Common Organic Solvents

Solvent	Boiling Point (°C)	Density (g/mL)
Acetic acid	118	1.05
Acetic anhydride	140	1.08
Acetone	56	0.79
Benzene*	80	0.88
Carbon tetrachloride*	77	1.59
Chloroform*	61	1.48
Cyclohexane	81	0.78
Dimethylformamide (DMF)	153	0.94
Dimethyl sulfoxide (DMSO)	189	1.10
Ethanol	78	0.80
Ether (diethyl)	35	0.71
Ethyl acetate	77	0.90
Heptane	98	0.68
Hexane	69	0.66
Ligroin	60–90	0.68
Methanol	65	0.79
Methylene chloride	40	1.32
Pentane	36	0.63
Petroleum ether	30–60	0.63
1-Propanol	98	0.80
2-Propanol	82	0.79
Pyridine	115	0.98
Tetrahydrofuran (THF)	65	0.99
Toluene	111	0.87
Xylenes	137–144	0.86

Solvents indicated in boldface type are flammable.

*Suspected carcinogen.

Atomic Mass Values for Selected Elements

Aluminum	26.98
Boron	10.81
Bromine	79.90
Carbon	12.01
Chlorine	35.45
Fluorine	18.99
Hydrogen	1.008
Iodine	126.9
Lithium	6.941
Magnesium	24.30
Nitrogen	14.01
Oxygen	15.99
Phosphorus	30.97
Potassium	39.09
Silicon	28.09
Sodium	22.99
Sulfur	32.07

Concentrated Acids and Bases

Reagent	**HCl**	**HNO_3**	**H_2SO_4**	**HCOOH**	**CH_3COOH**	**$NH_3(NH_4OH)$**
Density (g/mL)	1.18	1.41	1.84	1.20	1.06	0.90
% Acid or base (by weight)	37.3	70.0	96.5	90.0	99.7	29.0
Molecular weight	36.47	63.02	98.08	46.03	60.05	17.03
Molarity of concentrated acid or base	12	16	18	23.4	17.5	15.3
Normality of concentrated acid or base	12	16	36	23.4	17.5	15.3
Volume of concentrated reagent required to prepare 1 L of 1 M solution (ml)	83	64	56	42	58	65
Volume of concentrated reagent required to prepare 1 L of 10% solution (ml)*	227	101	56	93	95	384
Molarity of a 10% solution*	2.74	1.59	1.02	2.17	1.67	5.87

*Percent solutions by weight.

A Microscale Approach *to* Organic Laboratory Techniques

FIFTH EDITION

A Microscale Approach *to* Organic Laboratory Techniques

FIFTH EDITION

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This book is dedicated to
our organic chemistry laboratory students

Preface

STATEMENT OF MISSION AND PURPOSE IN REVISING THE TEXTBOOK

The purpose of this current edition of the microscale lab book is to teach students the techniques of organic chemistry. We desire to share our joy and love of the organic chemistry lab with our students! In this edition, we include many new up-to-date experiments that will demonstrate how organic chemistry is evolving. For example, there are new experiments involving nanotechnology and biofuels. We also include several new experiments based on Nobel Prize awards, such as using organometallic catalysts for synthesis (Sonogashira Coupling of Iodosubstituted Aromatic Compounds with Alkynes Using a Palladium Catalyst and Grubbs-Catalyzed Metathesis of Eugenol with 1,4-Butendiol to Prepare a Natural Product). Also included is a synthesis of the pharmaceutical drug Aleve® (naproxen) in a project-based experiment. This experiment includes a resolution step and makes extensive use of NMR spectroscopy. There are several new Green Chemistry experiments, and the "green" aspects of experiments from our previous book have been improved. We think that you will be enthusiastic about this new edition. Many of the new experiments will not be found in other laboratory manuals, but we have been careful to retain all of the standard reactions and techniques, such as the Friedel-Crafts reaction, the aldol condensation, Grignard synthesis, and basic experiments designed to teach crystallization, chromatography, and distillation.

SCALE IN THE ORGANIC LABORATORY

Experiments in organic chemistry can be conducted at different scales using varying amounts of chemicals and different styles of glassware. We have two versions of our laboratory textbooks that teach organic laboratory techniques. This microscale book (*A Microscale Approach to Organic Laboratory Techniques, Fifth Edition*) makes use of ₸ 14/10 standard-tapered glassware. Our version of a "macroscale" textbook (*A Small Scale Approach to Organic Laboratory Techniques*) uses the traditional larger scale ₸ 19/22 standard-tapered glassware. The third edition of our small scale book was published in 2011.

