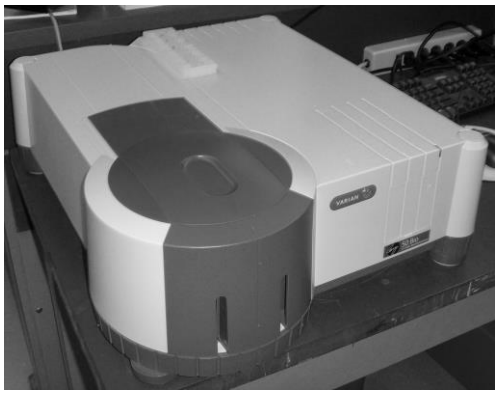
Cleaning Up:

Cleanup will vary according to the sample preparation method used.

1.) Solids pressed into neat solid holders must be rinsed out using a suitable solvent. The holders must be dried prior to returning to the sample case. Please check that no residue remains, as this will interfere with future users of the sample holder.
2.) Capillary tubes may be disposed of in the labeled containers along with m.p. sample tubes.
3.) NMR tube samples should be cleaned as one would normally clean an NMR tube. To clean your NMR tube, rinse the contents into the appropriate waste container. If any solids have formed, brush them out using a small test tube brush or pipe cleaner and rinse the tube with acetone and/or water. If clean, caps may be rinsed and reused. If damaged, caps may be discarded.
4.) If a cuvette is used, empty it into an appropriate organic or heavy metal waste container and rinse it thoroughly using acetone.

Varian Cary 50 Bio UV/Vis Spectrometer

Setting Up:



To access this instrument, one must log on to the accompanying computer (FISCEK-HSC06) using the following account:

Username: cary50
Password: user.

A variety of programs are available from the desktop; however most have highly similar interfaces. For collection of simple absorption spectra, "Scan" is recommended for beginning users. If the nature of your experiment requires only absorption values for one particular wavelength of radiation, "Simple Reads" is the recommended interface.

1.) Open the collection program of your choice from the desktop. Detailed instructions for "Scan" and "Simple Reads" interfaces are given below.
2.) Set up parameters for data collection by clicking the "Setup" button located toward the upper left corner of the interface.
   a.) "Scan" mode: It is usually sufficient to only set parameters using the general settings tab (the first one which opens with the "Setup" menu). Set the range of wavelengths you wish to scan under the "X mode" heading. This instrument is capable of scanning a maximum range of 900 nm to 190 nm.

   The level of detail which the instrument collects may be set using "Scan controls" (beginners should use the "simple" option for setting scan controls). This will allow selection from a range of preset scanning parameters which range from "Slowest" to "Survey" (very fast). Simply put, these preset options present a trade-off between quality of data and time required to collect. "Slowest" will collect a high quality spectrum, but take relatively more time to do so. "Survey" will only take a few moments, but the resultant spectrum will be of lower quality. All other presets range between these two extremes. For course purposes, the "Medium" to "Fast" settings are generally sufficient.

   One other setting of note is found under "Display Options" and has to do with the manner in which spectra are displayed. If you will be collecting a limited number of spectra of the same or closely related materials, it may be more simple to show all traces on one plot (this saves paper and is more concise). To do so, simply select "Overlay Data."

   Finally, note that absorbance is plotted on the Y-axis by default. If you wish to plot another parameter or change the default range, this may be done using the "Setup" menu as well. Click "Ok" to apply your settings.

   b.) "Simple Reads" mode: Set up is far more simple for this mode. If the nature of your experiment requires only information on the absorbance of a solution at a given

wavelength, set this wavelength in the "Read at wavelength" field of the setup menu (remember, the accessible range is 900 to 190 nm). Click "Ok" to apply your settings.

Preparing your sample:

1.) Prepare a dilute solution of your material of interest in an appropriate solvent. Since UV absorbance is often highly dependent on the nature of the material, the concentration required will vary according to the sample. Ideally, the peaks of a collected spectrum will range from near-zero absorbance to just below A = 1.0 on the Y-axis. Peaks slightly higher than A = 1.0 may be acceptable but if the majority of the spectrum is above approximately A = 0.8 on the Y-axis or if stronger peaks appear truncated, a more dilute solution should be prepared. If the collected spectrum is weak (the highest peak is below approximately A = 0.4) a more concentrated sample is necessary. If you do not know the nature of your material of interest, a solution with a concentration between 1.0×10^{-5} mol/L and 1.0×10^{-4} mol/L is often a good starting point. If you are constructing a calibration curve, your lab manual may suggest a range of concentrations to use.

2.) Obtain UV absorbance quartz cuvettes from your instructor. The cuvettes for this instrument are transparent on two opposing sides and frosted on the remaining two sides. The cuvette should be handled wearing gloves or only using the frosted sides (preferably both) to prevent depositing any skin oils or debris in the path of the UV radiation, which may alter the collected spectrum.

NOTE: The cuvette should always be placed in the instrument such that the UV radiation passes through the transparent sides of the cuvette. Facing the instrument, the path length is oriented perpendicular to the user's line of sight (so the frosted sides should be facing directly toward and away from the user).

ALSO NOTE: the cuvettes for the UV fluorimeter look quite similar to those for the Cary50, but are transparent on all 4 sides. These cuvettes should be reserved for users of the fluorimeter, as the fluorimeter cannot use absorbance cuvettes.

3.) If you have been supplied two cuvettes, fill one (approximately 80% full – overfilling accomplishes little and is likely to create a mess) with the solvent which you have used to prepare your sample and one with the sample solution itself. If only one cuvette is available, fill it with solvent and empty/refill it with sample prior to spectrum collection. Cap your cuvettes to minimize spillage. If the transparent sides of the cuvette have fingerprints or debris on them, polish them gently with a kimwipe.

NOTE: Many organic solvents are potentially damaging to the instrumentation or control computers. Never place or pour solvents on the instrument bench unnecessarily. A fume hood is available in the instrument room for sample preparation. Always fill cuvettes on a separate bench top or in a fume hood, as opposed to inside the instrument itself.

Using the instrument:

1.) A zero absorbance value must be set for the instrument to give accurate results. Slide the top of the sample chamber open and place your solvent cuvette (frosted sides toward the front and back) in the instrument's sample holder. Close the cover and click "Zero" (just

below "Setup"). All collections should be made with the sample chamber covered to minimize interference by ambient light and UV radiation.

2.) OPTIONAL: If you suspect that your solvent has any substantial UV absorbance, a baseline collection may help eliminate solvent absorption peaks. This option is available in the "Scan" program, but not in "Simple Reads." It may be selected from the "Setup" menu. The background collection should be performed at this time by clicking "Baseline." All baseline data is stored in the program until it is closed or until the baseline is overwritten with a new one. To verify that another user's baseline data is not applied to your spectrum (if the program was open when you arrived at the instrument), check that no baseline correction is selected in the "Setup" menu. Alternately, you may collect a blank spectrum by clicking "Start" to verify that your solvent does not absorb substantial amounts of UV radiation.

3.) Remove the solvent cuvette from the instrument and replace it with a sample cuvette.

4.) Click "Start" (top of the window in the middle). If you have not previously saved your data, you should be prompted to do so now. Locate your class' subfolder within C:/Data/ and give your file a name which indicates your identity (user initials) and the experiment which you are conducting. Click "OK."

5.) Name your sample when prompted and click "OK".

a.) For "Simple Reads" mode, you will simply see a list of absorbance values taken at the desired wavelength. To take additional readings, click "Start" again. One reading is taken each time "Start" is clicked. For simple reads, three to five collections are recommended as averaging these values can slightly improve accuracy.

b.) For "Scan" mode, a spectrum will now be collected. If the sample is too concentrated or too dilute, make the necessary adjustments and repeat "Preparing your sample" steps 1 and 3.

Preparing your spectrum:

1.) No spectrum preparation is needed for "Simple Reads" – proceed to step 2. For "Scan" mode, spectrum preparation is largely automated, but a visual inspection should be made to verify that the appropriate peaks have been identified. The spectrum may be modified using a variety of tools in the toolbar at the top of the spectrum window. Absorbance values for all labeled peaks will be automatically tabulated and are displayed below the printed spectrum. If you have several overlapping spectra, these values will be sorted according to sample name.

2.) Print your data from the "File" menu. The default printer is located in the instrument room next to the NMR processing computer.

3.) Save your data if you would like to keep it.

4.) Clear all traces from the window (scan mode) by right-clicking the spectrum and selecting "clear all traces" to prepare the instrument for the next user. If using simple reads mode, simply close the program.

Cleaning up:

Empty the quartz cuvettes into an appropriate organic or heavy metal waste container and rinse them thoroughly using acetone.

NOTE: Other facilities may use less expensive plastic cuvettes for UV absorbance. Never wash a plastic cuvette with acetone unless you know the nature of the material used – acetone may etch or corrode certain types of plastic.

Bruker Avance II 300 MHz NMR Spectrometer

NOTE: Due to high demand, use of the NMR spectrometer is only permitted during previously-scheduled times which may vary from semester to semester. Refer to the posted regulations for up-to-date information. Please consult your instructor to make special arrangements if you require access to this instrument outside of your regularly scheduled laboratory time.

Setting Up:

1.) If the control computer in the NMR room is powered off or locked, log in to the account:

Username: nmr user
Password: nmr

2.) If Bruker Biospin is not active, it may be started from the desktop. The lock display window (on the right screen) and BSMS control suite may be opened by clicking the corresponding options on the "NMR step-by-step" menu.

Preparing your sample:

1.) Place a 5 – 10 milligrams of the sample of interest (for a solid) or *one* drop (for a liquid) into an NMR tube and dissolve in approximately 0.75 mL of your chosen deuterated solvent. This will most likely be $CDCl_3$ but other solvents such as C_6D_6 or D_2O may be available depending upon the nature of your experiment.

2.) Cap, mix and label your NMR sample.

Using the instrument:

IMPORTANT NOTE: Please ask for assistance if you have never loaded a sample into the NMR spectrometer before. Improper loading may cause serious damage to the instrument.

ALSO NOTE: All NMR spectrometers generate powerful magnetic fields. As such, it is important that one never approaches a spectrometer while carrying any large metal objects (tools, etc.) or magnetic media (credit cards, magnetic storage media, etc.). In addition, one should not use an NMR spectrometer if they have a pacemaker or large metal plate within their body. While the Avance II is well-shielded, one should still keep metallic objects outside the area indicated by the yellow cones.

1.) Under "NMR Step-By-Step" menu, click "Create Dataset." Verify that the directory that you are working in corresponds to your course (ask for help if needed) and give your experiment a unique sample name. Include your name or initials in the sample name to help minimize confusion.

Also note the fields labeled "EXPNO" (experiment number) and "PROCNO" (procedure number). These may be used to help organize your experiments. The organizational scheme the program uses is as follows: maindirectory > yourclassdirectory > your experiment > EXPNO > PROCNO. For example, a Chem 3830 student with initials "BI"

may set up an experiment "BIexperiment2" and wish to run one ^{1}H spectrum and one $^{13}C\{^{1}H\}$ spectrum for each of three separate samples. All six spectra could be stored within the experiment "CHEM3830/BIexperiment2/…" if each dataset was given a unique EXPNO. You may use any organization scheme you wish, but each spectrum should be appropriately titled and all spectra from a single laboratory experiment should be within one sub-directory to keep clutter in the class directory to a minimum.

2.) If you wish to navigate between multiple open experiments, your datasets will become visible in the folder list on the left of the main window. If it is not found within the list, close and then re-open your course directory folder to refresh the list.

3.) Check that the top of the instrument is not capped (if it is, the sample lift will not initiate) and open the BSMS control suite (found in the NMR Step-By-Step menu, if it is not already open. It may be brought to the front by clicking the corresponding colour-coded tab on the top right of the main window). Select the "Main" control tab. Under sample, click "Lift." The button should turn green and the sample location indicator (at the very bottom of the control screen) should display "Up." You should hear gas flowing out of the top of the instrument.

4.) The tube height guide (at right) has both a blue plastic component (the "spinner") and a colourless glass component (the "guide"). Place the spinner into the top of the guide as shown, then carefully load your sample tube into the spinner so it touches (but is *no lower than*) the bottom of the glass guide. ***If your sample tube is too low when it is placed into the instrument, it will cause damage.*** Your solution should be approximately centered about the horizontal line on the side of the guide.

5.) *Without* removing your NMR tube from the blue spinner, lift it out of the colourless glass guide. Release your sample tube (along with the spinner) slowly over the top of the sample port *without* allowing it to drop. The sample should float on the stream of compressed air at the top of the sample port. If the flow rate is not high enough to support the sample without holding it, inform your instructor so that the necessary adjustments can be made.

6.) Using the BSMS controller, click "Lift" again. The sample location indicator should display "Missing" momentarily, followed by "Down." Your sample should be slowly lowered into the instrument. You may also notice an increase in the lock level, shown on the secondary monitor.

7.) Cap the sample port.

8.) Click on "NMR Step-By-Step" then "Lock." This will bring up a menu prompting you to select your solvent. Click on the solvent that you are using, then "OK." The instrument will automatically undergo a locking procedure. Once the "lock: finished" message appears at the bottom of the screen, proceed to the next step. This will likely take approximately one minute.

9.) Set up the experiment you wish to run using the appropriate "1D Experiments" or "2D Experiments" option under the "NMR Step-By-Step" menu. Some common 1D experiments you may wish to use are: 1d_proton (^{1}H), 1d_carbon_decoup ($^{13}C\{^{1}H\}$ – time permitting), 1d_P31_decoup ($^{31}P\{^{1}H\}$), or 1d_19F_wide (^{19}F, the "wide range"

experiment is recommended for any inorganic or organometallic species containing fluorine). Loading the default experiment parameters will likely be sufficient, though a number of customization options exist for each experiment. Consult your instructor if you would like to run a non-standard experiment.

10.) Tune and match the probe by clicking "Tune and Match" on the step-by-step menu. Allow the automated procedure to run until the "atma: finished" message appears. This will likely take 2-4 minutes, depending on the nucleus you wish to run and the instrument's previous settings. You may skip this step if the preceding user had the instrument tuned to the nucleus which you are interested in.

NOTE: the Bruker Avance II may be simultaneously tuned to two nuclei on two separate channels. One channel exists for collection of ^{1}H data while all non-H nuclei are run on the "x channel". In other words, you do not need to re-tune between running ^{1}H and ^{31}P spectra provided that you tune both to begin with. You do however need to re-tune between ^{31}P and ^{13}C. Selecting "Tune and Match" from within an "x channel" experiment (any non-H nucleus) will automatically tune the x channel to the selected nucleus and the proton channel. Selecting "Tune and Match" from within a ^{1}H experiment will not tune the "x channel."

11.) Click "Gradient Shimming" on the step-by-step menu and allow the automated shimming procedure to run until the "gradshimau: finished" message appears. This will likely take several more minutes. At this stage, the lock signal may have disappeared from the lock window. If this is the case, return to the BSMS control Suite. Under "Lock" click "Gain" then under "Value" click "Step –" or "Step +" as needed until the lock signal is visible. The signal should now approximate a horizontal line and should not fluctuate significantly over time.

12.) Click "acquire" to begin collecting your spectrum. The length of time this takes will vary from a few moments to several hours depending on the nature of your experiment (a simple 1D proton experiment should take no more than 3 minutes).

NOTE: At this stage you may wish to complete the section below ("Preparing Your Spectrum") before ejecting your sample. If you are not satisfied with your finished spectrum you may make adjustments to your experimental parameters and restart step 11. If you eject your sample and wish to collect a new spectrum, you must start again at step 1. If other users are waiting, you may briefly inspect your data but should relocate to the processing computer to generate your final spectrum.

13.) Uncap the sample port and click "LIFT" under "SAMPLE" on the BSMS control suite. Retrieve your sample then click "LIFT" again to stop the gas flow and re-cap the sample port. Remove your sample tube and replace the spinner into the guide.

Preparing Your Spectrum:

1.) If other users are waiting to use the NMR spectrometer, please relocate to the processing computer to prepare your spectrum. The processing computer is located immediately outside the NMR room (within the instrument room). The topspin program is available on this computer along with access to all data stored on the NMR harddrive. Note that files

are stored in the Z:/ directory (as opposed to C:/) as they are accessed remotely – your class directory should still be accessible from the left sidebar, but it will be a sub-folder of "Z:/". Also note that in order to protect original data, changes to spectra made from the processing computer will not overwrite any original files.

2.) Most basic spectral preparation and interpretation tools are found under the "NMR Step-By-Step" menu in the order that they should be completed. To visualize your spectrum once it has finished running, click "Exponential Multiplication" then "Fourier Transform." Beginning users should accept the default parameters in the subsequent pop-up windows.

3.) You should now see your spectrum, but it may not be completely in-phase. The most simple procedure for correcting this is the "Auto Phase Correct" tool, which is also in the "NMR Step-By-Step" menu.

4.) Locate your residual solvent peak or peaks and verify that the chemical shift(s) is(are) correct. If not, reset the shift of the most well-refined solvent peak to the correct value (see the supplied table next to the NMR control computer if you are unsure) by clicking the "Spectrum Calibration" tool (located on the main toolbar) then left-clicking the peak of interest. A popup window will appear allowing you to set the correct chemical shift for the peak.

    NOTE: You can change the view of your spectrum using the tools on the bottom row of the main toolbar (beginning with *2, /2, etc.). You can also zoom in on your spectrum by left-clicking the spectrum and dragging across the region of interest (this will not work if you are using the "Spectrum Calibration" tool or any other tool requiring you to click on the spectrum). Remember that there are tools on the aforementioned toolbar to reset your spectrum to the full collected width or to the default height.

5.) Next, select "Peak Picking" from the "NMR Step-By-Step" menu. This will activate peak picking mode, which will limit your ability to make other modifications to the spectrum until you have closed it. The toolbar in the peak picking window contains a number of options for defining new peaks and ranges; however, the most straightforward tool is called "Define New Peak Picking Range." This tool should toggle on once peak picking mode is activated and can be toggled on or off using the appropriate icon on the peak picking toolbar. When this option is toggled off, clicking and dragging on the spectrum will zoom as it does outside of peak picking mode. Other spectrum viewing and resizing tools remain active in peak picking mode.

    To define a peak picking range, toggle the appropriate tool on and click/drag to define a square around the top of any peaks of interest. Once drawn, peak picking regions may be deleted by right clicking on the region itself and selecting the appropriate "delete" command. Once you have selected all peaks of interest their markers (along with labels) should be visible on the spectrum. Save your changes by clicking the "Return, save changes" icon on the peak picking toolbar. This will return you to the main spectrum window and your peak labels should now be visible.

6.) Next, integration may be performed where appropriate. Enter integration mode from the "NMR Step-By-Step" menu. Integration mode is much like the peak picking mode in that it limits the manipulation options that are available. The icon for "Define New Region

Using Cursor" will appear in place of "Define New Peak Picking Range" and is toggled on or off similarly. Use this tool to define your integration regions as you defined your peak picking areas.

NOTE: Integration ranges are one-dimensional so one need only to define a region along the baseline. It is not necessary to draw a box around the peak of interest, as it was for Peak Picking.

Select a peak to serve as the "calibration" peak and right-click on the corresponding region. Select "calibrate" and set the value in the pop-up window to the known or expected integration value of that peak. The integration values for all other regions will adjust automatically. Right-clicking an integration region will also give the option to delete that region, analogous to deleting a peak picking region. Click "Return, save changes" to exit integration mode.

7.) Your spectrum should now appear essentially complete. If you wish to modify any peak picking or integration regions, you will have to re-enter the appropriate mode(s). Re-size the spectrum using the appropriate tools. You can print a spectrum using default display parameters from the file menu, or prepare your spectrum using the "Plot Editor" tool from the "NMR Step-By-Step" menu. Clicking "Plot Editor" will open a new program and load your spectrum automatically.

8.) If you choose to use the plot editor you may use a variety of tools such as region expansions, plot stacking, font and colour changes, and so on. These tools will not be discussed explicitly in this manual, but note that right clicking on a spectrum and clicking "1d/2d edit" from the main plot editor window will open a control window which allows for many of the same manipulations that you will have seen in the Bruker Biospin software (on the bottom row of the main toolbar). If you are interested in any more advanced spectral preparation tools, your instructor may be able to advise you further. When you have finished with the plot editor, print your spectrum from the "file" menu.

Cleaning Up:

NMR spectroscopy requires minimal cleanup – just be sure to leave the room at least as tidy as you found it. If you would like to save your NMR sample for future study, label it and keep it in the provided holder (lower left shelf of the cabinet) for short-term storage, or with your lab materials for longer periods of time. To clean up your NMR tube, rinse the contents into the appropriate waste container – acetone is often helpful here. If any solids have formed, brush them out using a small test tube brush or pipe cleaner and rinse the tube with acetone and/or water. If clean, caps may be rinsed and reused. If damaged, caps may be discarded.

Varian 431GC-210MS Gas Chromatograph – Mass Spectrometer

Setting Up:

1.) Verify that the main power supply to the GC-MS is on and start the control computer if this has not already been done. Log in to the computer using the following account:

    Username: Varian
    Password:

2.) Logging in to windows will automatically open the GC-MS control toolbar from which all necessary programs may be launched. Click "System Central" to open the main program and connect to the peripheral via the IP address 10.2.128.1.
3.) Open the "method builder" program by selecting "new method" from the main toolbar or by selecting "view/edit method" from the active method displayed (most likely Dailychecks.mth). From within the method builder program, open the method "CHEM3830default.mth" from the "methods" directory. You may wish to alter parameters for your experiment at this stage. If you wish to make changes to the CHEM 3830 default method, select "File" > "Save As" and save your method file in the "methods" directory with a name identifying your course number (be sure to include the user's initials and the date).
4.) Select "MS acquisition method" from the list of options at the left of the method builder. This will allow you to set the range of charge-to-mass ratios that the MS will survey. The maximum allowable range is 45 to 650. Surveying the full range is recommended unless you are interested in only a small, known region of the mass spectrum.
5.) Select "GC control" from the list within the method builder window. Set the time increments and desired temperature ranges using the provided spreadsheet. When run, the GC will adjust to the desired temperature, remain at this temperature for the indicated amount of time (not including the time required to reach this temperature), then increase to the next desired temperature. An estimate of the total time (including that required to adjust the temperature) is provided in the far right-hand column.
6.) Many other instrumental parameters may be set using the method builder tool; however, this should only be attempted by advanced users. Save your method file and exit from the method builder.

Preparing your sample:

It is important to analyze only samples which are highly volatile and completely free of salts. If this is not the case the column, which is very expensive, may become blocked and need to be replaced.

All samples should be dissolved in an appropriate non-reactive organic solvent (*e.g.* hexane, toluene, dichloromethane, etc.). Please note that aqueous solvents (*e.g.* alcohols, water) are not compatible with the column and will cause irreversible damage.

Mass spectrometers are extremely sensitive and only a very small amount of sample is required. While detection limits vary somewhat from sample to sample, a good starting concentration (to avoid overloading the detector) is 0.5 to 1.5 mg of sample/mL of solvent. At suitable concentration signal intensity should be between 1 tand 9 megacounts. If the signal intensity is significantly outside of this range, adjust the concentration accordingly and re-run the sample. Please note that if the detector is overloaded, subsequent runs may be contaminated with peaks from that sample.

All samples must be sealed within appropriate containers for the GC autosampler. These sample vials will be provided by your laboratory instructor at the beginning of the lab. The auto-sampler is only compatible with liquid (solution) samples.

Using the instrument:
Single sample injection may be run when only one sample is required. If numerous samples must be run on a single day, a batch run is most efficient. Both approaches will be briefly discussed.
Running a single sample:

1.) Place your sample (in a sealed sample holder) in the auto-sampler tray.
2.) Once your method has been set up, select "inject" > "single sample". When prompted, title your sample, identify the slot in the auto-sampler which holds it and indicate the method you wish to use (this will be CHEM3830default.mth if you have not set up your own method).
3.) When initiated, the auto-sampler will undergo a programmed sequence of actions which include rinsing the syringe and introduction of your sample to the GC column. Do not interfere with any moving parts or move any vials while this sequence is taking place.
4.) Allow the automated procedure to finish. A timer in the central "GC" window of the control software will indicate the amount of time remaining in the procedure. You will be able to watch the GC output in real time as your method is running. Once the procedure is complete, proceed to "Preparing your spectrum."

Running a batch of samples:
To begin a batch of samples, verify that all users have placed their sample containers in the autosampler and that the desired sample list is active in the "system central" window (see step 1 below). From the "Automation" menu, select "Begin Sample List". This will automatically sample and run each vial identified in the sample list according to the parameters outlined in the corresponding "methods" file.

1.) From the "system central" window, open the sample list by selecting "File" > "open sample list". Check which holder in the autosampler corresponds to your sample and name the corresponding field. In the last field, select "Daily Checks" method. This will run a routine diagnostic test once your sample run has completed. *Running the "Daily Checks" method at the end of each sample run is essential for the maintenance of the instrument and proper logging of GC-MS usage. Please do not neglect this step.*
2.) To begin the sample batch, select "Automation" > "Begin Sample List". The automated procedure described above will take place for each sample in the sample list.

Preparing your Spectrum:

1.) Once your sample has run, you may locate the corresponding GC-MS output in the …/VarianWS/data/ directory. To do this, launch the "Review/Process" program from the main toolbar and navigate to your dataset.
2.) A number of methods for visualizing output will be available. Select the GC output to display it in the main window. GC output will be automatically grouped into regions. Left click on a peak to view the corresponding mass spectrum for the region.
3.) You may resize your mass spectrum by clicking and dragging in the spectrum window (lower right by default). The "full scale" option will resize the spectrum to the full m/z range.
4.) Once your mass spectrum is appropriately sized, right click on the spectrum and select "Print". A new window will pop up; select "Print Active".
5.) This will output your file to a new window, from which you may review it, save it, or send it to the printer.

    NOTE: At present (Spring, 2009) hard copy printing has not yet been configured for the GC-MS computer. To output your file in a standard image format, select "export" > "to clipboard" from the print preview window. Paste the image into another program (*e.g.* MS paint) which is capable of saving in a standard image format (.jpg, .gif, etc.) and save it to the hard drive or to any portable data storage device. This can also be accomplished directly by selecting "export" > "to file"; however, the available format types are fairly limited.

Cleaning Up:

Once your sample has been run, rinse any residual material from your sample container into an appropriate waste container. Return the sample container to your laboratory instructor.

Glassblowing course

Fundamental Glass Manipulation

Cutting glass

There are a number of ways in which glass tubing can be cut, but some techniques are better than others. The preferred method is by flame cutting which is carried out in the following manner. Rotate the tube to be cut in the flame and when the glass reaches the working temperature, pull it apart. (Fig. I-6A) Redirect the flame to the front of the shoulder and pull off the existing "point" (Fig. I-6B). Reheat the end of the tubing again and blow it out (Fig. I-6C). With a piece of glass rod carefully chip off the feather edge and apply heat to the end of the tube until the wall thickness is uniform. With this method, the possibility of pinhole leaks when making a join is reduced and the seal can be worked so that it is invisible.

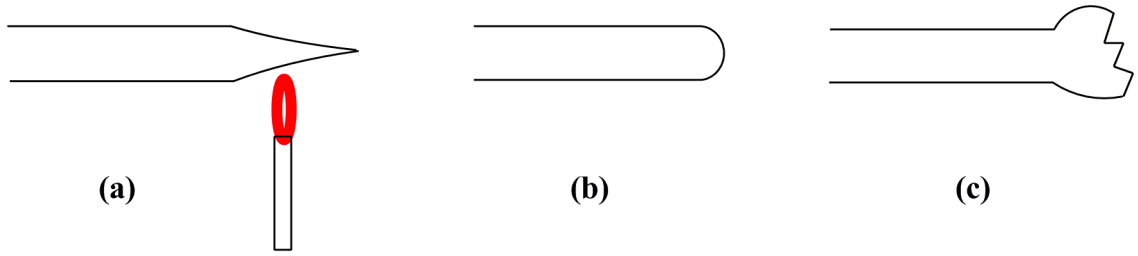


Figure I-6

The most common method of cutting tubing however, is the scratch technique. This is accomplished by placing a scratch with a glass knife perpendicular to the tube axis, and with the scratch facing up, apply downward pressure at the end of the tubing with the forearm and pulling up and outward with the thumb at the scratch. Fig. I-7 illustrates.

