Fifth Edition

The Organic Chem Lab Survival Manual

A Student's Guide to Techniques

James W. Zubrick

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To Cindy

Preface to the Second Edition

It is heartening to hear of your book being read and enjoyed, literally cover to cover, by individuals ranging from talented high-school science students to Professors Emeritus of the English language. Even better to hear that you have a chance to improve that book, based upon the above comments, comments by reviewers, and the experience gained from working with the text.

In this edition of *The Organic Chem Lab Survival Manual,* the section on notebooks and handbooks have been expanded to include typical notebook pages and actual handbook entries along with interpretation. There are new notes on cleaning and drying glassware, and how to find a good recrystallization solvent. Once their samples are purified, students may now find directions for taking a melting point with the Thomas–Hoover apparatus. Washing has been given the same importance as extraction, and a few more trouble spots—taking the pH of an organic layer, for one—have been smoothed. There are additional instructions on steam distillation using external sources of steam. Simple manometers, coping with air leaks, and the correct use of a pressure–temperature nomograph enhance the section on vacuum distillation. Refractometry has been added, as well as—by special request—sections on the theory of extraction and distillation, including azeotropes and azeotropic distillation, and, I believe, the first application of the Clausius–Clapyron equation as a bridge for getting from Raoult's Law (pressure and mole fraction) to the phase diagram (temperature and mole fraction).

Many people deserve credit for their assistance in producing this edition: my students, for helping me uncover what was lacking in the previous edition, with Mr. Ronald Pohadsky and Mr. Barry Eggleston making specific suggestions while working in the laboratory. A special thanks to Professor G.J. Janz, director of the Molten Salts Data Center at the Rensselaer Polytechnic Institute for his review of the physical chemistry sections of this edition, and to Professors Henry Hollinger and A. Rauf Imam for their help during the initial phases of that work. I would also like to thank

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for their valuable comments and suggestions in making this edition more useful for students of organic chemistry laboratory.

Finally, I'd like to thank Mr. Dennis Sawicki, Chemistry Editor at John Wiley & Sons, first, for one of the nicest birthday presents I've gotten in a while, and second, for his encouragement, guidance, and patience at some troubling points in the preparation of this edition. Ms. Dawn Reitz, Production Supervisor, Ms. Ann Meader, Supervising Copy Editor, and Mr. Glenn Petry, Copy Editor deserve a great deal of credit in bringing this second edition about.

J. W. Zubrick
Hudson Valley Community College
April 3, 1987

Preface to the First Edition

Describe, for the tenth time, an instrument not covered in the laboratory book, and you write a procedure. Explain, again and again, operations that are in the book, and you get a set of notes. When these produce questions you revise until the students, not you, finally have it right. It you believe that writing is solidified speech — with the same pauses, the same cadences — then a style is set. And if you can still laugh, you write this book.

This book presents the basic techniques in the organic chemistry laboratory with the emphasis of doing the work correctly the first time. To this end, examples of what can go wrong are presented with admonishments, often bordering on the outrageous, to forestall the most common of errors. This is done in the belief that it is much more difficult to get into impossible experimental troubles once the student has been warned of the merely improbable ones. Complicated operations, such as distillation and extraction, are dealt with in a straightforward fashion, both in the explanations and in the sequential procedures.

The same can be said for the sections concerning the instrumental techniques of GC, IR, NMR, and HPLC. The chromatographic techniques of GC and HPLC are presented as they relate to thin-layer and column chromatography. The spectroscopic techniques depend less on laboratory manipulation and so are presented in terms of similarities to the electronic instrumentation of GC and HPLC techniques (dual detectors, UV detection in HPLC, etc.). For all techniques, the emphasis is on correct sample preparation and correct instrument operation.

Many people deserve credit for their assistance in producing this textbook. It has been more than a few years since this book was first written, and a list of acknowledgements would approach the size of a small telephone directory — there are too many good people to thank directly.

For those who encouraged, helped, and constructively criticized, thanks for making a better book that students enjoy reading and learning from.

I'd like to thank the hundreds of students who put up with my ravings, rantings, put-ons, and put-downs, and thus taught me what it was they needed to know, to survive organic chemistry laboratory.

A special thanks to Dr. C.W. Schimelpfenig, for encouragement over many years when there was none, and whose comments grace these pages; Dr. D.L. Carson, whose comments also appear, for his useful criticism concerning the

presentation; Drs. R.A. Bailey, S.C. Bunce, and H.B. Hollinger for their constant support and suggestions; Dr. Mark B. Freilich, whose viewpoint as an inorganic chemist proved valuable during the review of manuscript; and Dr. Sam Johnson, who helped enormously with the early stages of the text processing. I also thank Christopher J. Kemper and Keith Miller for their valuable comments on the instrumental sections of the book.

Finally, I'd like to thank Clifford W. Mills, my patron saint at John Wiley & Sons, without whose help none of this would be possible, and Andrew E. Ford, Jr., vice president, for a very interesting start along this tortured path to publication.

Some Notes on Style

It is common to find instructors railing against poor usage and complaining that their students cannot do as much as to write one clear, uncomplicated, communicative English sentence. Rightly so. Yet I am astonished that the same people feel comfortable with the long and awkward passive voice, the pompous "we" and the clumsy "one," and that damnable "the student," to whom exercises are left as proofs. These constructions, which appear in virtually all scientific texts, do *not* produce clear, uncomplicated, communicative English sentences. And students do learn to write, in part, by following example.

I do not go out of my way to boldly split infinitives, nor do I actively seek prepositions to end sentences with. Yet by these constructions alone, I may be viewed by some as aiding the decline in students' ability to communicate.

E.B. White, in the second edition of *The Elements of Style* (Macmillan, New York, 1972, p. 70), writes

> Years ago, students were warned not to end a sentence with a preposition; time, of course, has softened that rigid decree. Not only is the preposition acceptable at the end, sometimes it is more effective in that spot than anywhere else. "A claw hammer, not an axe, was the tool he murdered her with." This is preferable to "A claw hammer, not an ax, was the tool with which he murdered her."
>
> Some infinitives seem to improve on being split, just as a stick of round stovewood does. "I cannot bring myself to really like the fellow." The sentence is relaxed, the meaning is clear, the violation is harmless and scarcely perceptible. Put the other way, the sentence becomes stiff, needlessly formal. A matter of ear.

We should all write as poorly as White.

With the aid of William Strunk and E.B. White in *The Elements of Style* and that of William Zinsser in *On Writing Well,* Rudolph Flesch in *The ABC of Style,* and D.L. Carson, whose comments appear in this book, I have tried to follow some principles of technical communication lately ignored in scientific texts: use the first person, put yourself in the reader's place, and, the best for last, use the active voice and a personal subject.

The following product names belong to the respective manufacturers. Registered trademarks are indicated here, as appropriate; in the text, the symbol is omitted.

Corning®	Corning Glass Works, Corning, New York
Drierite®	W. A. Hammond Drierite Company, Xenia, Ohio
Fisher–Johns®	Fisher Scientific Company, Pittsburgh, Pennsylvania
Luer-Lok®	Becton, Dickinson and Company, Rutherford, New Jersey
Mel-Temp®	Laboratory Devices, Cambridge, Massachusetts
Millipore®	Millipore Corporation, Bedford, Massachusetts
Swagelok®	Crawford Fitting Company, Solon, Ohio
Teflon®	E.I. DuPont de Nemours & Company, Wilmington, Delaware
Variac®	General Radio Company, Concord, Massachusetts

Forewords

Seldom does one have the opportunity to read and use a textbook that is completely useful, one that does not need substitutions and deletions. Zubrick's book is this type of resource for undergraduate organic students and their laboratory instructors and professors. I must heartily recommend this book to any student taking the first laboratory course in organic chemistry.

The Organic Chem Lab Survival Manual is filled with explanations of necessary techniques in much the same way that advanced techniques have been presented in books by Wiberg, Lowenthal, Newman, and Gordon and Ford. In larger universities, *The Survival Manual* is a valuable supplement to most laboratory manuals. It provides explanations that many graduate teaching assistants do not take time to give to their classes. Most teaching assistants of my acquaintance appreciate Zubrick's book because it supports their discussions during recitations (when each student has a personal copy), and it refreshes their memories of good techniques they learned and must pass on to a new generation of undergraduates.

The book is addressed to the undergraduate student audience. The informal tone appeals to most laboratory students. The illustrations are delightful. The use of different type fonts is effective for emphasis. Also, Zubrick always explains *why* the particular sequence of operations is necessary, as well as *how* to manipulate and support the apparatus and substances. This is a definite strength.

This book is an evolutionary product: Over the span of a decade, professors at major universities and liberal arts colleges have made suggestions for minor changes and improvements. I count myself fortunate to have used the forerunners, which have been published since 1973.

A large quantity of useful information has been collected, well organized, and presented with great care. This book is the handiwork of a master teacher.

C.W. Schimelpfenig
Dallas Baptist University
Dallas, Texas

The Organic Chem Lab Survival Manual is a book I have known about for a number of years in a variety of developmental stages. As it progressed, I watched with interest as Jim Zubrick struggled to achieve a balance between merely conveying information — what most books do — and conveying that

information efficiently to its very human audience. On the one hand, Jim insisted that his book contain all the necessary scientific detail; on the other hand, he also insisted that a "how to" book for organic chemistry lab need not be written in the dull and confusing prose which so often passes as the *lingua franca* of science. This book demonstrates that he has achieved both goals in admirable fashion.

In fact, *The Survival Manual* succeeds very well in following Wittgenstein's dictum that "everything that can be thought at all, can be thought clearly. Anything that can be said can be said clearly." It also follows the advice of Samuel Taylor Coleridge to avoid pedantry by using only words "suitable to the time, place, and company."

Although some few readers may take umbrage with this book because it is not, atypically couched in the language of a typical journal article, similar people no doubt also complained when William Strunk published *Elements of Style* in 1919. For Strunk also broke with tradition. Most other writing texts of the day were written in the convoluted language of the nineteenth century, and the material they contained consisted largely of lists of arcane practices, taboos, and shibboleths — all designed to turn students into *eighteenth-century* writers.

From Strunk's point of view, such texts were less than desirable for several major reasons. First, the medicine they offered students had little to do with the communication process itself; second, it had little to do with current practice; and third, taking the medicine was so difficult that the cure created more distress in the patients than did the disease itself.

Jim Zubrick proves in this book that he understands, as did Strunk, that learning reaches its greatest efficiency in situations where only that information is presented which is directly related to completing a specific task. In an environment fraught with hazards, efficiency of this sort becomes even more necessary.

The Survival Manual is an excellent book because it speaks to its audience's needs. Always direct — if sometimes slightly irreverent — the book says clearly what many other books only manage to say with reverent indirection. It never forgets that time is short or that the learning curve rises very slowly at first. The prose is straightforward, easy to understand, and is well supported by plentiful illustrations keyed to the text. It is also technically accurate and technically complete, but it always explains matters of laboratory technology in a way designed to make them easily understandable to students in a functional context.

All of these characteristics related to communication efficiency will natu-

rally make the laboratories in which the book is used safer labs; the improved understanding they provide serves as natural enhancement to the book's emphatic and detailed approach to laboratory safety.

Most important, however, all the elements of *The Survival Manual* come together in focusing on the importance of task accomplishment in a way which demonstrates the author's awareness that communication which does not efficiently meet the needs of its audience is little more than *pedantry* unsuitable to the time, place, and company.

David L. Carson
Director,
The Master of Science
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Contents

Safety First, Last and Always

The organic chemistry laboratory is potentially one of the most dangerous of undergraduate laboratories. That is why you must have a set of safety guidelines. It is a very good idea to pay close attention to these rules, for one very good reason:

The penalties are only too real.

Disobeying safety rules is not at all like flouting many other rules. *You can get seriously hurt.* No appeal. No bargaining for another 12 points so you can get into medical school. Perhaps as a patient, but certainly not as a student. So, go ahead. Ignore these guidelines. But remember—

You have been warned!

1. ***Wear your goggles.*** Eye injuries are extremely serious and can be mitigated or eliminated if you keep your goggles on *at all times.* And I mean *over your eyes,* not on top of your head or around your neck. There are several types of eye protection available, some of it acceptable, some not, according to local, state and federal laws. I like the clear plastic goggles that leave an unbroken red line on your face when you remove them. Sure, they fog up a bit, but the protection is superb. Also, think about getting chemicals or chemical fumes trapped under your contact lenses before you wear them to lab. Then don't wear them to lab. Ever.
2. ***Touch not thyself.*** Not a Biblical injunction, but a bit of advice. You may have just gotten chemicals on your hands, in a concentration that is not noticeable, and sure enough, up go the goggles for an eye wipe with the fingers. Enough said.
3. ***There is no "away."*** Getting rid of chemicals is a very big problem. You throw them from here, and they wind up poisoning someone else. Now there are some laws to stop that from happening. The rules were really designed for industrial waste, where there are hundreds of gallons of waste that have the same composition. In a semester of organic lab there will be much smaller amounts of different materials. Waste containers could be provided for everything, but this is not practical. If you don't see the waste can you need, ask your instructor. When in doubt, *ask.*
4. ***Bring a friend.*** *You must never work alone.* If you have a serious

accident and you are all by yourself, you might not be able to get help before you die. Don't work alone, and don't work at unauthorized times.

5. ***Don't fool around.*** Chemistry is serious business. Don't be careless or clown around in lab. You can hurt yourself or other people. You don't have to be somber about it; just serious.
6. ***Drive defensively.*** Work in the lab as if someone else were going to have an accident that might affect you. Keep the goggles on because *someone else* is going to point a loaded, boiling test tube at you. *Someone else* is going to spill hot, concentrated acid on your body. Get the idea?
7. ***Eating, drinking, or smoking in lab.*** Are you kidding? Eat in a chem lab? Drink in a chem lab??? Smoke, and blow yourself up????
8. ***Keep it clean.*** Work neatly. You don't have to make a fetish out of it, but try to be *neat.* Clean up spills. Turn off burners or water or electrical equipment when you're through with them.
9. ***Where it's at.*** Learn the location and proper use of the fire extinguishers, fire blankets, safety showers, and eyewashes.
10. ***Making the best-dressed list.*** No open-toed shoes, sandals, or canvas-covered footware. No loose-fitting cuffs on the pants or the shirts. Nor are dresses appropriate for lab, guys. Keep the mid-section covered. Tie back that long hair. And, a small investment in a lab coat can pay off, projecting that extra professional touch. It gives a lot of protection too. Consider wearing disposable gloves. Clear polyethylene ones are inexpensive, but the smooth plastic is slippery, and there's a tendency for the seams to open when you least expect it. Latex examination gloves keep the grip and don't have seams, but they cost more. Gloves are not perfect protectors. Reagents like bromine can get through and cause severe burns. They'll buy you some time though, and can help mitigate or prevent severe burns.
11. ***Hot under the collar.*** Many times you'll be asked or told to heat something. Don't just automatically go for the Bunsen burner. That way lies *fire.* Usually—

No Flames!

Try a hot plate, try a heating mantle (see Chapter 13, "Sources of Heat"). But try to stay away from flames. Most of the fires I've had to put out started when some bozo decided to heat some flammable sol-

vent in an open beaker. Sure, there are times when you'll HAVE to use a flame, but use it away from all flammables and in a hood (Fig. 1), and only with the permission of your instructor.

12. ***Work in the Hood.*** A hood is a specially constructed workplace that has, at the least, a powered vent to suck noxious fumes outside. There's also a safety glass or plastic panel you can slide down as protection from exploding apparatus (Fig. 1). If it is at all possible, treat every chemical (even solids) as if toxic or bad smelling fumes came from it, and carry out as many of the operations in the organic lab as you can *inside a hood,* unless told otherwise.

13. ***Keep your fingers to yourself.*** Ever practiced "finger chemistry?" You're unprepared so you have a lab book out, and your finger points to the start of a sentence. You move your finger to the end of the first line, and do that operation—

"Add this solution to the beaker containing the ice-water mixture"

And WOOSH! Clouds of smoke. What happened? The next line reads—

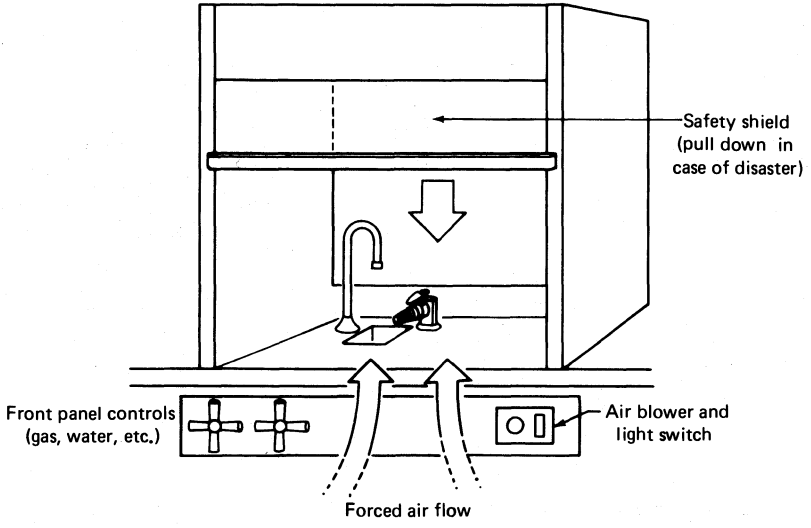


Fig. 1 A typical hood.

"very carefully as the reaction is highly exothermic."

But you didn't read that line, or the next, or the next. So you are a danger to yourself and everyone else. Read and take notes on any experiment before you come to lab (see Chapter 2, "Keeping a Notebook").

14. ***What you don't know can hurt you.*** If you are not sure about any operation, or you have any question about handling anything, *please* ask your instructor before you go on. Get rid of the notion that asking questions will make you look foolish. Following this safety rule may be the most difficult of all. Grow up. Be responsible for yourself and your own education.
15. ***Blue Cross or Blue Shield?*** Find out how you would get medical help, if you needed it. Sometimes during a summer session, the school infirmary is closed and you would have to be transported to the nearest hospital.

These are a few of the safety guidelines for an organic chemistry laboratory. You may have others particular to your own situation.

ACCIDENTS WILL NOT HAPPEN

That's an attitude you might hold while working in the laboratory. You are NOT going to do anything, or get anything done to you, that will require medical attention. If you do get cut, and the cut is not serious, wash the area with water. If there's serious bleeding, apply direct pressure with a clean, preferably sterile, dressing. For a minor burn, let cold water run over the burned area. For chemical burns to the eyes or skin, flush the area with lots of water. In every case, get to a physician if at all possible.

If you have an accident, *tell your instructor immediately. Get help!* This is no time to worry about your grade in lab. If you put grades ahead of your personal safety, be sure to see a psychiatrist after the internist finishes.

Keeping a Notebook

A **research notebook** is perhaps one of the most valuable pieces of equipment you can own. With it you can duplicate your work, find out what happened at leisure, and even figure out where you blew it. General guidelines for a notebook are:

1. The notebook must be bound permanently. No loose leaf or even spiral-bound notebooks will do. It should have a sewn binding so that the only way pages can come out is to cut them out. (8 1/2 x 11 in. is preferred).
2. *Use waterproof ink! Never pencil!* Pencil will disappear with time, and so will your grade. Cheap ink will wash away and carry your grades down the drain. Never erase! Just draw *one* line through ~~your errors~~ your errors so that they can still be seen. And never, never, never cut any pages out of the notebook!
3. Leave a few pages at the front for a table of contents.
4. Your notebook is your friend, your confidant. Tell it:

    a. What you have done. Not what it says to do in the lab book. What you, yourself, have done.

    b. Any and *all* observations: color changes, temperature rises, explosions . . . , anything that occurs. Any *reasonable* explanation *why* whatever happened, happened.

5. Skipping pages is *extremely* poor taste. It is NOT done!
6. List the IMPORTANT chemicals you'll use during each reaction. You should include USEFUL **physical properties:** the name of the compound, molecular formula, molecular weight, melting point, boiling point, density, and so. The *CRC Handbook of Chemistry and Physics,* originally published by the Chemical Rubber Company and better known as the *CRC Handbook,* is one place to get this stuff (see Chapter 3, "Interpreting a Handbook").

    Note the qualifier "USEFUL." If you can't use any of the information given, do without it! You look things up *before* the lab so you can tell what's staring back out of the flask at you during the course of the reaction.

Your laboratory experiments can be classified to two major types: a technique experiment or a synthesis experiment. Each requires different handling.

A TECHNIQUE EXPERIMENT

In a technique experiment, you get to practice a certain operation *before* you have to do it in the course of a synthesis. Distilling a mixture of two liquids to separate them is a typical technique experiment.

Read the following handwritten notebook pages with some care and attention to the *typeset* notes in the margin. A thousand words are worth a picture or so (Figs. 2–4).

Notebook Notes

1. Use a descriptive title for your experiment. *Distillation.* This implies you've done *all* there is in the *entire* field of distillation. You haven't? Perhaps all you've done is *The Separation of a Liquid Mixture by Distillation.* Hmmmmmm.
2. Writing that first sentence can be difficult. Try stating the obvious.
3. There are no large blank areas in your notebook. Draw sloping lines through them. Going back to enter observations after the experiment is over is *not professional.* Initial and date pages anytime you write anything in your notebook.
4. Note the appropriate changes in verb tense. Before you do the work, you might use the present or future tense writing about something that *hasn't happened yet.* During the lab, since you are supposed to write what you've actually done just after the time you've actually done it, a simple past tense is sufficient.

A SYNTHESIS EXPERIMENT

In a synthesis experiment, the point of the exercise is to prepare a clean sample of the product you want. All the operations in the lab (e.g., distillation,

Explanatory title

Numbered page

6

9/13/86

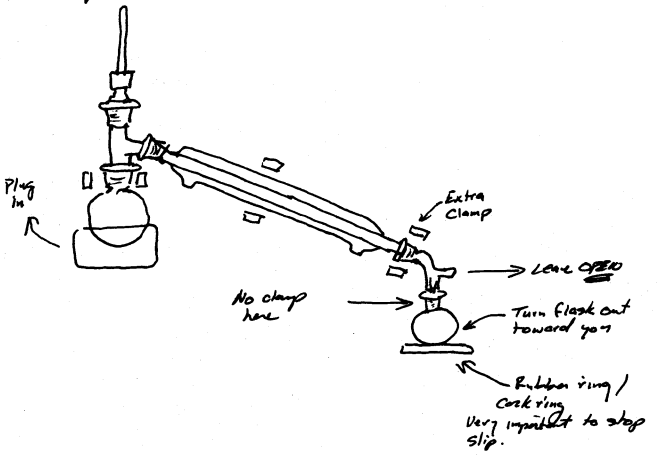
The Separation of a Liquid Mixture by Distillation

This is the Saturday before lab.

Distillation is one of the methods of separation and purification of liquids. We will be given an unknown liquid mixture and will have to separate it by distillation.

It's often hard to start. Hint: state the obvious.

After we get the unknown, should ~~dry it with~~ immediately dry the liquid over anhydrous magnesium sulfate. The setup is as detailed in the laboratory manual with some changes:



Local procedure change, probably from handout.

We will be using Thermowell heaters and will not need Variacs. Vacuum adapter clamped at angle, rotated toward me in order to make it easy to change flasks.

9/13/86 JEG

Fig. 2 Notebook entry for a technique experiment (1).

9/16/86 7

Separation of a Liquid Mixture (cont'd)

Obtained liquid unknown #20 from instructor & dried it over a slight xs of anhydrous magnesium sulfate. Set up distillation apparatus as described (p. 6), started with the smallest flask to collect fore-run as suggested by instructor. Filtered unknown into distilling flask with long-stem funnel. Set heat controller to 50. Mixture beginning to boil.

Instant modification.

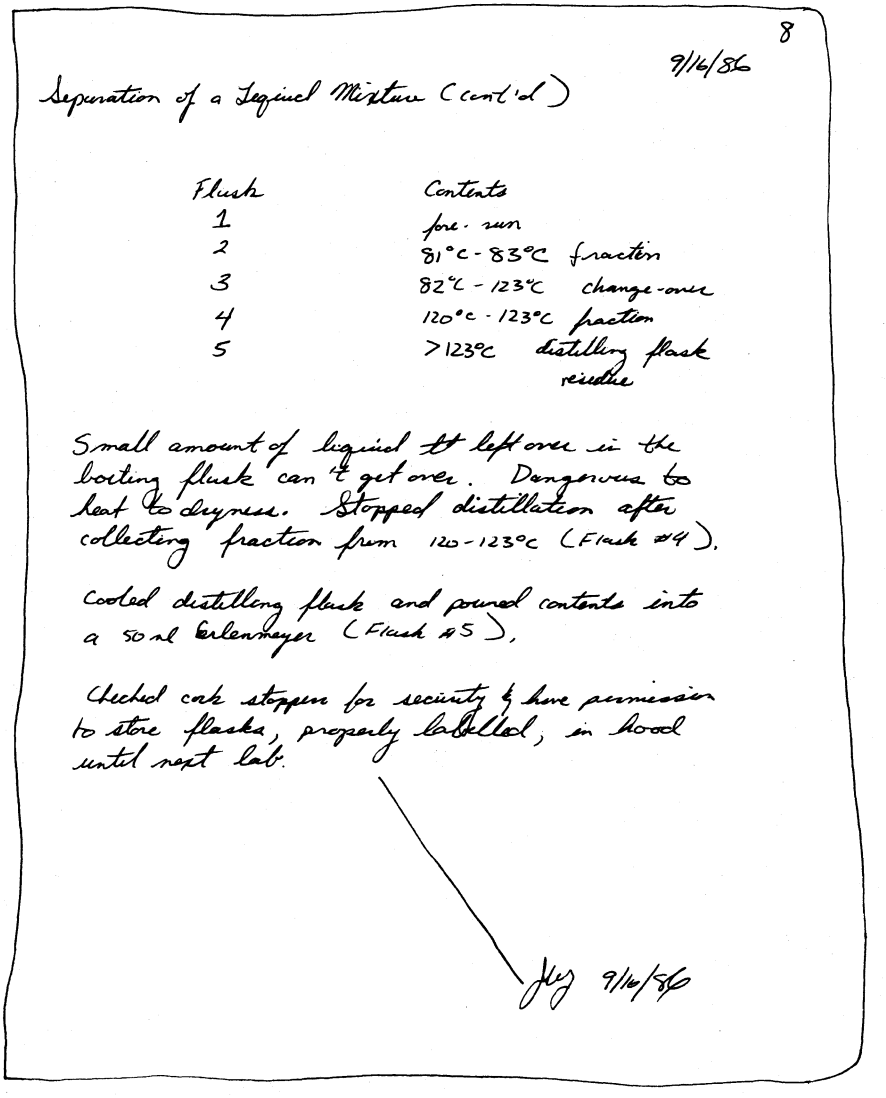
Liquid condensed on thermometer & temperature reading shot up to 79°C and stabilized at 81°C in a few seconds. Collected x 2 ml as fore-run. Will discard this later. Dropped Thermowell to remove heat to stop distillation and change receiving flasks. Started heating again.