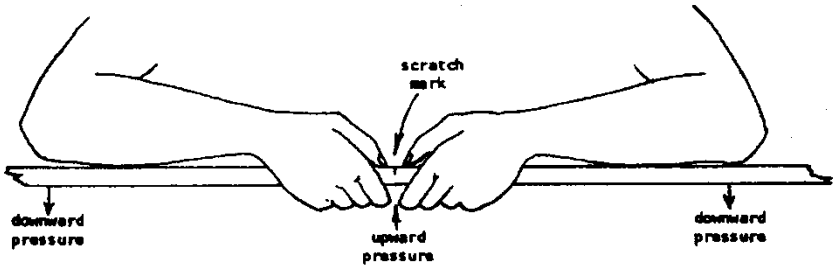


Figure I-7

In addition to the foregoing method, cracking or cutting of large tubing can be made easier if a piece of glass rod is heated to the melting point and is placed on the middle of the scratch previously made on the tube. Fig. I-8 illustrates.

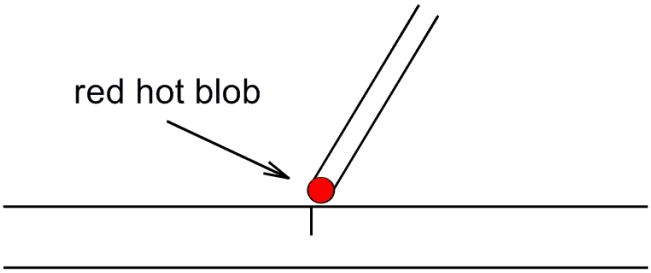


Figure I-8

Quite often a situation arises where a short section of glass tubing has to be removed. This can be a difficult task using the methods described. A simple method to accomplish this is as follows. Make a fairly long deep scratch perpendicular across the tube to be cut, and with the scratch facing up, apply an intense needle flame at the end of the scratch furthest away from you. The tube will fracture along the scratch and the short section can then be removed with the aid of tweezers. Fig. I-9 illustrates.

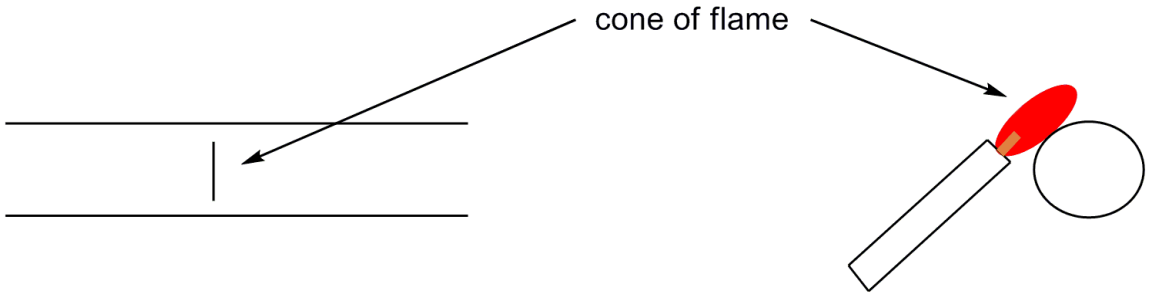


Figure I-9

Another cutting method which is ordinarily available in a professional shop only is a glass cutting saw.

Hand Working Technique

A glassblowing operation is done with the apparatus corked; a blow hose is also useful. The effects brought about by positive pressure in a closed system is expansion at the softened area; negative pressure will cause collapse. By varying the pressure, a piece of glass tubing can be given an entirely different shape simply by blowing or sucking on the blow hose while the glass is soft.

By applying heat to a piece of tubing and merely pulling on it, several things happen; the tube length is increased and the wall thickness becomes thin. Similarly, if the tubing is heated and the ends are pushed together, then the wall will be thickened and the overall length of the tube will be shortened.

When a piece of glass is heated to the working point, gravitational force will cause it to flow downward. For this reason, rotation of the glass while it is being worked is necessary.

Since the surface tension of glass is relatively high, glass protrusions when heated will tend to flow in causing the glass to become thick at that point.

As with most other compounds, superheating can cause changes in certain properties of glass. When these changes occur, the glass becomes cloudy in appearance and loses its flow properties when reheated to the working point.

When glass is cooled from the softening point, it goes through a crystallizing temperature range. If the glass is twisted or flexed in any way at these temperatures, it will become translucent and appear crystalline. This devitrification can be cured by reheating the glass to the working point.

Pulling A Point On Glass Tubing

There are many fundamental procedures with which a glass worker has to become familiar, but most involve the ability to rotate two pieces of glass tubing synchronously. Because this is quite difficult to master, a simple method called "Point Pulling" was devised. The following procedure illustrates this method.

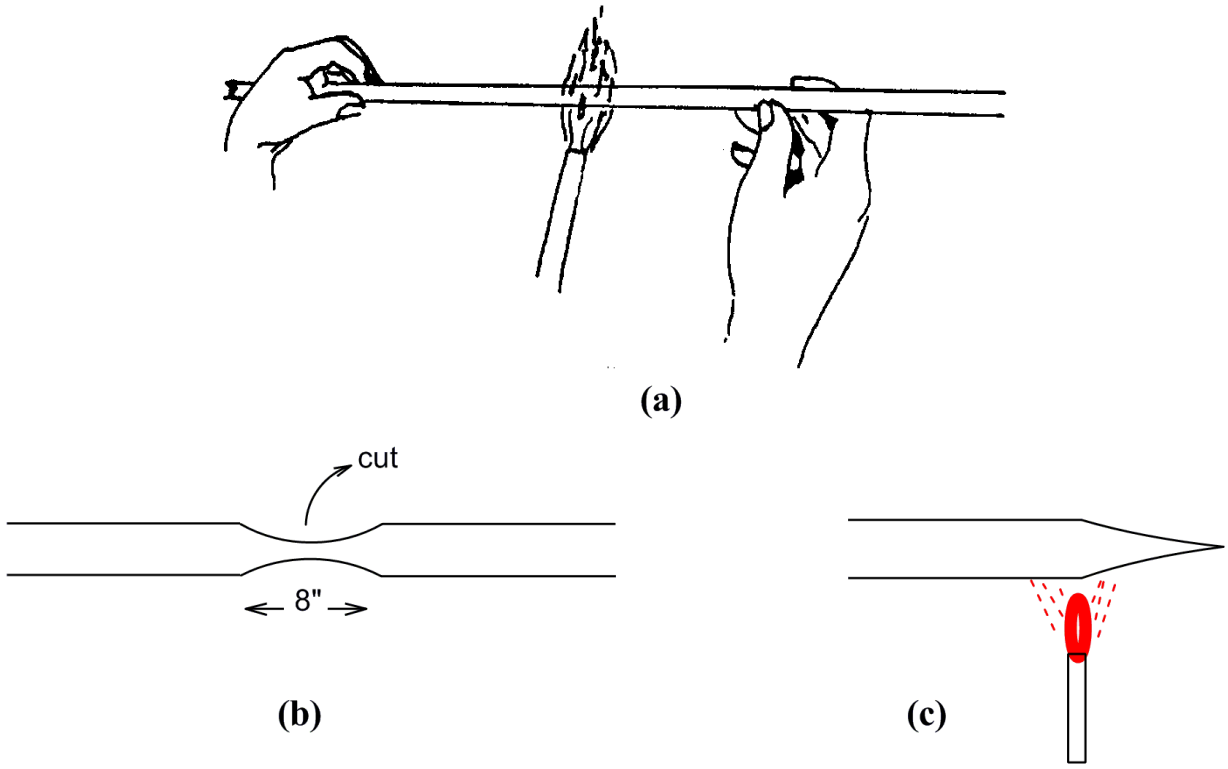


Figure I-10

A piece of tubing 12 or 13 mm in diameter, approximately 60 cm long, is cleaned and dried. The tube is then held in the hands as illustrated in Fig. I-10a. A soft bushy flame is directed to the midpoint of the tubing as it is being rotated. When the heated glass begins to soften the ends of the tube are pushed slightly together over a period of time until the softened glass area becomes thick. The tube is then removed from the flame and the ends slowly pulled

apart until the diameter at the midpoint is about 5 mm. When cool, the tubing is scratched with a knife at the narrowest point and separated into two pieces (Fig. I-10b)

The synchronous rotation of the tubing when in the softened state is of the utmost importance for two reasons:

(a) To attain uniformity of temperature around the entire periphery.
(b) To prevent twisting and/or buckling of the glass.

Now, take one of the pieces and hold it so that the right hand supports the point only and the flame is directed just back from the shoulder of the tubing. Fig. I-10c. This operation of Point Pulling is repeated until the point, when rotated in the fingers, is aligned with the axis of the tubing.

Constricting a Glass Tube

Illustrated in Fig. I-11 are two common types of constrictions. The method for fabricating these is as follows: hold and rotate the tubing in the usual manner and direct a bushy flame at a segment of it. If a constriction similar to Fig. I-11a is required, push on the tube ends to gather glass and thicken it at the point where it is heated. If a constriction similar to Fig. I-11b is desired, as a final step, pull on the tube ends slightly over a period of time until the desired internal diameter is achieved.

(a) **(b)**

Figure I-11

Assigned glassblowing projects

1. Joining Glass Tubing of the Same Diameter

Cut two pieces of 8 mm O.D. tubing to be 10 cm and 20 cm in length and cork one end of the 20 cm piece. Hold both pieces in the fingers as illustrated in Fig. I-10a. (The tubing must be held in this manner to allow the worker to blow into the end of the short piece and rotate the tubing simultaneously.) As the tubing is rotated, direct a soft bushy flame to the tube ends (Figure I-12a). When the glass begins to flow push the tubes together, then pull slightly in an attempt to thin the glass at the butt. Fig. I-12b. The joint is then reheated and expanded by

blowing into the open end of the tube. Fig. I-12c. The glass butt in reheated once again until the expanded section is reduced to the same diameter as the tubing. Fig. I-12d.

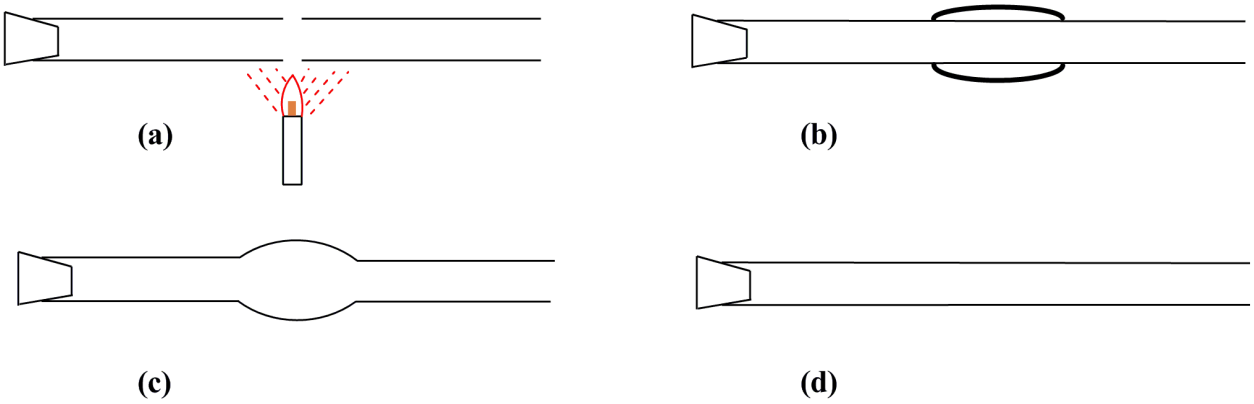


Figure I-12

2. Joining Glass Tubing of Different Diameters

Before tubing of different diameters can be joined, one end of the larger diameter must be modified as follows. Connect a blowhose assembly to one end of the larger diameter tube (20 mm) and rotate it with the left hand. Direct the flame to the other end of the tube as shown. Fig. I-13a. When the glass flows, with the aid of a pair of tweezers or glass rod, pull off the end as illustrated. Fig. I-13b. After the test tube end is accomplished (Fig. I-13c) reheat it and blow a hole of approximately the same diameter as the smaller tube (8 mm). Fig. I-13d, I-13e.

Cork one end of the tubing to be joined, then heat both ends. Fig. I-13e. (A greater portion of the flame should be directed to the larger diameter tube since more heat is required to soften it than to soften the smaller diameter tube.) When the ends begin to flow, join them and blow slightly. Fig. I-13f. Reheat the junction, expand the thickened glass by blowing, then pull the ends slightly. Fig. I-13g.

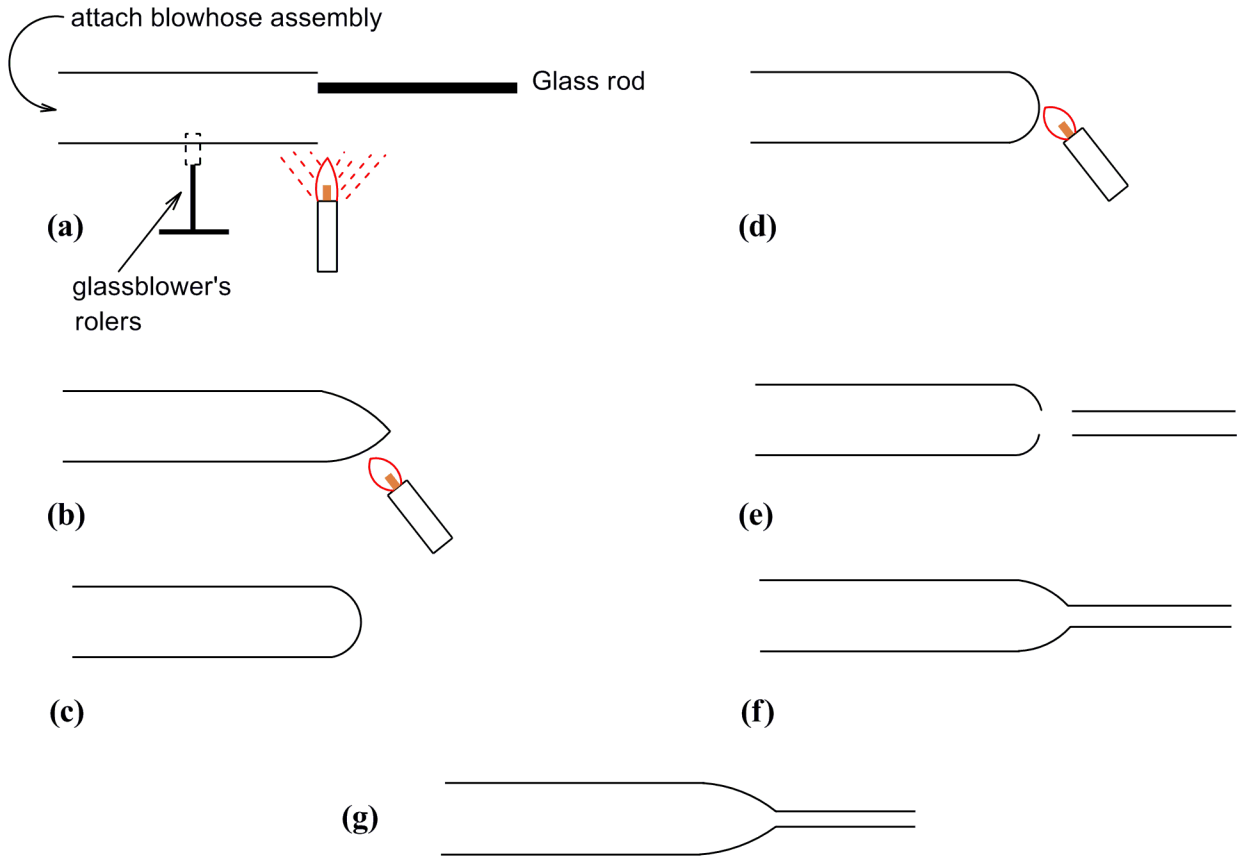


Figure I-13

3. Making T Pieces

From 8 mm O.D. tubing cut two pieces 15 cm and 8 cm in length. Cork one end of both tubes and fit a blowhose assembly over the open end of the longer piece. Direct a small needle flame to a spot near the midpoint of this tube. Do not rotate the tube. When the glass reaches the working temperature remove it from the flame and blow slightly. A slight bulge will appear. Fig. I-14a.

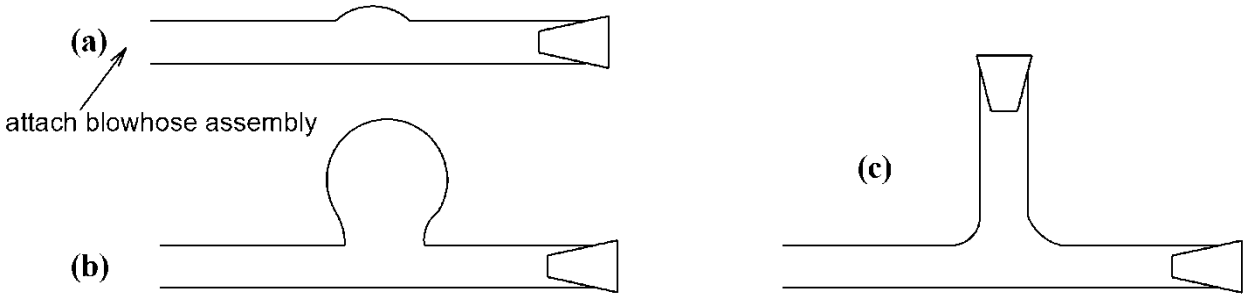


Figure I-14

Reheat the bulge until it collapses then quickly remove the tube from the flame and blow into the assembly until the wall ruptures. Fig. I-14b. (The hole should not be larger than the

diameter of the side arm to be joined.) After removing excess glass fragmentation with a piece of glass rod, direct a flame around the opening in an attempt to trim the uneven thin wall.

With the right hand position the short piece of glass tubing as shown in Fig. I-14c. Heat both openings, join the tubes together, then check "T" alignment. (If a small gap in the joint should result due to improper positioning, take a piece of glass rod and heat it and the gap simultaneously to the flow point and knit the pieces together. After the gap is closed, remove the excess glass by reheating the area, dabbing the glass rod on the thickened part and pulling it away.)

Work the glass at the joint by spot heating and blowing. This method ensures that rigidity of the "T" is maintained. (It is important that the entire area be kept reasonably warm while the joint is being worked, as severe thermal shock could cause the "strained" glass to fracture.) Anneal the glass immediately after the "T" piece is completed.

4. Bending Tubing at Right Angles

Bending small diameter tubing is relatively straightforward providing the worker follows this procedure. Cork one end of a piece of 8 mm O.D. tubing approximately 20 cm long and heat it in a wide bushy flame. Rotate the tubing in the usual manner, but in addition, move it from side to side in the flame while it is being rotated to heat a greater length along the tube. When the tubing reaches the working point, quickly remove it from the flame (stop rotating), bend the open end up toward the mouth and blow. Check the bend for alignment, etc. (Figure I-15).

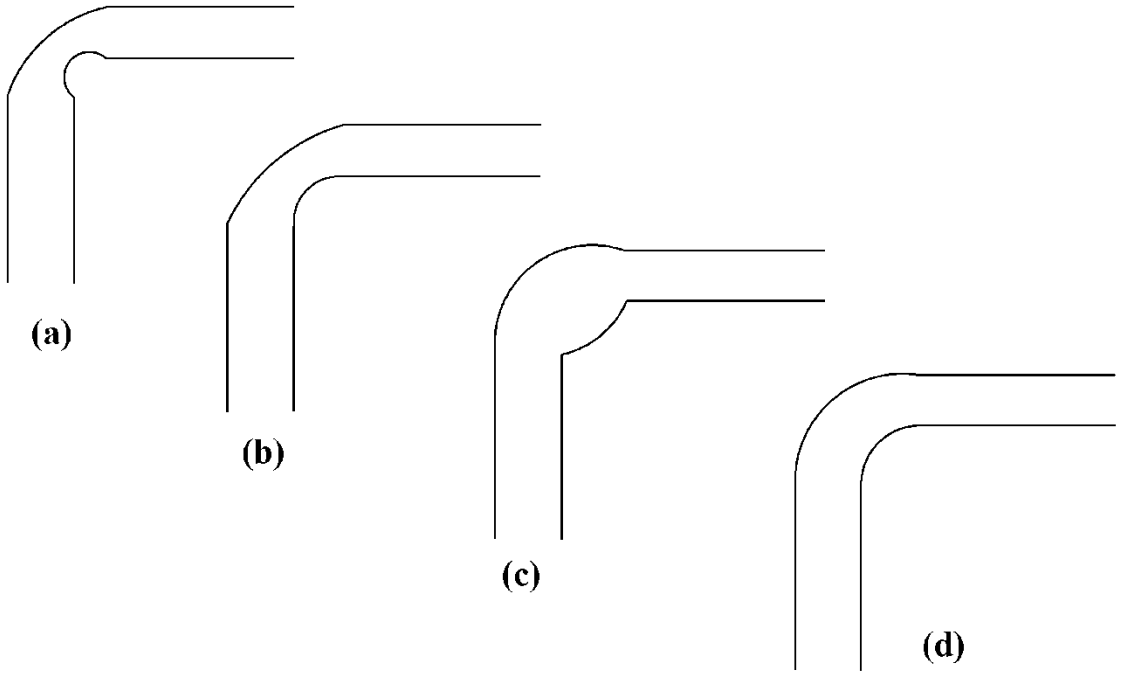


Figure I-15

(a) Bend is too sharp causing it to kink; a longer section of tubing should have been heated

(b) More air pressure should have been applied

(c) Too much air pressure was applied

(d) Satisfactory bend

5. Putting a side-arm on a test-tube (Schlenk tube)

Take a 20 cm length of 20 mm tubing, and heat the end to make a test-tube end (see Figure I-13a-d). Near the mid-point of the tubing, heat it in a low flame over a wide area around the attachment point. Make a narrow flame, and heat the attachment point to red heat (Figure I-16a). Blow out a small hole in the larger tube equal to the size of the side-arm to be attached (8 mm) (Figure I-16b). Reheat this bulge, and blow out a large bubble. Remove the devitrified glass from the hole (Figure I-16c). Attach the 8 mm tubing, which should be at least 10 cm long and be corked or sealed at the end, to the larger tube as follows. Heat both pieces to red heat and carefully join them at one point (figure I-16d). Now bend the tube in until it is attached at all points in the circumference.

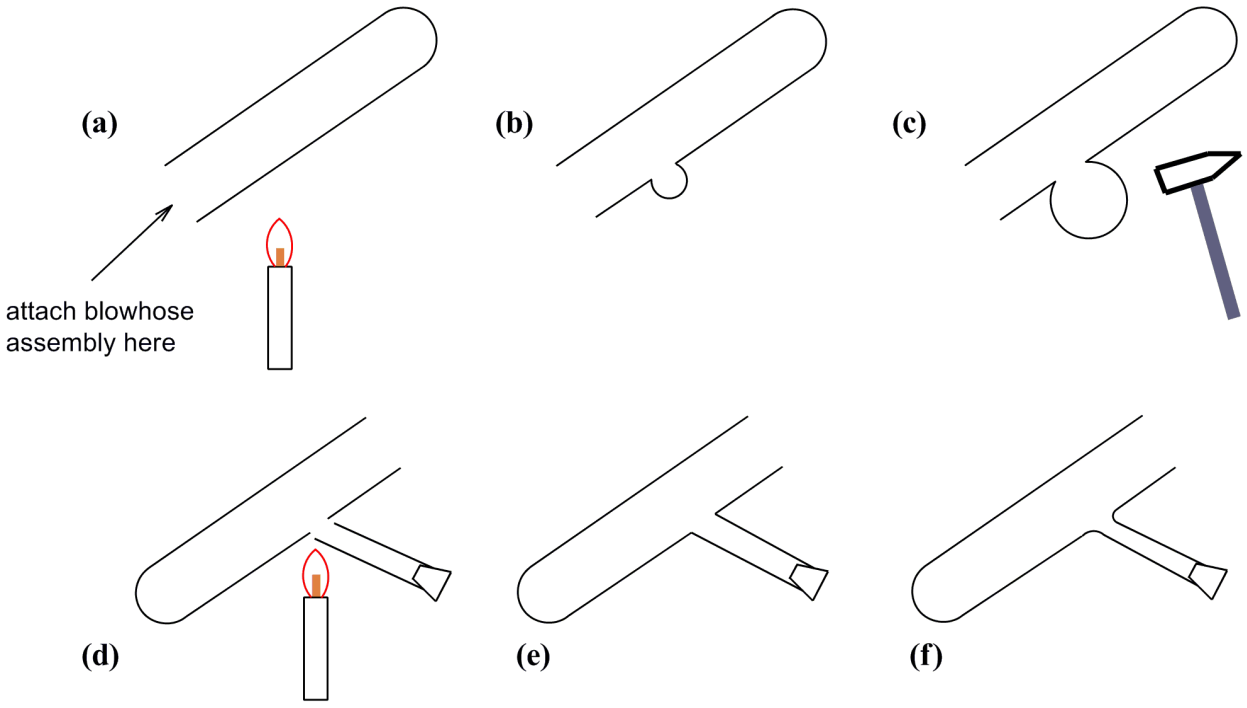


Figure I-16

Use gentle blowing to enlarge the size of the attachment point, with the goal of achieving a uniform thickness from the walls of the larger tube to the walls of the smaller tube. The excess

glass which has accumulated in the joining process is converted into increased diameter of the hole (Figure I-16e & f).

When a reasonable joint is obtained, carefully and thoroughly anneal the joint in a cool flame. After annealing and cooling, the side-arm can be cut about 2 cm from the larger tube, and the cut end is flame-polished to remove sharp edges. Finally, the open end of the larger tube is cut back to 3-4 cm above the attachement point and also flame-polished.

Evaluation

Bring the completed projects to your instructor (be sure to label them with your name), who will evaluate them according to functionality and, to a lesser extent, appearance. At least three of your projects must be judged "satisfactory" to pass the lab course. All glassblowing projects must be submitted no more than **two weeks** after the end of your assigned sessions.

Electrochemical Synthesis of the Hexabromodigallate(II) Ion

Introduction

The aqueous chemistry of the Group 13 elements is usually typified by aluminum rather than boron, since the latter has no cationic behaviour (i.e. B^{3+} does not exist). As the element, aluminum tends to be slightly less reactive than the other members of the group, as it is capable of protecting itself with a thin layer of oxide. Gallium has the unusual property of possessing an exceptionally low melting point (29.8 °C), yet it retains its group-characteristic boiling point (2070 °C). It thus has the longest liquid range of any known substance and is sometimes used as a thermometer fluid.

The usual oxidation state is 3+ for these elements, but both the 2+ and 1+ oxidation states is known in several cases. For gallium, these complexes are usually dimeric with Ga-Ga bonds, but other low-valent gallium species are known to be mixed-valence compounds, such as $Ga^{+}[GaCl_4]^{-}$, where the oxidation states are Ga(I) and Ga(III), respectively. The development of the chemistry of Ga(II) has been inhibited by unsuitable synthetic routes for true Ga(II) starting materials.

This experiment describes a technique that gives a good yield of pure $[PPh_3H]_2[Ga_2Br_6]$. Gallium metal is made the anode of an electrochemical cell, and a current is passed through an electrolyte containing suitable anions and triphenylphosphine. The IR and Raman spectra of the product will be used to chracterize it. The IR spectrum of $[Ph_3PH]Br$ will be recorded for comparison.

Instructional goals:

Properties of the following elements are highlighted: Ga, Br, P

(1) Establishing the molecular versus empirical formula of an inorganic anion.

(2) Structural evidence from a combination of far-IR and Raman spectroscopy.

(3) Experience with electrochemical synthesis of a metal compound.

Pre-lab exercise

1. Write a balanced chemical equation for the reaction in which $[PPh_3H]_2[Ga_2Br_6]$ is formed.
2. What is the structure of the hexabromodigallate anion? Create a HyperChem model of $Ga_2Br_6^{2-}$ and minimize it using the PM3 semi-empirical method. (Hint: you must check the "Allow Ions" box in the Periodic Table window in HyperChem to be able to draw this correctly.) Measure the optimized bond distances and angles.
3. What is the structure of the triphenylphosphonium ion? Create a HyperChem model of PPh_3H^{+} and minimize it using the PM3 semi-empirical method. (This also requires “Allow Ions”.) Measure the optimized bond distances and angles.

4. Does it matter which way the electrodes of the cell are connected to the power supply? Why? What physical evidence will you look for to confirm correct connection? (Hint: write the two electrochemical half reactions.) What crucial data must you record during the synthesis?
5. What signals do you expect to observe in the infrared spectrum of your product? What range of frequencies should you record in the IR analysis of the product?
6. Map out the timing of your afternoon's work. Use free gaps of time to do other operations. Be realistic in time allotted for each operation!

SAFETY NOTES

1. Gallium should be treated with respect as a heavy metal, and because it is easily liquified. Wear gloves.
2. Triphenylphosphine is poisonous if ingested or inhaled, but otherwise safe under normal laboratory use.
3. Concentrated HBr is corrosive and releases vapours of the acid. Handle only in a hood.
4. Mercury is also a toxic heavy metal. Use in a hood and dispose of in a special container.

Procedure

Preparation of the electrode and cell

Gallium metal can be cast around platinum wire to make a suitable electrode for the cell. Weigh about 3 g of gallium metal into a small beaker and then place the beaker into a larger container of warm water. The gallium will melt at 30 °C. Take about a 5 cm strip of the clean plastic tubing provided and pinch one end shut with a hose clamp. Carefully (over a drip pan) pour the liquid gallium into the open end of the plastic tube and insert the platinum wire (expensive, do not lose!) before the metal has had time to solidify. Allow the electrode to harden before cutting away the plastic mold (placing in a refrigerator for approximately 5 min may speed up the solidification). Rinse the electrode with water, then acetone and accurately weigh before and after each electrolysis.

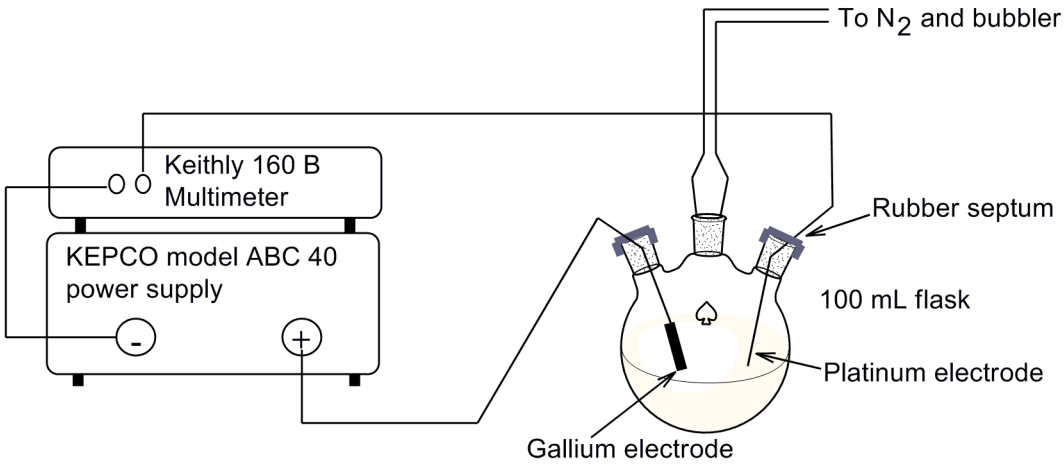


Figure II-1 Set-up of the electrolysis cell

Set up the cell as shown in the diagram. You will have to work near a nitrogen gas outlet, but it is not necessary to use a fume hood. Make sure that the anode (+) is the gallium electrode and that the platinum wire is the cathode (–). Do not switch on the current yet.

Preparation of $[PPh_3H]_2[Ga_2Br_6]$

Cool a 100 mL 3-neck ground-bottom flask in an ice bath and flush it through with nitrogen gas. Add 30 mL of acetonitrile, 0.5 g of triphenylphosphine, and 2 mL of conc. hydrobromic acid.

> *[Reagent grade solutions of HBr are often yellow/orange due to formation of small amounts of bromine. To remove this, shake the acid with 1 mL of mercury under nitrogen in a separating funnel until the solution is colorless. Dispose of the mercury in the waste container provided.]*

The gallium electrode may begin to react with the solution, but this reaction will be suppressed when the current is turned on. Apply a current of 50 mA for about 2 hours. Record the time exactly. The product will start to crystallize during the electrolysis (after 0.5 h). Collect the crystals on a small Büchner funnel in air and record the yield.

Record the loss in weight of the electrode and calculate the current efficiency (defined as moles of metal dissolved per Faraday of current passed). Melt the gallium electrode back into the container provided and cap for the next lab.

Characterization

Record the IR spectrum as follows: Record the IR spectra of your neat product and $[Ph_3PH]Br$ using the ATR IR spectrometer. In addition, record KBr pellet spectra over the full KBr range, of the product as well of $[Ph_3PH]Br$. Finally, record infrared spectra of $[Ph_3PH]Br$ and your product

as a nujol mull between CsI plates (600 to 200 cm^{-1}). *Beware of moisture contamination in the KBr!*

> ***NOTE**: CsI plates are extremely expensive (upwards of $300 per plate!) and are moisture-sensitive. Use them with great caution, and always clean them immediately (with CH_2Cl_2, NOT acetone or water!) and return to the desiccator for storage. These plates are very expensive and fragile - much more so than NaCl plates.*

Determine the melting point of your product and record Raman spectra of it and $[Ph_3PH]Br$.

Report

Hand in your product as well as the interpreted IR and Raman spectra.

At the end of your report, address the following additional questions:

1. Interpret the vibrational spectra using the information provided in the references.
2. How was the structure of hexabromodigallate and related compounds established unequivocally?
3. What is the reason for the instability of Ga(II), and how is this instability dealt with in $[Ga_2Br_6]^{2-}$?
4. Develop a qualitative molecular orbital bonding scheme for the dimeric anion. Show the orbital occupancy and topologies, and demonstrate why a dimer forms. (*Hint: first develop a picture for the two C_{3v} GaX_3 units, then bring them together along the z axis. You may use your HyperChem model as developed below to assist you in this task. However, do not simply cut and paste the result of the calculation, but rather use it to help you set up a qualitative MO scheme. A $GaBr_3^-$ model can also be calculated in HyperChem.*)

Molecular modelling

1. Use the model of $Ga_2Br_6^{2-}$ created in your Pre-lab exercise. Calculate and record the energy in PM3 (Hints: before starting your calculation, activate Start Log under the File menu; make sure that the correct charge and multiplicity are entered in the Setup menu). Report the geometry of this conformer – bond distances and angles.
2. Rotate one of the $GaBr_3$ groups by 60 degrees. (*i.e.* If you originally optimized the molecule in the staggered conformation, rotate the $GaBr_3$ group so you would form the eclipsed conformation.)
3. Re-optimize the geometry of this conformer, and record the energy. Report the geometry of this conformer – bond distances and angles.
4. Now calculate the energy difference in kJ/mol between the two structures (note that the default output of the program is in kcal/mol).
5. Use the model of PPh_3H^+ created in your Pre-lab exercise. Ensure that it is optimized under the PM3 semi-empirical model, with the correct charge and multiplicity entered for this molecule.

6. Describe the geometry of this ion, and record only the bond distances and angles for atoms directly connected to phosphorus.
7. Under the Compute menu, after peforming either a Geometry optimization, or if already optimized, a Single Point calculation, Compute Vibrations. This takes some time. Next and again under the Compute menu, Calculate Vibrational Spectrum.
8. In what region of the spectrum do you expect the P–H vibration to occur? Use the Animate Vibrations method to locate a normal mode of vibration that seems to be dominated by a P–H vibration. Record the calculated wavenumber for this vibration and compare it to your experimental value (Hint: remember that the calculation of molecular vibrations at this level of theory is quite approximate.)

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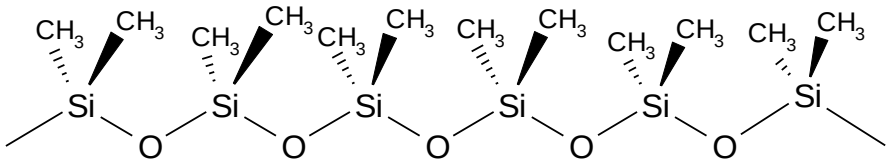
Inorganic Polymers: Preparation of Silicone Oligomers and Polymers

Introduction

Organic polymers have been known for a considerable time and include such compounds as polyethylene, polymethylmethacrylate ("plexiglass"), polyvinyl chloride (PVC), polyurethane, styrofoam and nylon. In general terms a polymer is a high molecular weight compound which is made from small repeating units. For instance, the repeating unit in polyvinyl chloride is $–CH_2–(CHCl)–$. Organic polymers of this type are limited in their applications by their tendency to thermally degrade above 250 °C. As a result attempts have been made to prepare thermally resistant polymers from inorganic starting materials. Of these, silicones $(R_2SiO)_x$ are the best known, although polyphosphazenes $(R_2PN)_x$ are finding widespread industrial applications.

Silicone polymers constitute one of the largest single economic components of chemical production in the western world. They consist of chains or networks of alternating silicon and oxygen atoms based on the repeating unit $–(Me_2SiO)_n–$ (see below), where n varies from several hundred to several thousand.



The precise properties desired (*e.g.* viscosity) can be systematically controlled by varying the chain length n; for light-weight oils n is approximately 100 while rubbers and resins have much higher molecular weights (n > 1000) and may exhibit cross-linking between adjacent chains. Small cyclic oligomers $(Me_2SiO)_n$, n = 3 – 8, can also be made.

Silicone polymers of this type are prepared by the controlled hydrolysis of dichlorodimethylsilane Me_2SiCl_2. The hydrolysis proceeds rapidly to completion since the Si–O bond energy (500 kJ/mol) in silicone (or siloxane) polymers considerably exceeds that of Si–Cl (350 – 375 kJ/mol). A notable feature of the reaction is the absence of any Si=O containing product, *i.e.* $Me_2Si{=}O$, the silicon analogue of acetone. This can be ascribed to the reduced stability of π-bonds involving $3p_\pi–2p_\pi$ versus $2p_\pi–2p_\pi$ overlap (as in acetone itself). The actual sequence of events is quite complex; the intermediate silanols $R_2Si(OH)_2$ are generally impossible to isolate as they immediately couple together in a condensation reaction with the concomitant elimination of H_2O (an **entropy** driven reaction).

The purity of Me_2SiCl_2 is very important in the formation of long-chain polymers (n > 1000). The actual chain length can be controlled by the addition of small amounts (< 0.05%) of chlorotrimethylsilane, Me_3SiCl. The trimethylsilanol formed by hydrolysis of Me_3SiCl condenses with the growing polymer chain, effectively terminating further polymerization at that point:

$$–O–SiMe_2–OH + HO–SiMe_3 \rightarrow –O–SiMe_2–O–SiMe_3 + H_2O$$

Conversely, if a trifunctional unit, as produced by the hydrolysis of trichloromethylsilane, is incorporated into the polymer chain, polymerization proceeds in three directions. This produces a cross-linked polymer and reduces the amount of linear polymerization. In the present experiment you will carry out the hydrolysis of Me_2SiCl_2 in diethyl ether. Under these conditions the cyclic trimer and tetramer, $(Me_2SiO)_3$ and $(Me_2SiO)_4$, are the major products. These will be separated by careful fractional distillation. You will also study the effect of the addition of cross-linking agents, *e.g.* B_2O_3, on the properties of the silicones.

Instructional goals:

Properties of the following elements are highlighted: Si, O, Cl

(1) Understanding condensation reactions of hydrolytically unstable halides.

(2) Experience with fractional distillation and use of a rotary evaporator.

(3) Performing IR spectroscopy.

Pre-lab exercise

1. Provide a balanced chemical reaction for the initial hydrolysis of dichlorodimethylsilane.
2. What reaction does this initial product undergo to form oligomers and polymers?
3. What are the formulae and structures of the "trimer" and "tetramer" prepared in this lab?
4. Produce HyperChem models of both molecules and optimize them using the PM3 semi-empirical method. (*Hint: draw a six-membered ring with alternating O-Si units. Then "Add hydrogens and model build". Change all of the H's to C's. Repeat "Add hydrogens and model build". Perform an intitial geometry optimization using MM+. Save this model. Finally, re-optimize the structure using PM3. Use a similar strategy for the tetramer*.)
5. Why must you use an NMR solvent containing no TMS for this experiment?
6. Map out the timing of your afternoon's work. Use free gaps of time to do other operations. Be realistic in time allotted for each operation!

SAFETY NOTES

1. Dichlorodimethylsilane reacts violently with water. Use caution in handling. The vapours are corrosive; dispense in a fume hood.
2. Silicone fluids are generally of low toxicity, but remember the breast implants! Avoid any unnecessary exposure to these and other laboratory chemicals.
3. CS_2 is an extremely flammable solvent, and must be used with extreme caution. Avoid any contact with a flame or spark source.

Procedure

Make a solution of dichlorodimethylsilane Me_2SiCl_2 (30 mL) in diethyl ether (50 mL) and place it in a 125 mL dropping funnel. Situate the dropping funnel so that the tip almost reaches the bottom of a 250 mL Erlenmeyer flask containing 100 mL of water. Slowly add the solution through the funnel while vigorously stirring the water by means of a magnetic stir bar. Hold the reaction mixture at 15 – 20 °C throughout the addition by surrounding the Erlenmeyer with an ice/water bath (Note: excessive cooling inhibits the reaction).

Separate the two phases with a separatory funnel (remembering to vent the funnel after agitation). Discard the lower (aqueous) phase and wash the ether phase (first with a solution of sodium carbonate (10 g of Na_2CO_3 in 50 mL of H_2O) and finally with another 50 mL of water). Remove and discard the lower (aqueous) phase after each step.

Allow the ether phase to stand over magnesium sulfate (add magnesium sulfate until clumping stops) in a sealed flask (!) for 20 minutes, then transfer the solution to a 100 mL round-bottomed flask. Using a rotary evaporator remove the ether (45 – 50 mL) from the solution and discard it properly. Transfer the remaining solution into a round-bottomed flask and set-up a distillation apparatus. Consult your instructor if assistance is required. The apparatus is built-up from Quickfit components with B14 joint sizes. All joints should be covered with a thin layer of silicone grease to prevent seizure, but use caution to prevent contamination of your products by the grease.

The distillation must be done slowly and carefully. The first fraction, the trimer $(Me_2SiO)_3$, b.p. 134 °C, is a solid at room temperature. Thus, it may be necessary to warm the still-head with a heat gun to prevent clogging and build up of pressure. Note that it is often practical to interupt the distillation and physically remove this solid product from the condenser. Get help from your instructor!

The second fraction is the tetramer $(Me_2SiO)_4$, b.p. 175 – 180 °C. It is usually the last pure fraction that can be obtained by distillation at atmospheric pressure. Attempts to collect further fractions (pentamers, hexamers, etc.) usually result in such high still-pot temperatures that the

high molecular weight diols ($HO[Me_2SiO]_nSiMe_2OH$) are pyrolyzed to cyclic dimethylsiloxanes and water. Thus a rather cloudy distillate, contaminated by trimer and tetramer, is produced.

Excluding any material formed by pyrolysis, the usual yields of trimer and tetramer are about 2 and 11 grams respectively. Record the yields and boiling ranges of your products; you should take more than one "cut" of each of your fractions and analyze their purities by ^{1}H and ^{29}Si NMR spectroscopy. The purest samples of trimer and tetramer can then be used for the other analyses, and for marking.

The residual silicone oil in the pot can be used to prepare "bouncing putty" by heating to approximately 200 °C with about 5% of its weight of boric oxide and an inert filler (try Celite). "Bouncing putty" slowly flows under its own weight, like a liquid, but bounces very well when formed into a ball and thrown at a hard surface (**please avoid your instructor!**).

Characterization

1. Record the IR spectra of your neat products using the ATR IR spectrometer. Record IR spectra of your distillation fractions. Use the b.p. data to try and identify those fractions that have the most of one of the given isomers present.
2. Record 300 MHz ^{1}H and ^{29}Si NMR spectra of both products. **Use $CDCl_3$ containing no TMS**; set the reference by the residual $CHCl_3$ signal at 7.25 ppm.
3. Interpret the mass spectra.

Report

At the end of your report, address the following additional questions:

1. Explain how the addition of B_2O_3 converts silicone oil into a rubbery material.
2. You can buy silicone sealants (for bath-tubs, etc.) at any hardware store. These are termed RTV (room temperature vulcanizing) polymers. What are these and how do they work?
3. How is Me_2SiCl_2 produced industrially? How would you make it in the laboratory?
4. Discuss the concept of catenation in the non-metallic elements. Which two elements form the most stable homocatenates? Why do the majority of other elements form heterocatenates? List as many examples as you can for heterocatenates among the non-metallic elements.

Molecular Modeling

1. Using the models created for your Pre-lab exercise, ensure that both rings are geometry optimized by the PM3 method. Describe the structures. Measure the bond distances and angles within the rings, as well as the torsional angles around the rings. Compare the values for the trimer and the tetramer.

2. Calculate the energy of the two isomers (*Hint: activate the Start Log command under the File menu to record your energies in a file*.) Can you think of a way to compare these energies to determine which isomer is more stable?

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Vacuum-line Preparation and IR Spectroscopic Characterization of Germane, GeH_4

Introduction

There is currently considerable interest in hydrides of the Group 13, 14, and 15 elements. They are used as gaseous precursors to semiconductor materials and as doping agents in the preparation of *p* and *q* junctions in elemental silicon for solid-state transistors and integrated circuits. These compounds were first studied in detail by Alfred Stock, who invented the modern chemical vacuum line in order to study reactive boranes, silanes and related compounds, including GeH_4.

In this lab you will prepare monogermane, the germanium analogue to methane. Both CH_4 and GeH_4 burn vigorously in air; however, GeH_4 inflames spontaneously, while methane has a considerable activation energy, and usually does not burn until ignited by heat or a spark. Therefore this experiment is performed entirely in an enclosed system built around a high-vacuum line. Vacuum lines have been designed for a variety of applications. The modification employed in this lab was designed specifically for this experiment. However it could be used for numerous other experiments requiring the manipulation of volatile materials. **Be very cautious in handling the line. Turn the stopcocks slowly with one hand, while holding the stopcock barrel with the other. Remember, glass is strong but fragile, and sudden shocks can break the line.**

Vacuum transfer of volatile compounds is very rapid in a totally evacuated apparatus. Cooling one region of the apparatus lowers the local pressure in that region and the gas moves there to re-establish equilibrium. (Figure II-2) In this way a volatile material can be moved around at will.

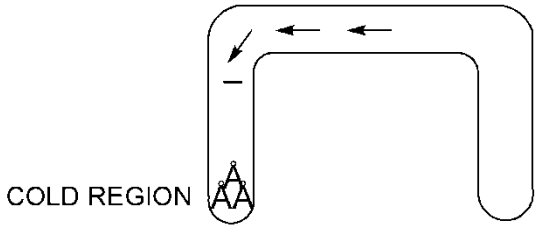

Figure II-2 Vapour transfer in *vacuo*

However, even a small amount of a **non-condensable** gas will severely retard transfer *in vacuo*. The definition of non-condensable depends on the cooling agent used. In practice, chemists use liquid N_2 or dry ice as coolants. *l*N_2 has a boiling point of –196 °C and dry ice sublimes at –78 °C under ambient pressure. Gases with boiling points close to these values will not readily condense. Typically, gases that do not condense when *l*N_2 is used as the coolant are the components of air, N_2 and O_2. At higher pressures, however, O_2 will condense quite readily in *l*N_2.

Never insert an open-ended tube or container in lN_2. In addition, be extremely suspicious if a large amount of liquid suddenly forms in your vacuum line (especially if it has a pale blue tint (lO_2 is blue). This is probably liquid air, because you have a leak in the apparatus. Leave the coolant around the trap containing the liquid air, and call your instructor or other qualified personnel. The rapid evaporation of a pool of liquid air (which can be caused by removing the coolant) can easily explode a glass apparatus. Furthermore, liquid air is enriched in lO_2, which is capable of oxidative reactions with organic matter, grease or dirt with explosive intensity.

Instructional goals:

Properties of the following elements are highlighted: Ge, B, H

(1) Understanding of, and experience with, a chemical vacuum line for the handling of volatile, reactive materials.

(2) Preparation of a volatile Group 14 hydride.

(3) Measurement of a gas-phase, "high-resolution" IR spectrum.

(4) Determination of the Ge–H bond length in GeH_4 by analysis of the vibrational-rotational spectrum.

Pre-lab exercise

1. Write a balanced chemical equation for the synthesis of germanium hydrides from GeO_2 and KBH_4.
2. What is a slush bath, and by what physical principle does it function?
3. What are the physical properties (*e.g.* m.p., b.p., vapour pressure) of GeH_4 and Ge_2H_6?
4. Create HyperChem models of GeH_4 and Ge_2H_6. Optimize their structures first using MM+ and then using the PM3 semi-empirical methods. Record all bond distances and bond angles.
5. Why is the IR spectrum recorded at a very low pressure in a cell with a 10 cm path length (much longer than the < 1 mm paths used in the liquid-film-between-NaCl-plates technique used in Chem. 2500/2600)?
6. Draw flow diagrams through schematic representations of the vacuum line to indicate the flow of vapours in the various stages of the preparation and purification of GeH_4. Include these in your lab notebook for consultation during the experiment.

SAFETY NOTES

1. Germanium dioxide is only mildly toxic by ingestion, but germane is a highly toxic gas. We make it in only very small quantity, and in a totally enclosed system. If the container of GeH_4 were accidentally broken, leave the immediate area until the gas has completely dispersed.
2. Potassium borohydride is toxic by ingestion. It reacts with water releasing hydrogen which represents a fire and explosion hazard. Use caution in handling.
3. Evacuated equipment represents an implosion hazard. Wear eye-protection and full face shields whenever you are near the reaction flask or vacuum line.
4. Ethyl bromide (bromoethane) is toxic by inhalation and ingestion. Its vapours are markedly irritating to the lungs on inhalation for even short periods. The vapours are also highly flammable. PREPARE THE SLUSH BATH IN A HOOD WITH THE SASH DOWN.
5. Chloroform is a suspected carcinogen, and is toxic by inhalation. It is not flammable. PREPARE THE SLUSH BATH IN A HOOD WITH THE SASH DOWN.
6. Dry ice is very cold (–78 °C) and cause severe tissue damage. This is particularly true if skin comes into contact with a dry ice solvent bath. Always wear gloves accordingly.

Procedure

Dewar Flasks

For the handling of cryogenic fluids, in this case liquid nitrogen (lN_2), and mixtures containing this coolant, you will employ Dewar flasks, or simply "Dewars" (Figure II-3). (The name is capitalized

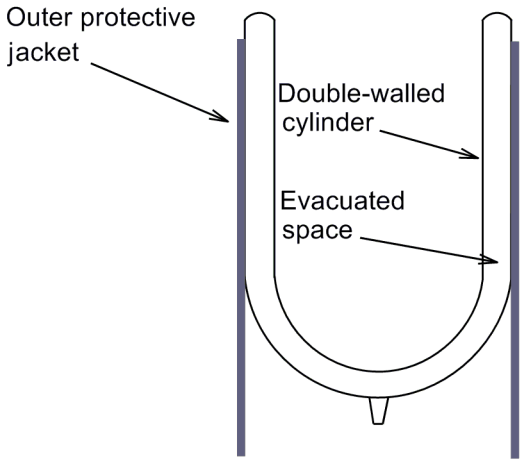

Figure II-3 Cross-section of a typical Dewar flask

because it refers to the inventor, Sir James Dewar, just as the Erlenmeyer flask honours Emil Erlenmeyer.) A typical Dewar is a double-walled cylindrical glass container, with the space

between the walls evacuated to a very low pressure. This means there are few molecules in the wall space to conduct thermal energy from the lab to the cryogen, and Dewar flasks are thus very good insulators. A further improvement in insulation is provided by silvering the glass to reflect radiant heat.

> *These flasks are very expensive and fragile! Moreover, since they are evacuated, when they break they implode with a loud report, and the glass fragments can cause serious injury.* ***Handle the Dewars with great care*** *in this and all other situations where you use them.*

Vacuum line setup

The vacuum line is attached to the lattice frame. A schematic representation is included as Figure II-4. Make sure that you view this line and understand how it correlates to the diagram. The apparatus for the experiment should be set up prior to starting as indicated in Figure II-5, and should be checked by the instructor before continuing. Connect the outlet tube to **port 2** on the vacuum line with **vacuum Tygon tubing**.

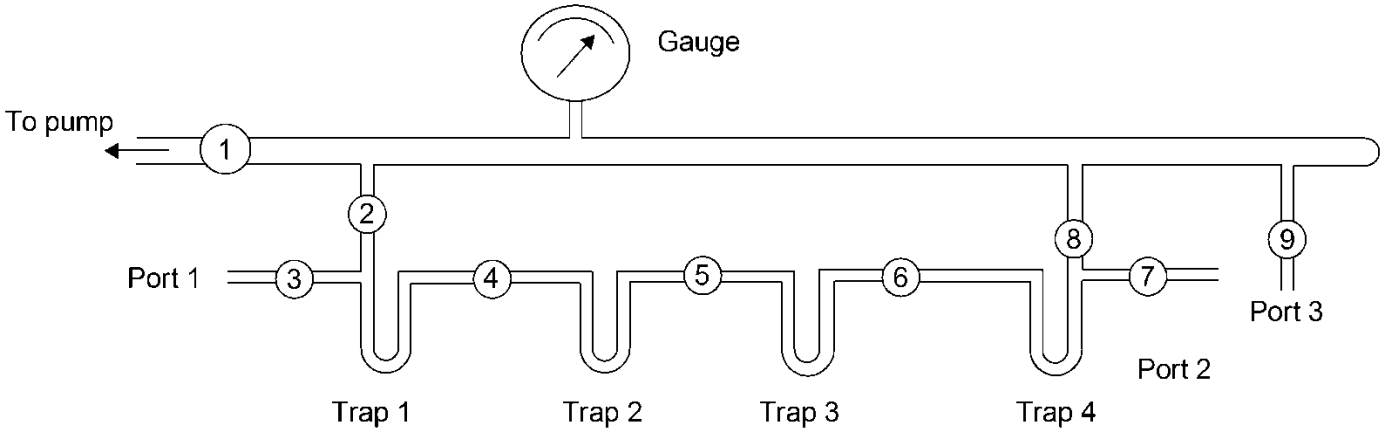

Figure II-4 Schematic diagram of vacuum line

Preparation of GeH_4

Charge a 250 mL RB flask with 60 mL of glacial acetic acid and a stirbar. Prepare a separate solution by dissolving, **in order**, 1 g of KOH, 0.5 g of GeO_2 and 0.75 g of KBH_4 in 15 mL of d H_2O in a 50 mL beaker. **Do not use a metal spatula to stir this mixture!** Pour this solution into the dropping funnel.

Put on a full face-shield without removing the normal safety glasses. Keep the shield down whenever facing the vacuum line or other evacuated containers.

Evacuate the vacuum line traps by opening stopcocks **1**, **2**, **4**, **5**, and **6**. Carefully open **7** with the stirrer running to evacuate the reaction flask. After the acetic acid stops bubbling, close **7** and cool all four traps by immersing them in Dewars filled with *l*N_2. Close **1**. Open **7**.