Do a bit of work and write a bit of text.

Collected liquid boiling from 81 to 83°C. Changed receiver as above. When new material came over thermometer read 82°C(!) for a few minutes (ml) then distillation stopped. Temperature began dropping! Turned heat up (70). Mixture starting to boil again and liquid came over @ 123°C. Collected a little of this then changed receiver as above. Shook distilling flask a little & added boiling stone before heating. Had to label flasks. So many of them.

9/16/86 Jay

Fig. 3 Notebook entry for a technique experiment (2).



8

9/16/86

Separation of a Liquid Mixture (cont'd)

Flask	Contents
1	fore-run
2	81°C - 83°C fraction
3	82°C - 123°C change-over
4	120°C - 123°C fraction
5	>123°C distilling flask residue

Small amount of liquid ~~it~~ left over in the boiling flask can't get over. Dangerous to heat to dryness. Stopped distillation after collecting fraction from 120-123°C (Flask #4).

Cooled distilling flask and poured contents into a 50 ml Erlenmeyer (Flask #5).

Checked cork stoppers for security & have permission to store flasks, properly labelled, in hood until next lab.

JKG 9/16/86

Fig. 4 Notebook entry for a technique experiment (3).

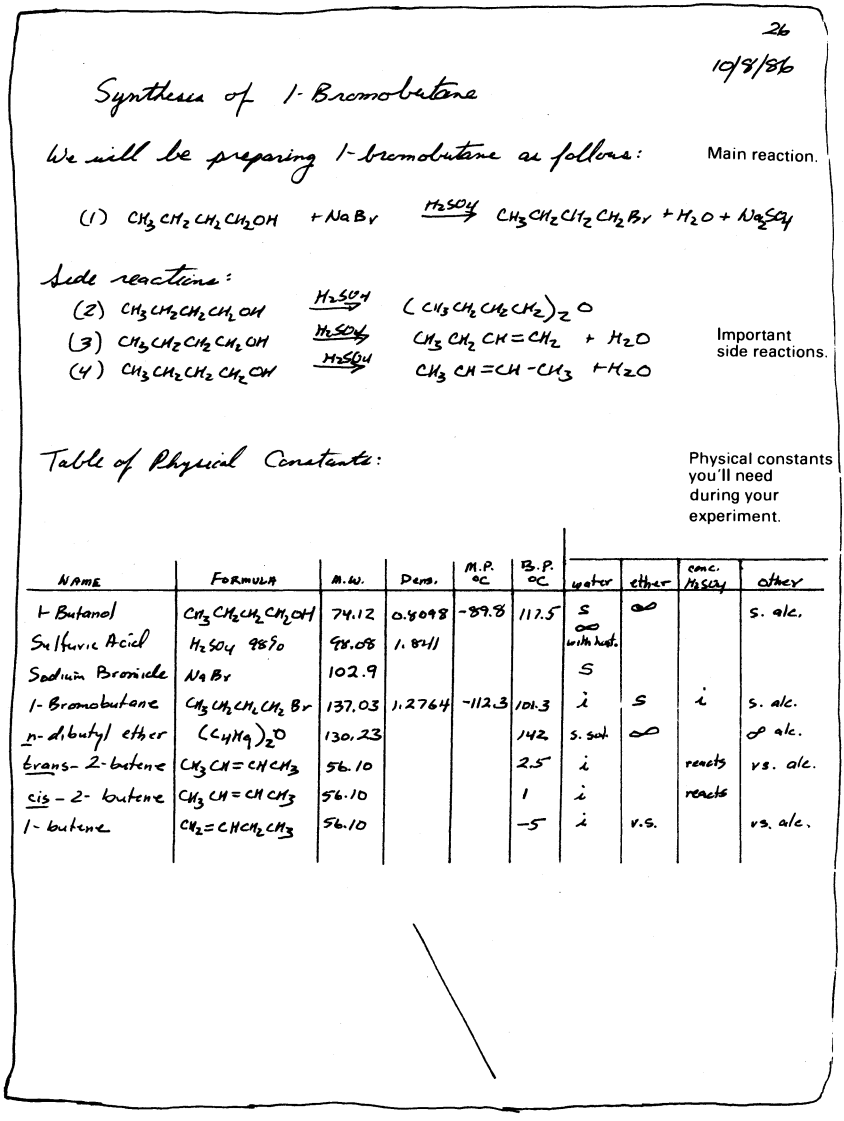
recrystallization, etc.) are just means to this end. The preparation of 1-bromobutane is a classic synthesis, and is the basis of the next series of handwritten notebook pages.

Pay careful attention to the typeset notes in the margins, as well as the handwritten material. Just for fun, go back and see how much was written for the distillation experiment, and how that is handled in this synthesis (Figs. 5–10).

Once again, if your own instructor wants anything different, do it. The art of notebook keeping has many schools — follow the perspective of your own.

Notebook Notes

1. Use a descriptive title for your experiment. *n-Butyl Bromide.* So what? Did you drink it? Set it on fire? What?! *The Synthesis of 1-Bromobutane from 1-Butanol* — now *that's* a title.
2. Do you see a section for unimportant side reactions? No. Then don't include any.
3. In this experiment, we use a 10% aqueous sodium hydroxide solution as a wash (see Chapter 11, "Extraction and Washing"), and anhydrous calcium chloride as a drying agent (see Chapter 7, "Drying Agents"). These are not listed in the Table of Physical Constants. They are neither reactants nor products. Every year, however, somebody always lists the physical properties of *solid* sodium hydroxide, calcium chloride drying agent, and a bunch of other reagents that have nothing to do with the main synthetic reaction. I'm specially puzzled by the listing of solid sodium hydroxide in place of the 10% solution.
4. **Theoretical yield** (not yeild) calculations always seem to be beyond the ken of a lot of you, even though these are exercises right out of the freshman year chemistry course. Yes, we do expect you to remember some things from courses past; the least of which is where to look this up. I've put a sample calculation in the notebook (Fig. 7), that gets the mass (g) of the desired product (1-bromobutane) from the volume (ml) of one reactant (1-butanol). Why from the 1-butanol and not from the sulfuric acid or sodium bromide? It's the 1-butanol we are trying to convert to the bromide, and we use a **molar excess** (often abbreviated XS) of everything else. The 1-butanol is, then, the **limiting reagent;** the reagent



26

10/8/86

Synthesis of 1-Bromobutane

We will be preparing 1-bromobutane as follows: Main reaction.

(1) $CH_3CH_2CH_2CH_2OH + NaBr \xrightarrow{H_2SO_4} CH_3CH_2CH_2CH_2Br + H_2O + Na_2SO_4$

Side reactions: Important side reactions.

(2) $CH_3CH_2CH_2CH_2OH \xrightarrow{H_2SO_4} (CH_3CH_2CH_2CH_2)_2O$

(3) $CH_3CH_2CH_2CH_2OH \xrightarrow{H_2SO_4} CH_3CH_2CH=CH_2 + H_2O$

(4) $CH_3CH_2CH_2CH_2OH \xrightarrow{H_2SO_4} CH_3CH=CH-CH_3 + H_2O$

Table of Physical Constants: Physical constants you'll need during your experiment.

NAME	FORMULA	M.W.	Dens.	M.P. °C	B.P. °C	water	ether	conc. H_2SO_4	other
1-Butanol	$CH_3CH_2CH_2CH_2OH$	74.12	0.8098	-89.8	117.5	S	∞		s. alc.
Sulfuric Acid	H_2SO_4 98%	98.08	1.8411			∞ with heat.			
Sodium Bromide	NaBr	102.9				S			
1-Bromobutane	$CH_3CH_2CH_2CH_2Br$	137.03	1.2764	-112.3	101.3	i	S	i	s. alc.
n-dibutyl ether	$(C_4H_9)_2O$	130.23			142	s. sol.	∞		∞ alc.
trans-2-butene	$CH_3CH=CHCH_3$	56.10			2.5	i		reacts	vs. alc.
cis-2-butene	$CH_3CH=CHCH_3$	56.10			1	i		reacts	
1-butene	$CH_2=CHCH_2CH_3$	56.10			-5	i	v.s.		vs. alc.

Fig. 5 Notebook entry for a synthesis experiment (1).

Calculations from freshman chemistry.

27

10/8/78p

Synthesis of 1-Bromobutane (cont'd.)

Theoretical yield of 1-bromobutane based on 17ml 1-butanol.

Mass of liquid from the density.

$17\ ml\ 1\text{-butanol} \times \frac{0.8098\ g\ 1\text{-butanol}}{1\ ml\ 1\text{-butanol}} = 13.77\ g\ 1\text{-butanol}$

Moles of starting material.

$13.77\ g\ 1\text{-butanol} \times \frac{1\ mole\ 1\text{-butanol}}{74.12\ g\ 1\text{-butanol}} = 0.1857\ moles\ 1\text{-butanol}$

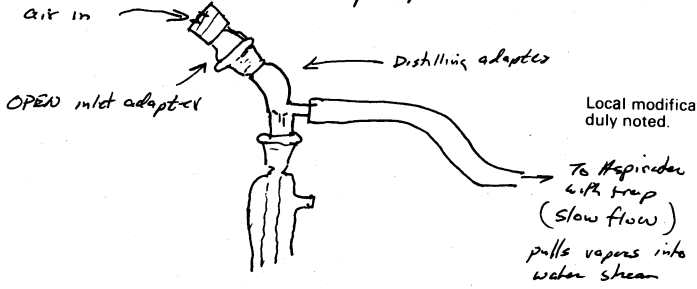
$0.1857\ moles\ 1\text{-butanol} \times \frac{1\ mole\ 1\text{-bromobutane}}{1\ mole\ 1\text{-butanol}} = 0.1857\ moles\ 1\text{-bromobutane}$

$0.1857\ moles\ 1\text{-bromobutane} \times \frac{137.03\ g\ 1\text{-bromobutane}}{1\ mole\ 1\text{-bromobutane}} = 25.44\ g\ 1\text{-bromobutane}$

Moles of product (calculated).

Grams of product (calculated). This is *theoretical yield.*

Apparatus: Reflux setup as in Zubrick with gas (HBr) trap at top of reflux condenser:



Local modification duly noted.

Fig. 6 Notebook entry for a synthesis experiment (2).

25
10/8/86

Syntheses of 1-Bromobutane (cont'd)

Outline of Procedure.

1. Place 24.0 g NaBr, 25 ml water, and 17 ml 1-butanol in a 250 ml R.B. flask and cool in ice-water bath to < 10°C.
2. SLOWLY add 20 ml. conc. H_2SO_4 with swirling.
3. Reflux this mixture over a flame for 30 min.
4. Let mixture cool. Distill mixture - receiver cooled in ice-water bath. Distill until distillate is NOT cloudy.
5. Collect a few drops of clear distillate in a test-tube. Add water and shake tube. If two layers form, continue distilling another 5-10 min. and repeat this test. If two layers do not form, distill for another 5-10 minutes and quit.
6. Wash distillate with 25 ml H_2O.
7. Wash distillate with 15 ml cold conc. H_2SO_4
8. Wash distillate with 15 ml 10% sodium hydroxide solution.
9. Dry with anhydrous $MgSO_4$ & filter (gravity) into small, dry R.B. flask.
10. Distill dried product using dried distillation apparatus.

jwz 10/8/86

Fig. 7 Notebook entry for a synthesis experiment (3).

29

10/9/86

Synthesis of 1-Bromobutane (cont'd.)

Placed 24.0 g NaBr, 25 ml water and 17 ml 1-butanol in a 250 ml R.B. flask & let cool in an ice-bath. When liquid reached 5°C, added H_2SO_4 with swirling. The mixture warmed up and turned a yellow color.

Set up for reflux with gas trap as on p.27. Mixture darkened as reflux continued.

Next step performed while reflux continues.

Placed 15 ml H_2SO_4 in erlenmeyer clamped to cool in ice-water bath for later.

After refluxing 30 min, let reaction mixture cool to room temp, then put in ice-water bath. There are two distinct layers in the flask, both an orange color. Color may be due to free bromine. One of the two layers is product.

Only a phrase recalls the distillation.

Distilled the mixture, and collected everything that came over up to 100°C. Initially, cloudy, white liquid came over (water + organic product?) then clear liquid. Stopped heating distilling flask, removed receiver and replaced it with test-tube in beaker with ice & water. Heated to distill over a few drops of liquid. Added a bit more than an equal amount of water - shook tube. NO LAYERS FORMED! Replaced receiving flask & distilled for 5 min. more.

Poured distillate into a 125 ml erlenmeyer separatory funnel & added 25 ml water. Water went into upper layer - upper layer is aqueous; lower is organic product. Save Lower Layer.

Note the recorded observations.

Fig. 8 Notebook entry for a synthesis experiment (4).

30

10/9/86

Synthesis of 1-Bromobutane (cont'd)

Washed product with the 15 ml cold conc. H_2SO_4. Solution warmed up as it shook flask!

Washed with the 15 ml 10% sodium hydroxide. Added 5 ml water and it stayed in upper layer. Tested aqueous layer with red litmus paper and it turned blue - so organic layer is NOT acidic.

Put product into 50 ml Erlenmeyer and added anhydrous magnesium sulfate in small amounts with swirling. Cloudy product turned clear and XS unused drying agent was swirling in the flask. Corked flask & put it away.

10/9/86 JWZ

10/14/86

Set up for distillation. Removed thermometer and thermometer adapter and put long-stemmed funnel into the flask. Gravity filtered my product directly into distilling flask. Dropped in boiling stone, replaced thermometer & adapter, and distilled liquid. Collected all that came over from 100-103°C

Fig. 9 Notebook entry for a synthesis experiment (5).

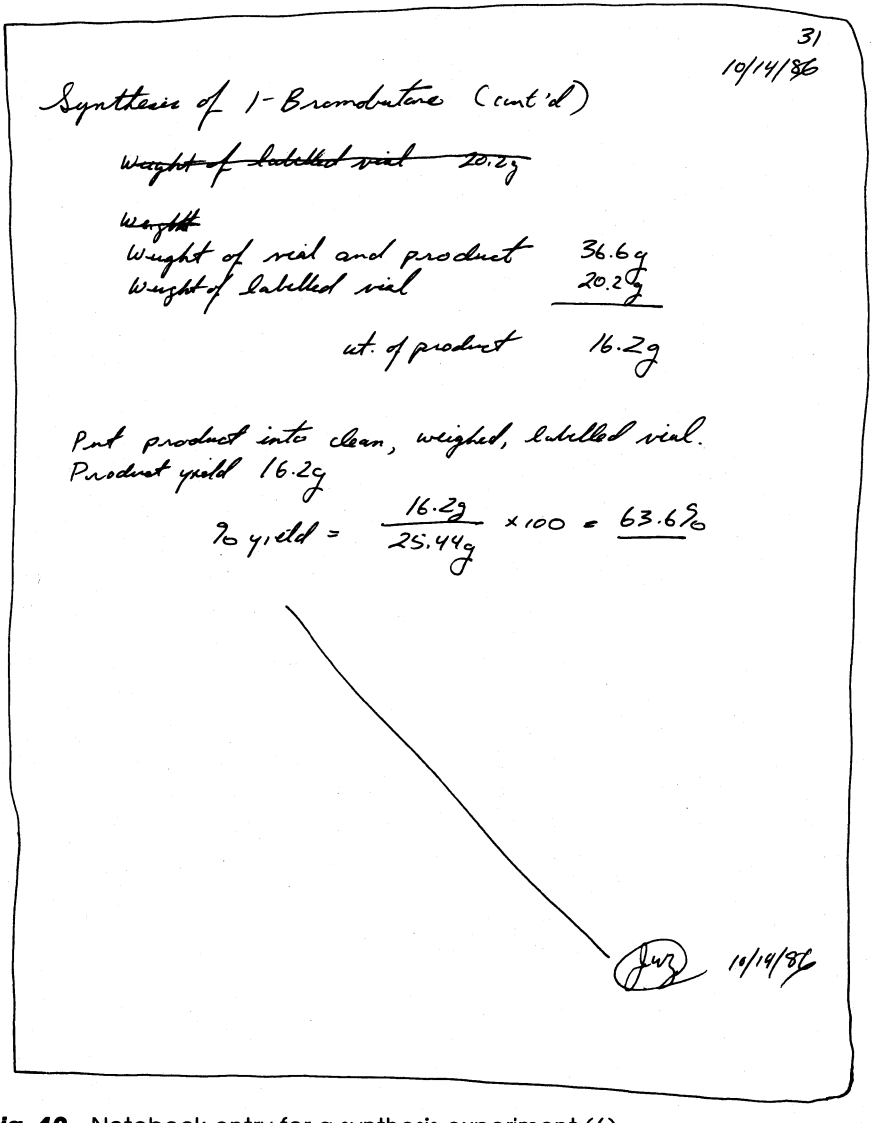


Fig. 10 Notebook entry for a synthesis experiment (6).

present in the smallest molar ratio. Note the use of the density to get from volume to mass (ml to g), molecular weight to go from mass to number of moles (g to mol), the stoichiometric ratio (here 1:1) to get moles of product from moles of limiting reagent, and finally reapplication of molecular weight to get the mass (g) of the product. Note that this mass is *calculated.* It is NOT anything we've actually produced. In THEORY, we get this much. That is theoretical yield.

5. I'm a firm believer in the use of units, factor-label method, dimensional analysis, whatever you call it. I KNOW I've screwed up if my units are (g 1-butanol)^2/mole 1-butanol.
6. Remember the huge writeup on the *Separation of a Liquid Mixture by Distillation,* drawings of apparatus and all? Well, the line "the mixture was purified by distillation," (Fig. 9) is all you write for the distillation during this synthesis.
7. At the end of the synthesis, you calculate the **percent yield.** Just divide the amount you *actually prepared* by the amount you calculated you'd get, and multiply this fraction by 100. For this synthesis, I *calculated* a yield of 25.44 g of product. For this reaction on the bench, I *actually* obtained 16.2 g of product. So:

$$(16.2\text{ g}/\ 25.44\text{ g})(100) = \mathbf{63.6\%\ yield}$$

Interpreting a Handbook

You should look up information concerning any organic chemical you'll be working with so that you know what to expect in terms of molecular weight, density, solubility, crystalline form, melting or boiling point, color, and so on. This information is kept in handbooks that should be available in the lab, if not in the library. Reading some of these is not easy, but once someone tells you what some of the fancy symbols mean, there shouldn't be a problem. Many of the symbols are common to all handbooks, and are discussed only once, so read the entire section even if your handbook is different. There are at least four fairly popular handbooks and I've included sample entries of 1-bromobutane and benzoic acid, a liquid and a solid you might come across in lab, to help explain things.

CRC HANDBOOK

(CRC Handbook of Chemistry and Physics, *CRC Press, Inc., Boca Raton, Florida.)* Commonly called "the *CRC*" as in, "Look it up in the *CRC*." A very popular book; a classic. Sometimes you can get the last year's edition cheaply from the publisher, but it's usually for an order of 10 or more.

Entry: 1-Bromobutane (Fig. 11)

1. ***No. 3683.*** An internal reference number. Other tables in the handbook will use this number, rather than the name.
2. ***Name, . . . Butane, 1-bromo.*** You get a systematic name and a formula.
3. ***Mol. wt. 137.03.*** The molecular weight of 1-bromobutane.
4. ***Color, ...*** Dots! This implies 1-bromobutane is a colorless liquid; nothing special really.
5. ***b. p. 101.6, 18.8^{30}.*** The **normaling boiling point,** at 760 torr, is 101.6°C. The 18.8 has a tiny superscript to tell you that 18.8°C is the boiling point at 30 torr.
6. ***m.p. − 112.4.*** The melting point of solid 1-bromobutane. Handbooks report only the TOP of the melting point range. You, however, should report the *entire* range.

7. ***Density. 1.2758$^{20/4}$.*** Actually, this particular number is a **specific gravity.** This is a mass of the density of the liquid taken at 20°C *referred to* (divided by) the density of the same mass of water at 4°C. That's what the tiny 20/4 means. Notice the units will cancel. A number without the modifying fraction is a true density (in g/ml) at the temperature given.
8. ***n_D 1.4401^{20}.*** This is the index of refraction (see Chapter 22, "Refractometry") obtained using the yellow light from a sodium lamp (the D line). Yes, the tiny 20 means it was taken at 20°C.
9. ***Solubility. al,eth,ace,chl.*** This is what 1-bromobutane must be soluble in. There are a lot of solvents, and here are the abbreviations for some of them:

al	alcohol	eth	ether
bz	benzene	chl	chloroform
peth	petroleum ether	w	water
aa	acetic acid	MeOH	methanol
lig	ligroin	CCl_4	carbon tetrachloride
to	toluene		

Some solvents have such a long tradition of use, they are our old friends and we use very informal names for them:
alcohol. Ethyl alcohol; ethanol.
ether. Diethyl ether; ethoxyethane.
pet. ether. Petroleum ether. Not a true ether, but a low boiling (30–60°C) hydrocarbon fraction like gasoline.
ligroin. Another hydrocarbon mixture with a higher boiling range (60–90°C) than pet. ether.

10. ***Ref. B1^4 258*** Reference to listing in a set of German handbooks called "Beilstein." Pronounce the German "ei" like the long i and stop yourself from saying "Beelsteen" or some such nonsense. 1-Bromobutane is in the fourth supplement (^{4}), Volume 1 (B1) on page 258.

PHYSICAL CONSTANTS OF ORGANIC COMPOUNDS (Continued)

No.	Name, Synonyms, and Formula	Mol. wt.	Color, crystalline form, specific rotation and λ_{max} (log ϵ)	b.p. °C	m.p. °C	Density	n_D	Solubility	Ref.
2531	Benzoic acid $C_6H_6CO_2H$	122.13	mcl lf or nd	249,133[10]	122.13	1.0749[130] 1.2659[15/4]	1.504[12]	al, eth, ace, bz, chl	B9[3], 360
2532	Benzoic acid, 2-acetamido 2-$(CH_3CONH)C_6H_4CO_2H$	179.18	nd (aa)	. . . . .	185	. . . . .	. . . . .	eth, ace, bz	B14[3], 922
3683	Butane, 1-bromo $CH_3CH_2CH_2CH_2Br$	137.03	. . . . .	101.6, 18.8[30]	−112.4	1.2758[20/4]	1.4401[20]	al, eth, ace, chl	B1[4], 258
3684	Butane, 1-bromo-4-chloro $BrCH_2CH_2CH_2CH_2Cl$	171.48	. . . . .	174–5[756], 63–4[10]	. . . . .	1.488[20/4]	1.4885[20]	al, eth, chl	B1[4], 264

Fig. 11 Sample *CRC* entries from the 61st edition.

Entry: Benzoic Acid (Fig. 11)

There are a few differences in the entries, what with benzoic acid being a solid, and I'll point these out. If I don't reexamine a heading, see the explanation back in the 1-Bromobutane entry for details.

1. ***Color, . . . mcl lf or nd.*** Monoclinic leaflets or needles. This is the shape of the crystals. There are many different crystalline shapes and colors and I can't list them all—but here's a few:

pl	plates	mcl	monoclinic
nd	needles	rh	rhombus
lf	leaves	ye	yellow
pr	prisms	pa	pale

   I've included #2532 (Benzoic acid, 2-acetamido) to show that you sometimes get a bonus. Here nd(aa) means you get needle-like crystals from acetic acid. Acetic acid (aa) is the recrystallization solvent (see Chapter 10, "Recrystallization"), and you don't have to find it on your own. Thus, pa ye nd (al) means that pale yellow needles are obtained when you recrystallize the compound from ethanol.
2. ***Density. 1.0749^{130}.*** This is an actual **density** of benzoic acid taken at 130°C. There is no temperature ratio as there is for the specific gravity ($1.2659^{15/4}$).

Nostalgia

I've included the entries from the 43rd and 49th editions of the *CRC* to show you that not all things improve with age.