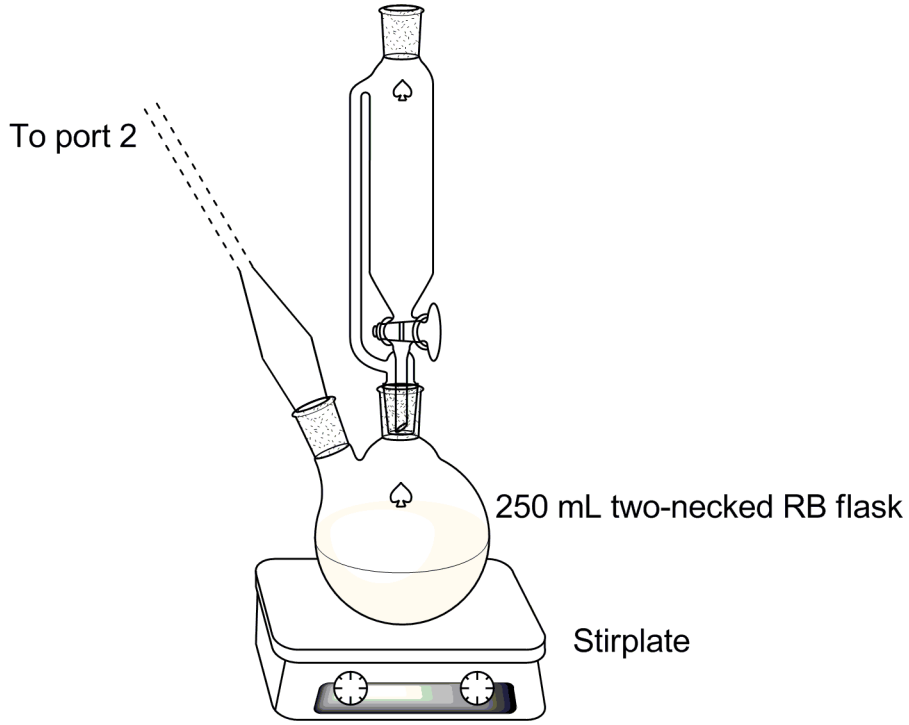

Figure II-5 Reaction flask set-up

Start the addition of reagent at a slow but steady rate such as to complete the addition over 10 minutes. Stop the addition with a drop or two of reagent left in the funnel. At this point stop the N_2 bleed, and open **1** completely for a few seconds. Close **7**. Open the bleed valve to bring the flask to atmospheric pressure with N_2. Disconnect the reaction flask and take it to a fume hood. Clean it out as soon as possible.

Preparation of slush baths

Slush baths are prepared **in a fume hood** by **slowly** adding liquid nitrogen to the stirred liquids in a Dewar, until the consistency of a thick milk shake is achieved. The stirring is done with a wooden stick to prevent breakage of the Dewar flask. Care must be taken not to add too much *l*N_2 or a difficult-to-melt solid mass will form. If the *l*N_2 is added too rapidly at the beginning, large amounts of the substance being cooled will be thrown out of the Dewar.

Trap-to-trap distillation

Remove the Dewars from traps **2**, **3**, and **4** allowing all the volatile materials to condense into trap 1. After several minutes only water may be left in these three traps. Close **2** and **4** and open **8**. Use the heat gun to evaporate away the water to the pump.

Immerse trap 2 in a Dewar filled with a $CHCl_3$ slush bath (–63.5 °C). Move the *l*N_2 Dewar from trap 1 to trap 3. Open **4**. As the mixture in trap 1 melts, the gases pass through the slush bath, removing acetic acid and water. **Do not hurry this along by warming the trap.**

When trap 1 is empty, close **5**, **6** and **8**. Remove the slush bath and open **2**. Heat traps 1 and 2 to drive the contents to the pump. When completely dry, cool them to room temperature. Attach the external Ascarite/magnesium perchlorate trap between ports 1 and 2. Open stopcock **3** and the stopcocks on the Ascarite trap to evacuate the trap. Close **2** and **4**, and then open **6** and **7**. Move the *l*N_2 Dewar from trap 3 to trap 1. The volatile germanes pass through the trap, but CO_2 and residual water are trapped by reaction with the trap materials. When trap 3 is empty, close all stopcocks and disconnect the Ascarite trap. **Ensure the stopcocks on the trap are closed; it can be used for many preparations if kept isolated from the atmosphere.**

Immerse trap 2 in an ethanol (99%) slush bath (–110 °C). Open **4** and **5**. Move the *l*N_2 Dewar to trap 3. This slush bath removes digermane. When trap 1 is empty, close **5**, open **2**, and remove the slush bath. Pump the residues in traps 1 and 2 away. **Do not lower the liquid nitrogen on the germane trap!**

<u>Characterization</u>

1. Measure the vapour pressure of your sample by closing **1** and **2**, opening **8**, and replacing the *l*N_2 Dewar with the ethyl bromide slush bath. This will liquefy the GeH_4, and the vapour in equilibrium with this liquid develops a pressure, which you can read from the pressure gauge. Pure germane has a vapour pressure of 182 mm Hg at –111.6 °C. When you are done with this measurement, cool again with liquid nitrogen to freeze the GeH_4 back into the trap. Close **8**.

2. You will perform a gas-phase IR spectrum of GeH_4 in high-resolution mode. This involves several differences in procedure, including the use of a different software package. Ask your instructor to assist with this data acquisition.

   The IR cell is a 10 cm path-length gas cell, with large KBr windows. It is stored in its own desiccator. This cell has vacuum stopcocks and ground-glass joints, enabling it to be directly attached to the vacuum line at port 3. The cell is evacuated by opening stopcock **9**. Now close **1**, open **8**, and remove the Dewar from trap 3 to vapourize the GeH_4. A pressure of only 10 – 20 mm Hg is required to observe the spectrum. Higher pressures lead to loss of resolution from **intermolecular** effects.

To empty the cell after analysis, reconnect the cell to the line and open the stopcocks on the cell and the line. The unused portion of GeH_4 can be stored in the container provided. Ask you instructor about the procedure for vacuum transfer to this container.

Report

Provide a full analysis of the high-resolution IR spectrum of GeH_4. The following will serve as an outline to guide you in this analysis.

Tetrahedral molecules are a special case of the class of molecules known as *spherical tops*, XYZ_3. The spectrum which you have recorded is an example of a vibrational-rotational spectrum, similar in all respects to the HCl spectrum studied in Chem 3730. However, the mathematical treatment of spherical top molecules is considerably more complex. Here follows a greatly abbreviated treatment. Each vibration has associated with it a *P, Q* and *R* "branch", with the *P* at lowest energy. The frequencies of the bands are identified by the *Q* branch. There are three in the spectrum of GeH_4: ν_3 at 2105 cm^{-1}, ν_2, an "IR-forbidden" band at 935 cm^{-1}, and ν_4 at 813 cm^{-1}. An analysis of the rotational "fine-structure" of ν_3 and ν_4 can give a value for the moment of inertia, I, for GeH_4. From this we can calculate the Ge–H bond length in this molecule by the following equation (defined for XY_4):

$$I = 8/3\, m_Y\, r_{XY}^2$$

where

$$r_{XY} = \sqrt{\frac{3I}{8m_H x 1.66710^{-24}}}$$

From the average spacing of the rotational lines in the *P* and *R* branches of the two fundamental vibrations, denoted $\Delta\nu_3$ and $\Delta\nu_4$, respectively, we can calculate values for the *estimated rotational constant, B*, for the tetrahedral molecule and the so-called Coriolis coupling constants, ζ_3 and ζ_4. These are related by the following equations:

$$\Delta\nu_3 = 2B\,(1 - \zeta_3)$$

$$\Delta\nu_4 = 2B\,(1 - \zeta_4)$$

$$\zeta_3 + \zeta_4 = ½$$

Thus:

$$B = (\Delta\nu_3 + \Delta\nu_4)/3$$

The estimated moment of inertia is obtained from B by the equation:

$$I_B = \frac{h}{8\pi^2 c B}$$

From the tabulated peak positions for the ν_3 and ν_4 lines, calculate values of *B*, *I*, and $r_{Ge\text{-}H}$. Remember to use average values, and remember the resolution limit of the spectrometer, and the resulting uncertainty in your answers.

At the end of your report, answer the following additional questions:

1. What is meant by the term fundamental vibration? Sketch the fundamental vibrations for a tetrahedral molecule.
2. Why are certain vibrations classified as "forbidden", and others "allowed" in the vibrational spectrum of GeH_4?
3. Compare your values for *B, I,* and $r_{Ge\text{-}H}$ with literature values.
4. Why is the rotational-vibrational method of determining structure and bond distances restricted to small molecules?

Molecular modeling

1. Using your PM3 optimized molecular model of GeH_4, perform a geometry optimization (this should just be identical to a single point calculation, but ensures that you truly have an optimized structure.)
2. Under the Compute menu, perform a Compute Vibrations. Then calculate the vibrational spectrum. Arrange your screen so that you can see both the spectrum window and your molecule. This may require re-sizing or translating your molecule on the screen.
3. Record the calculated vibrational frequencies (in cm^{-1}) and the symmetry labels of those vibrations. Then animate each vibration, and use this in conjunction with your answer to "additional question #1" above to identify the calculated vibrations using the conventional ν labeling system.
4. Construct a table comparing the calculated and measured vibrational energies of all of the vibrational bands. Indicate which bands are allowed and which are forbidden in the Infra-Red. Is the agreement between calculation and experiment good or poor? Explain.

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The Influence of Oxidation State on the Electronegativity of Tin

Introduction

The nature of the bonds between tin and its substituents is a function of both the oxidation state of the tin and the electronegativity of the second moiety. In general, the effective electronegativity of any atom increases with increasing oxidation state. Covalent character is a feature of bonds between systems with both reasonably high and similar electronegativities. In the tetravalent oxidation state tin is expected to form more covalent compounds with electronegative substituents such as carbon or chlorine. Thus, Sn(IV) has an extensive organometallic chemistry, involving covalent bonds to carbon-containing ligands.

Tin also has a stable divalent state which is much less electronegative. Bonding in Sn(II) compounds is therefore more ionic, and the compounds resemble those of divalent mercury. The trivalent oxidation state of tin, however, is not observed and attempts to prepare it usually result in a **disproportionation** reaction affording di- and tetravalent tin species. This type of reaction occurs in many other systems when the electronic configuration is particularly unstable. Specific examples include Tl(II), Au(II), Nb(II), etc. Disproportionation is essentially a mutual oxidation-reduction of the same element.

The reaction examined in this experiment is the oxidation of tin metal with benzyl chloride in which the attempt to produce Sn(III) results in a covalent Sn(IV) compound and an ionic Sn(II) species.

Instructional goals:

Properties of the following elements are highlighted: Sn, O, Cl

(1) Basic synthetic techniques; reflux, recrystallization in air.

(2) Synthesis of an organometallic compound by direct addition of an alkyl halide to the element.

(3) IR spectra by nujol mull.

(4) ^{1}H and ^{119}Sn NMR spectroscopy; use of heteronuclear NMR for an element with a minor isotope which is NMR active.

(5) Experience with mass spectrometry; use of isotope effects in the interpretation of the spectra of organometallic compounds.

Pre-lab exercise

1. Write a balanced chemical equation for the reaction performed in the first part of this experiment.
2. Write a balanced chemical equation for the reaction performed in the second part of this experiment.

3. What is the structure of $(PhCH_2)_3SnCl$? Create a HyperChem model of the structure. Optimize it in MM+ to get a good approximation of the true geometry. Improve your model by re-optimizing it using the PM3 semi-emprical method.
4. What range of frequencies should you record in the IR analysis of the product?
5. Map out the timing of your afternoon's work. Use free gaps of time to do other operations. Be realistic in time allotted for each operation!

SAFETY NOTES

1. Benzyl chloride is toxic and a possible carcinogen. Avoid breathing the fumes and wear disposable gloves when handling. Dispense it in the hood.
2. Tin metal and tin oxide have very low toxicity. All powdered metals are fire hazards.
3. Organotin compounds are highly toxic.
4. Glacial acetic acid is poisonous, corrosive, and a severe eye and skin irritant. It should always be dispensed and used in the hood with the sash down.
5. Ethyl acetate is very flammable. It is moderately toxic by inhalation. Use in the hood.

Procedure

Preparation of $(PhCH_2)_3SnCl$

Place 75 mL of water in a 250 mL, 2-neck RB flask equipped with a water-cooled condenser, heating mantle and a magnetic stir bar. The condenser should be attached to the central opening in the reflux position (vertical). While stirring vigorously, add 10 g of tin powder through the side arm of the flask. Bring the water to a boil and add 9.0 mL of benzyl chloride (density = 1.10 g/cm^3) via a disposable pipette, over a period of 2 minutes.

> *Benzyl chloride is toxic and a possible carcinogen. Avoid breathing fumes and wear disposable polyethylene gloves when handling! Dispense it in the fume hood.*

The mixture is kept at the boiling point with vigorous stirring for 1.5 hours after which point it is cooled to room temperature and the product collected and dried on a Büchner funnel (keep filter paper for later rinsing). **Save both the filtrate and the precipitate**. The cooling process may be shortened by using a water or ice/water bath.

> *NOTE: While refluxing you can complete other experiments, run spectra, etc. If for some reason you have to stop without filtering, break up the clumps as much as possible before storing.*

Transfer the precipitate along with the stir-bar into a 250 mL Erlenmeyer flask and remove the residue from the filter paper with 3 portions of 5 – 10 mL of HOT ethyl acetate. Allow the filtrate to drain into the same flask as the product. Heat the mixture until all of the large clumps are dissolved and then filter off the remaining grey precipitate. Evaporate the filtrate to dryness, stirring occasionally, using an air sweep. **Save a sample of this crude product for determination of its melting point.**

The crude product is then recrystallized from 30 mL of hot glacial acetic acid (**do this in the fume hood**). If the product does not completely dissolve using 30 mL add additional amounts in 5 mL portions. After recrystallization collect the crystals on a Büchner funnel, and wash them with 25 mL of **COLD** glacial acetic acid. Dry them with the air sweep. Weigh the purified product.

Isolation of Sn(II) from the reaction mixture

While in the fume hood, treat the filtrate from the initial reaction with 12 mL of conc. ammonia and heat the mixture to 70 °C. The white precipitate of $Sn(OH)_2$ is a positive test for tin(II). Collect, dry and weigh the solid.

Characterization

1. Obtain the m.p. of both the crude and recrystallized $(PhCH_2)_3SnCl$.
2. Record the ^{1}H, ^{13}C, and ^{119}Sn NMR spectra of $(PhCH_2)_3SnCl$.
3. Record the IR spectrum of $(PhCH_2)_3SnCl$ as a nujol mull. **NOTE**: If using KBr plates (as opposed to ATR IR) be exceedingly careful as they are very expensive and fragile – much more so than the NaCl plates. Wash them with CH_2Cl_2 (not acetone), and return them to the desiccator immediately after use.
4. Interpret the mass spectrum of $(PhCH_2)_3SnCl$.

Report

Hand in your two products as well as all the original spectra. Include a partial analysis of the vibrational spectrum, emphasizing the metal-halogen bands. Provide a full interpretation of the NMR spectra, including chemical shifts, coupling constants and intensities of all observed signals. Consult reference 4, p. 198 for background information on NMR. Assign the peaks in the mass spectrum using the "fragment" ion approach.

At the end of your report, address the following additional questions:

1. Why was the solid extracted with ethyl acetate instead of acetic acid?
2. From its solubility properties, does tribenzyltin chloride seem to be ionic or covalent? Explain.

3. Give a rationalization for the stability of Sn(II) and Sn(IV) versus Sn(III).
4. Despite the implications of this experiment, several exotic organometallic compounds of Sn(II) have recently been prepared and structurally characterized. What are some of these compounds, and how do they fit in to the general scheme of tin compounds put forward in the introduction?
5. The direct reaction of Sn with R–Cl is of crucial importance to key industries involving the Group 14 elements. What are some of these industries, and why is the direct reaction so important to them?
6. What effect do the differing isotopes of the atoms in your compound have on the mass spectrum? Account for the appearance of all peaks containing isotopes of significant (>5%) natural abundance.

Molecular Modeling

1. Use your PM3 optimized model of $(PhCH_2)_3SnCl$ from the Pre-lab exercise. Report the bond angles and distances for the atoms directly attached to Sn.
2. Organotin hydrides are important reagents in organic chemistry. Construct a model of $(PhCH_2)_3SnH$ and optimize it using MM+ and PM3. (*Hint: you can use the model of the chloride by removing the chlorine atom and using Model Build to Add Hydrogens. DO NOT Model Build or you lose all the optimization you have already performed!*)
3. Calculate Molecular Vibrations. This will take some time! Thereafter calculate the Vibrational Spectrum. Where do you expect the Sn–H stretching vibration to occur in the spectrum? Locate a normal mode of vibration that seems to be dominated by tin-hydrogen stretching. Record the number of this normal mode and its calculated energy at the PM3 level.
4. Would you expect that the Sn–H band would be easy to detect in the IR spectrum based on your calculations? Why or why not?

References

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Grignard Synthesis of Tetramethyldiphosphinedisulfide

Introduction

A major feature of the chemistry of the second and subsequent row elements is their ability to exist in high formal oxidation states, *e.g.* phosphorus(V) in PF_5 and sulfur(VI) in SF_6. Considerable interest has been shown over the years in the electronic reasons for the stability of these compounds, their stereochemical characteristics and their use as synthetic intermediates.

In the present experiment you will prepare and use methyl magnesium bromide (a Grignard reagent), a synthetic intermediate of fundamental importance to inorganic and organic chemists alike. The reagent will be generated by reacting magnesium with methyl bromide; subsequent treatment with thiophosphoryl chloride, $SPCl_3$, affords tetramethyldiphosphine disulfide $[Me_2PS]_2$. This procedure illustrates the use of main group organometallic compounds (in this case a Grignard reagent) in inorganic synthesis. This particular reaction is somewhat anomalous in that the expected product, $SPMe_3$, is not formed.

This anomaly is fortuitous; the isolated product is an extremely useful intermediate in its own right. In particular, it provides a useful route to high-coordinate phosphorus(V) compounds, *e.g.* Me_2PCl_3, by direct oxidation with chlorine

$$Me_2PS–SPMe_2 + 5\ Cl_2 \rightarrow 2\ Me_2PCl_3 + 2\ SCl_2$$

Instructional goals:

Properties of the following elements are highlighted: P, S

(1) Preparation and use of a Grignard reagent and understanding of the organometallic chemistry of magnesium.

(2) Preparation of a catenated phosphorus compound.

(3) Understanding and applications of ^{1}H and ^{31}P NMR spectroscopy.

(4) Awareness of 2nd order effects in NMR spectroscopy.

(5) Experience in the interpretation of high-resolution mass spectra for the characterization of inorganic compounds.

Pre-lab exercise

1. Provide balanced chemical equations for the preparation of the Grignard reagent and for the subsequent synthesis of $[Me_2PS]_2$.
2. What is the structure of $[Me_2PS]_2$? Build a molecular model in HyperChem for this molecule. How many conformers should you reasonably consider? Using the MM+ method, try to find the lowest energy conformation after geometry optimization.
3. How many signals do you expect in the ^{31}P NMR spectrum? Should the spectrum be acquired with or without broadband ^{1}H decoupling?

4. Map out the timing of your afternoon's work. Use free gaps of time to do other operations. Be realistic in time allotted for each operation!

SAFETY NOTES

1. Methyl bromide (bromomethane) is a highly toxic gas. It must only be used in a closed system and the whole apparatus must be kept in a fume hood.
2. Thiophosphoryl chloride is a moderately toxic liquid. It reacts vigorously with Grignard reagents.
3. Glacial acetic acid is poisonous, corrosive and a severe eye and skin irritant. It should always be dispensed and used in the hood with the sash down.
4. The solvents ethanol, and especially diethyl ether, are highly flammable liquids.

Procedure

Preparation of the methyl Grignard reagent

NOTE: This reaction must be performed in a fume hood and while preparing the Grignard reagent, due to the violent reaction that may occur, place a curved blast shield around the reaction vessel. Prior to doing the experiment, all glassware must be dried and 3 blocks of dry ice prepared.

Dry magnesium turnings (2.5 g) are added to a clean, dry 500-mL three-neck RB flask, equipped with a mechanical paddle stirrer (Figure III-1). To this flask, 250 mL of anhydrous diethyl ether and a crystal or two of iodine are added. The flask is then equipped with the large dry ice condenser to which the nitrogen line is attached. Attach a gas inlet to the right side-arm through which the MeBr will be added.

With nitrogen gas bubbling vigorously through the upper line, begin adding chunks of crushed dry ice to the condenser. When the cold finger is almost full, slowly add acetone (from a wash bottle) to the finger. After the initial effervescence the dry ice/acetone slurry will settle down into the finger. Further additions of small quantities of dry ice may be required to maintain the slurry throughout the reaction. You are now ready to commence preparation of the Grignard reagent, MeMgBr.

Slow down the flow of nitrogen to a steady rate of 2 bubbles per second. Fully open the main valve on the MeBr cylinder and open the regulator valve ½ turn for approximately 30 s to allow the gas to pass slowly into the reaction flask. You will notice the methyl bromide begin to condense on the cold finger and run back into the ether. After closing the valve, wait for 2-3 min for the reaction to start. The reaction between MeBr and Mg has a finite induction period, but once it commences it is quite exothermic, and may cause the ether to boil.

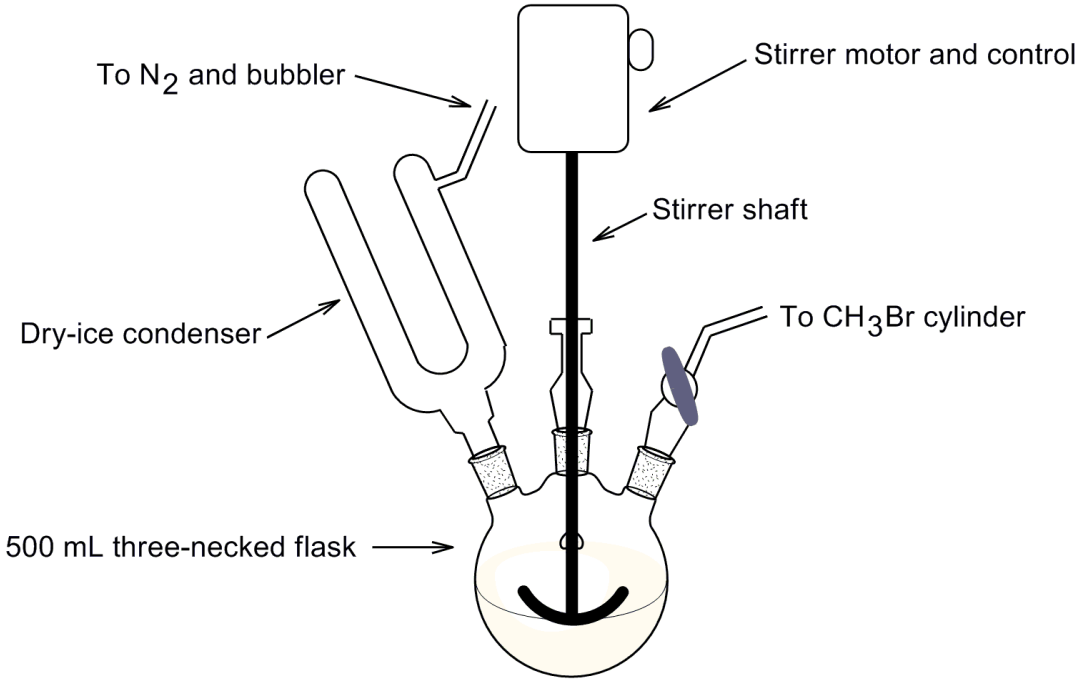

Figure III-1 Aparatus for preparation of Grignard reagent

The reaction between the MeBr and Mg is very vigorous. For this reason the cylinder must not initially be left open for longer than 30 s. If it is left open longer than 30 s, the build up of MeBr may cause the reaction to start violently enough to explode the reaction vessel and the attached apparatus. Hence the blast shield.

After the initial reaction subsides, reopen the cylinder for an additional 15 s. Repeat this process until all magnesium turnings have been dissolved. When this occurs, remove the gas inlet (make sure the cylinder valve is closed completely) and replace it with a glass stopper. Remove the dry-ice condenser and **immediately** replace it with the water condenser. (See Figure III-2.) Transfer the nitrogen line to the top of this condenser to maintain an inert atmosphere within the reaction flask. Leave the reaction mixture to stir at room temperature for 15 min; this will allow any excess methyl bromide to evaporate.

Preparation of $[Me_2PS]_2$

Measure out 3.0 mL (5.0 g) of thiophosphoryl chloride, $SPCl_3$, in a graduated cylinder and add this and 50 mL of anhydrous ether to an addition funnel. Attach the addition funnel to the stoppered side-arm of the reaction flask. Slowly add the $SPCl_3$/ether solution **while stirring vigorously**.

The first few drops will cause a very violent reaction. Therefore it is advisable to add this solution a few drops at a time while allowing the reaction to subside between additions. After approximately 1 mL has been added the rate can be gradually increased.

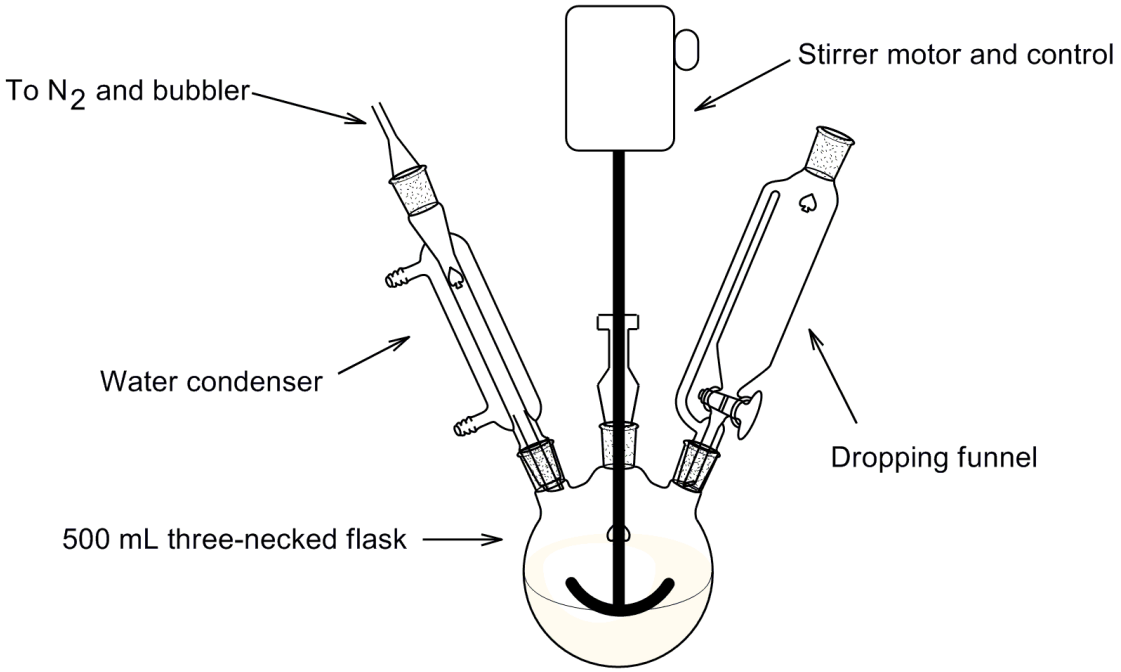

Figure III-2 Aparatus configured for second stage of reaction

This reaction is extremely exothermic and produces a heavy white porridge-like precipitate. (If a crust begins to form or the slurry becomes too thick to stir, stop the addition, remove the addition funnel and manually turn the mixture over with a spatula). When the addition is complete the mixture is quenched by the slow addition of 50 mL of 10% H_2SO_4.

The reaction is now essentially complete. Halt the nitrogen supply is halted and remove the addition funnel (and **clean it**). Pour the contents of the reaction flask into a 1-L beaker which is ¼ filled with crushed ice. Filter the resulting slurry through a Büchner funnel and wash the solid with 250 mL of water. Recrystallize the crude product by dissolving it in 150 mL of boiling ethanol in a 250 mL beaker and allow the solution to cool to room temperature. Collect the white crystalline needles of $[Me_2PS]_2$ by filtration and dry them in air.

Characterization

1. Weigh your product and determine the yield. Obtain its melting point and compare with literature values.
2. Record the ^{1}H, ^{13}C, and ^{31}P NMR NMR spectra (in $CDCl_3$).
3. Interpret the mass spectrum. Include a calculation of the exact mass of the main peak of the parent ion.

4. Measure the IR spectrum of the product.
5. Recorded a Raman spectrum of your product.

Report

Hand in your product as well as all original spectra. Provide a full interpretation of the NMR spectra, including chemical shifts, coupling constants, and relative intensities of all observed signals. Consult reference 4, p.198 for background information on NMR spectroscopy. Explain the phenomenon of "second-order effects in NMR spectroscopy", with specific reference to the ^{1}H NMR spectrum of $[Me_2PS]_2$. Assign as many peaks as possible in the mass spectrum.

At the end of your report, address the following additional questions:

1. Draw the structure of $[Me_2PS]_2$ and explain how this structure was determined (what other possibilities are there?). Explain what product might be formed if it were oxidized using a deficit of chlorine (*i.e.*, less than the 5 moles required by the equation on p. 5-1).
2. Me_2PCl_3 forms conducting solutions in acetonitrile (it is a 1:1 electrolyte). By contrast, Me_2PF_3 forms non-conducting solutions in acetonitrile. Interpret these observations in terms of the structural differences between the two compounds.
3. Explain how high-resolution mass spectroscopy can be used to identify a compound almost uniquely. Many journals now accept a correct high-resolution spectrum as proof for the existence of a new compound, *provided* the researchers can provide independent evidence of compound purity. What is the danger in using only the mass spectrum to substantiate the existence of a new compound?

Molecular Modeling

1. Use your electronic models as created for the Pre-lab exercise. Perform a careful comparative calculation of the three possible rotamers (*cis*, *trans* and staggered). Optimize each using the PM3 semi-empirical method. (*Hint: activate Start Log under the File menu to record the energies in a text file*.)
2. Make a table of the energies of the three conformers, using kJ/mol. Record all the bond distances and bond angles other than those involving the hydrogen atoms. Put these into your table as well.
3. Can you rationalize why the molecule adopts the more stable conformer?

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A Stable Inorganic Radical: 4-phenyl-1,2,3,5-dithiadiazolyl and Its Dimer

Introduction

Stable radicals are common in inorganic chemistry; nitric oxide, NO, and nitrogen dioxide, NO_2, are good examples. Fremy's salt, $K_2ON(SO_3)_2$, and organic nitroxides, ONR_2, are perhaps less well-known, but find important uses in the spectroscopic study of reactions involving radical intermediates. In the gas phase, and in solution, most of these radicals R• exist in equilibrium with a dimer, R–R. The characteristic conversion of brown NO_2 gas into a colourless liquid (N_2O_4) represents a classical example of such a process. Likewise, sodium dithionite, $Na_2S_2O_4$, really consists of a weakly associated pair of SO_2^- radical anions ($K_{diss}(S_2O_4)^{2-} = 10^{-9}$ M in H_2O), and as such, represents a useful and widely used reducing agent (1).

$$S_2O_4^{2-} \equiv 2\,SO_2^- \rightarrow 2\,SO_2 + 2\,e^- \quad (1)$$

Related to the dithionite anion are a series of cyclic p-radicals built from catenated –S=N– units; the two isomeric modifications (**1** and **2**) of the dithiadiazolyl are representative of this type of system.

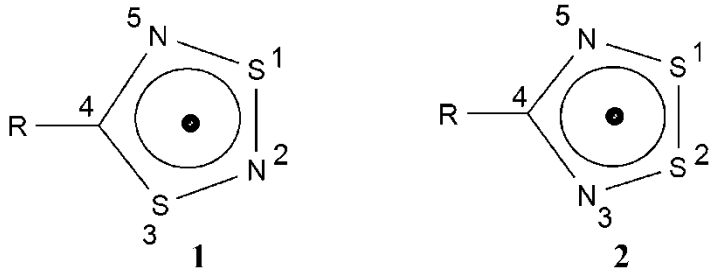

Figure III-3 1,3,2,5- and 1,2,3,5-dithiadiazolyl radicals

In the present experiment you will prepare the radical 4-phenyl-1,2,3,5-dithiadiazolyl by reduction of the corresponding dithiadiazolium cation, which can itself be prepared (as its chloride salt) by the reaction of *per*silylatedbenzamidine, $PhC(NSiMe_3)N(SiMe_3)_2$ with sulfur dichloride.

The reduction can be effected by a metal, such as zinc, or more conveniently, by the addition of triphenylstibine, Ph_3Sb (which is itself oxidized to Ph_3SbCl_2). The radical can be isolated as its dimer, a dark purple crystalline solid, and characterized by Electron Spin Resonance (ESR) spectroscopy, which provides information about the unpaired spin-density distribution.

Instructional goals:

Properties of the following elements are highlighted: S, N & Sb.

(1) The synthesis of moisture- and oxygen-sensitive materials under inert gas, using dry solvents.

(2) Understanding of stable free radicals, and the use of ESR spectroscopy to study free radicals.

(3) Provide an example of the application of ultraviolet photo-electron spectroscopy in inorganic chemistry.

(4) Familiarity with the use of molecular orbital theory in the interpretation of experimental data.

(5) Demonstrate the power of high-resolution mass spectrometry in chemical analysis.

Pre-lab exercise

1. What is the structure of $PhCN_2S_2^+ Cl^-$ and the dimer of $PhCN_2S_2^{\bullet}$?
2. Construct molecular models using HyperChem of the $PhCN_2S_2$ molecule. Be sure to make both the phenyl ring and the CN_2S_2 rings aromatic! Minimize it in MM+ and AM1 (for the latter calculation, be sure to set the charge and spin multiplicity correctly.) Now build a model of the dimer and minimize it using MM+. What is wrong with this model?
3. Provide balanced chemical equations for the synthesis of $PhCN_2S_2^+ Cl^-$ and $(PhCN_2S_2)_2$.
4. Describe in what way $PhCN_2S_2^+ Cl^-$ and $(PhCN_2S_2)_2$ are air-sensitive. What precautions are employed in their preparation to overcome these problems?
5. Map out the timing of your afternoon's work. Use free gaps of time to do other operations. Be realistic in time allotted for each operation!

SAFETY NOTES

1. *Per*silylatedbenzamidine can hydrolze to benzonitrile, which is moderately toxic and has an almond-like odour.
2. Sulfur dichloride is a poison by inhalation and ingestion. It decomposes on contact with water to form HCl and various sulfur acids. Handle only in the hood, and segregate wastes into the specially marked containers.
3. Triphenylantimony is toxic by ingestion, and should not be handled with bare hands.
4. Acetonitrile is a moderately toxic and highly flammable liquid. Use with care.

Procedure

Make sure that the glassware needed for this experiment is placed in an oven at 150 °C for at least 1 hour prior to starting the experiment. Do this before the lab period starts!

Preparation of $PhCN_2S_2^+ Cl^-$

Clamp a previously dried 250 mL side-arm flask, equipped with a water condenser, in the fume-hood and attach the side arm to the nitrogen bubbler. Add a small stir bar, 75 mL of **dry** acetonitrile (stored over molecular sieves) and 4.00 g of N,N,N'-*tris*trimethylsilylbenzamidine. Stopper the flask and use a heating mantle to warm the mixture to 50 °C (use a Variac setting of approximately 40%).

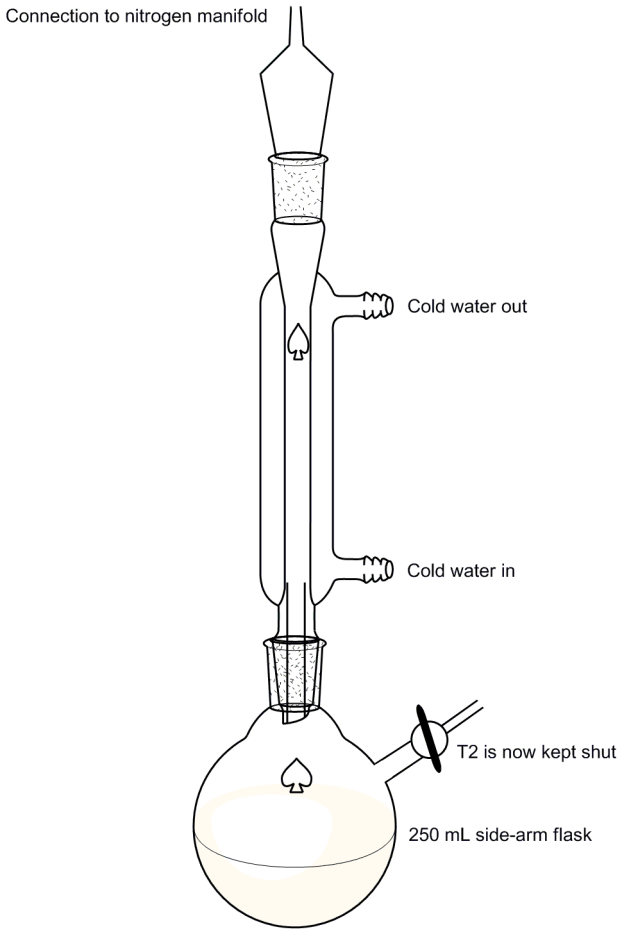

Figure III-4 Set-up for heating to reflux

Carefully open the bottle of sulfur dichloride (**STENCH**) and use a Pasteur pipette to inject ~3 mL of SCl_2 directly into the flask. A vigorous reaction ensues, producing a fluffy orange precipitate. Increase the Variac setting and heat the reaction mixture to a boil for about 30 minutes. Remove the heating mantle and allow the flask to cool, slowly forming orange crystals.

The orange crystalline product is moisture sensitive (especially when still wet with solvent). It is isolated by filtration with a "filter stick". (See figure III-5.) Replace the stopper of the 250 mL flask with one end of the filter stick, to the other end attach a 100 mL side-arm flask (Figure III-

5). Secure all the joints with clamps and, **with the assistance of your instructor**, slowly invert the apparatus so that the product flask is tipped down onto the glass frit. Apply a gentle vacuum at tap T1 to the lower flask using the double manifold vacuum line at the side of the lab. This will draw the solution through the upper flask and leave the precipitate on the sintered glass frit in the filter stick. When the filtration is complete remove the lower filled flask from the filter stick and replace it with the provided stopper.

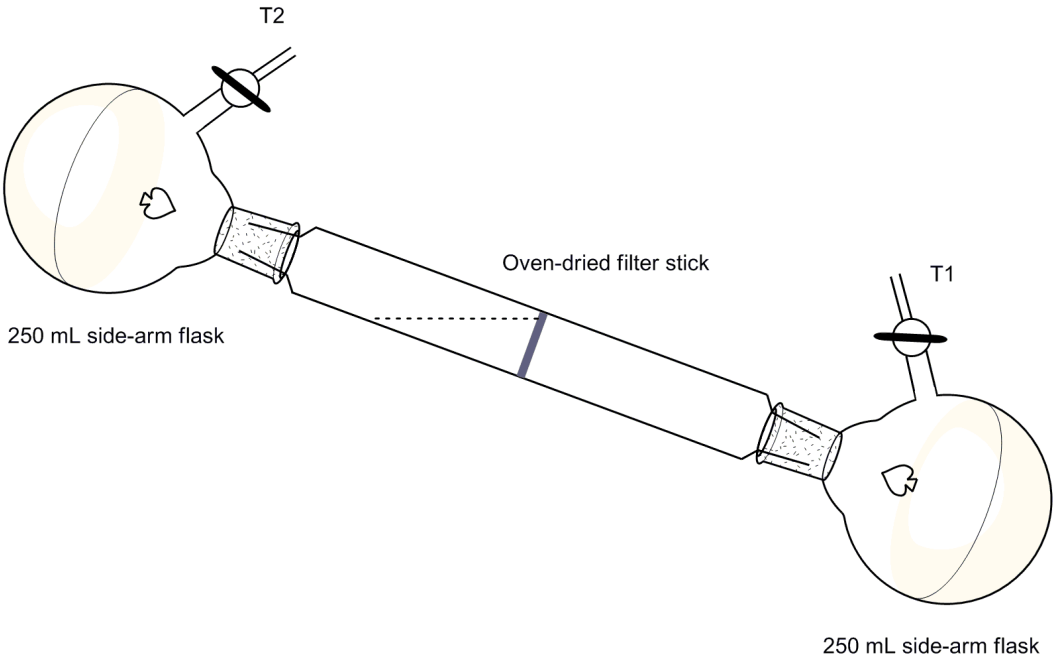

Figure III-5 Set-up for heating to reflux

Re-apply the vacuum via tap T2 and thoroughly dry the solid (about 10 min). Dispose of the (malodorous) sulfur waste in the designated waste bottle. When the solid is dry release the vacuum and **quickly** transfer the solid to a pre-weighed stoppered vial. Re-weigh the vial and record the yield of your product.

Characterization

1. Measure the m.p. of your product. Use a regular m.p. capillary tube. Dip the open end in silicone grease to provide a temporary seal against atmospheric moisture.
2. Record the IR spectrum.

Preparation of $[PhCN_2S_2]_2$

Add 10 mL of dry, oxygen-free, acetonitrile to a 200 mL side-arm flask. Attach the side-arm to a nitrogen bubbler in the fume hood. After flushing for about 5 min add 0.25 g of $PhCN_2S_2^+Cl^-$, followed immediately by 0.50 g of triphenylantimony while stirring with a small stir bar. The solution will darken and a fine black precipitate will be produced. Filter the mixture through a clean, dry filter stick, as described above. Dry the product under vacuum, and when dry fill the apparatus with N_2. Weigh the product and store it in a nitrogen flushed vial. *Consult your instructor regarding the purity of this sample. Further purification may be achieved by vacuum sublimation.*

Characterization

1. Measure the m.p. of your product, as described above.
2. Record the IR spectrum or the dimer. Be sure to print out the region of interest to the same scale as for the halide above. This will make visual comparison of the spectra much easier.
3. Interpret the ESR spectrum of the free radical dithiadiazolium in CH_2Cl_2 solution at room temperature which is included in this lab manual.
4. Interpret the mass spectrum. In each case, the source of the radical is solid dimer. The weak dimer bonds are broken in solution or in the gas phase. Include a calculation of what the exact mass of the parent ion main peak *should* be!

Report

Hand in your products as well as all original spectra, and record the yield of each compound prepared. Comment on the differences between the IR spectra of the cation and the neutral dimer. Do not attempt a complete analysis of the spectrum, but explain why this is omitted.

Provide an analysis of the ESR spectrum of the radical, *i.e.*, determine the nitrogen hyperfine coupling constants a_N and the g-value of the radical (you are given the *location* of the centre of the spectrum in Gauss units).

Interpret the mass spectrum of $PhCN_2S_2$ from the data provided. Clearly explain how this data provides strong corroboration for the proposed molecular formula. What aspect of the compound does the mass spectrum **not** show, and why is chemical analysis of new compounds still a required exercise?

Molecular Modeling

A knowledge of the electronic structure (orbitals and energies) of $PhCN_2S_2$ is required to answer the additional questions. Therefore be sure to do this section first. In order to avoid unnecessary

computational difficulties, in this and subsequent exercises we will use the model of $PhCN_2S_2^+$ that you optimized for the pre-lab exercises without further re-optimization. Be sure to follow the instructions carefully. Note that we use the AM1 semi-empirical method. PM3 is poorly parameterized for sulfur and nitrogen, and gives unreliable results.

1. Take the model of $PhCN_2S_2^+$ and perform a geometry optimization to ensure this is correctly modeled. Be sure to set the charge to +1 and the multiplicity to 1. Sketch the shape of the HOMO and the LUMO. Into which orbital does the extra electron in $PhCN_2S_2$ go?
2. Now change the charge to 0 and the multiplicity to 1. Perform a Single Point calculation, and look at the orbitals. Is there a well-defined SOMO? Sketch its shape. Which orbital in $PhCN_2S_2^+$ does it resemble?
3. Now create a realistic dimer of the radical $PhCN_2S_2$. You must do this manually, since neither the model builder nor the computational methods will provide accurate structures of the dimer. Proceed as follows. Under File, Merge onto your existing model of $PhCN_2S_2^+$ the same model. Save As a new file (*e.g.* "dimer"). Now you must place the two rings directly above and below each other. This is done by changing Select to Molecules, highlighting one of the molecules, and rotating/translating with the right mouse button depressed. You need to have the two rings co-planar and directly above each other. The two rings are slightly tilted apart, with the sulfur atoms closest and the Ph rings furthest apart. The separation at S is ~3.1 Å. Once you have a realistic model, be sure to save it.
4. Perform a Single Point AM1 calculation on the dimer (charge = 0, multiplicity = 1). Plot the orbitals and identify the HOMO. If this orbital does not extend between the rings, go into Plot Options on the Orbitals window, and *decrease* the orbital contour value slightly. Do not overdo this or the orbital will expand to cover the whole molecule. Now do the same for the LUMO of the dimer.
5. Sketch a simple energy level diagram, including orbital energies from HyperChem, for bringing together two dithiadiazole radicals to form a dimer. Your diagram should have two monomer SOMO's interacting to form a dimer HOMO and a dimer LUMO. Indicate the energies of the interaction and the paired and unpaired electrons in the usual manner.

At the end of your report, address the following additional questions:

1. Is your ESR spectrum consistent with your knowledge of the electronic structure of the radical, *i.e.* how many lines would you expect to see, and why? Use the MO plot of the SOMO from your molecular modeling exercise to answer this question.
2. The dimerization of $PhCN_2S_2$ is weak and reversible. In solution it appears to be largely in the monomer form. The low sublimation temperature is also in agreement with breaking apart of the dimer in the vapour phase. On the other hand, the dark colour of the solid is due to the dimer. Discuss.

3. The UV-PES spectrum of the radical is presented in ref. 5. Explain the method of UV-PES spectroscopy, and interpret the spectrum in light of the filled energy levels calculated for $PhCN_2S_2$.

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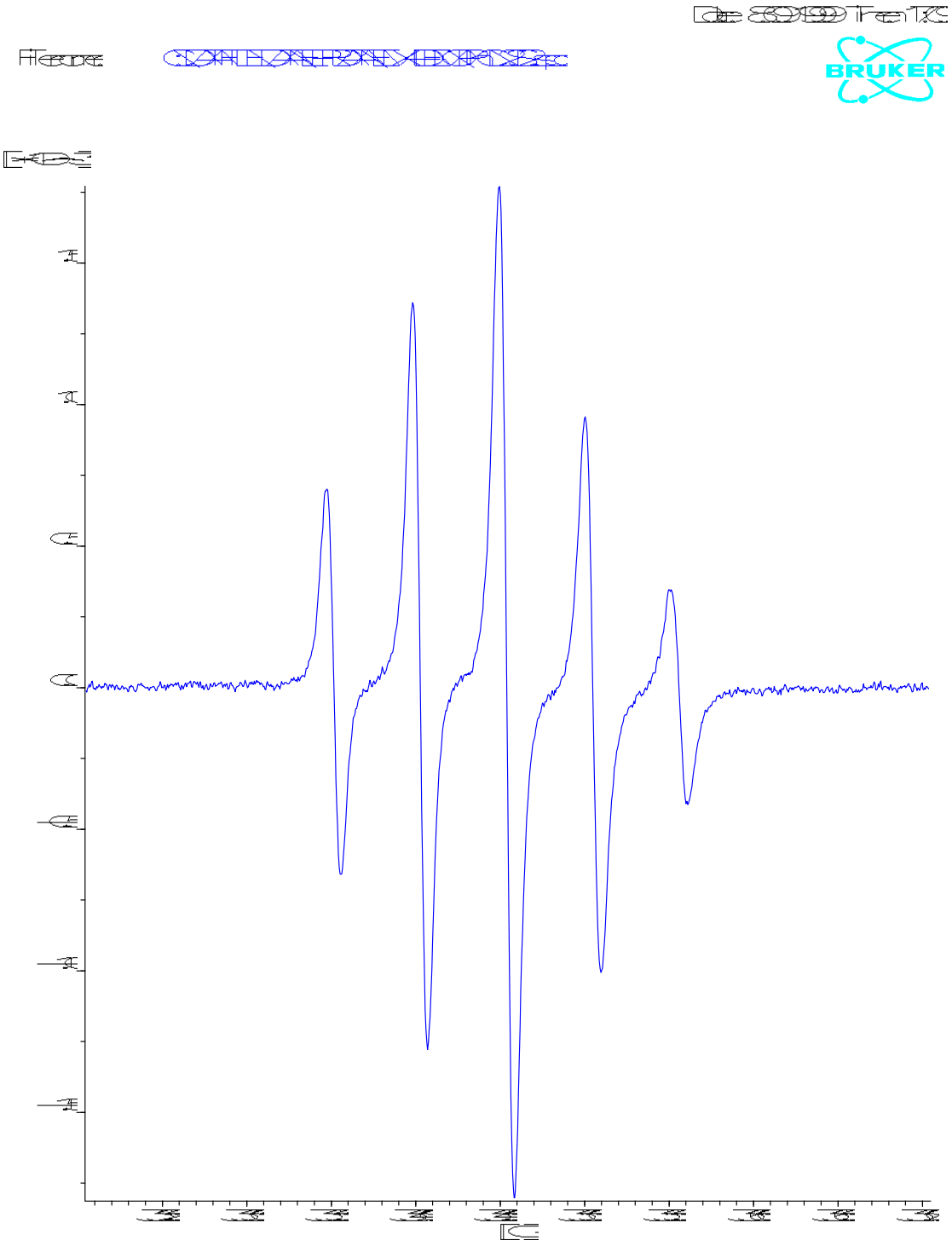
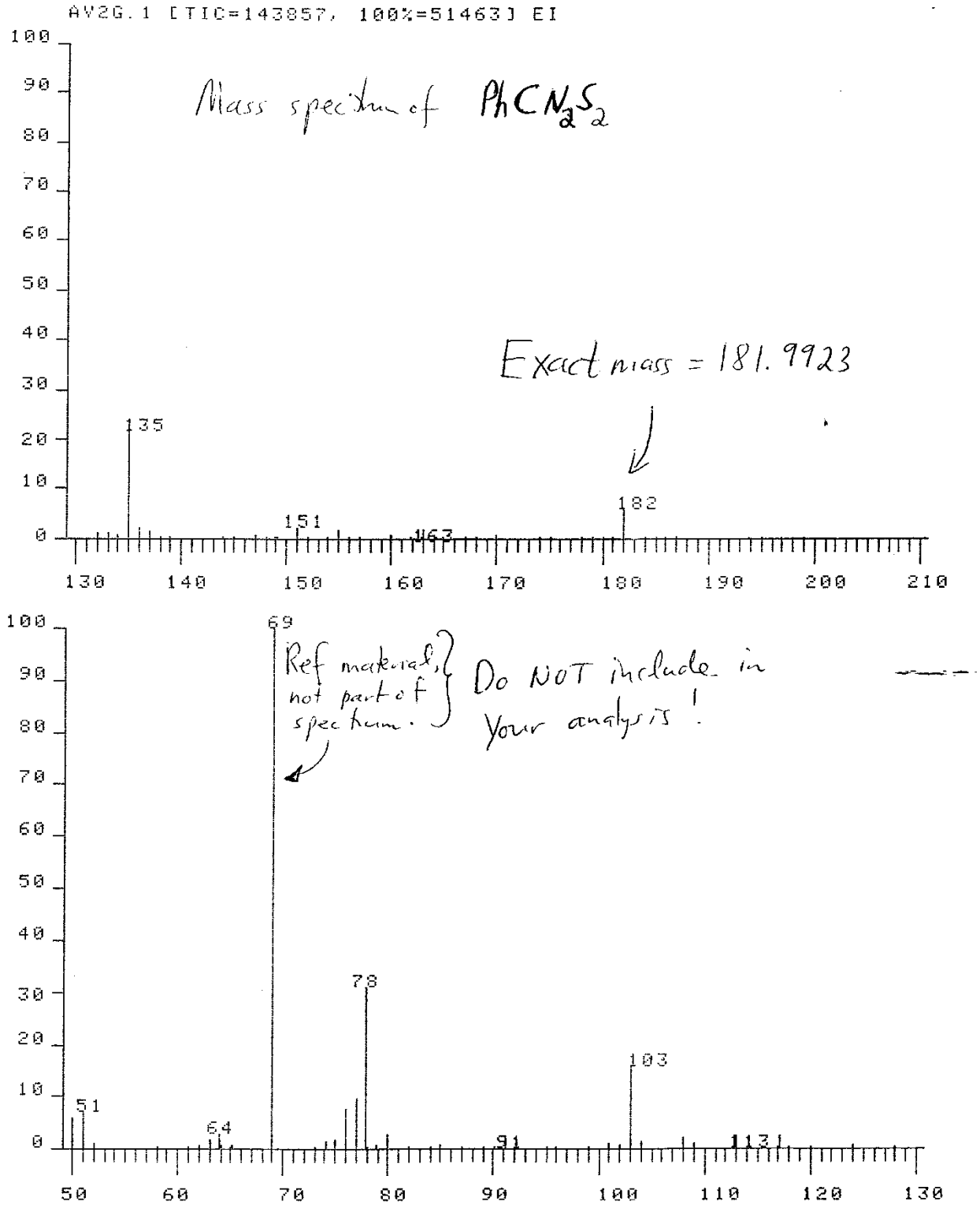


EPR spectrum of $PhCN_2S_2$ recorded in CH_2Cl_2 solution


AV2G.1 [TIC=143857, 100%=51463] EI
Mass spectrum of PhCN2S2
Exact mass = 181.9923
135
151
163
182
69
Ref material, not part of spectrum.
Do NOT include in your analysis!
51
64
78
91
103
113

Synthesis of Dinitrogen and Allotropes of Phosphorus

Introduction

Nitrogen

The elemental form of nitrogen is relatively inert. Thus, N_2 is commonly used as an inert atmosphere gas. There are limitations to this; for example, nitrogen reacts with lithium to form a coating of Li_3N on the exposed surface of the metal. In addition, some transition metal complexes react with gaseous N_2 at ambient pressure and temperature to form extremely stable speices. It is for this reason that under stringent conditions, argon is preferred over nitrogen as an inert gas. Liquefied nitrogen (b.p. –196 °C) is also an extremely useful coolant, in part because it evaporates to harmless nitrogen gas (except for the danger of asphyxiation in enclosed spaces.)

A nitrogen molecule is diatomic, N_2. It can be represented by the Lewis structure :N≡N: which implies a nitrogen-nitrogen triple bond. A great deal of energy is needed to break these bonds, and they must be broken before nitrogen atoms can react with atoms of other elements. This is one of the reasons why nitrogen molecules are so inactive. Conversely, the large bond energy of N_2 is one of the thermodynamic driving forces behind the explosive nature of many nitrogen compounds. When N_2 is formed during a chemical reaction there is concomitant release of a large quantity of heat and gas.

Nitrogen constitutes approximately 80% of the atmosphere. This high proportion of nitrogen might lead us to think of it as a plentiful element, but such is not the case. Indeed, nitrogen is a relatively scarce element, only about one-third as abundant as carbon. Then how can we explain the high proportion of nitrogen found in air? This is due to its chemical inactivity. In nature it forms relatively few compounds. Practically the only simple nitrogen compound in nature is Chile saltpeter ($NaNO_3$). Of course one cannot overlook that considerable quantities of nitrogen are involved in living systems and their remains (*e.g.* mineral oil.)

The inactivity of nitrogen has posed a crucial challenge for chemists. Since all plant and animal life depend on nitrogen-based compounds, nitrogen must therefore combine with other elements. Plant and animal cells consist of proteins which are highly complex compounds of carbon, hydrogen, oxygen and nitrogen (~17% nitrogen). A growing plant takes nitrogen from the minerals in the soil to make these proteins. The soil, which is steadily depleted of its nitrogen minerals, must be replenished, otherwise plants would starve, as would the animals which depend on plants.

The challenge to the chemist was therefore to learn how to make suitable nitrogen compounds which could serve as plant food. The way the chemist has met this challenge is one of the major scientific achievements of the last century.

Dinitrogen is needed to make various nitrogen compounds on an industrial scale, and for this purpose it is obtained by the fractional distillation of liquid air. Nitrogen is more volatile than oxygen (the boiling points are –196 °C for nitrogen and –183 °C for oxygen) and therefore, evaporates in the first fraction.

In the laboratory, an easier way to prepare nitrogen from air is simply to remove the more active oxygen by making it combine with another substance. For example, if air is passed over hot copper, the oxygen combines with it to form copper(II) oxide. If all the oxygen is used up, the residual gas is about 99% nitrogen; it contains small proportions of the inactive gases carbon

dioxide and argon, and water vapour. Alternatively, pure nitrogen (or chemical nitrogen) can be prepared by the decomposition of ammonium nitrite (NH_4NO_2). This compound readily decomposes at a low temperature to give nitrogen as the only gaseous product. This is an example of a comproportionation reaction.