1. ***General Organization.*** The 43rd and 49th editions make use of **boldface type** to list parent compounds, and lighter type to list derivatives. Benzoic acid is a parent; there are many derivatives (Fig. 12). The 61st edition lists all compounds with the same weight (Fig. 11).
2. ***Solubility tables.*** Here the older editions *really* shine. The 43rd edition gives numerical solubility data for benzoic acid: 0.18^{4}, 0.27^{18}, 2.2^{75}. These

PHYSICAL CONSTANTS OF ORGANIC COMPOUNDS (Continued)

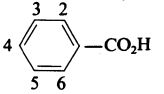
No.	Name	Synonyms and Formula	Mol. wt.	Crystalline form, color and specific rotation	m.p. °C	b.p. °C	Density	n_D	Solubility						Ref.
									w	al	eth	ace	bz	other solvents	
b1239	**Benzoic acid** . .	Benzenecarboxylic acid. 	122.12	mcl lf or nd	122.4	249^{760}	$1.3211^{23.3}$	1.504^{132}	δ	v	. v	. .	v	CCl_4 s lig δ	**B9**[2], 72
b1240	—, 4-acetamidopheyl ester	*p*-Benzoyloxyacetanilide. $C_{16}H_{13}NO_3$. *See* b1239	255.28	nd (al)	171	. . . . .	. . . . .	. . . . .	δ^h	v	. .	. .	v	aa v lig i	. . . . .
	Butane														
b2500	—, **1-bromo-*** .	*n*-Butyl bromide. $CH_2CH_2CH_2CH_2Br$	137.03	. . . . .	−112.3	101.3^{760}	1.2764_4^{20}	1.4398^{20}	1	∞	∞	. .	.	. . . . .	B1[3], 290

Fig. 12 Sample *CRC* entries from the 49th edition.

are the actual solubilities, in grams of benzoic acid per 100 g of water at 4, 18, and 75°C, respectively. The butyl bromide (1-bromobutane) entry has helpful solubility indicators: **i,** *insoluble* in water; ∞, *miscible* in alcohol; ∞, *miscible* in diethyl ether.

There are other abbreviations used for the solubility of a compound. Some of the more popular abbreviations are

s	soluble	i	insoluble
δ	slightly soluble	∞	miscible, mixes in all proportions.
h	solvent must be hot	v	very

What a big change from the 43rd to the 61st edition. Numerical solubility data missing, solubility indications gone, and even incomplete solubility reporting (Benzoic acid: chl, CCl_4, acet., me. al., bz, CS_2–43rd ed.; where are CCl_4, me. al., and CS_2 in the 61st?). The decrease in organizational structure, I can live with. But the new way of presenting the solubility data (what there is of it) is useless for many things you need to do in your lab. Reread the sample synthesis experiment (see Chapter 2, "Keeping a Notebook"). You need more useful solubility data for that experiment than you can extract from the most recent *CRC Handbook.* For my money, you want a fancy $17.50 doorstop, get a *CRC* 61st and up. You want useful information, get a *CRC* 60th and back. Or consult the handbook I want to talk about next.

LANGE'S

(Lange's Handbook of Chemistry, *McGraw-Hill Book Company, New York, New York.)* A fairly well known, but not well used handbook. The entries are similar to those in the *CRC Handbooks* so I'll only point out the interesting differences.

PHYSICAL CONSTANTS OF

No.	Name	Synonyms	Formula	Mol. Wt.
1449	**Benzoic acid** . . .	benzenecarboxylic acid*; phenylformic acid	C_6H_5COOH	122.12
1450	—, allyl ester. . .	allyl benzoate	$C_6H_5COOC_3H_5$ . .	162.18
1451	—, anhydride. .	See *Benzoic anhydride.*		
1452	—, benzyl ester .	benzyl benzoate; benzyl benzenecarboxylate	$C_6H_5COOCH_2C_6H_5$	212.24

*Name approved by the International Union of Chemistry.

846

PHYSICAL CONSTANTS OF

No.	Name	Synonyms	Formula	Mol. Wt.
2160	**Butyl bromide (*n*)** . .	1-bromobutane*	$CH_3(CH_2)_2CH_2Br$.	137.03
2161	***sec*-Butyl bromide** .	2-bromobutane*; methylethylbromomethane	$C_2H_5CH(CH_3)Br$.	137.03
2162	***tert*-Butyl bromide** .	2-bromo-2-methylpropane*; trimethylbromomethane	$(CH_3)_3CBr$	137.03

*Name approved by the International Union of Chemistry.

886

Fig. 13 Sample *CRC* entries from the 41st edition.

Entry: 1-Bromobutane (Fig. 14)

1. ***Name. Butyl bromide(n).*** Here, 1-bromobutane is listed as a substituted butyl group much like in the 43rd *CRC*. The systematic name is listed under synonyms.
2. ***Beil. Ref. I-119.*** The Beilstein reference; Volume 1, page 119, the original work (not a supplement).

ORGANIC COMPOUNDS (Continued)

No.	Crystalline form, color and index of refraction	Density g/ml	Melting point, °C	Boiling point, °C	Solubility in grams per 100 ml of		
					Water	Alcohol	Ether, etc.
1449	col. monocl. leaf. or need., 1.53974^{15}	1.2659^{15}_{4}	122	249	0.18^{4} 0.27^{18} 2.2^{75}	47.1^{15}	40^{15} eth.; s. chl., CCl_3, acet., me. al., bz., CS_2
1450	yel. liq	1.058^{15}_{15}	. . . . .	230	i.	s.	∞ eth.
1451							
1452	col. oily liq., or need. or leaf., 1.5681^{21}	1.114^{18}	21 (18.5)	323–4 (316–7)	i.	s.	s. eth., chl.; i. glyc.

For explanations and abbreviations see beginning of table.

847

ORGANIC COMPOUNDS (Continued)

No.	Crystalline form, color and index of refraction	Density g/ml	Melting point, °C	Boiling point, °C	Solubility in grams per 100 ml of		
					Water	Alcohol	Ether, etc.
2160	col. liq., 1.4398	1.299^{20}_{4}	−112.4	101.6	i.	∞	∞ eth.
2161	col. liq., 1.4344^{25}	1.2580^{20}_{4}	. . . . .	91.3	i.	. . . . .	. . . . .
2162	col, liq., 1.428 .	1.222^{20}_{4}	−20	73.3	i.	. . . . .	. . . . .

For explanations and abbreviations see beginning of table.

887

3. ***Crystalline form . . . lq.*** It's a liquid.
4. ***Specific gravity $1.275^{20/4}$.*** The tiny temperature notation is presented a bit differently, but the meaning is the same.
5. ***Solubility in 100 parts water. 0.06^{16}*** 0.06g of 1-bromobutane will dissolve in 100 g of water at 16°C. After that, no more.

Table 7-4 (*Continued*)
PHYSICAL CONSTANTS OF ORGANIC COMPOUNDS

No.	Name	Synonym	Formula	Beil. Ref.	Formula Weight
711	**Benzoic** acid	. . . . .	$C_6H_5 \cdot CO_2H$	IX-92	122.12
712	Na salt	sodium benzoate	$C_6H_5 \cdot CO_2Na \cdot H_2O$	IX-107	162.12

Benznaphthalide 765 Benzoic acid sulfamide 5671-3

Section 7

Table 7-4 (*Continued*)
PHYSICAL CONSTANTS OF ORGANIC COMPOUNDS

No.	Name	Synonym	Formula	Beil. Ref.	Formula Weight
1040	**Butyl** amine (**sec**)	. . . . .	$(C_2H_5)(CH_3):CH \cdot NH_2$	IV-160	73.14
1041	amine (***iso***)	. . . . .	$(CH_3)_2CH \cdot CH_2 \cdot NH_2$	IV-163	73.14
1057	bromide (***n***)	1-bromo-butane	$C_2H_5 \cdot CH_2 \cdot CH_2Br$	I-119	137.03
1058	bromide (**sec**)	2-bromo-butane	$C_2H_5 \cdot CHBr \cdot CH_3$	I-119	137.03
1059	bromide (***iso***)	1-Br-2-Me-propane	$(CH_3)_2CH \cdot CH_2Br$	I-126	137.03
1060	bromide (***tert***)	2-Br-2-Me-propane	$(CH_3)_3CBr$	I-127	137.03

Butyl borate 6117 Butyl carbinol (***iso***) 406 Butyl carbinol (***tert***) 410
Butyl carbamide 1138-9 Butyl carbinol (**sec**) 411 Butyl carbitol 2232
Butyl carbinol (*n*) 404

Fig. 14 Sample entries from Lange's 11th edition.

Entry: Benzoic Acid (Fig. 14)

1. ***Melting point. subl > 100.*** Benzoic acid starts to **sublime** (go directly from a solid to a vapor) over 100°C, before any crystals left melt at 122.4°C.

ORGANIC CHEMISTRY

Table 7-4 (*Continued*)
PHYSICAL CONSTANTS OF ORGANIC COMPOUNDS

No.	Crystalline Form and Color	Specific Gravity	Melting Point °C.	Boiling Point °C.	Solubility in 100 Parts		
					Water	Alcohol	Ether
711	mn. pr.	$1.316^{25°}_{4°}$	122.4; subl. > 100	250.0	$0.21^{17.5°}$; $2.2^{75°}$	$46.6^{15°}$, abs. al.	$66^{15°}$
712	col. cr.	. . . . .	$-H_2O$, 120	. . . . .	$61^{25°}$; $77^{100°}$	$2.3^{25°}$; $8.3^{75°}$	. . . .

Benzophenone oxide 6451

ORGANIC CHEMISTRY

Table 7-4 (*Continued*)
PHYSICAL CONSTANTS OF ORGANIC COMPOUNDS

No.	Crystalline Form and Color	Specific Gravity	Melting Point °C.	Boiling Point °C.	Solubility in 100 Parts		
					Water	Alcohol	Ether
1040	col. lq.	$0.724^{20°}_{4°}$	−104	66^{772mm}	∞	∞	∞
1041	col. lq.	$0.732^{20°}_{20°}$	−85	68-9	∞	∞	∞
1057	lq.	$1.275^{20°}_{4°}$	−112.4	101.6	$0.06^{16°}$	∞	∞
1058	lq.	$1.261^{20°}_{4°}$	−112.1	91.3	l.	. . . . .	. . . .
1059	lq.	$1.264^{20°}_{4°}$	−117.4	91.4	$0.06^{18°}$	∞	∞
1060	lq.	$1.220^{20°}_{4°}$	−16.2	73.3; d. 210	$0.06^{18°}$	∞	∞

Butyl carbonate 1892-4
Butyl chlorocarbonate 1077-8
Butyl citrate 6119
Butyl cyanide (*n*) 6405
Butyl cyanide (*iso*) 6413
Butyl cyanide (*tert*) 6246

2. ***Crystalline form . . . , mn. pr.*** monoclinic prisms. Here, *mn* is a variant of the *mcl* abbreviation used in the *CRC*. Don't let these small differences throw you. A secret is that all handbooks have a listing of abbreviations at the front of the tables. Shhhh! Don't tell *anyone*. It's a secret.

I like the Lange's format, redolent of the 43rd edition of the *CRC*. The one with the useful information. The organization based on common names, rather than systematic names, can make finding an entry a bit more difficult. There's a miniature gloss at the bottom of each page to help you find related compounds.

Butyl carbinol(n), at the bottom of Fig. 14, has an index number of *404.* If you're familiar with the carbinol naming scheme for alcohols, it isn't much to translate that to 1-pentanol. The entry still comes *before* the B's because Amyl alcohol(n), is another common name for 1-pentanol. On the page where 1-pentanol would show up, there's *only* a gloss entry: *1-Pentanol, 404.* This brings you right back to Amyl alcohol(n). Since most textbooks and labbooks are making it a *very big deal* these days to list none but the purest of pristine systematic nomenclature, you'd likely never expect the compounds to be listed this way, and that is a bit annoying. Even though you are missing out on a bit of the history in the field.

MERCK INDEX

***(The Merck Index,** Merck & Co., Inc., Rahway, New Jersey.)* This handbook is mostly concerned with drugs and their physiological effects. But useful information exists concerning many chemicals. Because of the nature of the listings, I've had to treat the explanations a bit differently than those for the other handbooks.

Entry: 1-Bromobutane (Fig. 15)

1. ***Top of page. 1522 n-Butylbenzene.*** Just like a dictionary, each page has headings directing you to the first entry on that page. So, 1522 is not the page number but the compound number for n-Butylbenzene, the first entry on page 216. The actual page number is at the bottom left of the page.
2. ***n-Butyl Bromide.*** Listed as a substituted butane with the systematic name given as a synonym.

3. ***C 35.06%, . . .*** Elemental analysis data; the percent of each element in the compound.
4. ***Prepd from. . . .*** A short note on how 1-bromobutane has been prepared, and references to the original literature (journals).
5. ***d_4^{25} 1.2686.*** The tiny 25 over 4 makes this a specific gravity. Note that the temperatures are given with the ***d*** and not with the numerical value as in *Lange's* and the *CRC.*

Entry: Benzoic Acid (Fig. 15)

1. ***Line 2. dracylic acid.*** What a synonym! Label your benzoic acid bottles this way and no one will ever "borrow" your benzoic acid again.
2. ***Lines 3–7.*** Natural sources of benzoic acid.
3. ***Lines 7–9.*** Industrial syntheses of benzoic acid. These are usually not appropriate for your lab bench preparations.
4. ***Lines 9–20.*** References to the preparation and characteristics of benzoic acid in the original literature (journals).
5. ***Structure.*** A structural formula of benzoic acid.
6. ***Lines 21–40. Physical data.*** The usual crystalline shape, density (note *two* values reported.), sublimation notation, boiling point data, and so on. *K at 25°* is the ionization constant of the acid; the pH of the saturated solution *(2.8 at 25°C)* is given. The solubility data *(Soly)* is very complete, including water solutions at various temperatures, a bit about the phase diagram of the compound, and solubility in other solvents. Note that numerical data is given where possible.
7. ***Lines 41–67.*** Properties of some salts of benzoic acid.
8. ***Line 68.*** Toxicity data for benzoic acid.
9. ***Lines 69–72.*** Some commercial uses of benzoic acid.
10. ***Lines 73–75.*** Therapeutic uses, both human and veterinary, for benzoic acid.

If all the chemical entries were as extensive as the one for benzoic acid, this would be the handbook of choice. Because benzoic acid has wide use in medi-

1522 ***n*-Butylbenzene**

1526. *n*-Butyl Bromide. *1-Bromobutane.* C_4H_9Br; mol wt 137.03. C 35.06%, H 6.62%, Br 58.32%. $CH_3(CH_2)_3Br$. Prepd from *n*-butyl alc and a hydrobromic-sulfuric acid mixture: Kamm, Marvel, *Org. Syn.* vol. 1, 5 (1921); Skau, McCullough, *J. Am. Chem. Soc.* 57, 2440 (1935). Colorless liquid. d_4^{25} 1.2686. bp_{760} 101.3° (mp −112°). n_D^{20} 1.4398. Insol in water; sol in alcohol, ether.

Page 216 *Consult the cross index before using this section.*

1093. Benzoic Acid. Benzenecarboxylic acid; phenylformic acid; dracylic acid. $C_7H_6O_2$; mol wt 122.12. C 68.84%, H 4.95%, O 26.20%. Occurs in nature in free and combined forms. Gum benzoin may contain as much as 20%. Most berries contain appreciable amounts (around 0.05%). Excreted mainly as hippuric acid by almost all vertebrates, except fowl. Mfg processes include the air oxidation of toluene, the hydrolysis of benzotrichloride, and the decarboxylation of phthalic anhydride: Faith, Keyes & Clark's *Industrial Chemicals*, F. A. Lowenheim, M. K. Moran, Eds. (Wiley-Interscience, New York, 4th ed., 1975) pp 138-144. Lab prepn from benzyl chloride: A. I. Vogel, *Practical Organic Chemistry* (Longmans, London α, 3rd ed, 1959) p 755; from benzaldehyde: Gattermann-Wieland, *Praxis des organischen Chemikers* (de Gruyter, Berlin, 40th ed. 1961) p 193. Prepn of ultrapure benzoic acid for use as titrimetric and calorimetric standard: Schwab, Wicher, *J. Res. Nat. Bur. Standards* 25, 747 (1940). *Review:* A. E. Williams in Kirk-Othmer *Encyclopedia of Chemical Technology* vol. 3 (Wiley-Interscience, New York, 3rd ed., 1978) pp 778-792.

Monoclinic tablets, plates, leaflets. d 1.321 (also reported as 1.266). mp 122.4°. Begins to sublime at around 100°. bp_{760} 249.2°; bp_{400} 277°; bp_{200} 205.8°; bp_{100} 186.2°; bp_{60} 172.8°; bp_{40} 162.6°; bp_{20} 146.7°; bp_{10} 132.1°. Volatile with steam. Flash pt 121-131°. K at 25°: 6.40×10^{-5}; pH of satd soln at 25°: 2.8. Soly in water (g/l) at 0° = 1.7; at 10° = 2.1;

Fig. 15 Sample entries from the Merck Index, 10th edition.

cine and food production, and it is very important to know the physical properties of drugs and food additives, a lot of information on benzoic acid winds up in the *Index*. 1-Bromobutane has little such use, and the size of the entry reflects this. Unfortunately, many of the compounds you come in contact with in the organic laboratory are going to be listed with about the same amount of information you'd find for 1-bromobutane, and not with the large quantities of data you'd find with benzoic acid.

at 20° = 2.9; at 25° = 3.4; at 30° = 4.2; at 40° = 6.0; at 50° = 9.5; at 60° = 12.0; at 70° = 17.7; at 80° = 27.5; at 90° = 45.5; at 95° = 68.0. Mixtures of excess benzoic acid and water form two liquid phases beginning at 89.7°. The two liquid phases unite at the critical soln temp of 117.2°. Composition of critical mixture: 32.34% benzoic acid, 67.66% water: *see* Ward, Cooper, *J. Phys. Chem.* 34, 1484 (1930). One gram dissolves in 2.3 ml cold alc, 1.5 ml boiling alc, 4.5 ml chloroform, 3 ml ether, 3 ml acetone, 30 ml carbon tetrachloride, 10 ml benzene, 30 ml carbon disulfide, 23 ml oil of turpentine; also sol in volatile and fixed oils, slightly in petr ether. The soly in water is increased by alkaline substances, such as borax or trisodium phosphate, *see also* Sodium Benzoate.

Barium salt dihydrate, $C_{14}H_{10}BaO_4.2H_2O$, *barium benzoate.* Nacreous leaflets. *Poisonous!* Soluble in about 20 parts water; slightly sol in alc.
very sol in boiling water.

Calcium salt trihydrate, $C_{14}H_{10}CaO_4.3H_2O$, *calcium benzoate.* Orthorhombic crystals or powder. d 1.44. Soluble in 25 parts water;

Cerium salt trihydrate, $C_{21}H_{15}CeO_6.3H_2O$, *cerous benzoate.* White to reddish-white powder. Sol in hot water or hot alc.

Copper salt dihydrate, $C_{14}H_{10}CuO_4.2H_2O$, *cupric benzoate.* Light blue, cryst powder. Slightly soluble in cold water, more in hot water; sol in alc or in dil acids with separation of benzoic acid.

Lead salt dihydrate. $C_{14}H_{10}O_4Pb.2H_2O$, *lead benzoate.* Cryst powder. *Poisonous!* Slightly sol in water.

Manganese salt tetrahydrate, $C_{14}H_{10}MnO_4.4H_2O$, *manganese benzoate.* Pale-red powder. Sol in water, alc. Also occurs with $3H_2O$.

Nickel salt trihydrate, $C_{14}H_{10}NiO_4.3H_2O$, *nickel benzoate.* Light-green odorless powder. Slightly sol in water; sol in ammonia; dec by acids.

Potassium salt trihydrate, $C_7H_5KO_2$. $3H_2O$, *potassium benzoate.* Cryst powder. Sol in water, alc.

Silver salt. $C_7H_5AgO_2$, *silver benzoate.* Light-sensitive powder. Sol in 385 parts cold water, more sol in hot water; very slightly sol in alc.

Uranium salt, $C_{14}H_{10}O_6U$, *uranium benzoate, uranyl benzoate.* Yellow powder. Slightly sol in water, alc.

Toxicity: Mild irritant to skin, eyes, mucous membranes.

USE: Preserving foods, fats, fruit juices, alkaloidal solns, etc: manuf benzoates and benzoyl compds, dyes; as a mordant in calico printing: for curing tobacco. As standard in volumetric and calorimetric analysis.

THERAP CAT: Pharmaceutic aid (antifungal agent).

THERAP CAT (VET): Has been used with salicylic acid as a topical antifungal.

THE ALDRICH CATALOG

(The Aldrich Catalog. *Aldrich Chemical Co., Inc., Milwaukee, Wisconsin.)* Not your traditional hard-bound reference handbook, but a handy book, nonetheless. The company makes many compounds, some not yet listed in the other handbooks, and often gives structures and physical constants for them. As Aldrich is in the business of selling chemicals to industry, many industrial references are given.

Entry: 1-Bromobutane (Fig. 16)

1. ***1-Bromobutane.*** Here it is listed *strictly* alphabetically as it is — with all the bromo-compounds — not as a butane, 1-bromo-, and only a cross reference as a butyl bromide.
2. ***[109-65-9].*** This is the Chemical Abstracts Service (CAS) Registry number. *Chemical Abstracts,* published by the American Chemical Society, is a listing of the abstract or summary written for any paper in the chemical literature. Every compound made gets a number. This makes for easy searching by computer, as well as by hand.
3. ***bp 100–104°.*** Without a tiny superscript this is the boiling point at 760 torr.
4. ***n_D^{20} 1.4390.*** Index of refraction. The temperature (20°) modifies the *n,* rather than the number as in the *CRC.*
5. ***d 1.276.*** The density in g/cc.
6. ***Fp 75°F(23°C) Flash point.*** Above 75°F, a mixture of 1-bromobutane and air and a spark will go up like gangbusters. Watch out!
7. ***Beil. 1,119.*** The Beilstein reference; Volume 1, page 119.
8. ***Merck Index 10, 1526.*** The Merck Index 10th ed. reference; compound #1526 (Fig. 15).
9. ***MSD Book 1, 236B.*** A reference to the page location of the entry in the *Sigma-Aldrich Library of Chemical Safety Data,* Edition 1.

Benzoic acid, 99+ %, GOLD LABEL, A.C.S. reagent **500g 17.20**
[*65-85-0*] **3kgt 80.65**
24,238-1 $C_6H_5CO_2H$ FW 122.12 mp 122-123° bp 249°
★ Fp 250°F(121°C) *Beil.* **9**,92 Fieser **1**,49 *Merck Index* **10**,1093 *FT-IR* **1**(2),186A *MSD Book* **1**,160A
RTECS# DG0875000 Disp. A *IRRITANT*

10,947-9 **Benzoic acid,** 99%, [*65-85-0*] **500gt 7.00**
★ $C_6H_5CO_2H$ **3kgt 31.00**

23,988-7 **1-Bromobutane,** 99+ %, GOLD LABEL [*109-65-9*] **50g 15.75**
★ (*n*-butyl bromide)
$CH_3(CH_2)_3Br$ FW 137.05 mp −112° bp 100-104°
n_D^{20} 1.4390 d 1.276 Fp 75°F(23°C) *Beil.* **1**,119 *Merck Index* **10**,1526 *MSD Book* **1**,236B *RTECS#* EJ6225000
Disp. D *FLAMMABLE LIQUID IRRITANT*
B5,949-7 **1-Bromobutane,** 99%, [*109-65-9*] (*n*-butyl bromide) **500g 17.40**
★ $CH_3(CH_2)_3Br$ **1kg 23.10**

Fig. 16 Sample entries from the Aldrich catalog, 1986–87.

10. ***RTECS# EJ6225000.*** The reference number in the *Registry of Toxic Effects of Chemical Substances (RTECS).* 1-Bromobutane is on the inventory of the EPA according to the Toxic Substances Control Act, PL9469, October 11, 1976 (TSCA).
11. ***Disp D.*** There are methods of disposal given in the *Aldrich Catalog.* Go to method D and throw 1-bromobutane out according to the rules. Remember, the methods given are for the disposal of large amounts of a single substance, as might be found in an industrial application. The rules for the disposal of the waste generated in your undergraduate laboratory may differ considerably.
12. ***FLAMMABLE LIQUID IRRITANT.*** Yep, it sure is.

Note the differences in prices for the 99+% GOLD LABEL and the merely 99% 1-bromobutane. Before you buy, check on the use of the chemical. Normally, you can buy the least expensive grade of the chemical, and distill or recrystallize it yourself before you use it, if necessary.

Entry: Benzoic Acid (Fig. 16)

1. ***Fieser 1, 49.*** A reference to Fieser & Fieser's *Reagents for Organic Synthesis,* Volume 1, page 49. This multivolume series gives syntheses and reactions of many organic compounds, along with references to the original literature.
2. **†.** Benzoic acid cannot be shipped by parcel post.
3. ***Beil. 9, 92.*** A reference to Beilstein, Volume 9, page 92.
4. ***FT-IR 1(2)186A.*** The Fourier-Transform Infra-Red spectrum of benzoic acid is in Edition 1, Volume 2, page 186A of *The Aldrich Library of FT-IR Spectra.*

NOT CLEAR—CLEAR?

One antonym for **clear** is **cloudy**. Another antonym for **clear** is **colored**. When you say you "obtained a clear liquid," do you mean that it is not cloudy, or that it is colorless?

Cloudiness usually means you've gotten water in your organic liquid. Colorless should be self-explanatory. You should always pair the turbidity and color designations:

"a clear, colorless liquid."
"a clear, blue liquid."
"a cloudy, colorless liquid."
"a cloudy, blue liquid."

I use clear to mean not cloudy, and *water-white* to mean not colored. Water-white is a designation found in the older chemical literature; **colorless** is more modern.

Is that clear?

Jointware

Using **standard taper jointware** you can connect glassware without rubber stoppers, corks, or tubing. Pieces are joined by glass connections built into the apparatus (Fig. 17). They are manufactured in standard sizes, and you'll probably use ₸19/22.