Nitric acid

Nitric acid is one of the most important acids in the chemical industry; it is used in the manufacture of fertilizers, drugs, dyes, and plastics. In industry, it is made by the catalytic oxidation of ammonia, the so-called Ostwald process, described by the following 3 equations. The Ostwald process is a cycle, in which the NO produced in step 3 is automatically sent back into the catalytic converter used in step 2.

$$4\,NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O$$
$$2\,NO + O_2 \rightarrow 2\,NO_2$$
$$3\,NO_2 + H_2O \rightarrow 2\,HNO_3 + NO$$

Pure nitric acid is a colourless liquid that boils at 86 °C. It decomposes in sunlight, or when heated, forming nitrogen dioxide (NO_2) which turns the solution brown. Water is usually added to retard this decomposition and, as a result, ordinary concentrated nitric acid contains about 68% acid and has a concentration of approximately 15M.

Nitric acid is a strong acid and can be thought of as completely ionized in dilute solution. Thus, reactions with metallic hydroxides, carbonates, or oxides are the same as those of dilute hydrochloric acid or dilute sulfuric acid. For example:

$$Na^+ + OH^- + H^+ + NO_3^- \rightarrow Na^+ + NO_3^- + H_2O$$

With metals, however, nitric acid does not yield hydrogen as is the case with the other acids. This is because both the hydrogen and nitrate ions (NO_3^-) are powerful oxidizers. We would expect the nitrate ion to be an oxidizer because nitrogen is in its highest oxidation state of +5. That is why free hydrogen is not usually a product when dilute nitric acid reacts with a metal. Indeed, the products of such a reaction depend upon the concentration of hydrogen and nitrate ions, the temperature of the reaction, and the activity of the reducing agent. In short, these reactions can be highly complicated, particularly with active metals.

Since dilute hydrochloric and sulfuric acids owe their oxidizing power solely to hydrogen ions, they will only react with metals above hydrogen in the emf series. But this is not the case with dilute nitric acid, which will react with all metals above hydrogen and most of the metals below hydrogen. Let us consider the reactions of nitric acid with copper.

$$Cu + 4\,HNO_3 \rightarrow Cu(NO_3)_2 + 2\,H_2O + 2\,NO_2$$

If dilute nitric acid is used, a colourless gas, nitric oxide (NO), is formed rather than the dark brown nitrogen dioxide.

$$3\,Cu + 8\,HNO_3 \rightarrow 3\,Cu(NO_3)_2 + 4\,H_2O + 2\,NO$$

To summarize: when concentrated nitric acid is the oxidizer, nitrogen dioxide is a product; when dilute nitric acid is the oxidizer, nitric oxide is a product. Notice also that in the more dilute acid, the nitrogen is reduced to a lower oxidation state! This complex behaviour can be summarized using the Latimer diagrams found in Ref.1, appendix 4.

Nitrates, the salts of nitric acid

An unusual but characteristic feature of nitrates is that their salts are all soluble in water. It is well to bear this in mind if a solution of a metallic ion is needed. Nitrates, like nitric acid, decompose when heated. Nitrates of the heavy metals decompose in an analogous manner to nitric acid; instead of O_2, they yield the metallic oxide:

$$2\ Pb(NO_3)_2 \rightarrow 2\ PbO + 4\ NO_2 + O_2$$

Nitrates of the alkali metals, however, are more strongly bound in their crystal lattices and, in consequence, are more difficult to decompose. When heated, they lose only oxygen to form the corresponding nitrite. For example:

$$2\ NaNO_3 \rightarrow 2\ NaNO_2 + O_2$$

It should be mentioned that ammonium nitrate is exceptional in the way it decomposes.

$$NH_4NO_3 \rightarrow N_2O + 2\ H_2O$$

This is because the ammonium ion is itself capable of being oxidized, and takes part in the decomposition to yield nitrous oxide, N_2O. This gas is used as an anaesthetic, and is sometimes referred to as laughing gas.

Phosphorus

Phosphorus is much more abundant than nitrogen. It occurs mainly as phosphate rock which contains a high percentage of calcium phosphate $Ca_3(PO_4)_2$. Phosphorus, like sulfur, occurs in allotropic forms, the two common ones being white (or yellow) phosphorus and red phosphorus.

White phosphorus is a soft, wax-like solid, exceedingly poisonous and very reactive chemically. It ignites spontaneously in air. White phosphorus is soluble in carbon disulfide but insoluble in water, and so it can be stored under water. Red phosphorus, however, does not oxidize rapidly at room temperature, although it burns very readily if it is sufficiently heated. Red phosphorus is much less poisonous than yellow phosphorus, and it is insoluble in carbon disulfide. These marked differences in properties suggest a difference in molecular structure.

The molecular weight of phosphorus, as determined experimentally from its vapour density, is 124. Therefore, phosphorus vapour consists of P_4 molecules. These molecules have an unusual tetrahedral shape, in which the four atoms are located at the corners of a regular tetrahedron. (Figure III-6) In contrast to nitrogen which forms N_2 in the gas phase with a triple bond, phosphorus forms P_4 which has four strained single bonds. (At least this is true below 800 °C; above this temperature the vapour consists of P_2 molecules.) This is consistent with the known weaker double bond versus

single bond strength on going down the periodic table. Indeed, compounds possessing stable P=P bonds were unknown until 1981.

Phosphorus vapour condenses to a liquid at 280 °C and then to a solid at 44 °C. The attractive forces between the molecules are van der Waals forces. If the solid or liquid is heated, the P_4 molecules separate and the vapour is formed. From this we conclude that the covalent bonds which bind atoms into molecules are generally stronger than the van der Waals forces which bind molecules into a liquid or solid.

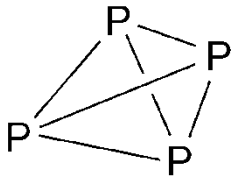


Figure III-6 The structure of white phosphorus

Red phosphorus is amorphous rather than crystalline. It is therefore much harder to obtain the detailed structure of this solid, since crystallographic methods cannot be used. The structure of red phosphorus is thought to be chains of ring-opened P_4 cages, as shown in Figure III-7. It is prepared from white phosphorus by heating in the absence of oxygen at atmospheric pressure. This thermal activation allows the ring-opening polymerization reaction to occur. If red phosphorus is heated to a sufficiently high temperature, the bonds between the atoms are broken and, on cooling, P_4 molecules are formed which condense to the liquid and solid forms of white phosphorus.

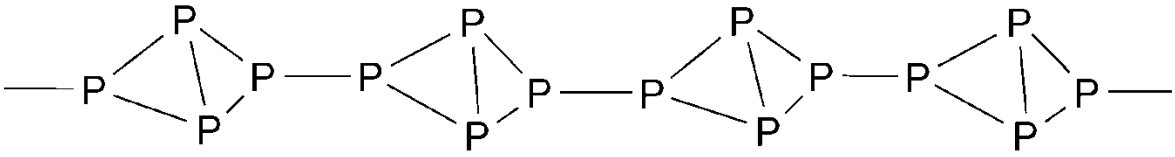


Figure III-7 Chain structure of amorphous red phosphorus

Instructional goals:

Properties of the following elements are highlighted: N & P.

(1) The synthesis of N_2.

(2) Provide an example of the oxidizing ability of nitric acid.

(3) Understanding different allotropes and reactivity of group 15 elements.

Pre-lab exercise

1. Construct a molecular orbital diagram for N_2.
2. Explain the differences between the properties of covalent and ionic compounds.
3. What are the major safety concerns associated with this lab? How will you address them?
4. Can different allotropes of an element give rise to different reactivity? Give an example.
5. Map out the timing of your afternoon's work. Use free gaps of time to do other operations. Be realistic in time allotted for each operation!

SAFETY NOTES

1. White phosphorus is spontaneously flammable in air. It also causes severe skin burns. Follow the guidelines in the procedure closely.
2. Nitric acid is extremely corrosive and can burn both the skin and respiratory tract. Use with care and only in a fume hood.
3. Nitric acid reacts violently with many organic compounds. Never dispose of nitric acid in the organic waste.
4. CS_2 is an extremely toxic and flammable solvent, and must be used with extreme caution. Avoid any contact with a flame or spark source.

Procedure

The preparation and properties of pure nitrogen

Assemble the apparatus illustrated in Figure III-8 in the fume hood, and clamp it securely. The generator is a clean, dry, 15 cm Pyrex test tube.

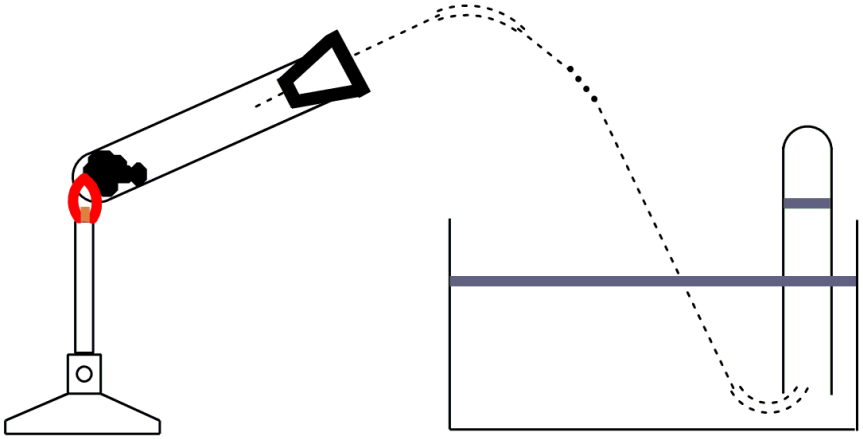


Figure III-8 Apparatus for the preparation of nitrogen gas

Place approximately 2 g of each NH_4Cl and $NaNO_2$ in the generator test tube, and add about 7 mL of water. Prepare to collect two large test tubes of gas by displacement of water. Warm the mixture slightly to start the reaction, then withdraw the flame. Since the reaction is exothermic, be prepared to loosen the clamp and immerse the generator in water to cool it. Permit the first gas generated (which will be mixed with air from the generator) to escape, then collect two test tubes of nitrogen.

In the fume hood:

(a) Observe the usual physical properties of the gas, such as colour, odour, solubility in water.
(b) Test the ability of the nitrogen to support combustion by inserting a deflagrating spoon containing burning sulfur (0.1 g S) into one of the tubes.
(c) Into the other tube, insert a deflagrating spoon with burning red phosphorus (0.03 g P).

Nitric acid as an oxidizing agent

(a) In a fume hood, put approximately 30 cm of iron wire and approximately 0.3 g of copper turnings into separate test tubes. Add 5 mL of 3 M HNO_3 to each test tube. Warm the test tubes to start the reaction and set aside for later use.

Place a few drops of 0.1 M $FeCl_3$ solution on a spotting plate, and add 15 M NH_4OH until a precipitate of $Fe(OH)_3$ forms. Note the form and colour of the $Fe(OH)_3$. Then do the same for a 0.1 M ferrous ammonium sulfate solution, which precipitates $Fe(OH)_2$.

After several minutes of reaction of the dilute HNO_3 with the iron and copper, observe the colour of the gas evolved. Take a few mL of the solution formed from the iron, add several volumes of water and then NH_4OH. Compare the precipitate with the one obtained with Fe^{2+} and Fe^{3+} and NH_4OH.

From the colour of the solution formed when HNO_3 acted on copper, and from the comparison of the precipitates, what were the products in each case?

(b) To 5 mL of 3 M HNO_3, add 3 cm strips of magnesium ribbon until the reaction is fairly slow. Remove the excess ribbon and transfer the solution to a 50 mL beaker and test for the presence of NH_4^+ ion. Add 2 mL of 1 M NaOH (or enough to produce slight cloudiness) to the solution. Attach a piece of moist red litmus paper to the underside of a watchglass, and place it on top of the beaker. Gently heat the solution on a hot plate (do not boil) and observe the litmus paper. [$NH_4^+ + OH^- \Leftrightarrow NH_3(g) + H_2O$]

(c) Add 2-3 mL of concentrated HNO_3 to 0.5 g of flowers of sulfur in a pyrex test tube and gently boil the mixture until the solution becomes clear. If necessary, remove the ball of free sulfur. Test it for the SO_4^{2-} ion. Add 2 mL of 0.3 M $BaCl_2$ to the solution. Centrifuge and discard the supernatant. Test the solubility of the precipitate in 6 M HCl. [$BaSO_4$ is insoluble in water and in acid; $BaSO_3$ is insoluble in water and soluble in 6 M HCl].

Decomposition of nitrates

(a) Have a wood splint available prior to starting this reaction. In a small Pyrex test tube melt 2 g of KNO_3. Heat the molten salt vigorously for approximately two minutes at the highest temperature possible with the Bunsen burner. During the decomposition, test the evolved gas by thrusting a glowing splint into the test tube (nearly to the surface of the liquid, but do not drop the splint into the molten salt). After the decomposition has continued for at least 2 min, allow the residue to solidify completely, then cool it in the air for about one minute. Add 1 – 2 mL of 3 M H_2SO_4 to the solid. Write equations for the decomposition and the reaction of the residue with H_2SO_4.

(b) Put 2 g of lead nitrate crystals into a Pyrex test tube and heat, holding the test tube directly in the flame. As soon as the decomposition products can be identified, discontinue the heating. The light yellow residue is PbO.

Allotropic forms of phosphorus

(a) From the side shelf obtain about 0.25 g of red phosphorus. While in the fume hood examine its physical structure. Heat approximately 0.05 g in an evaporating dish. Test the solubility of 0.05 g in 2 – 3 mL of CS_2.

(b) Obtain a piece of Pyrex tubing about 20 cm long. Heat the centre of the tube in the O_2 torch flame. When the glass has softened, draw out the tube to a capillary approximately 2 mm in diameter and seal off the constricted portion. In one of the tubes place a small amount of red phosphorus – no more than 20 mg. (See Figure III-9.) Heat the tube evenly until all of the red phosphorus has sublimed to white phosphorus on the cooler part of the tube.

Figure III-9 Apparatus for the preparation of white phosphorus

While the tube is cooling, observe the physical characteristics of the white phosphorus. When the tube has thoroughly cooled, add about 2 mL of CS_2, cork the tube and shake it until the phosphorus has dissolved. Pour the solution onto a piece of filter paper and lay it upon the counter in the fume hood to dry. Isolate it from all flammable materials and observe it carefully. (**Warning:** Do not spill the solution on the hands as white phosphorus causes severe burns. When disposing of the solution, pour it directly into the sink and NOT into the waste jars.)

Report

In this and all descriptive chemistry labs, you must record detailed observations in your lab notebook. Include this information in your report. Explain fully all reactions and write balanced chemical equations for each.

At the end of your report, address the following additional questions:

1. For each reaction consider the question, "Has an acid-base reaction occurred?" Is there a possibility of an oxidation/reduction reaction?
2. Can the observed changes be interpreted in terms of HSAB theory?
3. Can LeChatelier's principle explain the course of the reaction?
4. Is the material formed in each reaction ionic or molecular? Explain fully.

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Reactivity of Dioxygen and Allotropes of Sulfur

Introduction

Oxygen

Oxygen is one of the most abundant elements on earth. Large amounts of it are found in the molten mantle, the crust that forms the great land masses, the water of the oceans that cover most of the earth's surface, and in the gaseous atmosphere that surrounds the earth. Elemental oxygen can exist in two allotropic forms: diatomic molecules (O_2) and triatomic molecules (ozone, O_3). Allotropy is a characteristic property of all elements of this group. Only in the atmosphere is oxygen found in the elemental forms, primarily as the dioxygen molecule, O_2. O_3 is, however, an important component of the stratosphere, in which it exists in equilibrium with O_2. The O_2/O_3 cycle acts as a filter for long-wavelength ultra-violet solar radiation, a process which is commonly referred to simply as "the ozone layer."

Dioxygen reacts so avidly with both metals and nonmetals that the presence of a large amount of free O_2 in the atmosphere raises the question: where did all of that O_2 come from? Studies over the past 200 years have provided the general outline of the answer, but some important details are still being actively investigated. Most of the dioxygen on earth has been produced by plants, from the smallest algae to the majestic redwoods. Plants use water, carbon dioxide (CO_2) and sunlight to form carbohydrates and oxygen in a complex process called photosynthesis. Animals reverse this process. They react carbohydrates with oxygen inside their cells in a process called respiration, forming CO_2 and water. Thus, plants and animals exist together in a grand symbiotic cycle, each supplying the others' needs. The energy involved in this biological cycle is about 30 times the amount of energy expended each year by all of mankind's machines.

Oxygen may be prepared in the laboratory by a number of methods, most of which involve the decomposition of oxides. Mercuric oxide, HgO, is of historical significance, being used by Priestly in the discovery of oxygen in 1774 (by decomposing HgO with focussed sunlight.) In Experiment 7, you prepared O_2 by the decomposition of a nitrate:

$$2\ NaNO_3 \rightarrow 2\ NaNO_2 + O_2$$

A similar effect can be achieved by the thermal decomposition of potassium permanganate:

$$2\ KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$

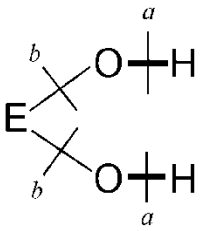
To observe and understand some of the chemistry of oxygen we will react O_2 with a variety of elements. The oxides formed will be dissolved in water and the solutions tested to see if they are acidic or basic.

Acids and bases from oxides

If EO stands for any element combined with oxygen, the oxide may react with water to form the molecule $E(OH)_2$

$$EO + H_2O \rightarrow E(OH)_2$$

(The number of OH groups will vary with different elements.) If the molecule $E(OH)_2$ is soluble in water, it will usually further react with water to form either hydronium ions, H_3O^+, or hydroxide ions, OH^-, depending on whether the O–H or the E–O bond breaks. (Figure III-10.)



Bond cleavage at point *a* yields an acid.

Bond cleavage at point *b* yields a base.

Figure III-10 Effect of bond cleavage on element-hydroxides

If a proton is given up (or donated) to a water molecule (corresponding to cleavage at point a), we can write the reaction as:

$$E(OH)_2 + H_2O \rightarrow H_3O^+ + E(O)OH^-$$

and by further dissociation:

$$E(O)OH^- + H_2O \rightarrow H_3O^+ + EO_2^{2-}$$

Thus, because it is a proton donor, the molecule formed from the oxide is an acid. On the other hand, suppose that the E–O bond breaks at point b. The $E(OH)_2$ molecule then dissociates in solution to give hydroxide ion, OH^-:

$$E(OH)_2 \rightarrow E(OH)^+ + OH^-$$
$$E(OH)^+ \rightarrow E^{2+} + OH^-$$

Because it produces the proton acceptor OH^-, the compound is called a base. If the oxide of an element forms an acid in water, it is termed an acidic oxide or acid anhydride. If the oxide in water forms a base, we speak of a basic oxide or base anhydride. To determine the formula of the anhydride of an oxy acid or base, simply subtract sufficient water to eliminate all hydrogen atoms. For example:

$$2\ NaOH_{(s)} - H_2O = Na_2O_{(s)}$$
$$Mg(OH)_{2(s)} - H_2O = MgO_{(s)}$$
$$2\ B(OH)_{3(s)} - 3\ H_2O = B_2O_{3(s)}$$

The tendency of $E(OH)_2$ to be either an acid or a base in water is controlled largely by the relative strengths of the interactions of water molecules with either H^+ and $E(O)OH^-$ or OH^- and $E(OH)^+$ and the nature of the element E. The variation in the nature of E is reflected by its position in the periodic table.

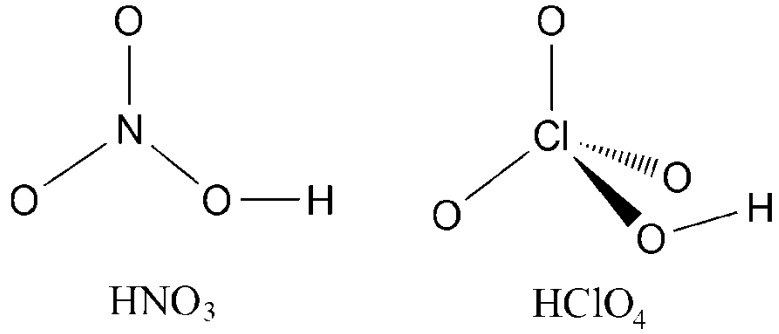
When the acidic oxide N_2O_5 is added to water, we might expect the following reaction to occur:

$$N_2O_5 \quad + \quad 5\,H_2O \quad \rightarrow \quad 2\,N(OH)_5$$

Instead, the partially hydrated oxo acid $N(OH)O_2$ is formed, which you may recognize as nitric acid when written with the more familiar formula HNO_3. Although acidic oxides seldom form fully hydrated oxo acids, it is still easy to determine the formula of the anhydride by subtracting water so as to leave no hydrogen atoms. For example, the formula of the anhydride of perchloric acid is obtained by subtracting one mole of water from two moles of perchloric acid.

$$2\,HClO_4 \; - \; H_2O \quad = \quad Cl_2O_7$$

Do not let the conventional way of writing the formulas for nitric acid and perchloric acid as HNO_3 and $HClO_4$, respectively, mislead you into thinking that the hydrogen atoms in the acids are directly bonded to the nitrogen or chlorine atoms. The structural formula for nitric acid might more accurately be written as $HONO_2$, and that for perchloric acid as $HOClO_3$. (See Figure III-11.)



HNO_3 $HClO_4$

Figure III-11 Structure of nitric and perchloric acids

Sulfur

Sulfur can behave chemically in two ways. First a sulfur atom can acquire two electrons to complete its octet, thereby forming the stable sulfide ion, S^{2-}, with the [Ar] electron configuration. It can also have positive oxidation states, particularly in the presence of powerful oxidizers such as fluorine and oxygen. Thus, as we already know, sulfur readily burns in air to form sulfur dioxide, a pungent gas. If sulfur reacts with metals (or hydrogen), it is the more electronegative partner in the resulting bonds, and its oxidation number is –2. On the other hand, if sulfur reacts with oxygen or fluorine, its oxidation number can be +1, +2, +3, +4, +5 or +6. Of these, the most common is +4, as in SO_2 and SF_4. In the presence of a suitable catalyst, sulfur dioxide will also combine with oxygen to form sulfur trioxide, SO_3; and SF_4 can be reacted with

excess fluorine to make SF_6. Interestingly, SF_6 is a very stable gas, and is used as an insulator in high-voltage electrical equipment, whereas SF_4 is a highly reactive compound. This is another example where a compound derives its stability from kinetic rather than from thermodynamic factors. SF_6 is unreactive because the crowded sulfur atom is kept away from nucleophiles by the six tightly-held fluorine atoms.

Both sulfur and oxygen atoms have 6 electrons in their outermost energy levels. It would, therefore, be reasonable to expect that sulfur, like oxygen, would form diatomic molecules, S_2. Actually, sulfur forms diatomic molecules only at high temperatures. At ordinary temperatures it forms a ring of 8 sulfur atoms bound together by covalent bonds (Figure III-12). The origin of this difference lies in the relative strengths of the single (*e.g.* O–O vs S–S) and double bonds (O=O vs S=S). Only for the elements of the second period of the periodic table is the bond energy of a double bond greater than the sum of two single bonds.

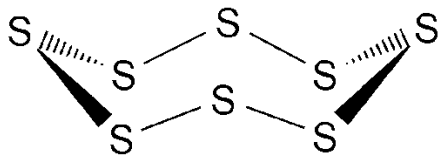


Figure III-12 The crown shape of the sulfur molecule, S_8

As one would expect, the van der Waal's forces are considerably greater in cyclic S_8 than in O_2. Sulfur molecules are nonpolar and will thus dissolve in nonpolar liquids such as carbon tetrachloride, carbon disulfide, and hexane, but not in water.

Sulfur has several allotropic forms, the most important of which are rhombic and monoclinic. Crystals of rhombic and monoclinic sulfur differ only in the internal arrangement of the crown-8 rings with respect to one another. The resulting crystals are observably different, belonging as they do to two different symmetry classes.

Rhombic sulfur consists of yellow octahedral crystals (see Figure III-13). It is stable at ordinary temperatures, and is therefore the more familiar allotrope. It melts at 114 °C, is insoluble in water and quite soluble in carbon disulfide. Sizable crystals of rhombic sulfur can be grown by slowly evaporating a carbon disulfide solution of sulfur.

Monoclinic sulfur consists of long needle-shaped crystals (see Figure III-13). These can be formed by melting rhombic sulfur and then allowing it to cool and crystallize. This is because monoclinic sulfur is stable at temperatures above 96 °C; it is unstable below this temperature and slowly reverts to the rhombic form. A more convenient way of preparing monoclinic sulfur is to let it crystallize from solution in hot toluene.

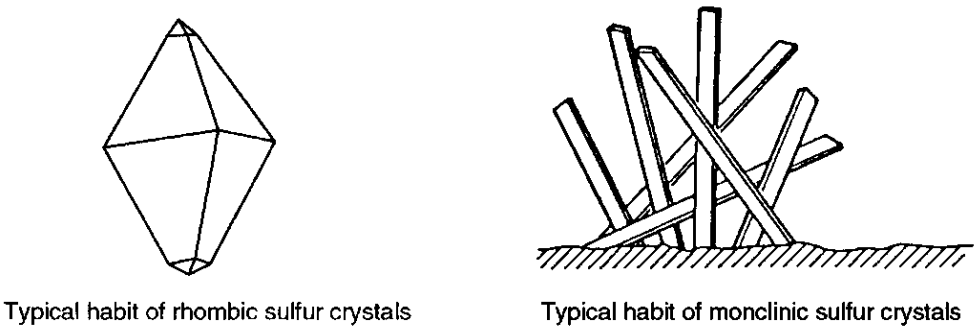


Figure III-13 Common appearance of the two main allotropes of sulfur

Near its melting point, sulfur is a mobile liquid, which is consistent with the interpretation that at this point it consists almost entirely of S_8 rings and that these rings interfere only slightly with each other's motion. However, as the temperature is raised, the kinetic energy of the molecules increases, causing bond-breaking and re-forming to occur. As such the rings become entangled and the viscosity of the liquid increases dramatically. As the temperature is raised still further, more extensive bond-breaking occurs and a variety of short-chain sulfur molecules are formed. This allows some of the entangled chains to free themselves, and, as a result, the viscosity decreases. Finally, if the hot liquid is suddenly chilled by cold water, the chains again become so entangled that the sulfur solidifies and becomes rubber-like in texture. On long standing, the entangled chains eventually revert to S_8 rings, and this so-called plastic sulfur reverts to the rhombic crystalline form.

By sharing its electrons with more electronegative elements, such as oxygen, sulfur attains positive oxidation states. There are numerous sulfur oxides, and myriad oxo acids and anions, involving several sulfur oxidation states, and –S–O–S– catenation. We will consider only the most common ones here. (Figure III-14.)

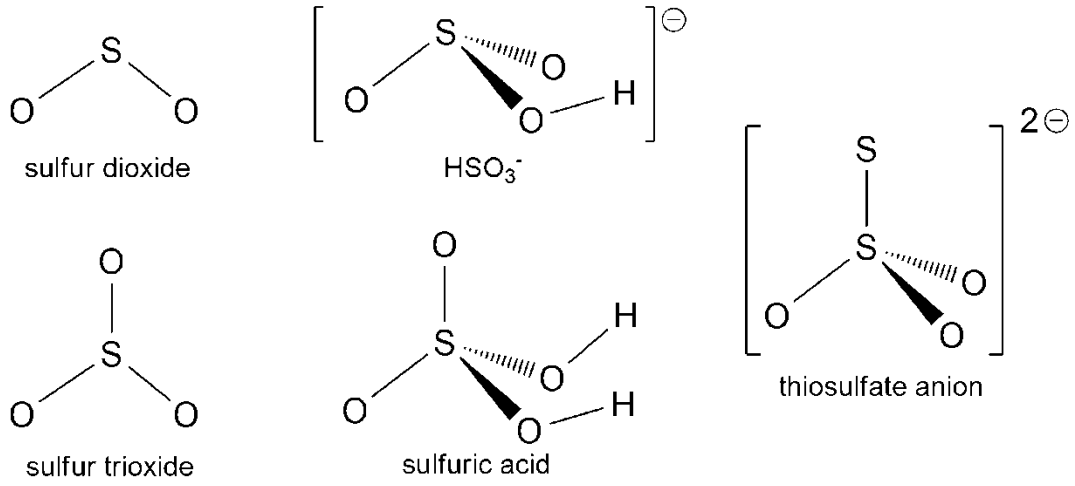


Figure III-14 Structures of common sulfur oxides and the related acids and anions

In sulfur dioxide, four of the sulfur electrons are involved in bonding with oxygen. SO_2 is the anhydride of sulfurous acid, H_2SO_3, which is a weak acid, and forms some $H^+ + HSO_3^-$. In

basic solutions the equilibria are shifted to the right, to form more bisulfite and sulfite ions and water.

$$SO_2 + 2\,H_2O \rightarrow H_3O^+ + HSO_3^-$$
$$HSO_3^- + OH^- \rightarrow SO_3^{2-} + H_2O$$

SO_2 can be detected by the formation of a bright yellow precipitate when the gas is bubbled through an aqueous solution of hydroquinone. The crystals are composed of a hydroquinone clathrate. This is a type of cage structure in which SO_2 molecules are trapped in the holes formed when hydroquinone forms a hydrogen-bonded network solid. The cage only forms when "guest" molecules of certain size are added to the hydroquinone solution.

In sulfur trioxide all six of the sulfur electrons are involved in bonding. Sulfur trioxide is the anhydride of sulfuric acid, H_2SO_4, one of the most important industrial inorganic chemicals. It is a strong acid whose aqueous solutions contain large concentrations of H^+ and HSO_4^- ions. In basic solutions the SO_4^{2-} ion is the predominant species.

$$SO_3 + 2\,H_2O \rightarrow H_3O^+ + HSO_4^-$$
$$HSO_4^- + 2\,H_2O \rightarrow H_3O^+ + SO_4^{2-}$$
$$HSO_4^- + OH^- \rightarrow SO_4^{2-} + H_2O$$

A third sulfur oxide is known principally as the oxo anion, which is the thiosulfate ion. Note that in the thiosulfate ion the sulfur atom that replaces the oxygen in the sulfate structure may be assigned a –2 oxidation number and that the central sulfur atoms has an oxidation number of +6, just as it has in sulfate. The +2 oxidation number assigned to sulfur in thiosulfate is obtained by finding the average of +6 and –2, *i.e.* (+6 – 2)/2 = +2.

H_2SO_4 and SO_4^{2-} are mild oxidizing agents, whereas H_2S, S^{2-}, H_2SO_3, SO_3^{2-} and $S_2O_3^{2-}$ are reducing agents. In addition, since S, $S_2O_3^{2-}$, SO_3^{2-}, and H_2SO_3 represent intermediate oxidation states, they can act as oxidizing agents with a strong reducing agent and as reducing agents with a strong oxidizing agent.

Instructional goals:

Properties of the following elements are highlighted: O & S.

(1) Understanding the properties and reactivity of O_2.

(2) Preparation and understanding of several different allotropes of sulfur.

(3) Understanding the relationship between acid and base anhydrides.

Pre-lab exercise

1. Construct a molecular orbital diagram for O_2.
2. Distinguish between three different allotropes of sulfur. How are their chemical structures similar? How are they different?
3. What are the major safety concerns associated with this lab? How will you address them?

4. The preparation of oxides as outlined below represent elements from groups 2, 14, 15, and 16, in the periodic table. To complete the series, consider an oxide or hydroxide from each of the other principal groups 1, 13, and 17.
5. Map out the timing of your afternoon's work. Use free gaps of time to do other operations. Be realistic in time allotted for each operation!

SAFETY NOTES

1. Sample odours of evolved gases by wafting the air above the mouth of the test tube towards your nostrils. NEVER inhale directly from the test tube into your nose or mouth! (See Figure III-15.)
2. Magnesium burns extremely bright, especially in high concentrations of oxygen. Do not look directly at the brilliant light as this can cause severe damage to the eyes.
3. Sulfuric acid is extremely corrosive and can burn both the skin and respiratory tract. Use with care and only in a fume hood.
4. Nitric acid is extremely corrosive and can burn both the skin and respiratory tract. Use with care and only in a fume hood.
5. Nitric acid reacts violently with many organic compounds. Never dispose of nitric acid in the organic waste.
6. CS_2 is an extremely toxic and flammable solvent, and must be used with extreme caution. Avoid any contact with a flame or spark source.

Procedure

The properties and reactions of pure oxygen

Since O_2 was prepared chemically in Experiment 7, we will save time in this laboratory by using oxygen from a compressed gas cylinder. Collect 6 bottles of oxygen gas from the O_2 tank by displacement of water from the inverted bottles in a trough. Your instructor will demonstrate. Note the physical state, color, odor, density (compared with air) and solubility in water of $O_{2(g)}$.

(a) Prepare oxides of the following elements by burning them in oxygen gas as described, keeping the bottles covered as much as possible. Number or label each bottle to avoid confusion. Immediately after each combustion, add 10 – 15 mL of water, replace the watch glass, shake the bottle to dissolve the oxide formed, and set it aside for later use.

(i) Magnesium

Ignite an 8 cm length of magnesium ribbon, holding it with the crucible tongs and at once thrust it into a bottle of oxygen.

(ii) Carbon

Ignite a small piece of charcoal, holding it with the tongs or in a clean deflagrating spoon, and thrust the glowing charcoal into a bottle of oxygen.

(iii) Phosphorus and (iv) Sulfur

For each of these, clean the deflagrating spoon, and burn out any combustible residue. Add no more than 0.01 g of sulfur, or 0.03 g of phosphorus (use red phosphorus). Heat these over the burner and if necessary ignite with the hot tip of a file. Then thrust them into separate bottles of oxygen. After each combustion dies down, reheat the deflagrating spoon to burn out all remaining phosphorus or sulfur.

(v) Iron

Ignite a small ball of steel wool (*ca.* 3 cm in size) using a Bunsen burner. Thrust the burning wool into a bottle of O_2. Remove the tongs when combustion dies down, removing any unburnt iron still held in them.

(b) Test each of the solutions formed with both red and blue litmus paper. If the solution does not give a positive test with either red or blue litmus paper, divide the solution in half and test one half with phenolphthalein indicator and the other half with bromcresol purple. Phenolphthalein is colorless in acid and pink in base; bromcresol purple is purple in base and yellow in acid.

Allotropic forms of sulfur

(a) In a fume hood, add 2 mL of CS_2 to a level spatula spoonful (or 1 g) of flowers of sulfur in a test tube. Shake for about 30 s and then filter the solution through a dry filter paper, catching the filtrate in a clean watch glass. Set the watch glass under the hood and allow the CS_2 to evaporate undisturbed. When all of the CS_2 has evaporated, examine the residue under low magnification of a microscope.

(b) Place about 1 gram of sulfur in a 25 × 150 mm test tube. Pour about 20 mL of toluene into the test tube and then heat it in an oil bath at 110 °C with frequent stirring until much sulfur has dissolved. (This takes about 5 minutes.) In the meantime, heat a watchglass over a water bath. When some sulfur has gone into solution let the precipitate settle and decant the clear liquid into the watchglass. Allow the toluene to evaporate in the fume hood and examine the crystals.

(c) Fill a 400 mL beaker about two-thirds with cold H_2O. Add about 10 g of flowers of sulfur to a 25 × 150 mm test tube and melt the sulfur slowly. Then heat it until it boils, noting the changes in color and viscosity. Heat the side of the test tube that will be the path of the sulfur as it is poured. Pour the boiling sulfur into the H_2O in the beaker. Discard the film on the surface of the H_2O and remove the sulfur from the bottom of the beaker.

Sulfur dioxide and sulfite ion: oxidation +4

(a) Place about 2 g of Na_2SO_3 in a large test tube. Add 6 M HCl dropwise until you can smell the odour of the gas (SO_2) given off. Now add about 15 mL of water and stir until all the solid dissolves.

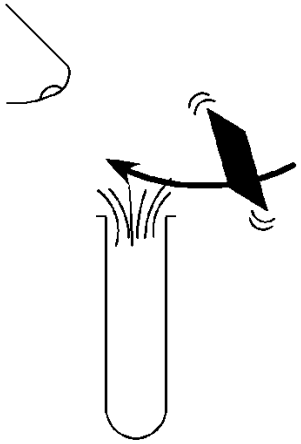


Figure III-15 Safe sampling of evolved gases by "wafting" toward the nose

(b) Divide the solution equally among three smaller test tubes. To one portion add a few milliliters of 0.1 M $BaCl_2$. What is the precipitate formed? Is it soluble in 6 M HCl (added a drop at a time)? (Ignore a slight turbidity, which is due to air oxidation of sulfite to sulfate.) Save this solution for later comparison. To another portion add 5 – 6 mL of saturated bromine water, drop by drop. How do you account for the decolorization that takes place? Now add a few milliliters of 0.1 M $BaCl_2$ to this test tube. What is the precipitate formed? Is it soluble in 6 M HCl? (When testing the solubility of the precipitates in acid, it is suggested that the sample be centrifuged, the supernatant discarded, and the remaining ppt be shaken with the acid.) Add a little of the third portion, a few drops at a time, to a test tube containing 5 mL of 3 M H_2SO_4 and some mossy zinc. Observe the odour of the gas, and note the precipitate formed.

Sulfuric acid, sulfates: oxidation state +6

(a) Is the dilution of concentrated H_2SO_4 exothermic or endothermic? To what do you attribute this result? Place a few drops of 18 M H_2SO_4 on a few crystals of sugar in a small evaporating dish. Heat if necessary. Repeat the test on a small piece of paper or wood (such as a match stick). How do you explain the results?

(b) Add 3 mL of 0.1 M Na_2SO_4 to 3 mL each of the following solutions in separate 10 cm test tubes (0.1 M $Ca(NO_3)_2$, 0.1 M $BaCl_2$, 0.1 M $Pb(NO_3)_2$. Test the solubility of any precipitates in dilute nitric acid by adding 1 mL of 6 M HNO_3 to each precipitate.

Report

In this and all descriptive chemistry labs, you must record detailed observations in your lab notebook. Include this information in your report. Explain fully all reactions and write balanced chemical equations for each.

At the end of your report, address the following additional questions:

1. Is there a relation between the acidity or basicity of the aqueous solution of these oxides and the position of the element in the periodic table?
2. Is there a difference in the vigor of reaction (rate, light and heat evolved, etc.) of the different elements with oxygen that can be related to the position of the element in the periodic table?
3. Is the material formed in each reaction ionic or molecular? Explain fully.

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Halide Ions as Ligands: Preparation and Characterization of Hexahalogenotellurates(IV)

Introduction

All the halide ions have the ability to function as ligands and they are by far the most common of all ligand types, forming perhalogeno complexes with all metal and many metalloid ions, *e.g.*, $FeCl_4^-$, $IrCl_6^-$, SiF_6^{2-}, as well as many mixed complexes in conjunction with other ligands, *e.g.*, $[Co(NH_3)_5Br]^{2+}$. In this course we are focusing on the main-group elements, and in this experiment we will prepare and study perhalogeno complexes of the metalloid tellurium. Tellurium is a member of Group-16 of the periodic table, so this experiment is a study of both Group-16 and Group-17 elements.

One of the important general questions that arises concerns the relative affinities of the halide ions for a given metal or metalloid. There is no simple answer to this question, however. For crystalline materials it is obvious that lattice energies play an important role. In considering the stability of the complex ions in solution, it is important to recognize that (a) the stability of a complex involves not only the absolute stability of the M–X bond, but also its stability relative to the that of ion-solvent bonds, and (b) in general an entire series of complexes will exist, M^{n+}*(aq)*, $MX^{(n-1)+}$*(aq)*, $MX_2^{(n-2)+}$*(aq)*, --- $MX_x^{(n-x)+}$*(aq)*, where x is the maximum coordination number of the metal ion. Of course, these two points are of importance in all types of complex ions in solution, but they have probably been best studied for halide complexes.

A survey of the available data on the stability of halide complexes shows that generally the stability decreases in the series F > Cl > Br > I, but with some metal ions the order is the opposite, namely F < Cl < Br < I. We may use the Hard and Soft Acids and Bases theory to rationalize such trends. The underlying theory behind the applicability of the HSAB rules include the charge-radius ratio, polarizability, and ability to use empty outer d orbitals for back-bonding. From the available results it appears that for complexes where the replacement stability order is Cl < Br < I, the actual order of M–X bond strength is Cl > Br > I. Thus, ionic size and polarizability appear to be the critical factors.

For hexahalogenotellurates(IV), the fluorides are by far the least stable and have not been isolated to this date. The stability of the remaining halogenates (Figure IV-1: Cl, **1**; Br, **2**; I, **3**) is found to be Cl > Br > I.

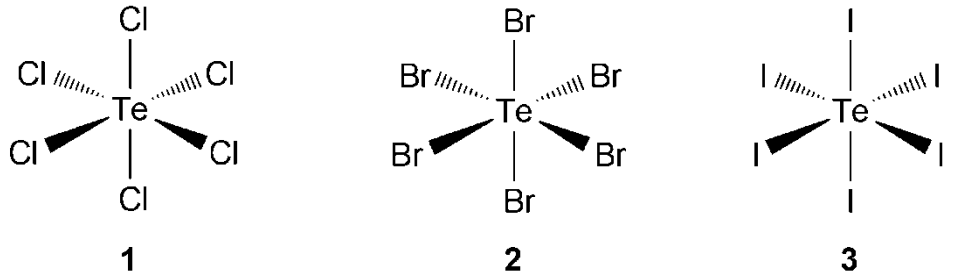

Figure IV-1 Hexahalogenotellurates

These six-coordinate anions are isoelectronic with IF_6^- and XeF_6. There has therefore been persistent interest in the physical structures of these compounds since they should possess a lone pair. This therefore poses a challenge to the VSEPR model of structure prediction. In fact, it has been speculated that the lone pair might be stereochemically inactive. Since our laboratory is not equipped to prepare the noble-gas fluorides, this experiment is also meant as a "model system" for this aspect of the chemistry of Xe.

Instructional goals:
Properties of the following elements are highlighted: Cl, Br, I, Te, {Xe}

(1) The preparation of salts of non-metal halogen complex ions.
(2) Experience in the use of vibrational spectroscopy for the study of high-symmetry complex ions.
(3) Experience in the use of electronic absorption spectroscopy for the study of the electronic structure of inorganic compounds.
(4) To gain an understanding of Mössbauer spectroscopy and its insights into chemical structure.
(5) To acquaint the student with the concept of "stereochemically inactive lone pairs", and the resulting controversies.

Pre-lab exercise

1. Write balanced equations for Part 1 and Part 2 of the preparation you are following (*i.e.* either A, B or C).
2. What is the structure of $[TeCl_6]^{2-}$ as predicted by the VSEPR model of chemical structures? Sketch the structure and assign the point group. Now prepare a model using HyperChem. For this function, draw Te with six Cl atoms attached. Then add a lone pair from the HC periodic table. Invoke model build. No further optimization is possible.
3. What is the actual structure of $[TeCl_6]^{2-}$ in its salts? Sketch this structure and assign its point group. To build this model, take the previous example and optimize it using the PM3 method. Be sure to set the charge correctly.
4. What range of IR frequencies do you need to record to get the data required for this experiment?

5. Map out the timing of your afternoon's work. Use free gaps of time to do other operations. Be realistic in time allotted for each operation!

SAFETY NOTES

1 Tellurium and tellurium compounds are toxic. They are converted in the body to dimethyl telluride which imparts a garlic-like odour to the breath and sweat. Heavy exposures may, in addition, result in headache, drowsiness or respiratory arrest.

2. Precautions: handle in a fume hood at all times – wear polyethylene disposable gloves – place ALL the solid wastes, including the gloves, in the special waste container!

3. Concentrated HCl, HBr, and HI are corrosive and release vapours of the acid. Handle only in the fume hood.

4. Aqueous wastes from this experiment go into their own separate waste container, and NOT down the drain!

Procedure 9A - Preparation of $K_2[TeCl_6]$ and $[NBu_4]_2[TeCl_6]$

Part 1 - Preparation of $K_2[TeCl_6]$

Tellurium(IV) oxide (2.0 g), TeO_2, is dissolved in a minimum quantity, up to 30 mL, of concentrated hydrochloric acid. A saturated solution of two molar equivalents of KCl in water is added with stirring. The solution is evaporated on a steam bath (**FUME HOOD!**) and stirred until the yellow crystals settle. The salt is recrystallized from 4 M HCl and is dried in a vacuum desiccator over solid NaOH.

Part 2 - Preparation of $[NBu_4]_2[TeCl_6]$

K_2TeCl_6 (1.0 g) is dissolved in 4 M HCl and two molar equivalents of tetra-n-butylammonium chloride in 1 M HCl is added. If the solution of NBu_4Cl is cloudy due to organic impurities, it must be filtered by gravity through a fine filter paper before it is added to the tellurate. The yellow precipitate, which is formed immediately, is filtered off on a Büchner funnel, washed twice with a small amount of 1 M HCl, and dried in a vacuum dessicator.

Procedure 9B - Preparation of $K_2[TeBr_6]$ and $[NBu_4]_2[TeBr_6]$

Part 1 - Preparation of $K_2[TeBr_6]$

Tellurium(IV) oxide (2.0 g), TeO_2 is dissolved in a minimum quantity, up to 30 mL, of concentrated hydrobromic acid. A saturated solution of two molar equivalents of KBr in water is added with stirring. The solution is evaporated on a steam bath (**FUME HOOD!**) and stirred

until the orange crystals settle. The salt is recrystallized from 4 M HBr and is dried in a vacuum desiccator over solid NaOH.

Part 2 - Preparation of $[NBu_4]_2[TeBr_6]$

K_2TeBr_6 (1.0 g) is dissolved in 4 M HBr and two molar equivalents of tetra-n-butylammonium bromide in 1 M HBr is added. If the solution of NBu_4Br is cloudy due to organic impurities, it must be filtered by gravity through a fine filter paper before it is added to the tellurate. The orange precipitate, which is formed immediately, is filtered off on a Büchner funnel, washed twice with a small amount of 1 M HBr, and dried in a vacuum dessicator.

Procedure 9C - Preparation of $K_2[TeI_6]$ and $[NBu_4]_2[TeI_6]$

Part 1 - Preparation of $K_2[TeI_6]$

Tellurium(IV) oxide (2.0 g), TeO_2, is dissolved in a minimum quantity, up to 30 mL, of concentrated hydroiodic acid. A saturated solution of two molar equivalents of KI in water is added with stirring. The solution is evaporated on a steam bath (**FUME HOOD!**) and stirred until the black crystals settle. The salt is recrystallized from 4 M HI and is dried in a vacuum desiccator over solid NaOH.

Part 2 - Preparation of $[NBu_4]_2[TeI_6]$

K_2TeI_6 is (0.5 g) dissolved in 4 M HI and two molar equivalents of tetra-n-butylammonium iodide in 1 M HI is added. If the solution of NBu_4I is cloudy due to organic impurities, it must be filtered by gravity through a fine filter paper before it is added to the tellurate. The black precipitate, which is formed immediately, is filtered off on a Büchner funnel, washed twice with a small amount of 1 M HI, and dried in a vacuum dessicator.

Characterization

Make sure that the samples are completely dried before attempting to characterize them! Obtain the melting points and IR spectra of all compounds prepared. Be very careful to keep the samples dry during the required manipulation. Also collect an IR spectrum of the corresponding $[NBu_4]X$ salts to aid in the interpretation of your IR spectra. Record the UV-visible absorption spectra of the $[NBu_4]_2[TeX_6]$ salt as a dilute solution (0.1 mM) in CH_2Cl_2 (quartz cells, not plastic!) Prepare solutions of accurately known concentration, and use 1 cm quartz cuvettes to measure the spectra. It may be necessary to use solutions of different concentration in differing regions of the spectrum.

Molecular Modeling

1. Use the PM3 optimized octahedral structure of $TeCl_6^{2-}$ for *all parts* of this lab. Bromide and iodide complexes are difficult to model by quantum mechanics, but we can asume that the same principles apply to all three halide complexes, and indeed to that of the fluoride as well.
2. Calculate a PM3 geometry optimization of the dianion (set charge and multiplicity correctly). Then calculate the orbitals. Note that you may have to adjust the Orbital Exponent term in the Plot Orbital menu box in order to "see" what is going on in this calculation. Usually this means that you will have to *increase* the exponent value, which has the effect of shrinking the outside surface of the orbital. Once you do this correctly, you should have no difficulty in identifying the consituent atomic orbitals in the MO's. Also, be sure to use Align Molecule from the Edit menu (primary axis to *z*, secondary to *x*) before performing your calculation.
3. Carefully look at all of the oribtals in the MO diagram. They are situated in three large groups. What is the nature of the lower group? Should you ignore these in any interaction diagram? Which set of orbitals constitute *net bonding* between the chloride ions and tellurium? Which correspond only to the 18 lone pairs expected on the halogens?
4. Using your analysis of the PM3 MO diagram, construct your own interaction diagram. Use only those symmetry adapted orbitals for the halogens that interact with Te. Ignore all that are lone pair in character. Show bonding and antibonding interactions, and occupy with the right number of net electrons, *i.e.*, ignore core or lone pair electrons. Identify the HOMO. What is the nature of the HOMO?

Report

Hand in your products as well as all original spectra. Identify the bands in the IR spectra according to their origin, and attempt a vibrational analysis of the Te—X bands. Write a full report according to the instructions given at the front of the laboratory manual.

At the end of your report, address the following additional questions:

1. What is meant by "stereochemical inactive lone pair"? Discuss how this concept applies to $[TeX_6]^{2-}$ ions, and to the isoelectronic compounds BrF_6^-, IF_6^- and XeF_6. Is there any evidence that the lone pair in these EX_6L molecules can be streochemically active?
2. Briefly describe the principles of Mössbauer spectroscopy. (See ref. 20 for a simplified discussion of this technique.) Discuss the results reported in the literature for the Mössbauer spectra of $[TeX_6]^{2-}$ salts. Contrast the three halides.

3. Briefly discuss the origin of the UV-visible absorption bands using a molecular orbital approach. (Hint: use the octahedral MO diagram you developed in the computational exercise and determine the number of filled orbitals. Transitions between filled and empty orbitals show up as absorptions in the UV-visible region of the electromagnetic spectrum.)
4. Describe the colours of the Cl, Br and I complexes. Put this on a quantitative basis by preparing a table of for the various bands of the three types of complexes. What does this data suggest about the strength of the Te–X bonds?

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Covalent and Ionic Derivatives of Iodine in the +1 Oxidation State

Introduction

The most familiar oxidation states of the halogens are zero in the elements F_2, Cl_2, Br_2, and I_2 and (–1) in the halides of most of the other elements. However, in combination with electronegative elements the heavier halogens must be assigned a positive oxidation number. The oxyhalo acids such as chloric ($HClO_3$), perchloric ($HClO_4$), bromic ($HBrO_3$), and periodic (HIO_4 or H_5IO_6) are examples.

A second class of compounds with positive oxidation states for halogens is the interhalogen type. Compounds including IF, IF_3, IF_5, and IF_7 are known, as are many other possible combinations. Here the iodine is assigned oxidation numbers of +1, +3, +5, and +7, respectively. In the case of the first two oxidation numbers, the fluoride ion may be replaced by other oxidizing anions (*i.e.* those not oxidized by the iodine). Positive iodine nitrates, sulfates, phosphates, and carboxylates have all been characterized. The positive iodine ion displays some metallic behaviour. It can be complexed with numerous different ligands, the most effective being aromatic amines such as pyridine.

Recently, hypervalent iodine compounds, *i.e.*, compounds with iodine in a positive oxidation state, have found application in organic chemistry (ref. 6).

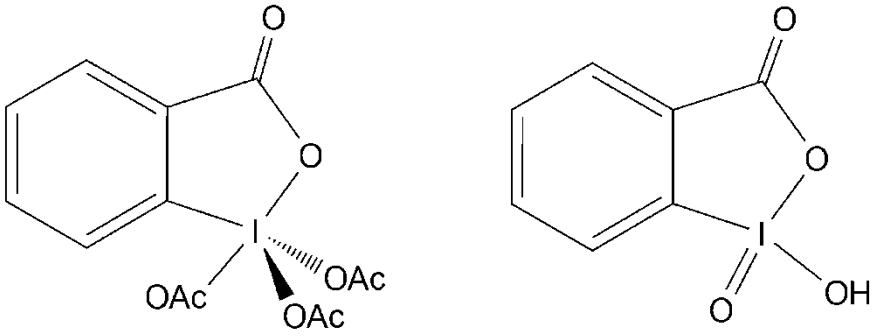

Figure IV-2 Hypervalent Iodine Compounds

The interhalogen compounds, while polar, are essentially covalently bonded. They behave as neutral molecules and display the low melting and boiling points expected of such species. The addition of complexing agents can lead to both cationic and anionic derivatives, and an example of each is prepared in this experiment.

Instructional goals:

Properties of the following elements are highlighted: I, Br

(1) To prepare and study positive iodine compounds of the interhalogen and complex ion type.

(2) To use the VSEPR model to discuss the structures of interhalogen compounds, and to understand the bonding in these compounds by molecular orbital methods.

(3) Provide experience with sublimation.

(4) Use of electronic absorption spectroscopy in the understanding of electronic structure of inorganic compounds.

Pre-lab exercise

1. Write balanced chemical equations for the synthesis of the products in parts (A), (B), and (C).
2. Sketch the structures of IBr, $[Ipy_2]^+$, and $[ICl_2]^-$. Use the VSEPR model to derive the correct structures. Assign the point groups of these molecules and ions. Now use HyperChem to produce models of these three species using PM3 optimization. For $[Ipy_2]^+$, it is simplest to use a model in which the two pyridine rings are co-planar. You may need to rotate the C–N bonds to bring these rings into co-planarity.
3. What are the physical properties of IBr? What kind of a compound is it, and how is this reflected in the operations performed on it in this experiment?
4. What is sublimation? How does variation in applied pressure affect this process?
5. Map out the timing of your afternoon's work. Use free gaps of time to do other operations. Be realistic in time allotted for each operation!

SAFETY NOTES

1. Chlorine is a toxic gas by inhalation. It causes severe irritation of the mucous membranes of the eye and lungs. Use only in a fume hood with the sash down. Wear gloves to prevent skin burns.
2. Bromine is a liquid with a high vapour pressure. The vapours are toxic by inhalation, with very similar effects to those of chlorine. Bromine also causes severe skin burns. Antidote: wash with KI solution.
3. IBr must be treated with all the caution used for bromine.
4. Pyridine is moderately toxic, and has an extremely unpleasant odour. It is known to cause sterility in laboratory rats. Use only in the hood. Rinse wastes away (aqueous down the hood sinks, organic rinsed into the waste container with acetone) before removing glassware from the hood for washing.
5. Disposable polyethylene gloves are provided. These have superior chemical resistance to vinyl or latex gloves. The latter are not to be used in the Chem 3830 laboratory!
6. All iodine compounds should be treated as poisons, and gloves worn at all times during handling.

Procedure

Note: Prepare a KI antidote solution by dissolving 5 g of KI in 100 mL of H_2O in a 400 mL beaker. Keep this solution handy at all times while handling Br_2 or IBr. Wash any spills on the skin with this solution. Br_2 will oxidize the I^- to I_2, which leaves harmless Br^- and I_2 on the skin, which merely stains the skin rather than burning it.

(A) Iodine Bromide

Place 3.2 g of iodine in a test tube and add 1 mL of bromine (bromine in excess). Close the test tube with a cork (**not** a rubber stopper) and allow to stand for ten minutes at room temperature. (Start step 1 of part (B) at this time.) The crude solid obtained is transferred **in the fume hood** to the vacuum sublimation apparatus. Most of the excess bromine should evaporate during this transfer procedure. Carry the sealed sublimer to the vacuum line.

Ensure that the trap is filled with liquid N_2 to protect the pump from the corrosive halogens.

Evacuate the sublimation apparatus for 30 s being careful to avoid opening the stopcock to the vacuum line too quickly, since this causes extreme bumping and splattering. Cold water is then

passed through the cold finger and the crude solid gently warmed using a water bath (it is also possible to use only the heat from the palm of your hand).