The symbol ₸ means **standard taper.** The first number is the size of the joint at the widest point, in millimeters. The second number is the length of the joint, in millimeters. This is simple enough. Unfortunately, life is not all that simple, except for the mind that thought up this next devious little trick.

STOPPERS WITH ONLY ONE NUMBER

Sounds crazy, no? But with a very little imagination, and even less thought, grave problems can arise from confusing the two. Look at Fig. 18, which shows all glass stoppers are not alike. Interchanging these two leads to **leaking joints** through which your **graded** product can escape. Also, the ₸19/22 stopper is much more expensive than the ₸19 stopper, and you may *have to*

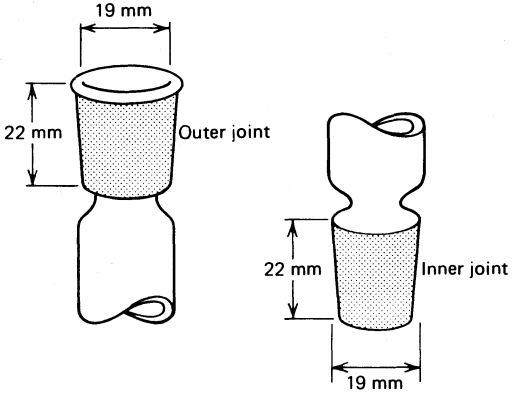


Fig. 17 Standard taper joints (₸ 19/22).

pay money to get the correct one when you check out at the end of the course. Please note the emphasis in those last two sentences. I appeal to your better nature and common sense. So, take some time to check these things out.

As you can see from Fig. 18, that single number is the width of the stopper at its top. There is no mention of the length, and you can see that it is too short. The T19 stopper *does not* fit the T19/22 joint. Only the T19/22 stopper can fit the T19/22 joint. Single-number stoppers are commonly used with volumetric flasks. Again, they will leak or stick if you put them in a double-number joint.

With these delightful words of warning, we continue the saga of coping with ground-glass jointware. Fig. 19 shows some of the more familiar pieces of jointware you may encounter in your travels. They may not be so familiar to you now, but give it time. After a semester or so, you'll be good friends, go to reactions together, maybe take in a good synthesis. Real fun stuff!

These pieces of jointware are the more common pieces that I've seen used in the laboratory. You may or may not have *all* the pieces shown in Fig. 19. Nor will they necessarily be called EXACTLY by the names given here. The point is *find out* what each piece is, and *make sure* that it is in good condition *before* you sign your life away for it.

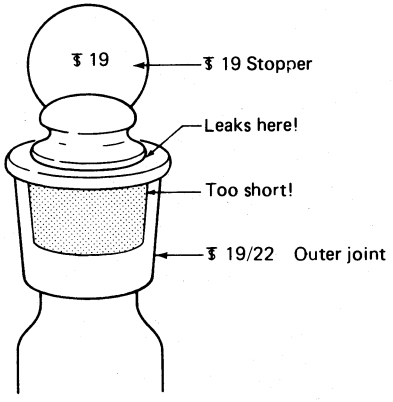


Fig. 18 A T 19 nonstandard stopper in a T19/22 standard taper joint.

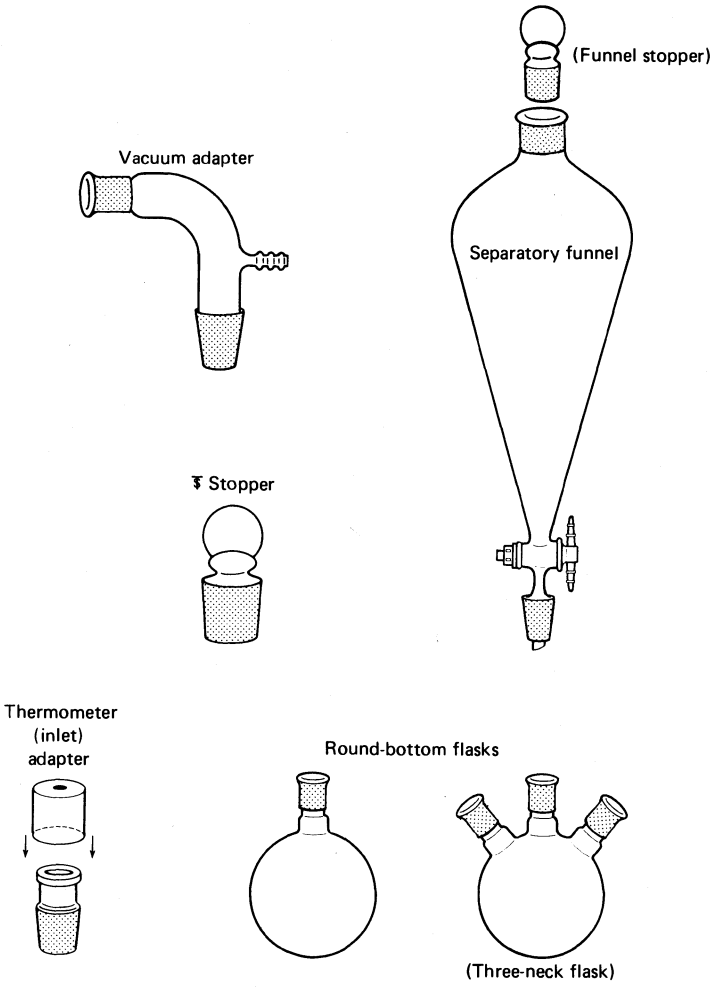
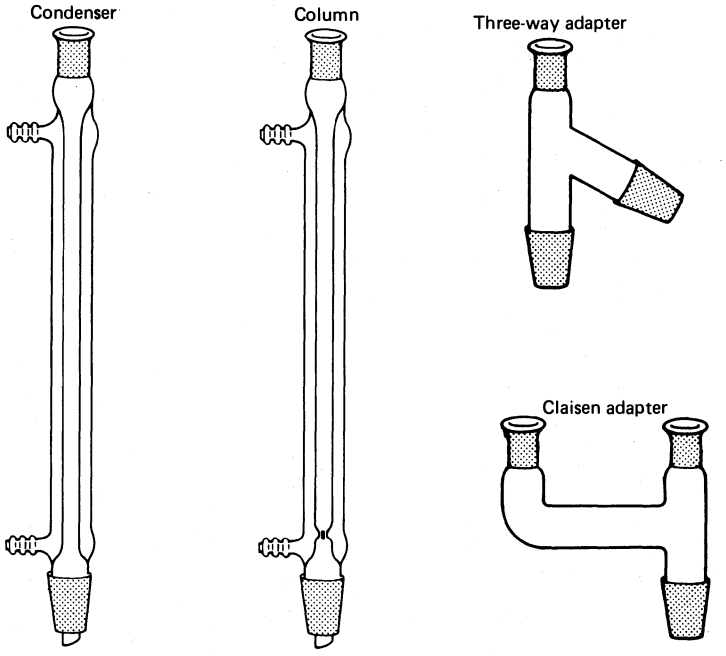


Fig. 19 Some jointware.

ANOTHER EPISODE OF *LOVE OF LABORATORY*

"And that's $28.46 you owe us for the separatory funnel."
"But it was broken when I got it!"
"Should've reported it then."



"The guy at the next bench said it was only a two-dollar powder funnel and not to worry and the line at the stockroom was long anyway, and . . . and . . . anyway the stem was only cracked a little . . . and it worked O.K. all year long . . . Nobody said anything. . . . "
"Sorry."

Tales like these are commonplace, and ignorance is no excuse. Don't rely on expert testimony from the person at the next bench. He may be more confused than you are. And equipment that is "slightly cracked" is much like a person who is "slightly dead." There is no in-between. If you are told that you *must* work with damaged equipment because there is no replacement available, you would do well to get it in writing.

HALL OF BLUNDERS AND THINGS NOT QUITE RIGHT

Round-Bottom Flasks

Round-bottom (R.B.) jointware flasks are so round and innocent looking, that you would never suspect they can turn on you in an instant.

1. ***Star cracks.*** A little talked about phenomenon that turns an ordinary R.B. flask into a potentially explosive monster. Stress, whether prolonged heating in one spot, or indiscriminate trouncing upon hard surfaces, can cause a flask to develop a **star crack** (Fig. 20) on its backside. Sometimes they are hard to see, but if overlooked, the flask can split asunder at the next lab.
2. ***Heating a flask.*** Since they are cold-blooded creatures, flasks show more of their unusual behavior while being heated. The behavior is usually unpleasant if certain precautions are not taken. In addition to star cracks, various states of disrepair can occur, leaving you with a benchtop to clean. Both humane and cruel heat treatment of flasks will be covered in (see Chapter 13, "Sources of Heat"), which is on the SPCG (Society for the Prevention of Cruelty to Glassware) recommended readings list.

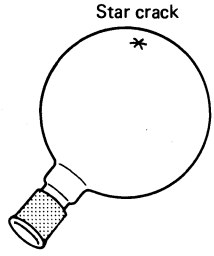


Fig. 20 R. B. flask with star crack.

Columns and Condensers

A word about **distilling columns** and **condensers:**

Different!

Use the **condenser** as is for **distillation** and **reflux** (see Chapter 15, "Distillation," and Chapter 16, "Reflux"). You can use the *column with or without column packing* (bits of metal or glass or ceramic or stainless-steel sponge — whatever)! That's why the column is wider and it has *projections* at the end (Fig. 21). These projections help hold up the column packing if you use any packing at all (see Fig. 80).

If you jam column packing into the skinny condenser, the packing may never come out again! Using a condenser for a packed column is bad form and can lower your esteem or grade, whichever comes first.

You might use the column as a condenser.
Never use the condenser as a packed column!

The Adapter with Lots of Names

Fig. 22 shows the one place where joint and nonjoint apparatus meet. There are two parts: a rubber cap with a hole in it and a glass body. Think of the

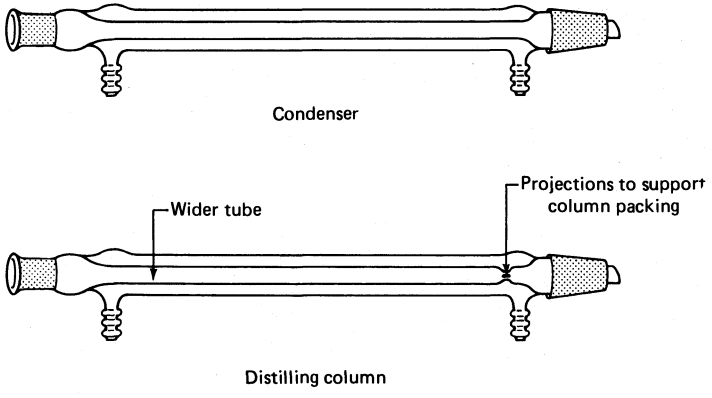


Fig. 21 Distilling column versus condenser.

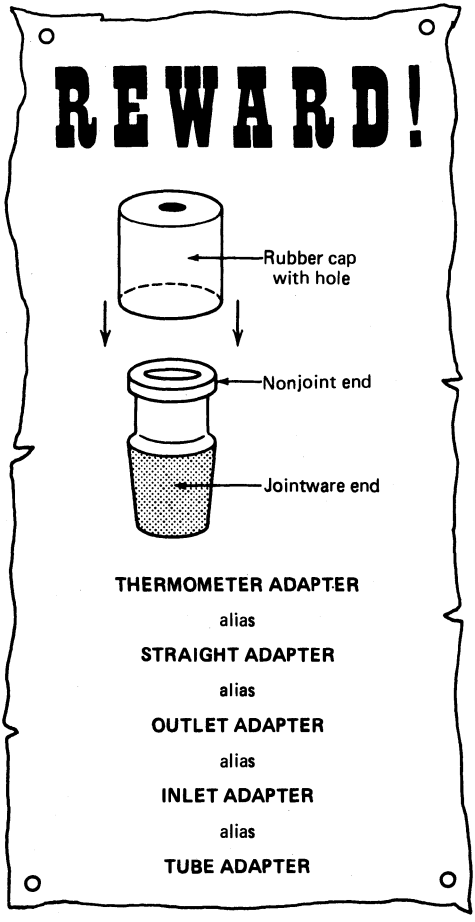


Fig. 22 Thermometer adapter.

rubber cap as a rubber stopper through which you can insert thermometers, inlet adapters, drying tubes, and so on.

CAUTION! Do not force. You might snap the part you're trying to insert. Handle both pieces through a cloth; lubricate (water) and then insert carefully.

The rubber cap fits over the **nonjoint** end of the glass body. The other end is a **ground glass joint** and *fits only other glass joints.* The rubber cap should

neither crumble in your hands nor need a 10-ton press to bend it. If the cap is shot, get a new one. Let's have none of these corks, rubber stoppers, chewing gum, or any other type of plain vanilla adapter you may have hiding in the drawer.

And remember: Not only thermometers, but **anything** that resembles a glass tube can fit in here! This includes unlikely items such as **drying tubes** (they have an outlet tube) and even a **funnel stem** (you may have to couple the stem to a smaller glass tube if the stem is too fat).

The imaginative arrangements shown in Fig. 23 are acceptable.

Forgetting the Glass

Look, the Corning people went to a lot of trouble to turn out a piece of glass (Fig. 24) that fits perfectly in *both* a glass joint *and* a rubber adapter, so *use it!*

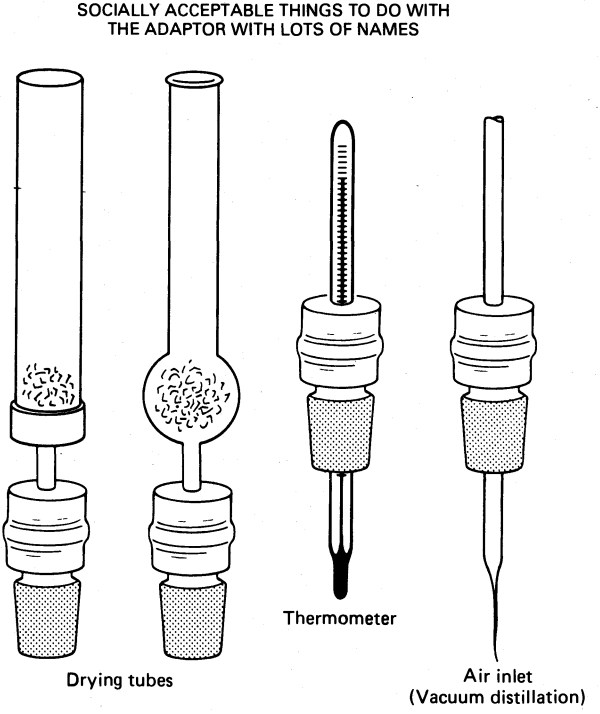


Fig. 23 Unusual, yet proper uses of the adapter with lots of names.

THINGS **NOT** TO DO WITH
THE ADAPTER WITH LOTS OF NAMES

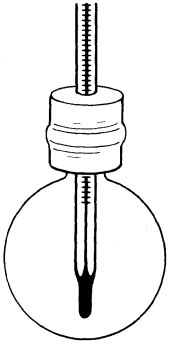


Fig. 24 The glassless glass adapter.

Inserting Adapter Upside Down

This one (Fig. 25) is really ingenious. If you're tempted in this direction, go sit in the corner and repeat over and over,

"Only glass joints fit glass joints"

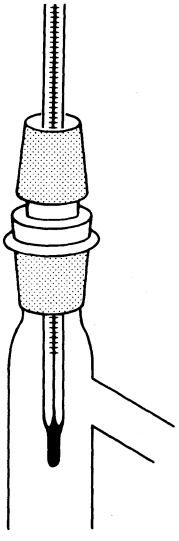


Fig. 25 The adapter stands on its head.

Inserting Adapter Upside Down *Sans* Glass

I don't know whether to relate this problem (Fig. 26) to glass forgetting, or upside-downness, since it is both. Help me out. If I don't see you trying to use an adapter upside down without the glass, I won't have to make such a decision. So, don't do it.

GREASING THE JOINTS

In all my time as an instructor, I've never had my students go overboard on greasing the joints, and they never got them stuck. Just lucky, I guess. Some instructors, however, use grease with a passion, and raise the roof over it. The entire concept of greasing joints is not as slippery as it may seem.

To Grease or Not To Grease

Generally you'll grease joints on two occasions. One, when doing vacuum work to make a tight seal that can be undone; the other, doing reactions with

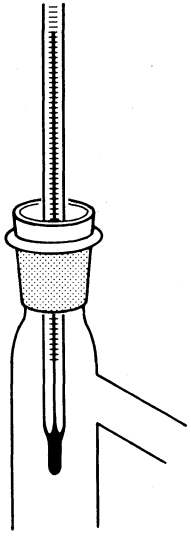


***Fig.* 26** The adapter on its head, without the head.

strong base that can etch the joints. Normally you don't have to protect the joints during acid or neutral reactions.

Preparation of the Joints

Chances are you've inherited a set of jointware coated with 47 semesters of grease. First wipe off any grease with a towel. Then soak a rag in any hydrocarbon solvent (hexane, ligroin, petroleum ether — and *no flames,* these burn like gasoline) and wipe the joint again. Wash off any remaining grease with a strong soap solution. You may have to repeat the hydrocarbon–soap treatments to get a clean, grease-free joint.

Into the Grease Pit (Fig. 27)

First, use only enough to do the job! Spread it thinly along the upper part of the joints, only. Push the joints together with a twisting motion. The joint should turn clear from one third to one half of the way down the joint. *At no time should the entire joint clear!* This means you have *too much grease* and must start back at *Preparation of the Joints.*

Don't interrupt the clear band around the joint. This is called **uneven greasing** and will cause you headaches later on.

STORING STUFF AND STICKING STOPPERS

At the end of a grueling lab session, you're naturally anxious to leave. The reaction mixture is sitting in the joint flask, all through reacting for the day, waiting in anticipation for the next lab. You put the correct glass stopper in the flask, clean up, and leave.

The next time, the stopper is stuck!

Stuck but good! And you can probably kiss your flask, stopper, product and grade goodbye!

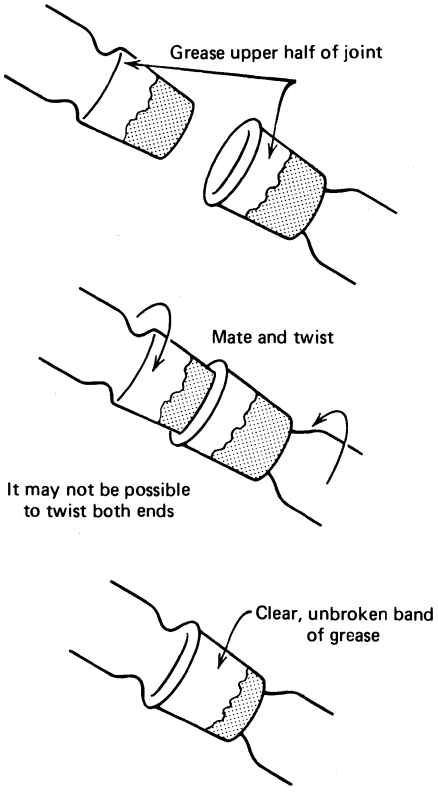


Fig. 27 Greasing ground glass joints.

Frozen!

Some material has gotten into the glass joint seal, dried out, and cemented the flask shut. There are a few good cures, but several excellent preventive medicines.

Corks!

Yes, corks. Old-fashioned, non-stick-in-the-joint corks.

If the material you have to store *does not attack cork,* this is the cheapest, cleanest method of closing off a flask.

A well-greased glass stopper *can* be used for materials that attack cork, but

only if the stopper has a good coating of stopcock grease. Unfortunately, this grease can get into your product.

Do not use rubber stoppers!

Organic liquids can make rubber stoppers swell up like beach balls. The rubber dissolves and ruins your product, and the stopper won't come out either. Ever.

The point is

Dismantle all ground glass joints before you leave!

CORKING A VESSEL

If winemakers corked their bottles like some people cork their flasks, there'd be few oneophiles and we'd probably judge good years for salad dressings rather than wines. You don't just take a new cork and stick it down into the neck of the flask, vial, or what have you. You must press the cork first. Then as it expands, it makes a very good seal and doesn't pop off.

A brand new cork, **before pressing** or **rolling**, should fit only about one-quarter of the way into the neck of the flask or vial. Then you roll the lower half of the cork on your *clean* benchtop to soften and press the small end. *Now* stopper your container. The cork will slowly expand a bit and make a very tight seal (Fig. 28).

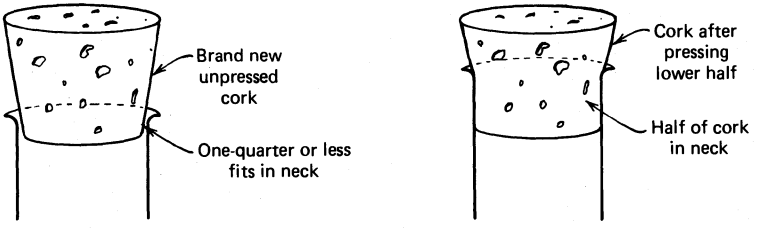


Fig. 28 Corking a vessel.

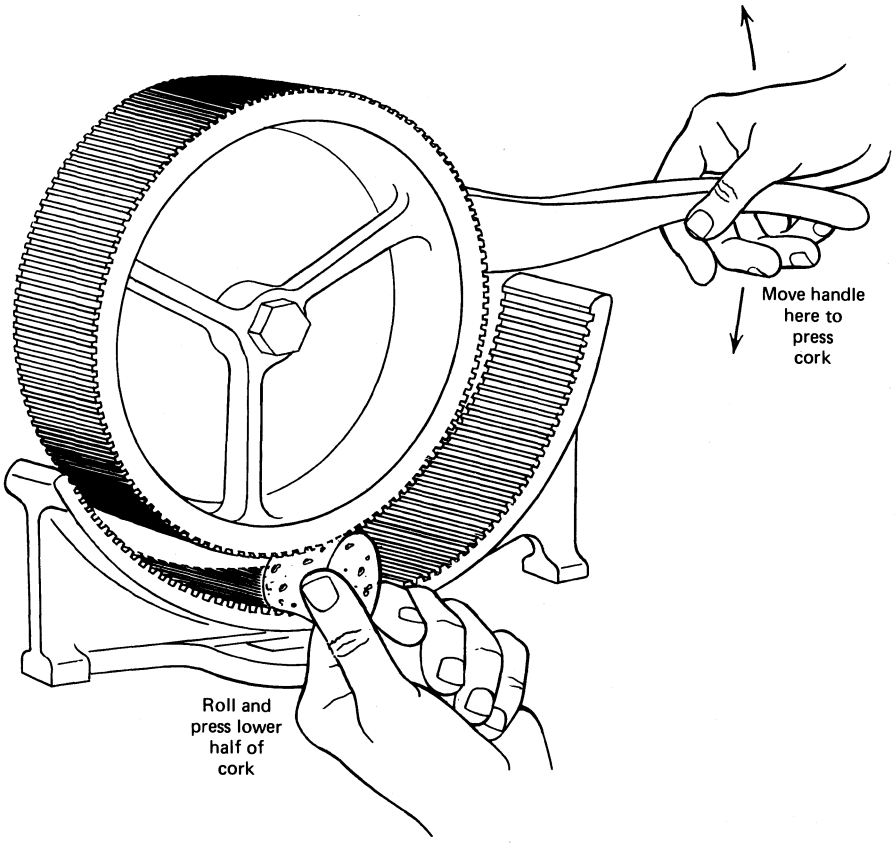


Fig. 29 A wall-mounted cork press.

THE CORK PRESS

Rather than rolling the cork on the benchtop, you might have the use of a **cork press.** You put the small end of the cork into the curved jaws of the press, and when you push the lever up and down, the grooved wheel rolls and mashes the cork at the same time (Fig. 29). Mind your fingers!

Other Interesting Equipment

An early edition of this book illustrated some equipment specific to the State University of New York at Buffalo, since that's where I was when I wrote it. It's now a few years later, and I realize that you can't make a comprehensive list.

Buffalo has an unusual "pear-shaped distilling flask" that I've not seen elsewhere. The University of Connecticut equipment list contains a "Bobbitt Filter Clip" that few other schools have picked up.

So if you are disappointed that I don't have a list and drawing of every single piece of equipment in your drawer, I apologize. Only the most common organic lab equipment is covered here. Ask your instructor "Whattizzit?" if you do not know.

I assume that you remember Erlenmeyer flasks, and beakers and such from the freshman lab. I'll discuss the other apparatus as it comes up in the various techniques. This might force you to read this book before you start lab.

Check out Fig. 30. Not all the mysterious doodads in your laboratory drawer are shown, but the more important are.

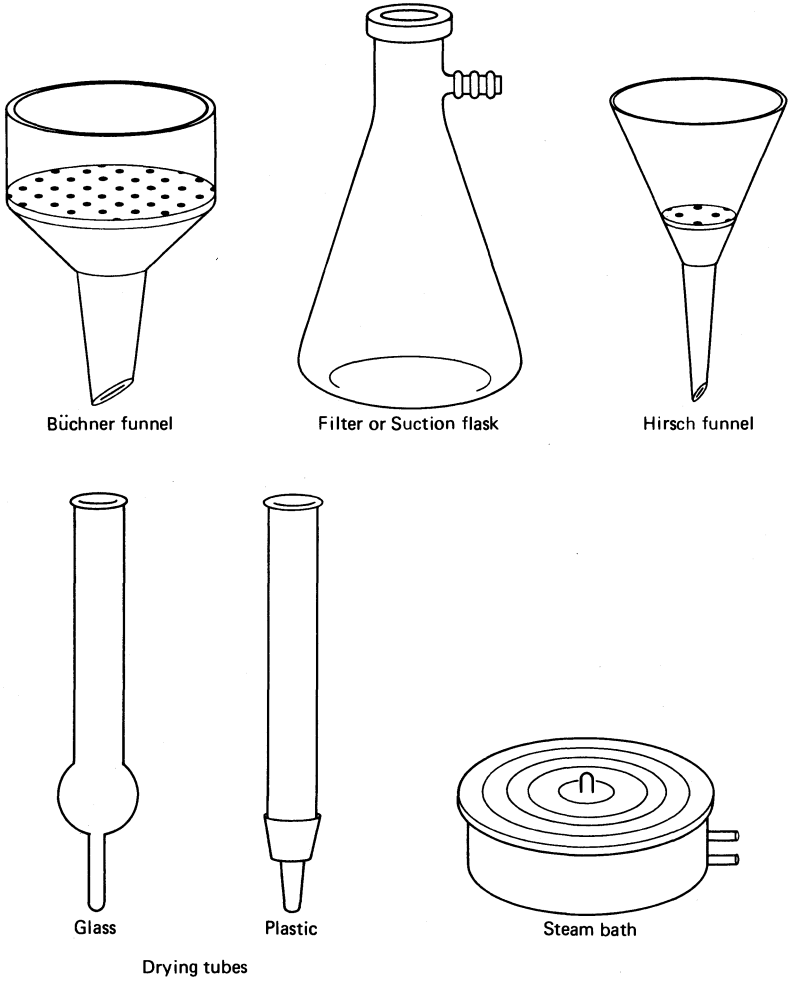


Fig. 30 Some stuff from your lab drawer.

Clean and Dry

Once you've identified your apparatus, you may find you have to clean it.

1. Wash your glassware at the *end* of the lab day. That way you'll have clean and dry glassware, ready to go for the next lab. This may be difficult to do if you perform an experiment on the day you check in.
2. A *little* solvent, a *little* detergent, and a *lot* of elbow grease. These are the correct proportions for a cleaning solution. You do not need all the soap on the planet, nor do you have to fill the glassware to overflowing with soap solution. *Agitation* is the key here. The more you agitate a small amount of soap solution, the less you agitate your instructor by wasting your time and supplies, and the more effective your cleaning will be.
3. Special Buchner funnel cleaning alert. The standard ceramic Buchner funnel is not transparent, and you can't see whether or not the bums who used the funnel the last time to collect a highly colored product, didn't clean the funnel properly. The first time you Buchner filter crystals from an alcohol solution, the colored impurity dissolves, bleeds up into your previously clean crystals, and you may have to redo your entire experiment. I'd rinse the Buchner funnel with a bit of hot ethanol before I used it, just for insurance.

DRYING YOUR GLASSWARE WHEN YOU DON'T NEED TO

"It's late. Why haven't you started the experiment yet?"
"I washed all my glassware and spent half an hour drying it."
"What technique are we doing?"
"Steam distillation."
"Steam goes through the entire setup, does it?"
A nodding head responds.
"What's condensed steam?"
"Water. . . . "

There are all sorts of variations, but they boil down to this: You've taken all this time to dry your glassware only to put water in it. Writers of lab manuals are very tricky about this. Perhaps they say you'll be using *steam.* Or maybe 5% *aqueous* sodium bicarbonate solution. Or even that a byproduct of your reaction is H_2O. Condense *steam* and you get *what?* An *aqueous* solution has *what* for a solvent? H_2O is *what?*

Look for sources of water other than plain water. If a "water-and"mixture is going to be in the equipment anyway, drying to perfection is silly.

DRYING YOUR GLASSWARE WHEN YOU NEED TO

If you wash your glassware *before* you quit for the day, the next time you need it, it'll be clean and dry. There are only a few reactions you might do that need superclean, superdry apparatus, and you should be given special instructions when that's necessary. (In their new book, *Experimental Organic Chemistry,* 2nd. Edition, McGraw-Hill, 1986, authors H. D. Durst and G. W. Gokel make the claim that glassware dried overnight is dry enough for the Grignard reaction, an *extremely* moisture-sensitive reaction, and flame drying can be avoided unless the laboratory atmosphere is extremely humid.)

Don't use the compressed air from the compressed air lines in the lab for drying anything. These systems are full of dirt, oil, and moisture from the pumps, and will get your equipment dirtier than before you washed it.

Yes, there are a few quick ways of drying glassware in case of emergency. You can rinse *very wet* glassware with a small amount of acetone, *drain the glassware very well,* and put the glassware in a drying oven (about 100°C) for a short spell. The acetone not only washes the water off the glassware very well (the two liquids are **miscible**, that is, they mix in all proportions.), the liquid left behind is acetone-rich, and evaporates faster than water. Don't use this technique unless absolutely necessary.

Drying Agents

When you've prepared a liquid product, you must dry the liquid before you finally distill and package it, by treating the liquid with a **drying agent.** Drying agents are usually certain anhydrous salts that combine with the water in your product and hold it as a **water of crystallization.** When all of the water in your sample is tied up with the salt, you gravity filter the mixture. The dried liquid passes through the filter paper and the *hydrated salt* stays behind.

TYPICAL DRYING AGENTS

1. **Anhydrous calcium chloride.** This is a very popular drying agent, inexpensive and rapid, but of late I've become disappointed in its performance. It seems that the calcium chloride powders a bit upon storage and abuse, and this *calcium chloride dust* can go right through the filter paper with the liquid. So a caution: If you must use anhydrous calcium chloride, be sure it is granular. Avoid powdered calcium chloride, or granular anhydrous calcium chloride that's been around long enough to become pulverized. And don't add to the problem by leaving the lid off the jar of drying agent; that's the abuse I was talking about.

   Anhydrous calcium chloride tends to form *alcohols of crystallization,* so you really can't use it to dry alcohols.
2. **Anhydrous sodium carbonate and anhydrous potassium carbonate.** These are useful drying agents that are basically *basic.* As they dry your organic compound, any carbonate that gets dissolved in the tiny amounts of water in your sample can neutralize any tiny amounts of acid that may be left in the liquid. If your product is *supposed* to be acidic (in contrast to being *contaminated* with acid), you should avoid these drying agents.
3. **Anhydrous magnesium sulfate.** In my opinion, anh. $MgSO_4$ is about the best all-around drying agent. It has a drawback, though. Since it is a fine powder, lots of your product can become trapped on the surface. *This is not the same as water of crystallization.* The product is *only on the surface, not inside the crystal structure,* and you may wash your product off.

4. **Drierite.** Drierite, one commercially available brand of anhydrous calcium sulfate, has been around a long time and is a popular drying agent. You can put it in liquids and dry them or pack a drying tube with it to keep the moisture in the air from getting into the reaction setup. But be warned. There is also *Blue Drierite.* This has an indicator, a cobalt salt, that is *blue when dry, pink when wet.* Now you can easily tell when the drying agent is no good. Just look at it. Unfortunately, this stuff is not cheap, so don't fill your entire drying tube with it just because it'll look pretty. Use a small amount mixed with white Drierite, and when the blue pieces turn pink, change the entire charge in your drying tube. You can take a chance using Blue Drierite to dry a liquid directly. Sometimes the cobalt compound dissolves in your product. Then you have to clean and dry your product all over again.

USING A DRYING AGENT

1. Put the liquid or solution to be dried into an Erlenmeyer flask.
2. Add *small* amounts of drying agent and swirl the liquid. When the liquid is no longer cloudy, the water is gone, and the liquid is dry.
3. Add just a bit more drying agent and swirl one final time.
4. Gravity filter through filter paper (see Fig. 44).
5. If you've used a carrier solvent, then evaporate or distill it off, whichever is appropriate. Then you'll have your clean, dry product.

FOLLOWING DIRECTIONS AND LOSING PRODUCT ANYWAY

"Add 5 g of anhydrous magnesium sulfate to dry the product." Suppose your yield of product is lower than that in the book. Too much drying agent — not enough product — Zap! It's all sucked onto the surface of the drying agent. Bye bye product. Bye bye grade.

Add the drying agent slowly to the product in small amounts

Now about those small amounts of product (usually liquids).

1. Dissolve your product in a *low boiling point solvent.* Maybe ether or hexane or the like. Now dry this whole solution, and gravity filter. Remove the solvent carefully. Hoo-ha! Dried product.
2. Use chunky dehydrating agents like anhydrous calcium sulfate (Drierite). Chunky drying agents have a much smaller surface area, so not much of the product gets adsorbed.

On Products

The fastest way to lose points is to hand in messy samples. Lots of things can happen to foul up your product. The following are unforgiveable sins!

SOLID PRODUCTS

1. **Trash in the sample.** Redissolve the sample, gravity filter, then evaporate the solvent.
2. **Wet solids.** Press out on filter paper, break up, let dry. The solid shouldn't stick to the sides of the sample vial. Tacky!
3. **Extremely wet solids (solid floating in water).** Set up a gravity filtration (see "Gravity Filtration") and filter the liquid off of the solid. Remove the filter paper cone with your solid product, open it up, and leave it to dry. Or remove the solid and dry it on fresh filter paper as above. Use lots of care though. You don't want filter paper fibers trapped in your solid.

LIQUID PRODUCTS

1. **Water in the sample.** This shows up as droplets or as a layer of water on the top or the bottom of the vial, or *the sample is cloudy.* Dry the sample with a drying agent (see Chapter 7, "Drying Agents") and gravity filter into a clean dry vial.
2. **Trash floating in the sample.** For that matter, it could be on the bottom, lying there. Gravity filter into a clean, dry vial.
3. **Water in the sample when you don't have a lot of sample.** Since solid drying agents can absorb lots of liquid, what can you do if you have a tiny amount of product to be dried? Add some solvent that has a low boiling point. It must dissolve your product. Now you have a lot of liquid to dry, and *if a little gets lost, it is not all product.* Remove this solvent after you've dried the solution. Be careful if the solvent is flammable. *No flames!*

THE SAMPLE VIAL

Sad to say, but an attractive package can sell an inferior product. So why not sell yours. Dress it up in a **neat new label.** Put on

1. **Your name.** Just in case the sample gets lost on the way to camp.
2. **Product name.** So everyone will know what is in the vial. What does "Product from part C" mean to you? Nothing? Funny, it doesn't mean anything to instructors either.
3. **Melting point (solids only).** This is a range, like "M.P. 96–98°C" (see Chapter 9, "The Melting Point Experiment").
4. **Boiling point (liquids only).** This is a range "B.P. 96–98°C" (see Chapter 15, "Distillation").
5. **Yield.** If you weigh the empty vial and cap, you have the **tare weight.** Now add your product and weigh the full vial. Subtract the *tare weight* from this *gross weight* to get the **net weight** (yield, in grams) of your product.
6. **Percent yield.** Calculate the percent yield (see Chapter 2, "Keeping a Notebook") and put it on the label.

You may be asked for more data, but the things listed above are a good start down the road to good technique.

P.S. Gummed labels can fall off vials, and pencil will smear. *Always use waterproof ink!* And a piece of transparent tape over the label will keep it on.

HOLD IT! DON'T TOUCH THAT VIAL

Welcome to "You Bet Your Grade." The secret word is **dissolve.** Say it slowly as you watch the cap liner in some vials dissolve into your nice, clean product and turn it all goopy. This can happen. A good way to prevent this is to cover the vial with aluminum foil before you put the cap on. Just make sure the product does not react with aluminum. Discuss this at length with your instructor.

The Melting Point Experiment

A **melting point** is the temperature at which the first crystal just starts to melt until the temperature at which the last crystal just disappears. Thus the melting point (abbreviated M.P.) is acually a **melting range.** You should report it as such, even though it is *called* a melting point, for example, M.P. 147–149°C.

People always read the phrase as melting *point* and never as *melting* point. There is this uncontrollable, driving urge to report one number. No matter how much I've screamed and shouted at people *not* to report one number, they almost always do. It's probably because handbooks list only one number, the upper limit.

Generally, melting points are taken for two reasons.

1. ***Determination of purity.*** If you take a melting point of your compound and it starts melting at 60°C and doesn't finish until 180°C you might suspect something is wrong. A melting range *greater than 2°C* usually indicates an impure compound (As with all rules, there are exceptions. There aren't many to this one, though.).

2. ***Identification of unknowns.***

   a. If you have an unknown solid, take a melting point. Many books (ask your instructor) contain tables of melting points and lists of compounds that may have a particular melting point. One of them may be your unknown. You may have 123 compounds to choose from. A little difficult, but that's not all the compounds in the world. Who knows?? Give it a try. If nothing else, you know the melting point.

   b. Take your unknown and mix it *thoroughly* with some chemical you think might be your unknown. You might not get a sample of it, but you can ask. Shows you know something. Then:

      1) If the mixture melts at a *lower* temperature, over a *broad range,* your unknown is NOT the same compound.

      2) If the mixture melts at the *same temperature, same range,* it's a good bet it's the *same compound.* Try another one, though, with a different ratio of your unknown and this compound just to be sure. A *lower* melting point with a *sharp range* would be a special point called a **eutectic mixture,** and you, with all the other

troubles in lab, just might accidentally hit it. On lab quizzes, this is called

"Taking a mixed melting point."

Actually, "taking a mixture melting point," the melting point of a mixture, is more correct. But I have seen this expressed both ways.

SAMPLE PREPARATION

You usually take melting points in thin, closed end tubes called **capillary tubes.** They are also called **melting point tubes** or even **melting point capillaries.** The terms are interchangeable, and I'll use all three.

Sometimes you may get a supply of tubes that are open on *both ends!* You don't just use these as is. Light a burner, and close off one end, *before* you start. Otherwise your sample will fall out of the tube (see "Closing Off Melting Point Tubes," following).

Take melting points on *dry, solid* substances ONLY, *never* on liquids or solutions of solids *in* liquids or on wet or even damp solids.

Only on dry solids!

To help dry damp solids, place the damp solid on a piece of filter paper and fold the paper around the solid. Press. Repeat until the paper doesn't get wet. Yes, you may have to use fresh pieces of paper. Try not to get filter paper fibers in the sample, OK?

Occasionally, you may be tempted to dry solid samples in an oven. *Don't*—unless you are specifically instructed to. I know some students who have decomposed their products in ovens and under heat lamps. With the time they save quickly decomposing their product, they can repeat the entire experiment.

Loading the Melting Point Tube

Place a small amount of *dry* solid on a new filter paper (Fig. 31). Thrust the open end of the capillary tube into the middle of the pile of material. Some

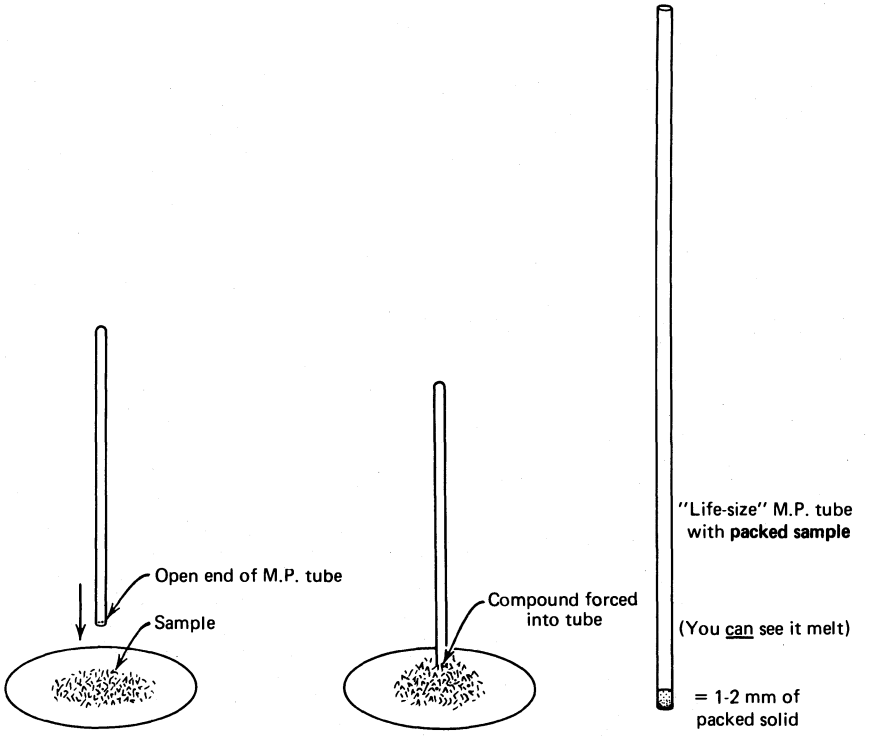


Fig. 31 Loading a melting point tube.

solid should be trapped in the tube. Turn the tube over, closed end down. Remove any solid sticking to the outside. The solid must now be packed down.

Traditionally, the capillary tube, turned upright with the *open end up,* is stroked with a file, or tapped on the benchtop. Unless done *carefully,* these operations *may break the tube.* A safer method is to drop the tube *closed end down,* through a length of glass tubing. You can even use your condenser or distilling column for this purpose. When the capillary strikes the benchtop, the compound will be forced into the closed end. You may have to do this several times. If there is not enough material in the M.P. tube, thrust the open end of the tube into the mound of material and pack it down again. Use your own judgment; consult your instructor.

Use the smallest amount of material that can be seen to melt

Closing Off Melting Point Tubes

If you have melting point tubes that are *open at both ends* and you try to take a melting point with one, it should come as no surprise when your compound falls out of the tube. You'll have to *close off one end,* to keep your sample from falling out (Fig. 32). So light a burner and get a "stiff" small blue flame. SLOWLY touch the end of the tube to the side of the flame, and hold it there. You should get a yellow sodium flame, and the tube will close up. There is no need to rotate the tube. And remember, *touch—just touch*—the edge of the flame, and hold the tube there. Don't feel you have to push the tube way into the flame.

MELTING POINT HINTS

1. Use only the smallest amount that you can see melt. Larger samples will heat unevenly.
2. Pack down the material as much as you can. Left loose, the stuff will heat unevenly.
3. Never remelt any sample. They may undergo nasty chemical changes such as oxidation, rearrangement and decomposition.
4. Make up more than one sample. One is easy, two is easier. If something goes wrong with one, you have another. Duplicate, even triplicate runs are common.

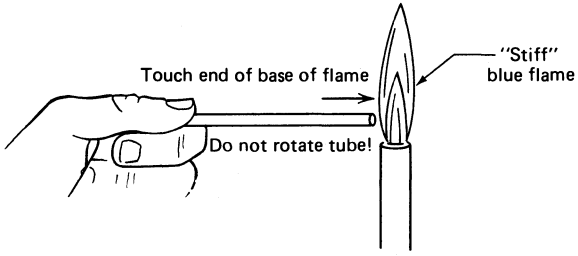


Fig. 32 Closing off a M. P. tube with a flame.

THE MEL-TEMP APPARATUS

The Mel-Temp apparatus (Fig. 33) substitutes for the Thiele tube or open beaker and hot oil methods (see "Using the Thiele Tube"). Before you use the apparatus, there are a few things you should look for.

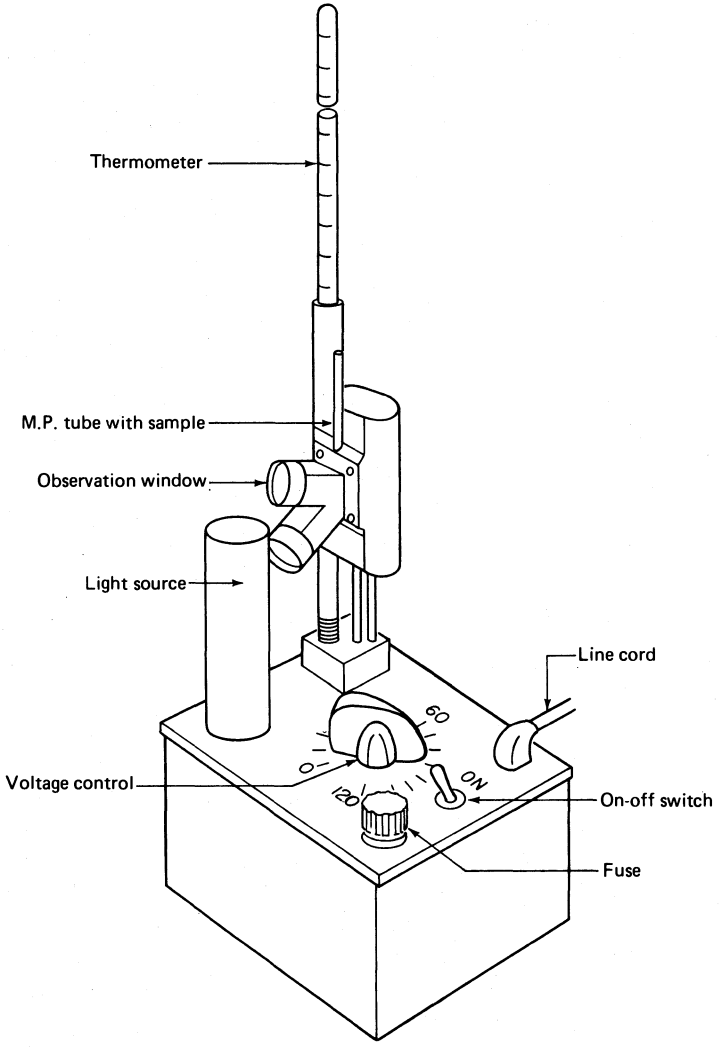


Fig. 33 The Mel-Temp apparatus.

1. ***Line cord.*** Brings a.c. power to unit. Should be plugged into a live wall socket [See J. E. Leonard and L. E. Mohrmann, *J. Chem. Educ.*, **57**,119 (1980), for a modification in the wiring of older units, to make them less lethal. It seems that even with the three-prong plug, there can still be a shock hazard. *Make sure your instructor knows about this!*].
2. ***On–off switch.*** Turns the unit on or off.
3. ***Fuse.*** Provides electrical protection for the unit.
4. ***Voltage control.*** Controls the *rate* of heating, *not the temperature!* The higher the setting, the faster the temperature rise.
5. ***Light source.*** Provides illumination for samples.
6. ***Eyepiece.*** Magnifies the sample (Fig. 34).
7. ***Thermometer.*** Gives temperature of sample, and upsets the digestion when you're not careful and you snap it off in the holder.

OPERATION OF THE MEL-TEMP APPARATUS

1. *Imagine yourself getting burned if you're not careful.* Never assume the unit is cold.

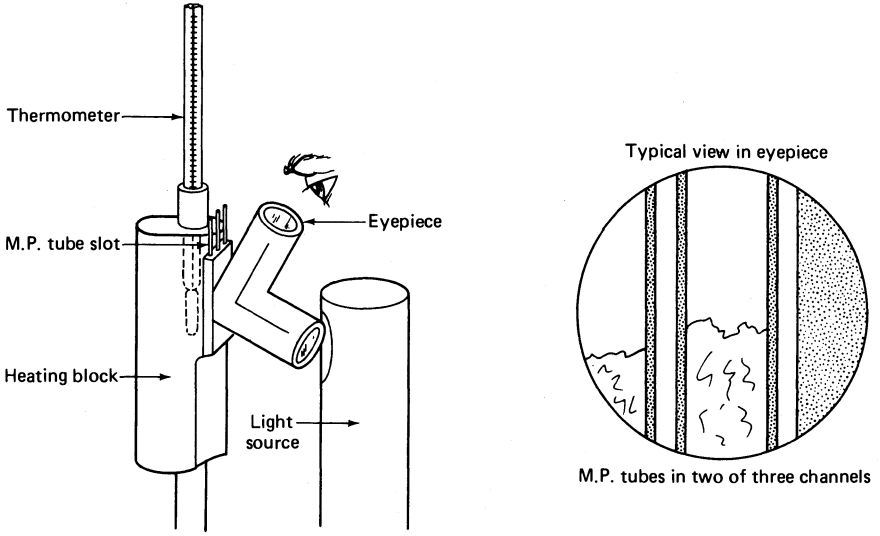


Fig. 34 Closeup of the viewing system.

2. Place loaded M.P. tube in one of the three channels in the opening at the top of the unit (Fig. 34).
3. Set the voltage control to zero if necessary. There are discourteous folk who do not reset the control when they finish using the equipment.
4. Turn the on–off switch to *ON*. The light source should illuminate the sample. If not, call for help.
5. Now science turns into art. Set the *voltage control* to *any* convenient setting. The point is to get up to *within 20°C* of the *supposed* melting point. Yep, that's right. If you have no idea what the melting point is, it may require several runs as you keep skipping past the point with a temperature rise of 5–10°C per minute. A convenient setting is *40*. This is just a suggestion, not an article of faith.
6. After you've melted a sample, *throw it away!*
7. Once you have an idea of the melting point (or looked it up in a handbook, or were told), *get a fresh sample,* and bring the temperature up quickly at about *5–10°C per minute* to *within 20°C* of this approximate melting point. Then turn down the *voltage control* to get a *2°C per minute rise.* Patience!
8. When the first crystals *just start to melt,* record the temperature. When the *last crystal just disappears,* record the temperature. If both points appear to be the same, either the sample is extremely pure, or the temperature rise was *too fast.*
9. Turn the on–off switch to *OFF.* You can set the voltage control to zero for the next person.
10. Remove all capillary tubes.

Never use a wet rag or sponge to quickly cool off the heating block. This might permanently warp the block. You can use a cold metal block to cool it if you're in a hurry. Careful. If you slip, you may burn yourself.