In about 15 min most of the solid will have sublimed to the cold finger. The system is then **slowly** returned to atmospheric pressure with dry nitrogen. The sublimation apparatus is then opened **in the fume hood** and the purified solid transferred to a vial.

(B) Dipyridyliodonium acetate

Step 1

Place 4.7 g of iodine in 50 mL of chloroform in a 125 mL Erlenmeyer flask. Add 1 mL of bromine and swirl the flask gently to mix the reagents. Allow the flask to stand corked at room temperature for 30 minutes.

Step 2

As a test for complete reaction dip a glass rod into the solution, allow it to dry in the fume hood and observe the crystals. They should resemble those produced in part (A). This however does not always work because of the volatility of the crystals.

Add 5.9 mL of 0.98 g/mL pyridine (**in the fume hood**) **dropwise** to the reaction mixture (cooled in an ice bath) while continuously swirling to mix the reagents. Continue mixing until the solution clears. This reaction is **strongly exothermic** and will boil the solvent violently if the pyridine is added too quickly. Allow the solution to sit in the ice bath for 5 min and then add 6.2 g of silver acetate through a solid addition funnel. Swirl the mixture; this should produce a yellow solution and a dense precipitate. Allow the precipitate (**what is it?**) to settle, then decant it onto fluted filter paper, keeping the filtrate. Save the white precipitate in a marked bottle.

With constant mixing slowly add 70 mL of ligroine to the yellow filtrate and allow the mixture to stand. Cool in an ice bath if no crystals form. If still no crystals form, stopper the flask and store until the next day. Vacuum filter the yellow precipitate and store the product in a stoppered vial.

(C) Preparation of $[NEt_4]^+ ICl_2^-$

The equipment consists of a hotplate/stirrer, an Erlenmeyer flask containing a magnetic stirbar, and a glass tube to deliver the Cl_2 below the surface of the solution. Prepare a solution of 3.5 g of tetraethylammonium chloride in 35 mL of H_2O in the flask. Add 2.6 g of iodine to the flask. Warm the solution to at least 30 – 40 °C with stirring. Bubble chlorine vigorously from the cylinder (**use the fume hood**) until the iodine just dissolves and the orange oily mass that forms

solidifies. Cool to precipitate the yellow product and collect it by filtration on a Büchner funnel. Record the yield.

Characterization

1. Obtain the IR spectra of the products of parts (B) and (C). Measure the solution IR spectrum of IBr in ligroine using the polyethylene solution cells (below 600 cm^{-1}.)
2. Obtain the IR spectrum of $[NEt_4]Cl$. Find the IR spectrum of pyridine in the Sadtler reference collection. (Pyridine is too obnoxious to run a spectrum of as a neat liquid.)
3. Record the mp of the products of parts (A), (B) and (C). Note: some compounds may decompose without melting. This is a valid observation – record the decomposition temperature.
4. Record the visible spectrum of IBr in CCl_4 in the range 600 to 200 nm. Then add a little 99% ethanol so as to make the solution ~1% in alcohol, and re-run the spectrum, noting any changes.
5. Record the visible spectrum of $[NEt_4]ICl_2$ in $CHCl_3$ solution in the range 600 to 200 nm.

Molecular modeling

1. Using your PM3 model of IBr calculate the orbitals for this molecule. Using the HyperChem output as a guide, describe the bonding in IBr by constructing and orbital interaction diagram between a bromine and an iodine atom. Provide correct symmetry labels for the orbitals and sketch the orbital topologies. Assign the visible spectrum as measured in CCl_4 (electronic absorption spectrum) using your MO diagram.
2. Now add to your IBr model a molecule of ethanol, without joining them by a bond. Ensure that they are arranged as in Figure IV-3, with the ethanol oxygen placed about 1.9 Å from the iodine. (This is because in such adducts, iodine is the Lewis acid, and oxygen the Lewis base, contrary to what you might expect from the behaviour of halide anions. Why?) Perform a PM3 MO calculation and note the shape and energy of the HOMO and the LUMO. To what can you attribute the colour change and the subsequent alteration in the visible spectrum upon the addition of ethanol to the CCl_4 solution of IBr? Create an MO interaction diagram to show the interaction between the two oxygen orbitals and the IBr orbitals that causes the change in the energy levels and MO patterns.

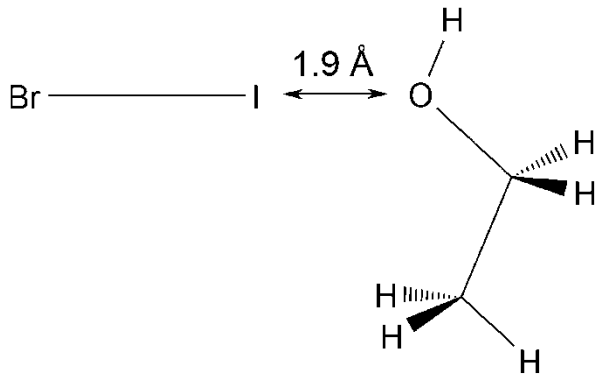

Figure IV-3 IBr + Ethanol Model

3. Use your PM3 model of the $[ICl_2]^-$ ion to calculate and display the orbital shapes and energies. Use this HyperChem result as a guide to construct an MO interaction diagram for the combination of two Cl^- ions with a central I^+ ion. Use the symmetry adapted orbital approach. Provide correct symmetry labels for the orbitals, and sketch the orbital topologies. Assign the visible spectrum using your MO diagram.
4. Use your PM3 model to calculate and display the orbitals of $[Ipy_2]^+$. Use the results of the HyperChem calculation to describe the bonding in this ion using a simplified molecular orbital approach by treating pyridine as a point source of N; think what type of orbital on the N atom would participate in bonding to the iodine cation. Provide correct symmetry labels for the orbitals and sketch the orbital topologies.

Report

Describe the appearance of each product and determine the percent yield, showing the equation and your reasoning. What is the oxidation state of iodine in each compound? What does the volatility of IBr suggest about bonding (*i.e.*, is it covalent, van der Waals, ionic, etc.)? Briefly explain.

Discuss the IR spectra of (B) and (C). What are the observed bands due to? Explain, using normal vibrations for the respective symmetry point groups as well as force constant arguments, the complete absence of certain species from the IR spectra.

What other methods of characterization could be used to determine the structures of these products? These may not be techniques available to us at the U. of L. What evidence do you have that the description of the product of part (B) is correctly described by $[Ipy_2]CH_3CO_2$? What experiments can you think of to prove this?

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Synthesis and Properties of the Halogens

Introduction

Under normal conditions fluorine is a yellow gas, chlorine is a green gas, bromine is a dark red liquid, and iodine a shiny black solid. All the halogens are poisonous and should be handled with great care. It is interesting to note that the toxicity of the members of the halogen family decreases with increasing atomic number.

The ionization energies are usually high. As a result, the halogens do not normally tend to lose electrons in chemical reactions but rather, they tend to gain them. Ionization of halogens to positive oxidation states usually occurs only in compounds with more electronegative elements. For fluorine, there are none! For chlorine, there are a number of oxygen compounds (χ(O) = 3.50). Bromine and iodine also form some (unstable) nitrogen compounds. In recent years an extensive chemistry of polyiodide cations has developed, with the help of "superacids" (see p. 410 of ref. 1).

The tendency of the halogens to gain electrons in chemical reactions is consistent with their status as non-metals. This tendency is quantified by the electron affinity, or enthalpy of electron attachment, to use the more modern term (the signs used in the table below follow the latter definition). When a halogen atom acquires an electron to form an ion it releases energy, thereby entering a lower energy state, or a more stable state. Thus electron affinity can be defined as the energy released when an electron enters the outermost orbital of an atom.

Element	**F**	**Cl**	**Br**	**I**	**At**
Electron affinity (kJ mol^{-1})	-328	-349	-325	-295	-270

However, the exact size of the electron affinity is not as easy to correlate with orbital character. For example, since fluorine is anomalously small, its electron affinity is reduced from what it might be due to electron-electron repulsion. When we look at chemical behaviour, however, we find that the oxidizing power of the halogens decreases as we proceed down the group from fluorine, to chlorine, to bromine to iodine, in accord with the predictions of simple theory.

Because of their great chemical activity it is not surprising that the halogens do not occur free in nature. Chlorine is by far the most abundant of the halogens. It occurs as chloride ion in sea water and as rock salt in large mineral deposits.

The halogens may complete their inert gas configurations either by gaining an electron to form an ionic bond or by sharing an electron to form a covalent bond. An example of the first kind of reaction is the combination of sodium and fluorine.

$$Na + \tfrac{1}{2} F_2 \rightarrow NaF$$

The electronegativity of fluorine is high and it captures an electron to form a stable ion, with little tendency for back donation of charge. The resulting compound is thus an ionic solid. An example of the second kind of reaction is the combination of atoms of the same kind to form diatomic molecules, such as:

$$F + F \rightarrow F_2$$

The van der Waal's forces between fluorine molecules are very weak and, as a result, there is little attraction between the molecules and little tendency for fluorine gas molecules to condense to a liquid. (The boiling point of fluorine is –188 °C.) The van der Waal's forces are much stronger for bromine, strong enough to hold the molecules together to form a liquid at ordinary temperatures. (The boiling point of bromine is 59 °C.) The forces in iodine are so strong that the molecules condense to a solid at ordinary temperatures. (The boiling point of iodine is 183 °C, although at atmospheric pressure iodine sublimes rather than forming a liquid.)

Fluorine is the most powerful of all oxidizers. The oxidation number of fluorine is –1 in all its compounds.

Chlorine is prepared in the laboratory by the chemical oxidation of the chloride ion. (Industrially it is prepared by the electrolysis of brine, which effectively means the electrochemical oxidation of chloride ions.) Hydrochloric acid is a good source of chloride ions and manganese dioxide is a suitable oxidizer.

Chlorine is a strong oxidizer. It combines directly with most metals to form chlorides. The vigor of the reaction depends upon the activity of the metal. Sodium, for instance, bursts into flame if placed in chlorine. The reaction with iron is interesting because iron(III) chloride is formed:

$$2\ Fe + 3\ Cl_2 \rightarrow 2\ FeCl_3$$

In this reaction, chlorine is a strong enough oxidizer to capture one of the "buried" electrons of iron, an electron in the next-to-the outermost shell. If iron reacts with chlorine, iron(III) chloride is formed; if iron reacts with hydrochloric acid, iron(II) chloride is formed. Chlorine is clearly a more powerful oxidizer than hydrogen ion. Since chlorine is a stronger oxidizer than bromine or iodine, it will displace bromine from bromides and iodine from iodides:

$$Cl_2 + 2\ Br^- \rightarrow 2\ Cl^- + Br_2$$

$$Cl_2 + 2\ I^- \rightarrow 2\ Cl^- + I_2$$

These replacement reactions serve as a test by which bromides and iodides can be identified.

Chlorine dissolves in water to a small degree. The total concentration for a saturated aqueous solution at 25 °C is 0.091 M. Of this total, $[Cl_2] = 0.061$ and $[HOCl] = 0.030$. The equilibrium for the disproportionation of Cl in neutral solution is:

$$H_2O + Cl_2 \rightarrow HCl + HOCl$$

One chlorine atom forms chloride ion in water solution and the other forms a covalent bond with oxygen. One of the chlorine atoms in this reaction is reduced and the other oxidized. This disproportionation is favoured in basic solution, where quantitative solutions of NaOCl can be prepared (*i.e.* bleach)

Preparation of and test for iodine in aqueous solution

Both industrially and in the laboratory iodine is prepared from iodide solutions (some natural brines have a high iodine content; otherwise iodine can be isolated from certain types of seaweed.) Iodine is appreciably soluble in water, but the presence of even a small excess I^- sets up a powerful equilibrium as follows:

$$I_2 + I^- \rightarrow I_3^-$$

Solutions of I_2 and I_3^- in water are brown in colour, due to a Lewis acid/base interaction with the water molecules. This makes it virtually impossible to tell aqueous Br_2 from aqueous I_2, or to identify iodine in any kind of coloured solution. However, a positive identification of both these halogens is readily made by using a phase-transfer solvent. Normally CCl_4 is used, a totally non-polar liquid. Both Br_2 and I_2 are very soluble in this solvent, and as an additional benefit, there is no Lewis acid/base interaction to alter the colours. Thus, Br_2 in CCl_4 is orange-brown in colour (depending on concentration) and I_2 is deep purple. When doing an iodine test, always be sure to add sufficient chlorine water to lower the I^- concentration to the level where the following reaction will tend to go towards the product side. Otherwise the iodine may stay as I_3^- in aqueous solution despite the presence of CCl_4.

$$I_{2(H2O)} \rightarrow I_{2(CCl4)}$$

Hydrogen halides

A method of preparing hydrogen halides is to treat a metal halide with concentrated sulfuric acid. The principle is that the other acid must be a sufficiently strong Brønsted acid to protonate the halide ion, which is a Brønsted base. Concentrated sulfuric acid is used in the preparation of volatile acids because it is strong enough of an acid, and its boiling point, at approximately 330 °C, enable the HX acids to be removed from solution by distillation.

Hydrogen fluoride is prepared by treating fluorspar with concentrated sulfuric acid:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2\,HF$$

By far the most important of the hydrogen halides is hydrogen chloride. It is prepared by the reaction between common salt and concentrated sulfuric acid as shown in the equation:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$

Neither HBr nor HI can be prepared by the methods used to prepare HF and HCl. You will recall that the halogens are oxidizing agents and that, in oxidizing power, $F_2 > Cl_2 > Br_2 > I_2$. It therefore follows that the halide ions are reducing agents and that, in reducing power, $I^- > Br^- > Cl^- >$ F. Concentrated H_2SO_4 is a strong oxidizer. Bromide and iodide ions react with, and reduce, concentrated H_2SO_4; in one case sulfur dioxide is the reduction product and in the other, hydrogen sulfide.

It should now be apparent that HBr and HI cannot be prepared from their halide salts by the reaction of an acid that is a strong oxidizer. Instead, phosphoric acid may be used. The equations for the preparation of these two gases would then be:

$$3\ NaBr + H_3PO_4 \rightarrow Na_3PO_4 + 3\ HBr$$
$$3\ KI + H_3PO_4 \rightarrow K_3PO_4 + 3\ HI$$

Fluorides, chlorides, bromides, and iodides of the elements

In general, the halides are quite soluble in water. There are, however, some exceptions to this rule, for example, the chlorides, bromides and iodides of silver, mercury(I), and lead are only slightly soluble in water. Halide ions are also capable of acting as ligands in complexation reactions, and replacing other ligands around the central (usually metallic) atom. For example, the blood-red complex $[FeSCN(OH_2)_5]^{+2}$ can be converted to the colourless complex $[FeX_6]^{3-}$ by reaction with excess halide. Likewise, the water molecules of hydration on blue $Cu^{+2}_{(aq)}$ can be replaced by excess halide ion to form yellow or green $[CuX_4]^{2-}$ complexes.

Higher oxidation states of chlorine.

Chlorine and its compounds show a marked tendency to undergo self-(or auto)-oxidation-reduction, in which some molecules or ions of a species are oxidized to a high state while others are reduced to the stable –1 state. This process is called disproportionation. It is possible to oxidize Cl^- (oxidation state –1) to free chlorine, $Cl_{2(g)}$ (oxidation state 0), and then carry out a series of disproportionation reactions in which the chlorine is successively oxidized to the +1, +5, and finally the +7 oxidation states, as indicated on the flow chart in Figure IV-4.

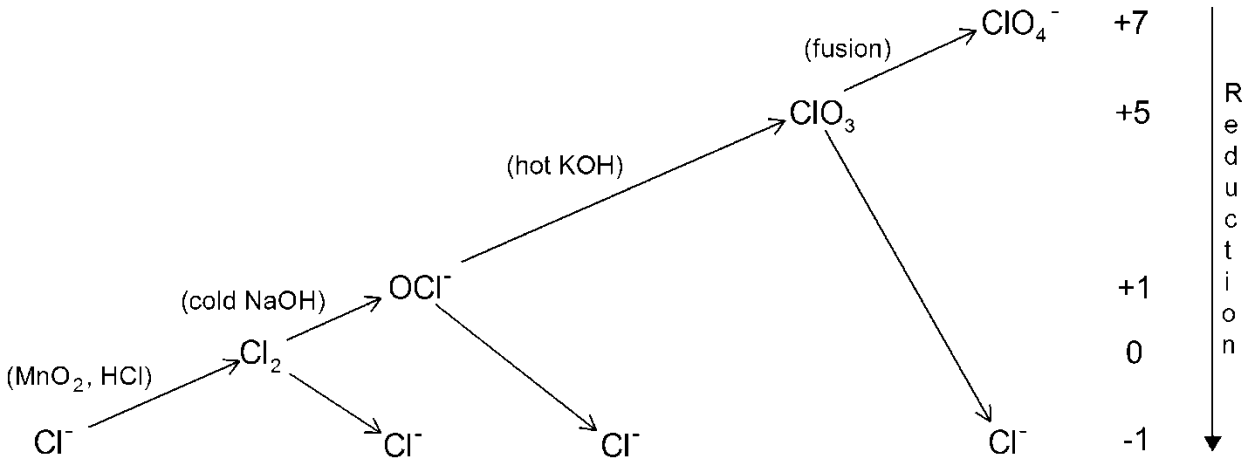

Figure IV-4 Dispropotionation interconversion of chlorine and its oxo anions in basic solution

Instructional goals:

Properties of the following elements are highlighted: F, Cl, Br & I.

(1) Understanding the relative oxidizing and reducing properties of the halides.

(2) Preparation and reactivity of Cl_2 and I_2.

(3) Understanding the reactivity of Br_2.

Pre-lab exercise

1. Construct a molecular orbital diagram for F_2.
2. Why do the van der Waal's forces of the halogens become progressively stronger as the atomic number increases?
3. Why is Cl_2 gas collected in an upright jar, as opposed to water displacement from an inverted jar (as in experiment 7)?
4. What are the major safety concerns associated with this lab? How will you address them?
5. Map out the timing of your afternoon's work. Use free gaps of time to do other operations. Be realistic in time allotted for each operation!

SAFETY NOTES

1. Anhydrous hydrogen halides are extremely corrosive, HF is particularly dangerous since it attacks tissue and cannot be rinsed away once it has contacted flesh. WEAR DISPOSABLE POLYETHYLENE GLOVES DURING THIS STEP, AND DURING THE CLEANUP OF YOUR APPARATUS, WHICH SHOULD BE DONE IMMEDIATELY AFTERWARDS.
2. Sample odours of evolved gases by wafting the air above the mouth of the test tube towards your nostrils. NEVER inhale directly from the test tube into your nose or mouth!
3. Elemental chlorine and bromine are dangerous chemicals. Work in such a way that body parts are never exposed to these reagents. Bromine is a liquid with a high vapour pressure. The vapours are toxic by inhalation, with very similar effects to those of chlorine. Bromine also causes severe skin burns. Antidote: wash with KI solution.
4. All iodine compounds should be treated as poisons, and gloves worn at all times during handling.
5. CCl_4 is a suspected carcinogen, and is toxic by inhalation or ingestion. It is not flammable. Use only in a fume hood.

Procedure

The preparation and reactions of pure chlorine

Arrange an apparatus as shown in Figure IV-5. The delivery tube should extend to the bottom of the bottle through a piece of paper covering its top. Place 3 g of MnO_2 in a 25 x 100 mm Pyrex test tube and add 10 mL of concentrated HCl. Immediately attach the delivery tube to the test tube and gently heat the latter until Cl_2 gas is evolved. Collect 2 bottles of the gas, placing a white paper behind each bottle as it is filling to discern when sufficient Cl_2 has been obtained. Cover each bottle with a glass plate. Add H_2O to the generator and immediately flush the contents down the drain with plenty of water.

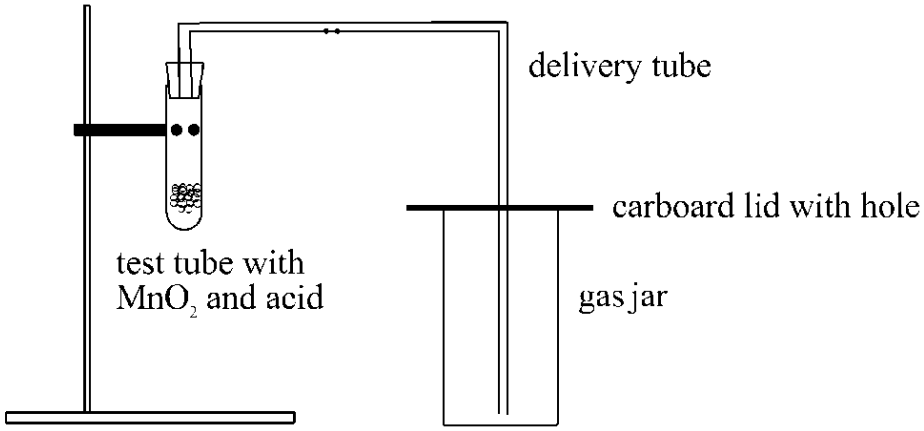

Figure IV-5 Apparatus for the preparation of Cl_2

Pack steel wool into a small (4 mm) tight ball, but leave a few ends protruding. Move a bottle of chlorine close to the burner, grasp the protruding ends of the steel wool ball with the tongs, heat the iron until red hot, then quickly thrust and hold it into the bottle of chlorine (do not drop – the bottle may crack). After the reaction is complete, add 10 mL of water. Pour the solution into a 15 × 10 mm test tube and add a few drops of 0.2 M KSCN. A blood-red product of $Fe(SCN)^{+2}$ indicates the iron metal was oxidized to the +3 state.

Moisten a piece of blue litmus paper and while holding it with forceps, thrust it briefly into the second bottle of chlorine. Immediately replace the glass plate.

Obtain two pieces of each red litmus paper, paper with ink and pencil marks, and paper with black typing. Wet one of each of the above items and drop them into the second bottle of chlorine. Also drop in the dry pieces. Leave these until the end of the lab class and then observe the results. (Grass or flowers may also be added.)

In separate test tubes put 2 mL of 0.1 M KI solution and 2 mL of 0.1 M KBr solution. Add a few drops of chlorine water from the side shelf. Note the colors produced in the two tubes. Add approximately 1 mL of CCl_4 to each of the test tubes and shake them well. Allow the liquids to separate and observe the relative concentration of colors in the two layers.

<u>Bromine</u>

Add chlorine water drop by drop to 1 mL of 0.1 M KI solution in a test tube until there is a definite change in the color of the mixture. Identify the colored product, using CCl_4.

The preparation and reactions of pure iodine

Set up a 50 mL beaker with an evaporating dish as depicted in Figure IV-6. Put 0.5 g of KI crystals and about the same quantity of MnO_2 into the beaker. Fill the drying dish about two-thirds with cold H_2O. Moisten the solids in the beaker with 1 or 2 drops of H_2O and add about 1 mL of concentrated H_2SO_4. Place the dish back on the beaker and apply just enough heat to keep the beaker filled with iodine fumes for 3 or 4 minutes. Empty the dish and beaker and invert the dish on the table-top to allow the crystals to dry. If adequate crystals have not formed on the dish, use the crystals sublimed onto the sides of the beaker.

Using the spatula, put several of the iodine crystals in 2 mL of ethanol in a test tube, and shake the tube to cause dissolution. Put a few drops of the solution into a 25 × 200 mm test tube and dilute to 10 mL with H_2O. Add a few drops of starch solution (suspension). This is an excellent test for free iodine and, vice versa, for starch.

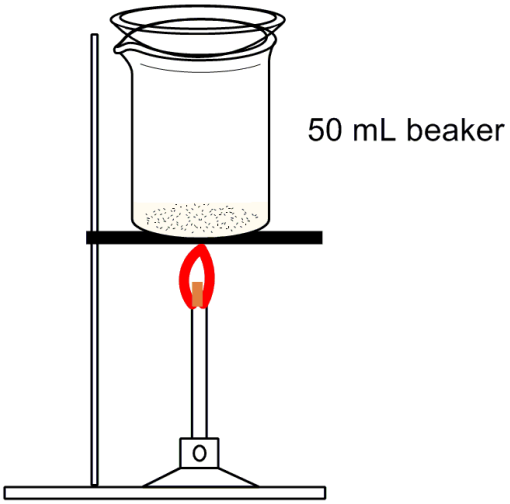

Figure IV-6 Apparatus for the preparation of I_2

Add 0.1 M $Na_2S_2O_3$ solution to the remainder of the alcohol solution dropwise until a change is noted.

Using the collected data, arrange the halogens in order of their activity, and consider atomic-structural explanations for this trend.

Preparation and properties of the hydrogen halides

In separate dry 20 × 150 mm test tubes place about one gram of CaF_2, NaCl, KBr, and KI. Have four moist strips of blue litmus paper ready on a glass plate; also have a stirring rod and a container of 15 M NH_4OH available. Add approximately 1 mL of concentrated (~80%) H_3PO_4 to each of the halide salts. If necessary heat to cause a reaction. After the air in the test tubes has been displaced by the gases generated, blow gently across the mouth of each of the tubes. (The

formation of a fog indicates the presence of a water-soluble gas. The gases may fume in the air itself. **DO NOT INHALE THE GASES!** Using tongs, briefly hold the pieces of blue litmus paper in the mouth of the test-tubes. Also hold a stirring rod wet with NH_4OH solution near the test-tube mouths.

Repeat the above treatment with new small quantities of CaF_2, NaCl, KBr, and KI and concentrated H_2SO_4 instead of the phosphoric acid. If necessary warm to initiate reaction. Observe any noteworthy differences between the methods of preparation. Take particular note of the colour changes.

In each of 3 small test tubes, place 4 mL of 0.002 M $KMnO_4$ and 2 mL of dilute H_2SO_4. Add 4 drops of 0.1 M KCl solution one test tube, 0.1 M KBr solution to a second, and 0.1 M KI solution to the third. After reaction occurs, add about 1 mL of CCl_4 to each of the tubes whose contents show a change in colour, and shake well. Observe the appearance of the denser CCl_4 layer.

Complexing ability of the halide ions

Put 2 mL of 0.1 M $Fe(NO_3)_3$ solution in a test tube. Add 2 drops of 0.2 M KSCN solution. Divide the red solution between two test tubes. Add approximately 0.1 g of solid NaF to one test tube and a similar amount of solid NaCl to the other. Stir the content of both test tubes. If the color does not disappear add more solid until the solution becomes saturated. On the basis of these results what would you predict would happen when using Br^- and I^- ions?

Add 1 drop of 1 M $CuSO_4$ solution to 1 mL of 12 M HCl. Compare the appearance of this solution to that of 1 mL of 1 M $CuSO_4$ in a separate test tube. Add 2 mL of water to both test tubes and make a fresh comparison.

Chemical properties of the hypochlorite ion

Since solid NaOCl cannot be easily isolated without decomposition, we shall test portions of the solution of a commercial bleach obtained at the grocery store. It was prepared by passing chlorine into a solution of NaOH. Pour several drops of NaOCl solution on red and blue litmus to note its acidity or basicity. Note any bleaching effect.

Add 1 mL of 0.5 M $AgNO_3$ to a 3 mL portion of the NaOCl solution. What is the precipitate? (Compare with the behavior of a drop of 6 M NaOH on 0.5 M $AgNO_3$.) Is it soluble in 6 M HNO_3, and does any other precipitate remain? Explain your observations.

Place 2 mL of 0.1 M KI and 1 mL of CCl_4 in a test tube. Add 5% NaOCl solution dropwise (shaking the test tube after each drop) and note any color change in the CCl_4 layer. Is there any evidence for the formation of I_2? An excess of NaOCl must be avoided because it will remove the color, owing to further oxidation of the initial product to the colorless IO_3^- ion.

Repeat this test using 2 mL of 0.1 M KBr in place of KI. Is there any evidence for the formation of Br_2 detected by a color change in the CCl_4 layer? (No more than 5 drops should be needed to cause a change.) Where would you place the ClO^- ion with respect to Br_2 and I_2 in a scale of oxidizing strength? Acidify the test solution with 5 M HCl and shake, noticing any color formed in the CCl_4 layer. Does the oxidizing strength of ClO^- change when the solution is acidified?

Report

In this and all descriptive chemistry labs, you must record detailed observations in your lab notebook. Include this information in your report. Explain fully all reactions and write balanced chemical equations for each.

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