THE FISHER–JOHNS APPARATUS

The Fisher–Johns apparatus (Fig. 35) is different in that you don't use capillary tubes to hold the sample. Instead, you sandwich your sample be-

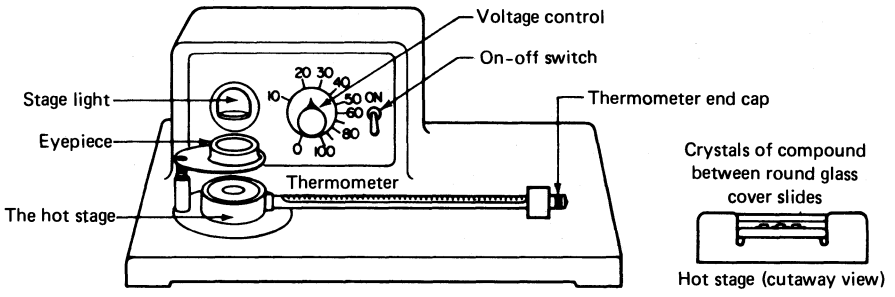


Fig. 35 The Fisher–Johns apparatus.

tween two round microscope cover slides (thin windows of glass) on a heating block. This type of melting point apparatus is called a **hot stage.** It comes complete with spotlight Look for the following.

1. ***Line Cord*** (at the back). Brings a.c. power to unit. Should be plugged into a live wall socket.
2. ***On–off switch.*** Turns the unit on or off.
3. ***Fuse*** (also at the back). Provides electrical protection for the unit.
4. ***Voltage control.*** Controls the *rate* of heating, *not the temperature!* The higher the setting, the faster the temperature rise.
5. ***Stage light.*** Provides illumination for samples.
6. ***Eyepiece.*** Magnifies the sample.
7. ***Thermometer.*** Gives temperature of sample.
8. ***Thermometer end cap.*** Keeps thermometer from falling out. If the cap becomes loose, the thermometer tends to go belly-up, and the markings turn over. Don't try to fix this while the unit is hot. Let it cool so you won't get burned.
9. ***The hot stage.*** This is the heating block that samples are melted on.

OPERATION OF THE FISHER–JOHNS APPARATUS

1. *Don't assume that the unit is cold.* That is a good way to get burned.
2. Keep your grubby fingers off the cover slides. Use tweezers or forceps.

3. Place a clean round glass cover slide in the well on the hot stage. *Never melt any samples directly on the metal stage.* Ever!
4. Put a few crystals on the glass. Not too many. As long as you can see them melt, you're all right.
5. Put another cover slide on top of the crystals to make a sandwich.
6. Set the voltage control to zero if it's not already there.
7. Turn on–off switch to *ON.* The light source should illuminate the sample. If not, call for help!
8. Now science turns into art. Set the *voltage control to any* convenient setting. The point is to get up to *within 20°C* of the *supposed* melting point. Yep, that's right. If you have no idea what the melting point is, it may require several runs as you keep skipping past the point with a temperature rise of 5–10°C per minute. A convenient setting is *40.* This is just a suggestion, not an article of faith.
9. After you've melted a sample, let it cool, and remove the sandwich of sample and cover slides. *Throw it away!* Use an appropriate waste container.
10. Once you have an idea of the melting point (or looked it up in a handbook, or you were told), *get a fresh sample,* and bring the temperature up quickly at about *5–10°C per minute to within 20°C* of this approximate melting point. Then turn down the *voltage control* to get a *2°C per minute rise.* Patience!
11. When the first crystals *just start to melt,* record the temperature. When the last crystal *just disappears,* record the temperature. If both points appear to be the same, either the sample is extremely pure, or the temperature rise was *too fast.*
12. Turn the on–off switch to *OFF.* Now set the voltage control to zero.
13. Let the stage cool, then remove the sandwich.

THE THOMAS–HOOVER APPARATUS

The Thomas–Hoover apparatus (Fig. 36) is the electromechanical equivalent of the Thiele tube or open beaker and hot oil methods (see "Using the Thiele Tube"). It has lots of features, and you should look for the following.

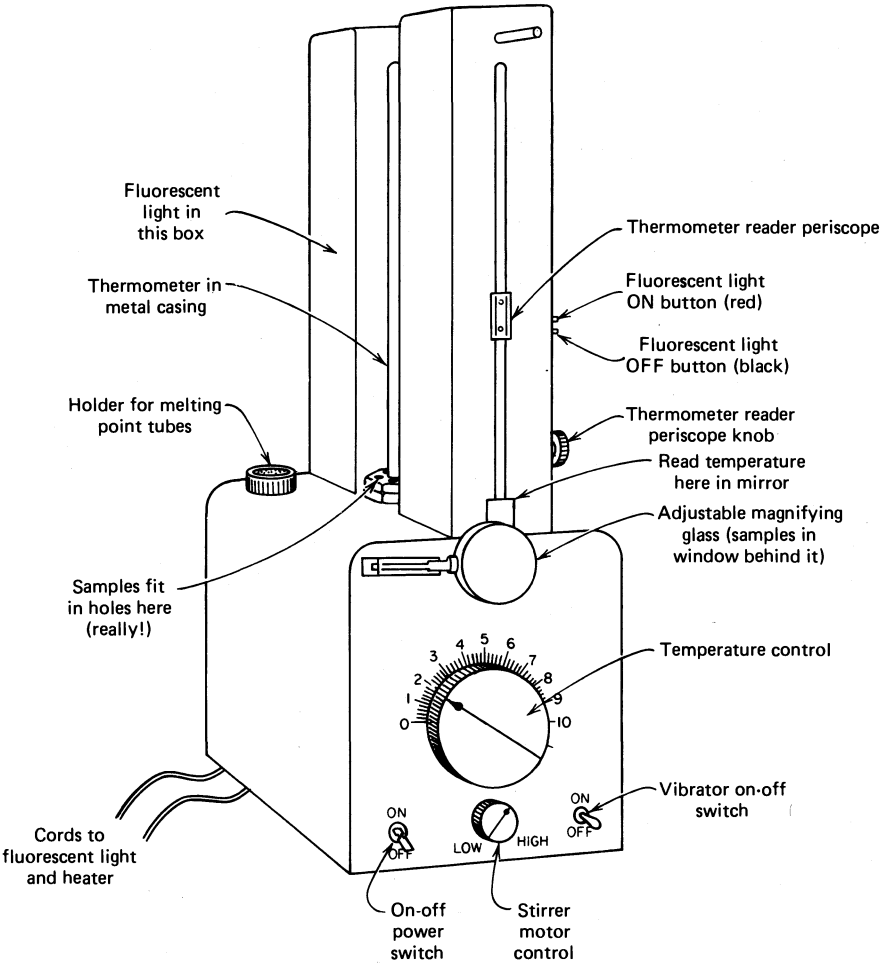


Fig. 36 The Thomas–Hoover apparatus.

1. ***Light box.*** At the top of the device, towards the back, a box holds a fluorescent light bulb behind the thermometer. On the right side of this box are the fluorescent light switches.
2. ***Fluorescent light switches.*** Two buttons. Press and hold the red button down for a bit to light the lamp; press the black button to turn the lamp off.

3. ***Thermometer.*** A special 300° thermometer in a metal jacket is immersed in the oil bath that's in the lower part of the apparatus. Two slots have been cut in the jacket to let light illuminate the thermometer scale from behind, and to let a thermometer periscope read the thermometer scale from the front.
4. ***Thermometer periscope.*** In front of the thermometer, this periscope lets you read a small magnified section of the thermometer scale. By turning the small knob at the lower right of this assembly, you track the movement of the mercury thread, and an image of the thread and temperature scale appear in a stationary mirror just above the sample viewing area.
5. ***Sample viewing area.*** A circular opening cut in the front of the metal case such that you can see your samples in their capillary tubes (and the thermometer bulb) all bathed in the oil bath. You put the tubes into the oil bath through the holes in the capillary tube stage.
6. ***Capillary tube stage.*** In a semicircle about the bottom of the jacketed thermometer, yet behind the thermometer periscope, are five holes through which you can put your melting point capillaries.
7. ***Heat.*** Controls the rate of heating, not the temperature. The higher the setting, the faster the temperature rise. At Hudson Valley Community College, we've had a stop put in and you can only turn the dial as far as the number 7. When it gets up to 10, you always smoke the oil. Don't do that.
8. ***Power on–off switch.*** Turns the unit on or off.
9. ***Stirrer control.*** Sets the speed of the stirrer from low to high.
10. ***Vibrator on–off switch.*** Turns the vibrator on or off. It's a spring-return switch so you must hold the switch in the on position. Let go, and it snaps off.
11. ***Line cords.*** One brings a.c. power to the heater, stirrer, sample light, and vibrator. The other cord brings power to the fluorescent light behind the thermometer. Be sure both cords are plugged into live wall sockets.

OPERATION OF THE THOMAS–HOOVER APPARATUS

1. If the fluorescent light for the thermometer is not lit, press the red button at the right side of the light box and hold it down for a bit to start the lamp. The lamp should remain lit after you release the button.

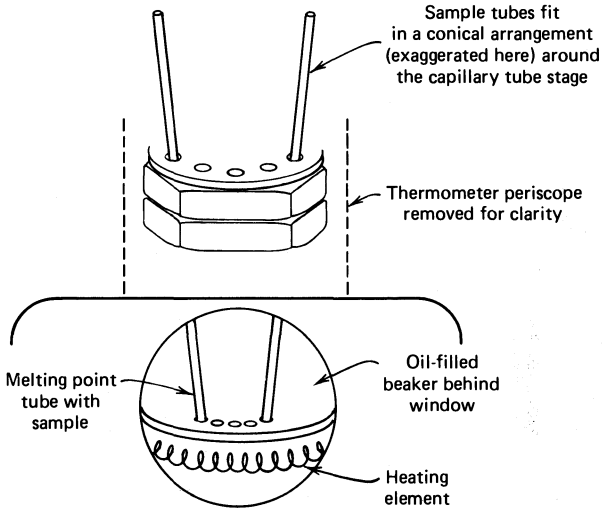


Fig. 37 Closeup of the viewing system.

2. Look in the thermometer periscope, turn the small knob at the lower right of the periscope base, and adjust the periscope to find the top of the mercury thread in the thermometer. Read the temperature. Wait for the oil bath to cool if the temperature is fewer than 20 Celsius degrees below the approximate melting point of your compound. You'll have to wait for a room temperature reading if you have no idea what the melting point is. You don't want to plunge your sample into oil that is so hot it might melt too quickly, or at an incorrect temperature.
3. Turn the voltage control to zero if it isn't there already.
4. Turn the power on–off switch to *ON*. The oil bath should become illuminated.
5. Insert your capillary tube in one of the capillary tube openings in the capillary tube stage. *This is not simple.* Be careful. If you snap a tube at this point, the entire unit may have to be taken apart to remove the pieces. It appears you have to angle the tube toward the center opening and angle the tube toward you (as you face the instrument) at the same time (Fig. 37). It's as if they were placed on the surface of a conical funnel.
6. Adjust the magnifying glass for the best view of your sample.

7. Turn the stirrer knob so that the mark on the knob is about half of the way between the SLOW and FAST markings on the front panel. That's just a suggestion. I don't have any compelling reasons for it.
8. Adjust the thermometer periscope to give you a good view of the top of the mercury thread in the thermometer.
9. Now science turns into art. Set the *heat control* to *any* convenient setting. The point is to get up to *within 20°C* of the *supposed* melting point. If you have no idea what the melting point is, it may require several runs as you keep skipping past the point with a temperature rise of 5–10°C per minute. A convenient setting is *4*. This is just a suggestion, not an article of faith.
10. Remember, you'll have to keep adjusting the thermometer periscope to keep the top of the mercury thread centered in the image.
11. After you've melted a sample, *throw it away!*
12. Once you have an idea of the melting point (or looked it up in a handbook, or were told), *get a fresh sample,* and bring the temperature up quickly at about *5–10°C per minute* to *within 20°C* of this approximate melting point. Then turn down the *heat control* to get a *2°C per minute rise.* Patience!
13. When the first crystals *just start to melt,* record the temperature. When the *last crystal just disappears,* record the temperature. If both points appear to be the same, either the sample is extremely pure, or the temperature rise was *too fast.* If you record the temperature with the horizontal index line in the mirror matched to the lines etched on both sides of the periscope window and the top of the mercury thread at the same time, you'll be looking at the thermometer scale head on. This will give you the smallest error in *reading* the temperature (Fig. 38).
14. Don't turn the control much past 7. You can get a bit beyond 250°C at that setting, and that should be *plenty* for any solid compound you might prepare in this lab. Above this setting, there's a real danger of smoking the oil.
15. Turn the power switch to *OFF.* You can also set the *heat control* to zero for the next person.
16. Press the black button on the right side of the light box and turn the fluorescent light off.
17. Remove all capillary tubes.

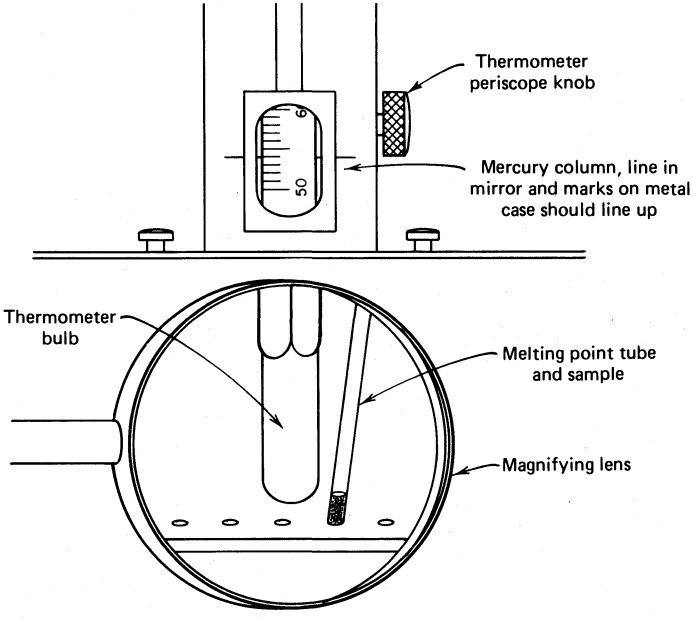


Fig. 38 Reading the temperature.

There are a few more electric melting point apparati around, and much of them work the same. A **sample holder, magnifying eyepiece,** and **voltage control** are common, and an apparently essential feature of these devices is that dial markings are almost *never* temperature settings. That is, a setting of **60** will not give a temperature of 60°C, but probably much higher.

USING THE THIELE TUBE

With the Thiele tube (Fig. 39) you use hot oil to transfer heat evenly to your sample in a melting point capillary, just like the metal block of the Mel-Temp apparatus does. You heat the oil in the sidearm and it expands. The hot oil goes up the sidearm, warming your sample and thermometer as it touches them. Now, the oil is cooler and it falls to the bottom of the tube where it is heated again by a burner. This cycle goes on automatically as you do the melting point experiment in the Thiele tube.

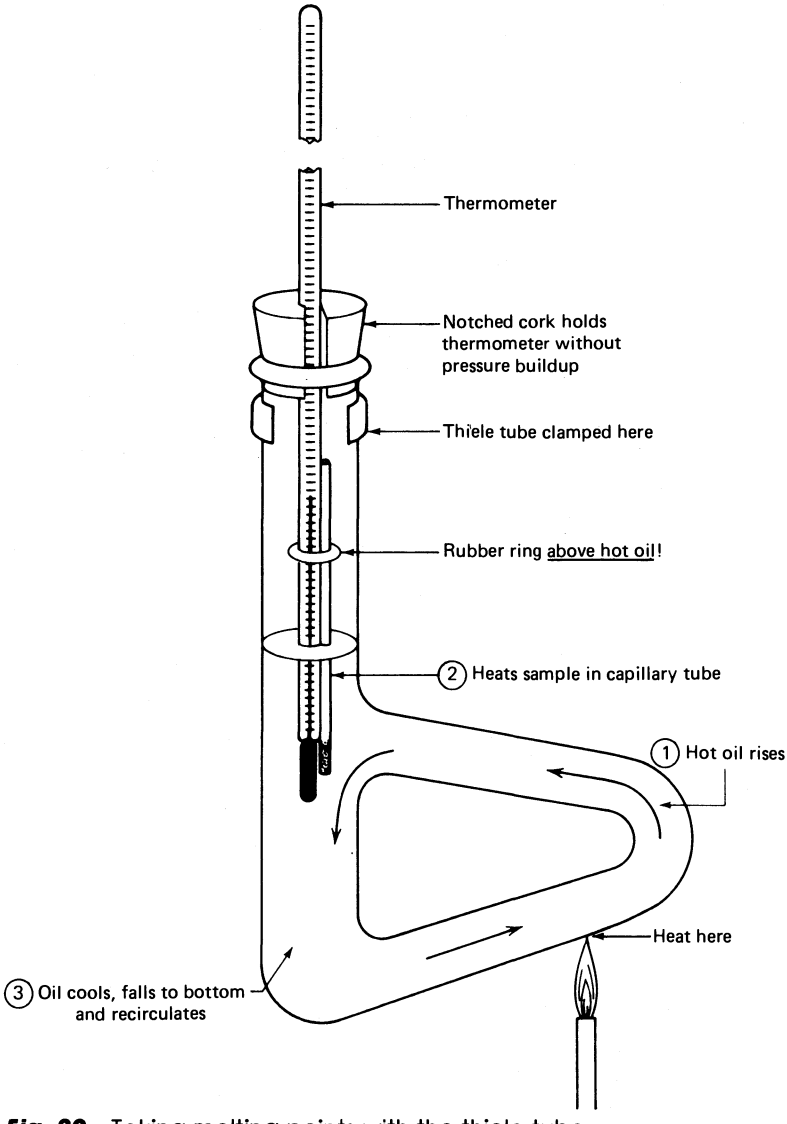


Fig. 39 Taking melting points with the thiele tube.

Don't get any water in the tube or when you heat the tube the water can boil and throw hot oil out at you. Let's start from the beginning.

Cleaning the Tube

This is a bit tricky, so don't do it unless your instructor says so. Also, check with your instructor *before* you put fresh oil in the tube.

1. Pour the old oil out into an appropriate container and let the tube drain.
2. Use a hydrocarbon solvent (hexane, ligroin, petroleum ether—and *no flames!*) to dissolve the oil that's left.
3. Get out the old soap and water and elbow grease, clean the tube, and rinse it out really well.
4. Dry the tube in a drying oven (usually $> 100°C$) thoroughly. Carefully take it out of the oven and let it cool.
5. Let your instructor examine the tube. If you get the OK, *then* add some fresh oil. Watch it. First, *no water.* Second, don't overfill the tube. Normally, the oil expands as you heat the tube. If you've overfilled the tube, oil will crawl out and get you.

Getting the Sample Ready

Here you use a loaded melting point capillary tube (see "Loading the Melting Point Tube") and attach it directly to the thermometer. The thermometer, unfortunately, has bulges; there are some problems, and you may snap the tube while attaching it to the thermometer.

1. Get, or cut, a thin rubber ring from a piece of rubber tubing.
2. Put the *bottom* of the loaded M.P. tube *just above* the place where the thermometer constricts (Fig. 40), and carefully roll the rubber ring onto the M.P. tube.
3. Reposition the tube so that the sample is near the center of the bulb and the rubber ring is near the open end. *Make sure the tube is vertical.*

Dunking the Melting Point Tube

There are more ways of keeping the thermometer suspended in the oil than I care to list. You can cut or file a notch on the side of the cork, drill a hole, and

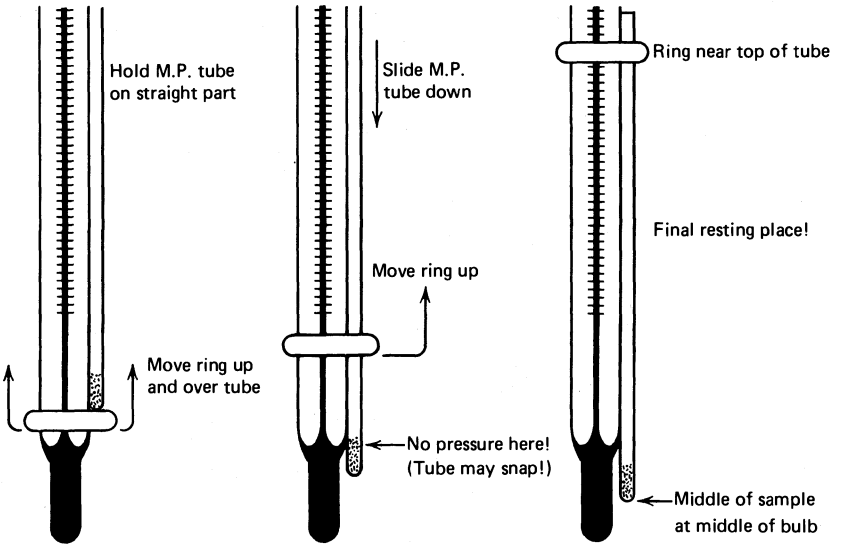


Fig. 40 Attaching M. P. tube to thermometer without a disaster.

insert the thermometer *(Be careful!)* Finally, cap the Thiele tube (Fig. 39). The notch is there so that pressure will not build up as the tube is heated. *Keep the notch open, or the setup may explode.*

But this requires drilling or boring corks, something you try to avoid (why have ground glass jointware in the undergraduate lab?). You can *gently* hold a thermometer and a cork in a clamp (Fig. 41). Not too much pressure, though!

Finally, you might put the thermometer in the **thermometer adapter** and suspend that, clamped gently by the rubber part of the adapter, not by the ground glass end. Clamping ground glass will score the joint.

Heating the Sample

The appropriately clamped thermometer is set up in the Thiele tube as in (Fig. 39). Look at this figure *now* and remember to heat the tube *carefully — always carefully — at the elbow. Then:*

1. If you don't know the melting point of the sample, heat the oil fairly quickly, *but no more than 10°C per minute* to get a rough melting point.

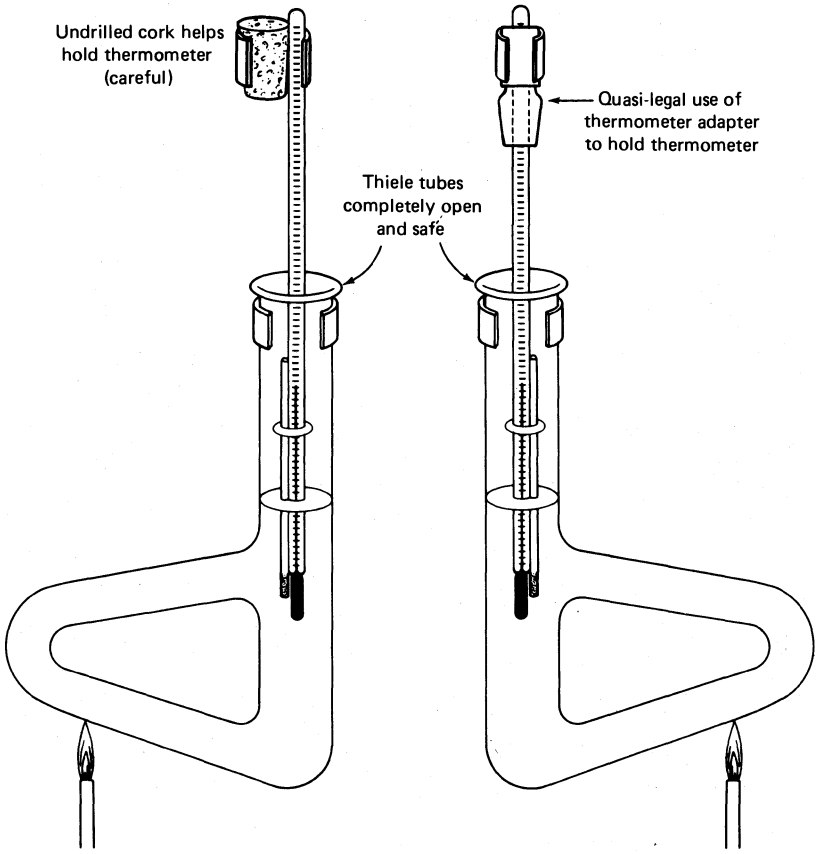


Fig. 41 Safely suspended thermometer with Thiele tube.

And it will be rough indeed, since the temperature of the thermometer usually lags that of the sample.

2. After this sample has melted, lift the thermometer and attached sample tube *carefully (it may be HOT)* by the thermometer up at the clamp, until they are *just out of the oil.* This way the thermometer and sample can cool, and the hot oil can drain off. Wait for the thermometer to cool to about room temperature before you remove it entirely from the tube. Wipe off some of the oil, reload a melting point tube *(never remelt melted samples),* and try again. And heat at 2°C per minute this time.

Recrystallization

The essence of a recrystallization is a **purification.** Messy, dirty, compounds are cleaned up, purified, and can then hold their heads up in public again. The sequence of events you use will depend a lot on how messy your crude product is, and just how soluble it will be in various solvents.

In any case, you'll have to remember a few things.

1. Find a solvent that will *dissolve the solid while hot.*
2. The same solvent *should not dissolve it while cold.*
3. The *cold solvent* must keep impurities dissolved in it *forever or longer.*

This is the major problem. And it requires some experimentation. That's right! Once again, art over science. Usually, you'll know what you should have prepared, so the task is easier. It requires a trip to **your notebook,** and possible, a **handbook** (see Chapter 2, "Keeping a Notebook" and Chapter 3, "Interpreting a Handbook"). You have the data on the solubility of the compound in your notebook. What's that you say? *You don't have the data in your notebook?* Congratulations, you get the highest F in the course.

Information in the notebook (which came from a handbook) for your compound might say, for alcohol (meaning *ethyl* alcohol), **s.h.** Since this means **s**oluble in **h**ot alcohol, it implies **i**nsoluble in cold alcohol (and you wondered what the **i** meant). Then alcohol is probably a good solvent for recrystallization of that compound. Also, check on the **color** or **crystalline form.** This is important since

1. A color in a supposedly white product is an impurity.
2. A color in a colored product is *not* an impurity.
3. The *wrong color* in a product is an impurity.

You can usually assume impurities are present in small amounts. Then you don't have to guess what possible impurities might be present or what they

might be soluble or insoluble in. If your sample is really dirty, the assumption can be fatal. This doesn't usually happen in an undergraduate lab, but you should be aware of it.

FINDING A GOOD SOLVENT

If the solubility data for your compound are not in handbooks, then

1. Place 0.1 g of your solid (weighed to 0.01g) in a test tube.
2. Add 3 ml of a solvent, stopper the tube, and shake the bejesus out of it. If *all of the solid dissolves at room temperature,* then your solid is **soluble.** Do *not* use this solvent as a recrystallization solvent. (You must make note of this in your notebook, though).
3. If none (or very little) of the solid dissolved at room temperature, unstopper the tube and heat it (*Careful — no flames!*) and shake it and heat it and shake it. You may have to heat the solvent to a gentle boil (*Careful!* Solvents with low boiling points often boil away). If it does *not* dissolve at all, then do not use this as a recrystallization solvent.
4. If the sample *dissolved when HOT,* and *did NOT dissolve at room temperature,* you're on the trail of a good recrystallization solvent. One last test.
5. Place this last test tube in an ice-water bath, and cool it to about 5°C or so. If lots of crystals come out, this is good, and this is your recrystallization solvent.
6. Suppose your crystals don't come back when you cool the solution. Get a glass rod into the test tube, stir the solution, rub the inside of the tube with the glass rod, agitate that solution. If crystals still don't come back, perhaps you'd better find another solvent.
7. Suppose, after all this, you still haven't found a solvent. Look again. Perhaps your compound *completely* dissolved in ethanol at room temperature, and would *not* dissolve in water. AHA! Ethanol and water are **miscible** (i.e., they mix in all proportions) as well. You will have to perform a **mixed-solvent recrystallization** (see "Working with a Mixed-Solvent System").

GENERAL GUIDELINES FOR A RECRYSTALLIZATION

Here are some general rules to follow for purifying any solid compound.

1. Put the solid in an Erlenmeyer flask, not a beaker. If you recrystallize compounds in beakers, you may find the solid climbing the walls of the beaker to get at you as a reminder. A 125-ml Erlenmeyer usually works. Your solid should look comfortable in it, neither cramped, nor with too much space. You probably shouldn't fill the flask more than one fifth to one fourth full.
2. Heat a large quantity of a proven solvent (see preceding) to the boiling point, and *slowly add the hot solvent. Slowly!* A word about solvents: *Fire!* Solvents burn! *No flames!* A hot plate here would be better. You can even heat solvents in a *steam or water bath.* But — *No flames!*
3. Carefully add the hot solvent to the solid to just dissolve it. This can be tricky, since hot solvents evaporate, cool down, and so on. Ask your instructor.
4. Add a slight excess of the hot solvent (5–10 ml) to keep the solid dissolved.
5. If the solution is only slightly colored, the impurities will stay in solution. Otherwise, the big gun, **activated charcoal,** may be needed (see "Activated Charcoal"). Remember, if you were working with a colored compound, it would be silly to try to get rid of all the color, since you would get rid of all the compound and probably all your grade.
6. Keep the solvent hot (*not boiling*) and look carefully to see if there is any trash in the sample. This could be old boiling stones, sand, floor sweepings, and so on. Nothing you'd want to bring home to meet the folks. *Don't confuse real trash with undissolved good product!* If you add more hot solvent, good product will disolve, and trash will not. If you have trash in the sample, do a **gravity filtration** (see following).
7. Let the Erlenmeyer flask and the hot solution cool. Slow cooling gives better crystals. Garbage doesn't get trapped in them. But this can take what seems to be an interminable length of time. (I know, the entire lab seems to take an interminable length of time.) So, after the flask cools and it's just *warm* to the touch, then put the flask in an ice-water bath to cool. *Watch it!* The flasks have a habit of turning over in the water baths

and letting all sorts of water destroy all your hard work! Also, a really hot flask will shatter if plunged into the ice bath, so again, watch it.

8. When you're through cooling, filter the crystals on a **Buchner funnel.**
9. Dry them and take a melting point, as described in Chapter 9.

GRAVITY FILTRATION

If you find yourself with a flask full of hot solvent, your product dissolved in it, along with all sorts of trash, this is for you. You'll need more hot solvent, a ringstand with a ring attached, possibly a clay triangle, some filter paper, a clean, dry flask, and a **stemless funnel.** Here's how **gravity filtration** works.

1. Fold up a **filter cone** out of a piece of filter paper (Fig. 42). It should fit nicely, within a single centimeter or so of the top of the funnel. For those who wish to filter with more panache, try using **fluted filter paper** (see "world famous fan-folded fluted filter paper," Fig. 52).
2. Get yourself a **stemless funnel,** or, at least, a **short-stemmed funnel.** Why? Go ahead and *use* a stem funnel and watch the crystals come out in the stem as the solution cools, blocking up the funnel (Fig. 43).
3. Put the **filter paper cone** in the **stemless funnel.**
4. Support this in a ring attached to a ringstand (Fig. 44). If the funnel is too small and you think it could fall through the ring, you may be able to get a **wire** or **clay triangle** to support the funnel in the ring (Fig. 45).

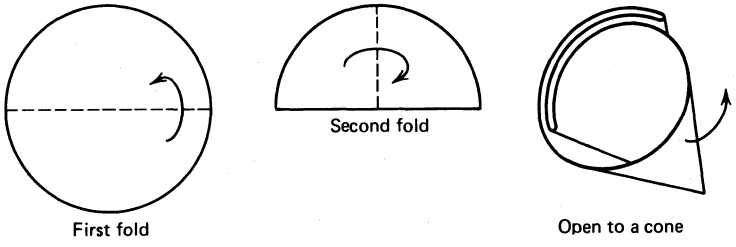


Fig. 42 Folding filter paper for gravity filtration.

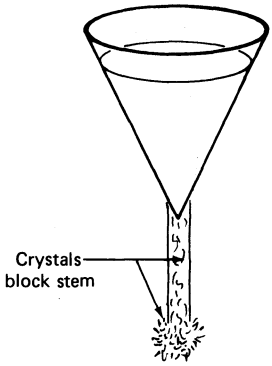


Fig. 43 The too long a funnel stem—Oops!

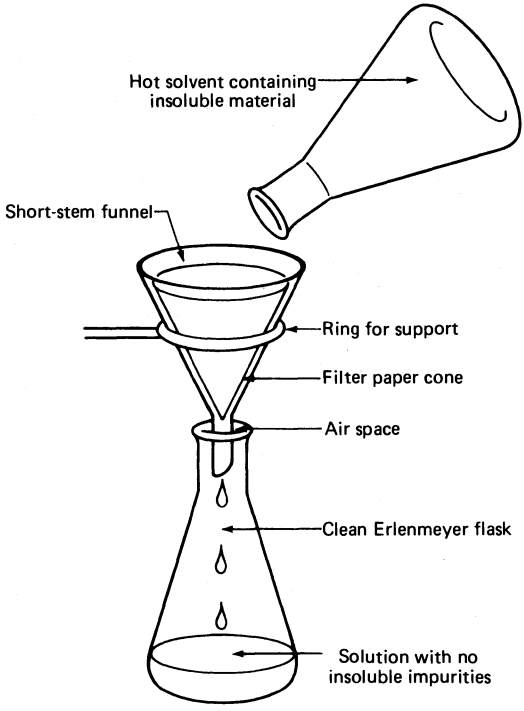


Fig. 44 The gravity filtration setup with a funnel that fits the iron ring.

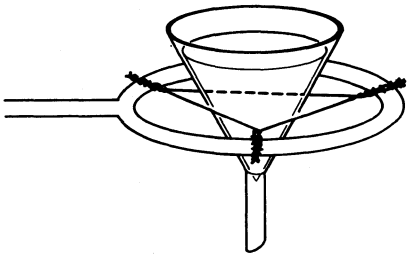


Fig. 45 A wire triangle holding a small funnel in a large iron ring for gravity filtration.

5. Put the new, *clean, dry flask* under the funnel to catch the hot solution as it comes through. All set?
6. Get that flask with the solvent, product and trash hot again. (*No flames!*) You should get some fresh, clear solvent hot as well. (*No flames!*)
7. Carefully pour the hot solution into the funnel. As it is, some solvents evaporate so quickly that product will probably come out on the filter paper. It is often hard to tell the product from the insoluble trash. Then—
8. Wash the filter paper down with *a little hot solvent.* The product will redissolve. The trash won't.
9. You now let the *trash-free* solution cool and clean crystals should come out. Since you have probably added solvent to the solution, *don't be surprised if no crystals come out of solution. Don't panic either!* Just boil away some of the solvent, let your solution cool, and wait for the crystals again. If they *still* don't come back, just repeat the boiling.

Do not boil to dryness!

Somehow, lots of folk think recrystallization means dissolving the solid, then boiling away all the solvent to dryness. *NO!* There must be a way to convince these lost souls that *the impurities will deposit on the crystals.* After the solution has cooled, crystals come out, sit on the bottom of the flask, and *must be covered by solvent!* Enough solvent to keep those nasty impurities dissolved and off the crystals.

THE BUCHNER FUNNEL AND FILTER FLASK

The **Buchner funnel** (Fig. 46) is used primarily for separating crystals of product from the liquid above them. If you have been *boiling your recrystallization solvents dry, you should be horsewhipped* and forced to reread these sections on recrystallization!

1. Get a piece of filter paper large enough to cover all the holes in the bottom plate, yet *not* curl up the sides of the funnel. It is placed *flat* on the plate (Fig. 46).
2. Clamp a **filter flask** to a ringstand. This filter flask, often called a **suction flask,** is a very heavy-walled flask with a sidearm on the neck. A piece of heavy-walled tubing connects this flask to the **water trap** (see Fig. 48).

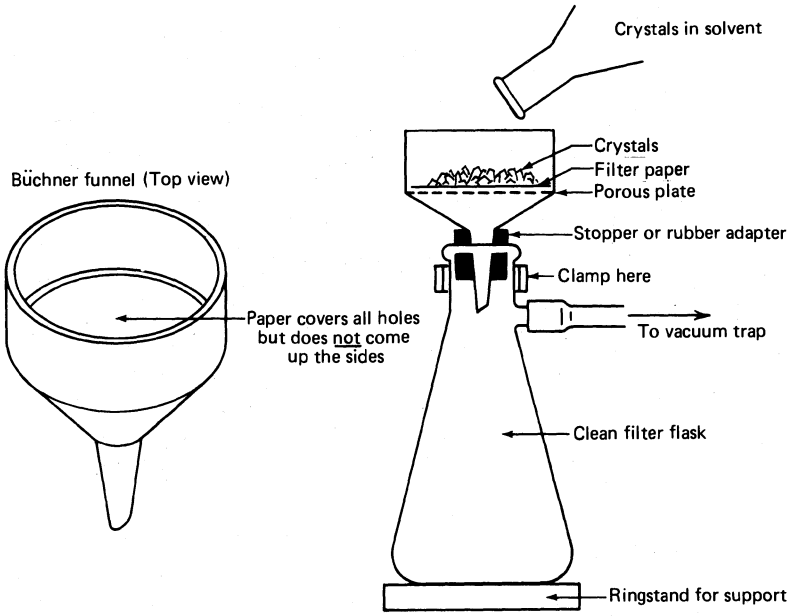


Fig. 46 The Buchner funnel at home and at work.

3. Now use a **rubber stopper** or **filter adapter** to stick the Buchner funnel into the top of the filter flask. The Buchner funnel makes the setup top-heavy and prone to be prone — and broken. Clamp the flask first, or go get a new Buchner funnel to replace the one you'll otherwise break.
4. The **water trap** is in turn connected to a source of vacuum, most likely, a **water aspirator** (Fig. 47).
5. The faucet on the **water aspirator** should be turned on *full blast!* This should suck down the filter paper, which you now *wet with some of the cold recrystallization solvent.* This will make the paper stick to the plate. You may have to push down on the Buchner funnel a bit to get a good seal between the rubber adapter and the funnel.
6. Swirl and pour the crystals and solvent *slowly, directly into the center of the filter paper,* as if to build a small mound of product there. *Slowly!* Don't flood the funnel by filling it right to the brim, and waiting for the level to go down. If you do that, the paper may float up, ruining the whole setup.
7. Use a very small amount of the same cold recrystallization solvent and a spatula to remove any crystals left in the flask. Then you can use some of the *fresh, cold recrystallization solvent* and slowly pour it over the crystals to wash away any old recrystallization solvent and dissolved impurities.
8. Leave the aspirator on and let air pass through the crystals to help them dry. You can put a thin rubber sheet, a **rubber dam,** over the funnel. The vacuum pulls it in and the crystals are pressed clean and dry. And you won't have air or moisture blowing through, and possibly decomposing, your product. Rubber dams are neat.
9. When the crystals are dry, *and you have a* **water trap,** just turn off the water aspirator. Water won't back up into your flask. [If you've been foolhardy and filtered without a water trap, just remove the rubber tube connected to the filter flask sidearm (Fig. 47)].
10. At this point, you may have a *cake of crystals* in your Buchner funnel. The easiest way to handle this is to *carefully lift the cake* of crystals out of the funnel *along with the filter paper,* plop the whole thing onto a larger piece of filter paper, and let the whole thing dry overnight. If you are pressed for time, *scrape the damp filter cake from the filter paper, but*

don't scrape any filter paper fibers into the crystals. Repeatedly press the crystals out between dry sheets of filter paper, changing sheets until the crystals no longer show any solvent spot after pressing. Those of you who use **heat lamps** may find your white crystalline product turning into instant charred remains.

11. When your cake is *completely dried,* weigh a vial, put in the product, and weigh the vial again. Subtracting the weight of the vial from the weight of the vial and sample will give the weight of the product. This **weighing by difference** is easier and less messy than weighing the crystals directly on the balance. This weight should be included in the label on your **product vial** (see Chapter 8, "On Products").

Just a Note

I've said that a Buchner funnel is used primarily for separating crystals of product from the liquid above them. And in the section on drying agents, I tell people to use a gravity filtration setup to separate a drying agent from a liquid product. Recently, I've had some people get the notion that you can Buchner filter products from drying agents. I don't advise that. You will probably lose a lot of your product, especially if it has a low boiling point (<100°C). Under this *vacuum filtration* your product simply evaporates along with your grade.

ACTIVATED CHARCOAL

Activated charcoal is ultrafinely divided carbon with lots of places to suck up big, huge, polar, colored impurity molecules. Unfortunately, if you use too much, it'll suck up **your product!** And, if your product was white, or yellow, it'll have a funny gray color from the excess charcoal. Sometimes, the impurities are untouched and only the product gets absorbed. Again, it's a matter of trial and error. Try not to use too much. Suppose you've got a *hot solution* of some solid, *and the solution is highly colored.* Well,

1. First, *make sure your product should not* **be** *colored!*
2. Take the flask with your filthy product off the heat and swirl the flask.

This dissipates any superheated areas so that when you add the activated charcoal, the solution doesn't foam out of the flask and onto your shoes.

3. *Add the activated charcoal.* Put a small amount, about the size of a pea, on your spatula, then throw the charcoal in. Stir. The solution may turn black. Stir and heat.
4. Set up the **gravity filtration** and filter off the carbon. It is especially important to *wash off any product caught on the charcoal,* and it is really hard to see anything here. You should take advantage of **fluted filter paper.** It should give a more efficient filtration.
5. Yes, have some extra fresh solvent heated as well. You'll need to add a few milliliters of this to the hot solution to help keep the crystals from coming out on the filter paper. And you'll need more to help wash the crystals off of the paper when they come out on it anyway.
6. This solution should be *much cleaner* than the original solution. If not, you'll have to *add charcoal and filter again.* There is a point of diminishing returns, however, and one or two treatments is usually all you should do. Get some guidance from your instructor.

Your solid products should not be gray. Liquid products (yes, you can do liquids!) will let you know that you didn't get all the charcoal out. Often, you can't see charcoal contamination in liquids while you're working with them. The particles stay suspended for awhile, but after a few days, you can see a layer of charcoal on the bottom of the container. Sneaky, those liquids. By the time the instructor gets to grade all the products — *voila* — the charcoal has appeared.

THE WATER ASPIRATOR: A VACUUM SOURCE

Sometimes you'll need a vacuum for special work like **vacuum distillation** and **vacuum filtration** as with the Buchner funnel. An inexpensive source of vacuum is the **water aspirator** (Fig. 47).

When you turn the water on, the water flow draws air in from the side port on the aspirator. The faster the water goes through, the faster the air is drawn in. Pretty neat, huh? I've shown a plastic aspirator, but many of the older metal varieties are still around.

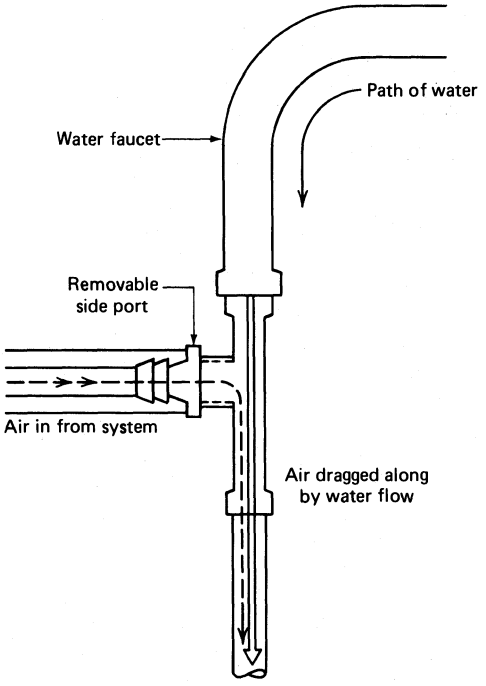


Fig. 47 A water aspirator.

You may have to pretest some aspirators before you find one that will work well. It'll depend upon the water pressure in the pipes, too. Even the number of people using aspirators on the same water line can affect the performance of these devices. You can test them by going to an aspirator and turning the faucet on *full blast.* It does help to have a sink under the aspirator. If water leaks out the side port, *tell your instructor and find another aspirator.* Wet your finger and place it over the hole in the side port to feel if there is any vacuum. If there is *no vacuum,* tell your instructor and find another aspirator. Some of these old, wheezing aspirators have a very weak vacuum. You must decide for yourself if the suction is "strong enough." There should be a **splash guard** or rubber tubing leading the water stream directly into the sink. This will keep the water from going all over the room. If you check and don't find such protection, see your instructor. All you have to do with a fully tested and satisfactory aspirator is hook it up to the **water trap.**

THE WATER TRAP

Every year I run a chem lab and when someone is doing a **vacuum filtration,** suddenly I'll hear a scream and a moan of anguish, as water backs up into someone's filtration system. Usually there's not much damage, since the filtrate in the suction flask is generally thrown out. For **vacuum distillations,** however, this **suck-back** is disaster. It happens whenever there's a pressure drop on the water line big enough to cause the flow to decrease so that there is a *greater vacuum in the system than in the aspirator.* Water, being water, flows into the system. Disaster.

So, for your own protection, make up a **water trap** from some stoppers, rubber tubing, a thick-walled Erlenmeyer or filter flask, and a screw clamp (Fig. 48). *Do not use garden variety Erlenmeyers; they may implode without warning.* Two versions are shown. I think the setup using the filter flask is more flexible. The screw clamp allows you to let air into your setup at a controlled rate. You might clamp the water trap to a ringstand when you use it. The connecting hoses have been known to flip unsecured flasks, two out of three times.

WORKING WITH A MIXED-SOLVENT SYSTEM—THE GOOD PART

If, after sufficient agony, you cannot find a single solvent to recrystallize your product from, you may just give up and try a *mixed-solvent system.* Yes, it does mean you mix more than one solvent, and *recrystallize using the mixture.* It should only be so easy. Sometimes, you are told what the mixture is and the correct proportions. Then it is easy.

For an example, I could use "solvent 1" and "solvent 2," but that's clumsy. So I'll use a rethe ethanol–water system and point out the interesting stuff as I go along.

The Ethanol–Water System

If you look up the solubility of water in ethanol (or ethanol in water) you find an ∞. This means they mix in all proportions. Any amount of one dissolves

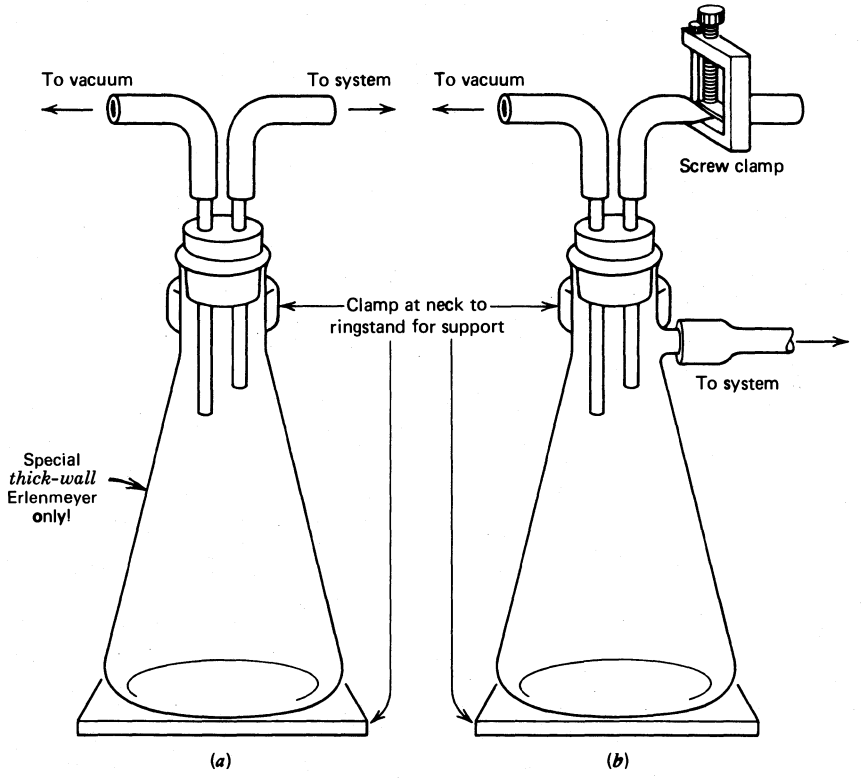


Fig. 48 A couple of water traps hanging around.

completely in the other—no matter what. Any volumes, any weights. You name it. The special word for this property is **miscibility.** Miscible solvent systems are the kinds you should use a mixed solvents. They keep you out of trouble. You'll be adding amounts of water to the ethanol, and ethanol to the water. If the two weren't miscible, they might begin to separate and form two layers as you changed the proportions. Then you'd have REAL trouble. So, go ahead. You *can* work with mixtures of solvents that aren't miscible. But don't say you haven't been warned.

The ethanol–water mixture is so useful because

1. *At high temperatures, it behaves like alcohol!*
2. *At low temperatures, it behaves like water!*

From this, you should get the idea that it would be good to use a mixed solvent to recrystallize compounds that are *soluble in alcohol* yet *insoluble in water.* You see, each solvent alone cannot be used. If the material is soluble in the alcohol, not many crystals come back from alcohol alone. If the material is insoluble in water, you cannot even begin to dissolve it. So, you have a *mixed solvent,* with the best properties of *both* solvents. To actually perform a *mixed-solvent recrystallization* you

1. Dissolve the compound in the smallest amount of *hot ethanol.*
2. Add *hot water* until the solution turns cloudy. This **cloudiness** is *tiny crystals of compound coming out of solution.* Heat this solution to dissolve the crystals. If they do not dissolve completely, add *a very little hot ethanol* to force them back into solution.
3. Cool, and collect the crystals on a **Buchner funnel.**

Any solvent pair that behaves the same way can be used. The addition of hot solvents to one another can be tricky. It can be *extremely dangerous* if the boiling points of the solvents are very different. For the *water–methanol mixed solvent,* if 95°C water hits *hot methanol* (B.P. 65.0°C), watch out!

There are other miscible, mixed-solvent pairs, pet. ether and diehyl ether, methanol and water, and ligroin and diethyl ether among them.

A MIXED-SOLVENT SYSTEM—THE BAD PART

Every silver lining has a cloud. More often than not, compounds "recrystallized" from a mixed-solvent system don't form crystals. Your compound may form an *oil* instead.

Oiling out is what it's called; more work is what it means. Compounds usually oil out if *the boiling point of the recrystallization solvent is higher than the melting point of the compound,* though that's not the only time. In any case, if the oil solidifies, the impurities are trapped in the now solid "oil," and you'll have to purify the solid again.

Don't think you won't ever get oiling out if you stick to single, unmixed solvents. It's just that with two solvents, there's a greater chance you'll hit upon a composition that will cause this.

Temporarily, you can

1. Add more solvent. If it's a mixed-solvent system, try adding more of the solvent the solid is NOT soluble in. Or add more of the OTHER solvent. No contradiction. The point is to *change the composition.* Single solvent or mixed solvent, changing the composition is one way out of this mess.
2. Redissolve the oil by heating, then shake up the solution as it cools and begins to oil out. When these smaller droplets finally freeze out, they may form crystals that are relatively pure. They may not. You'll probably have to clean them up again. Just don't use the same recrystallization solvent.

Sometimes, once a solid oils out, it doesn't want to solidify at all, and you might not have all day. Try removing a sample of the oil with an eyedropper or disposable pipette. Then get a glass surface (watch glass) and add a few drops of a solvent that the compound is known to be *insoluble* in (usually water). Then use the rounded end of a glass rod to *triturate the oil with the solvent.* **Trituration** can be described loosely as the beating of an oil into a crystalline solid. Then you can put these crystals back into the rest of the oil. Possibly they'll act as seed crystals and get the rest of the oil to solidify. Again, you'll still have to clean up your compound.

SALTING-OUT

Sometimes you'll have to recrystallize your organic compound from water. No big deal. But sometimes your organic compound is more than ever so slightly insoluble in water, and not all the compound will come back. Solution? Salt solution! A pinch of salt in the water raises the **ionic strength.** There are now charged ions in the water. Some of the water that solvated your compound goes to be with the salt ions. Your organic compound does not particularly like charged ions anyway, so more of your organic compound comes out of the solution.

You can dissolve about 36 g of common salt in 100 ml of cold water. That's

the upper limit for salt. You can estimate how much salt you'll need to practically saturate the water with salt. Be careful though—if you use too much salt, you may find yourself collecting salt crystals along with your product (see also the application of salting-out when you have to do an extraction; "Extraction Hints").

WORLD FAMOUS FAN-FOLDED FLUTED FILTER PAPER

Some training in origami is *de rigueur* for chemists. It seems that the regular filter paper fold is inefficient, since very little of the paper is exposed. The idea here is to **flute** or **corrugate** the paper, increasing the surface area in contact with your filtrate. You'll have to do this several times to get good at it.

Right here let's review the difference between **fold** and **crease.** Folding is folding; creasing is folding, then stomping on it, running fingers and fingernails over a fold over and over and over. Creasing so weakens the paper, especially near the point, that it may break at an inappropriate time in the filtration.

1. Fold the paper in half, then in half again, then in half again (Fig. 49). Press on this wedge of paper to get the fold lines to stay, but *don't crease. Do this in one direction only.* Either always fold toward you or away from you, but not both.

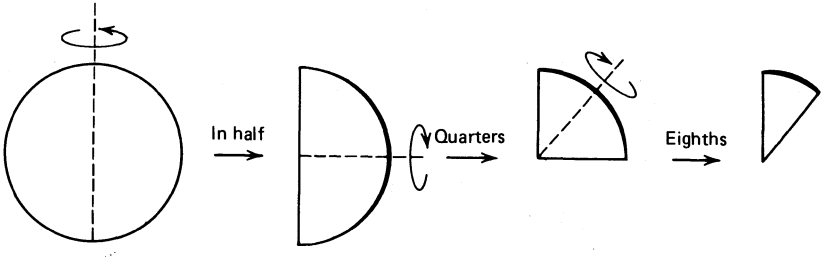


Fig. 49 Folding filter paper into eighths.

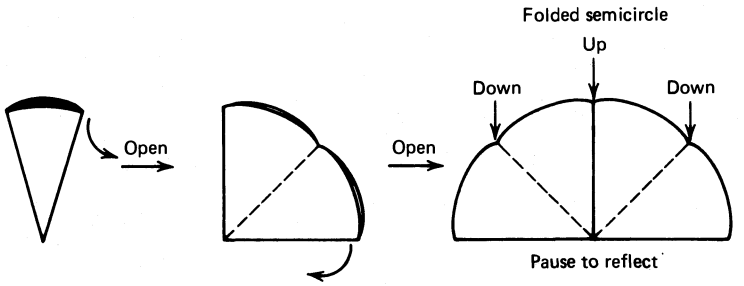


Fig. 50 Unfolding to a sort of bent semicircle.

2. Unfold this cone *twice* so it looks like a semicircle (Fig. 50), and put it down on a flat surface. Look at it and think for not less than two full minutes the first time you do this.
3. OK. Now try a "fan fold." You alternately fold, first in one direction then the other, every individual eighth section of the semicircle (Fig. 51).
4. Open the fan and play with it until you get a fairly fluted filter cone (Fig. 52).
5. It'll be a bit difficult, but try to find the two opposing sections that are NOT folded correctly. Fold them inward (Fig. 52), and you'll have a fantastic fan-folded fluted filter paper of your very own.

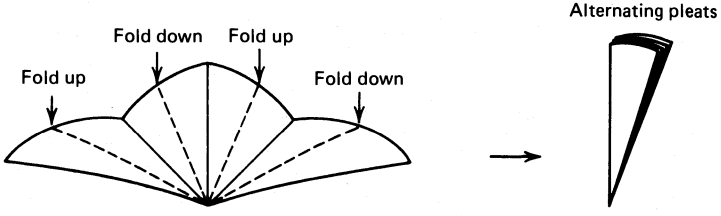


Fig. 51 Refolding to a fan.

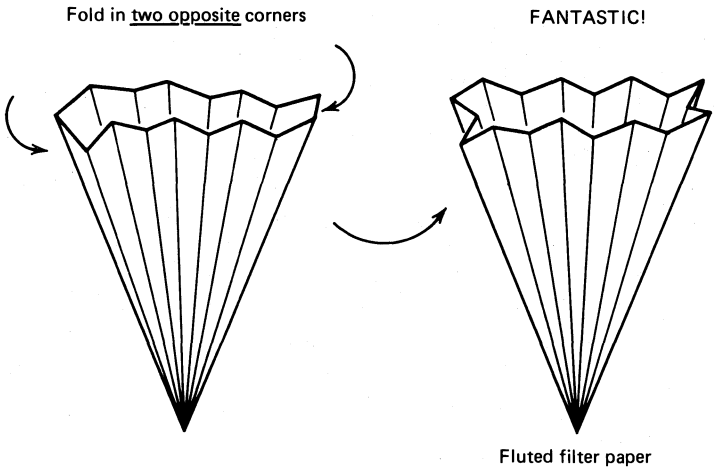


Fig. 52 Finishing the final fluted fan.

P.S. For those with more money than patience, prefolded fan-folded fluted filter paper is available from suppliers.

Extraction and Washing

Extraction is one of the more complex operations you'll do in the organic chemistry lab. For this reason, I'll go over it especially slowly and carefully. Another term you'll see used simultaneously with **extraction** is **washing.** That's because extraction and washing are really the same operation, but each leads to a different end. How else to put this?

Let's make some soup. Put the vegetables, fresh from the store, in a pot. You run cold water in and over them to clean them and throw this water down the drain. Later, you run water in and over them to cook them. You keep this water — it's the soup.

Both operations are similar. Vegetables in a pot in contact with water the first time is a **wash.** You remove unwanted dirt. *You washed with water.* The second time, vegetables in a pot in contact with water is an **extraction.** You've **extracted** essences of the vegetables *into water.* Very similar operations; very different ends.

To put it a little differently,

You would extract good material from an impure matrix.

You would wash the impurities from good material.

The vegetable soup preparation is a *solid-liquid extraction.* So is coffee making. You extract some component(s) of a solid directly into the solvent. You might do a solid-liquid extraction in lab as a separate experiment; *liquid-liquid extractions are routine.* They are so common that if you are told to do an extraction or a washing, *it is assumed,* you will use *two liquids — two INSOLUBLE liquids — and a separatory funnel.* The separatory funnel, called a **sep funnel** by those in the know, is a special funnel that you can separate liquids in. You might look at the section on separatory funnels (later in this chapter) right now, then come back later.

Two insoluble liquids in a separatory funnel will form **layers;** one liquid will float on top of the other. You usually have compounds dissolved in these layers, and either the compound you want is *extracted from one to the other,* or junk you don't want is *washed from one layer to the other.*

Making the soup, you have *no* difficulty deciding what to keep or what to throw away. First you throw the water away; later you keep it. But this can change. In a sep funnel, the layer you want to keep one time may not be the layer you want to keep the next time. Yet, if you throw one layer away prematurely, you are doomed.

NEVER-EVER LAND

**Never, never, never, never,
ever throw away any layer, until you are absolutely sure you'll never need it again. Not very much of your product can be recovered from the sink trap!**

I'm using a word processor, so I can copy this warning over and over again, but let's not get carried away. One more time, WAKE UP OUT THERE!

**Never, never, never, never,
ever throw away any layer, until you are absolutely sure you'll never need it again. Not very much of your product can be recovered from the sink trap!**

STARTING AN EXTRACTION

To do any extraction, you'll need two liquids, or solutions. *They must be insoluble in each other.* **Insoluble** here has a practical definition:

When mixed together, the two liquids form two layers.

One liquid will float on top of the other. A good example is ether and water. Handbooks say that ether is slightly soluble in water. When ether and water are mixed, yes, some of the ether dissolves; most of the ether just floats on top of the water.

Really soluble or *miscible liquid pairs are no good* for extraction and washing. When you mix them, *they will not form two layers!* In fact, they'll *mix in all proportions.* A good example of this is acetone and water. What kinds of problems can this cause? Well, for one, *you cannot perform any extraction with two liquids that are miscible.*

Let's try it. A mixture of say, some mineral acid (is HCl all right?) and an organic liquid, "Compound A," needs to have that acid washed out of it. You dissolve the compound A–acid mixture in some acetone. It goes into the sep funnel, and you now add water to wash out the acid.

Acetone is miscible in water. No layers form! You lose!

Back to the lab bench. Empty the funnel. Start over. This time, having called yourself several colorful names because you should have read this section thoroughly in the first place, you dissolve the Compound A–acid mixture in ether and put it into the sep funnel. Add water, and *two layers form!* Now you can wash the acid from the organic layer to the water layer. The water layer can be thrown away.

Note that the acid went into the water, *then the water was thrown out!* So we call this a **wash**. If the water layer had been saved, we'd say the acid had been **extracted into the water layer.** It may not make sense, but that's how it is.

Review:

1. You *must have two insoluble liquid layers* to perform an extraction.
2. *Solids must be dissolved in a solvent,* and that solvent must be insoluble in the other extracting or washing liquid.
3. If you are washing or extracting an organic liquid, dissolve it into another liquid, *just like a solid,* before extracting or washing it.

So these terms, **extraction and washing** are related. Here are a few examples.

1. Extract with ether. Throw ether together with the solution of product and pull out *only the product into the ether.*
2. Wash with 10% NaOH. Throw 10%NaOH together with the solution of product and pull out *everything but product into the NaOH.*
3. You can even extract with 10% NaOH.
4. You can even wash with ether.

So extraction is pulling out what you want from all else!
Washing is pulling out all else from what you want.

And please note—*you ALWAYS do the pulling from ONE LAYER INTO ANOTHER.* That's also *two immiscible liquids.*

You'll have to actually do a few of these things before you get the hang of it, but bear with me. When your head stops hurting, reread this section.

DUTCH UNCLE ADVICE

Just before I go on to the separatory funnel, I'd like to comment on a few questions I keep hearing when people do washings and extractions.

1. ***"Which layer is the water layer?"*** Look at both layers in the funnel and get an idea of how big they are in relation to one another. Now *add water to the funnel.* Watch where the water goes. Watch which layer grows. Water to water. That's how you find the water (aqueous) layer. Don't rely on odor or color. Enough ether dissolves in water to give the water layer the odor of an ether layer; just enough of a highly colored substance in the wrong layer can mislead you.
2. ***"How come I got three layers?"*** Sometimes, when you pour fresh water or some other solvent into the funnel, you get a small amount hanging at the top, and it looks like there are three different layers. Yes, it *looks* as if there are three different layers, but there are not three different layers. Only two layers, where part of one has lost its way. Usually, this mysterious third layer looks just like its parent, and you might gently swirl the funnel and its contents to reunite the family.
3. ***"What's the density of sodium hydroxide?"*** You've just done a wash with 5–10% sodium hydroxide solution, you've just read something about finding various layers in the funnel by their densities, and, by this question, you've just shown that you've missed the point. Most wash solutions are 5 to 10% active ingredient dissolved in water. This means they are 90 to 95% water. Looking up the density of the solid reagents then, is a waste of time. The density of these solutions is *very close* to that of water. (10% NaOH has a specific gravity of 1.1089.)
4. ***"I've washed this organic compound six times with sodium bicarbonate solution so why's it not basic yet?"*** This involves finding the pH of the organic layer. I'll give it away right now. *You cannot find the pH of an organic layer.* Not directly. You find the pH of the aqueous layer that's been in contact with the organic layer. If the aqueous layer is on the top, dip a glass rod into it and touch the glass rod to your test paper. If the aqueous layer is on the bottom and your sep funnel in a ring, let a drop of the aqueous layer out of the funnel to hang on the outlet tip. Transfer the drop to your test paper. Warning. Be *sure* you are testing the

aqueous layer. Some organics are very tenacious and can get onto your glass rod. The organic layer may WET the test paper, but without water any color you see doesn't mean much.

THE SEPARATORY FUNNEL

Before going on to some practical examples, you might want to know more about where all this washing and extracting is carried out. I've mentioned that it's a special funnel called a **separatory funnel** (Fig. 53) and that you can impress your friends by calling it a **sep funnel.** Here are a few things you should know.

The Stopper

At the top of the sep funnel is a T glass stopper. There is a number, commonly T 22, possibly T 19/22, on the stopper head. *Make sure this number is on the head and that it is the same as the number marked on the funnel.* If this stopper is not so marked, you may find the product leaking over your shoes when you turn the sep funnel upside down. Try *not to grease this stopper* unless you plan to sauté your product. Unfortunately, these stoppers tend to get stuck in the funnel. The way out is to be sure you don't get the ground glass surfaces wet with product. How? Pour solutions into the sep funnel as carefully as you might empty a shotglass of Scotch into the soda. Maybe *use a funnel.* To confuse matters, I'll suggest you use a light coating of grease. Unfortunately, my idea of light and your idea of light may be different.

Consult your instructor!

The Glass Stopcock

This is the time-honored favorite of separatory funnel makers everywhere. There is a notch at the small end that contains either a rubber ring *or* a metal clip, *but not both!* There are two purposes for the ring.

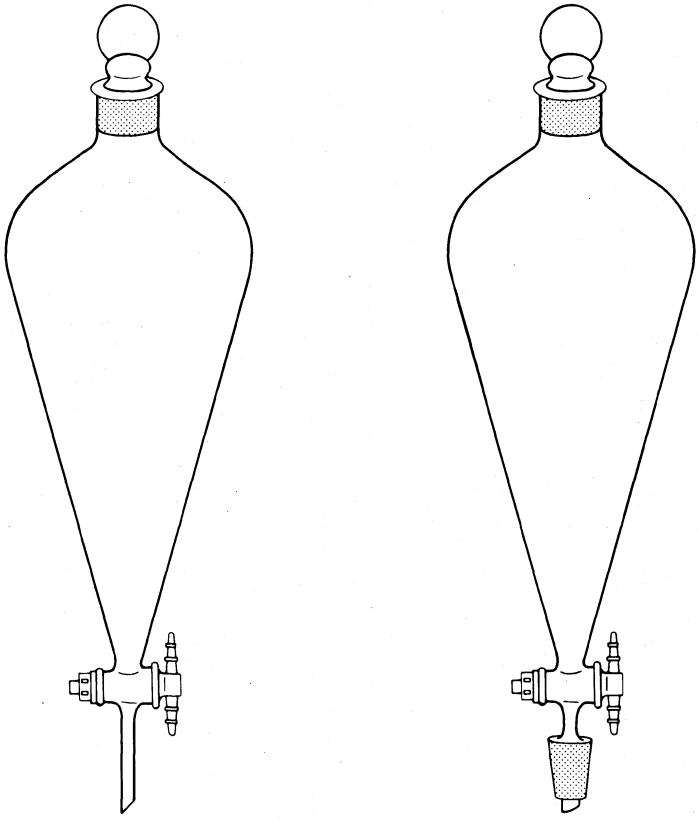


Fig. 53 Garden variety separatory funnels.

1. To keep the stopcock from falling out entirely. Unfortunately, the rubber rings are not aware of this and the stopcock falls out anyway.
2. To provide a sideways pressure, pulling the stopcock in, so that it will not leak. Names and addresses of individuals whose stopcocks could not possibly leak and did so anyway will be provided on request. So provide a little sideways pressure of your own.

When you grease a glass stopcock (and you must), do it very carefully so

that the film of grease does *not* spread into the area of the stopper that comes in contact with any of your compound (Fig. 54).

The Teflon Stopcock

In wide use today, the **Teflon stopcock** (Fig. 55) requires no grease and will not freeze up! The glass surrounding the stopcock *is not ground glass and cannot be used in funnels that require ground glass stopcocks!* The Teflon stopcocks are infinitely easier to take care of. There is a Teflon washer, a rubber ring, and, finally, a Teflon nut, placed on the threads of the stopcock. This nut holds the whole thing on. Any leakage at this stopcock results from

1. A loose Teflon nut. Tighten it.
2. A missing Teflon washer or rubber ring. Have it replaced.

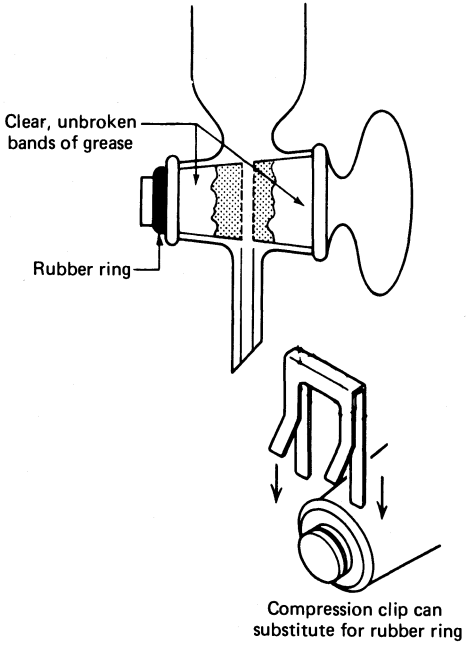


Fig. 54 The infamous glass stopcock.

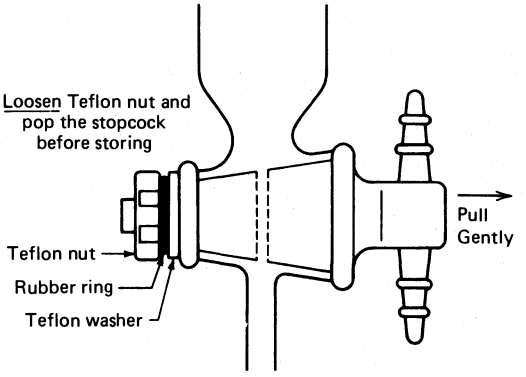


Fig. 55 Extreme closeup of teflon stopcock popping ritual.

3. An attempt to place the wrong size or taper Teflon stopcock into the funnel. This is extremely rare. Get a new funnel.

Emergency stopcock warning!

Teflon may not stick, *but it sure can flow!* If the stopcock is extremely tight, the Teflon will bond itself to all the nooks and crannies in the glass in interesting ways. When you're through, always loosen the Teflon nut and "pop the stopcock" by pulling on the handle. The stopcock should be loose enough to spin freely when spun with one finger — *then remember to tighten it again before you use it.*

It seems to me that I'm the only one that reads the little plastic bags that hold the stopcock parts. Right on the bags it shows that after the stopcock goes in, *the Teflon washer goes on the stem first,* followed by the rubber ring, and then the Teflon nut (Fig. 55). So why do I find most of these things put together incorrectly?

THE STEM

The stem on a sep funnel can either be straight or have a ground glass joint on the end (Fig. 53). The ground glass joint fits the other jointware you may have and can be used that way as an **addition funnel** to add liquids or solutions

into a setup (see "Addition and Reflux"). You can use this type of separatory funnel as a sep funnel. You can't, however, use the straight-stem separatory funnel as an addition funnel without some help; remember, straight glass tubes don't fit ground glass joints (see "The Adapter With Lots of Names").

WASHING AND EXTRACTING VARIOUS THINGS

Now, getting back to extractions, there are really only four classes of compounds that are commonly handled in undergraduate extractions or washings.

1. ***Strong Acids.*** The mineral acids, and organic acids (e.g., benzoic acid). You usually *extract these into sodium bicarbonate solution or wash them with it.*
2. ***Really weak acids.*** Usually phenols, or substituted phenols. Here, you'd use a *sodium hydroxide solution for washing or extraction.* You need a *strong base* to work with these weak acids.
3. ***Organic bases.*** Any organic amine (aniline, triethylamine, etc.). As you use bases to work with acids, use a ***dilute acid*** (5 to 10% HCl, say) to extract or wash these bases.
4. ***Neutral compounds.*** All else, by these definitions (e.g., amides, ethers, alcohols, hydrocarbons).

HOW TO EXTRACT AND WASH WHAT

Here are some practical examples of washings and extractions, covering various types and mixtures and separations and broken down into the four classifications listed above.

1. ***A strong organic acid.*** Extract into sat'd (saturated) sodium bicarbonate solution.

(**CAUTION!** *Foaming and fizzing and spitting and all sorts of carrying on.)* The weak base turns the strong acid into a salt, and the salt dissolves in the water–bicarbonate solution. Because of all the fizzing, you'll have to be very careful. Pressure can build up and blow the stopper out of the funnel. Invert the funnel. *Point the stem AWAY FROM EVERYONE up and toward the BACK OF THE HOOD*—and open the stopcock to vent or "burp" the funnel.

a. *To recover the acid,* add conc. (concentrated) HCl until the solution is acidic. Use pH or litmus paper to make sure. Yes, the solution really fizzes and bubbles. You should use a large beaker so material isn't thrown onto the floor if there's too much foam.

b. *To wash out the strong acid,* just throw the solution of bicarbonate away.

2. ***A weakly acidic organic acid.*** Extract into 10% NaOH–water solution. The strong base is needed to rip the protons out of weak acids (they don't want to give them up) and turn them into salts; Then they'll go into the NaOH–water layer.

a. *To recover the acid,* add conc. HCl until the solution of base is acid when tested with pH or litmus paper.

b. *To wash out the weak acid,* just throw this NaOH–water solution away.

3. ***An organic base.*** Extract with 10% HCl–water solution. The strong acid turns the base into a salt (This *turning the whatever into a salt that dissolves in the water solution* should be pretty familiar to you by now. Think about it.). Then the salt goes into the water layer.

a. *To recover the base,* add ammonium hydroxide to the water solution until the solution is *basic* to pH or litmus paper. *Note that this is the reverse of the treatment given to organic acids.*

b. *To wash out an organic base, or any base,* wash as above and throw out the solution.

4. ***A neutral organic.*** If you've extracted strong acids first, then weak acids, then bases, there are only neutral compound(s) left. If possible, just remove the solvent that now contains *only your neutral compound.* If you have *more than one neutral compound,* you may want to extract one from the other(s). You'll have to find *two different immiscible organic liquids,* and *one liquid must dissolve ONLY the neutral organic compound you want!* A tall order. You must count on *one neutral organic compound being more soluble in one layer than in the other.* Usually the separation is *not clean — not complete.* And you have to do more work.

What's "more work"? That depends on the results of your extraction.

The Road to Recovery — Back-Extraction

I've mentioned **recovery** of the four types of extractable materials, but that's not all the work you'll have to do to get the compounds in shape for further use.

1. If the recovered material is *soluble in the aqueous recovery solution,* you'll have to do a **back-extraction.**

   a. Find a solvent that dissolves your compound, and is *not miscible in the aqueous recovery solution.* This solvent should boil at a low temperature (<100°C), since you will have to remove it. Ethyl ether is a common choice. *(***Hazard!** *Very flammable).*

   b. *Then you extract your compound BACK FROM THE AQUEOUS RECOVERY SOLUTION into this organic solvent.*

   c. Dry this organic solution with a drying agent (see Chapter 7, "Drying Agents").

   d. Now you can remove the organic solvent. Either distill the mixture or evaporate it, perhaps on a steam bath. All this is done away from flames and in a hood.

   When you're through removing the solvent and you're product is not pure, clean it up. If your product is a liquid, you might distill it; if a solid, you might recrystallize it. Make sure it is clean.

2. If the recovered material is *insoluble in the aqueous recovery solution,* and *it is a solid,* collect the crystals on a Buchner funnel. If they are *not pure,* you should recrystallize them.
3. If the recovered material is *insoluble in the aqueous recovery solution* and *it is a liquid,* you can use your separatory funnel to *separate the aqueous recovery solution from your liquid product. Then dry your liquid product and distill it if it is not clean. Or, you might just do a back-extraction* as just described. This has the added advantage of getting out the small amount of liquid product that dissolves in the aqueous recovery solution and increases your yield. Remember to dry the back-extracted solution before you remove the organic solvent. Then distill your liquid compound if it is not clean.

A SAMPLE EXTRACTION

I think the only way I can bring this out is to use a typical example. This may ruin a few lab quizzes, but if it helps, it helps.

Say you have to separate a mixture of *benzoic acid (1), phenol (2), p-toluidine (4-Methylanaline) (3),* and *anisole (methoxybenzene) (4)* by extraction. The numbers refer to the class of compound, as previously listed. We're assuming that none of the compounds react with any of the others and that you know we're using all four types as indicated. Phenol and 4-methylanaline are corrosive toxic poisons and if you get near these compounds in lab, *be very careful.* When they are used as an example on these pages, however, you are quite safe. Here's a sequence of tactics.

1. Dissolve the mixture in ether. Ether is insoluble in the water solutions you will extract into. Ether happens to dissolve all four compounds. Aren't you lucky? You bet! It takes lots of hard work to come up with the "typical student example."
2. Extract the ether solution with 10% HCl. This converts *only* compound 3, the basic p-toluidine, into the hydrochloride salt, which dissolves in the 10% HCl layer. You have just *extracted a base with an acid solution.* Save this solution for later.
3. Now extract the ether solution with sat'd sodium bicarbonate solution.