Over the years that we have been involved with developing experiments, we have learned that students can easily adjust to working with small laboratory equipment. Perhaps we can thank our colleagues who teach analytical techniques in general chemistry for demonstrating that students can learn to be meticulous and work with small amounts of material in many traditional experiments. As students and faculty learn to appreciate the impact of laboratory experiments on the environment, they become more aware that it is not necessary to consume large quantities of chemicals. Students come to appreciate the importance of reducing waste generated in the organic laboratory. All of us, students and faculty alike, are becoming more "green."

MAJOR FEATURES OF THE TEXTBOOK THAT WILL BENEFIT THE STUDENT

Organic chemistry significantly impacts our lives in the real world. Organic chemistry plays a major role in industry, medicine, and consumer products. Composite plastics are increasingly used in cars and airplanes to cut weight while increasing strength. Biodiesel is a hot topic today as we try to find ways of reducing our need for petroleum, and replacing it with materials that are renewable. We need to replace the resources that we consume.

A number of experiments are linked together to create multistep syntheses. The advantage of this approach is that you will be doing something different from your neighbor in the laboratory. Wouldn't you like to be doing something different from your neighbor? You may be synthesizing a new compound that hasn't been reported in the chemical literature! You will not be all doing the same reaction on the same compounds: an example of this is the chalcone reaction, followed by the green epoxidation and cyclopropanation of the resulting chalcones.

NEW TO THIS EDITION

Since the fourth edition of our microscale textbook appeared in 2007, there have been new developments in the teaching of organic chemistry laboratory. This fifth edition includes many new experiments that reflect these new developments and includes significant updating of the essays and techniques chapters.

New experiments added for this edition include:

Experiment 1	Solubility: Part F Nanotechnology Demonstration
Experiment 27	Biodiesel
Experiment 31	Borneol oxidation to camphor, new procedure
Experiment 34	Sonogashira Coupling of Iodoaromatic Compounds with Alkynes
Experiment 35	Grubb's-Catalyzed Metathesis of Eugenol with *cis*-1,4-Butenediol
Experiment 44	N,N-Diethyl-m-toluamide (OFF), new procedure
Experiment 48	Diels-Alder Reaction with Anthracene-9-methanol
Experiment 52	Identification of Unknowns, revised procedure
Experiment 55	Competing Nucleophiles in S_N1 and S_N2 Reactions: Investigations Using 2-Pentanol and 3-Pentanol
Experiment 56	Friedel-Crafts, more substrates added
Experiment 58	Aqueous-Based Organozinc Reactions

Experiment 59	Synthesis of Naproxen (Aleve®) by palladium catalysis
Experiment 62	Green Epoxidation of Chalcones
Experiment 63	Cyclopropanation of Chalcones

We have included a new essay "Biofuels." Substantial revisions were made to the "Petroleum and Fossil Fuels" essay and "The Chemistry of Sweeteners" essay. Other essays have been updated as well.

We have made a number of improvements in this edition that significantly improve safety in the laboratory. We have added several new experiments that incorporate the principles of Green Chemistry. The Green Chemistry experiments decrease the need for hazardous waste disposal, leading to reduced contamination of the environment. These experiments involve techniques such as solid phase extraction and the use of a microwave reactor. Other experiments have been modified to reduce their use of hazardous solvents. The "Green Chemistry" essay has been revised. In our view, it is most timely that students begin to think about how to conduct chemical experiments in a more environmentally benign manner. Many other experiments have been modified to improve their reliability and safety.

In keeping with the Green Chemistry approach, we have suggested an alternative way of approaching qualitative organic analysis. This approach makes extensive use of spectroscopy to solve the structure of organic unknowns. In this approach, some of the traditional tests have been retained, but the main emphasis is on using spectroscopy. In this way, we have attempted to show students how to solve structures in a more modern way, similar to that used in a research laboratory. The added advantage to this approach is that waste is considerably reduced.

New techniques have been introduced in this edition. Chiral gas chromatography has been included in the analysis of the products obtained from the resolution of α-phenylethylamine (Experiment 30) and the products from the chiral reduction of ethyl acetoacetate (Experiment 28). A new method of obtaining boiling points using a temperature probe with a Vernier LabPro interface or digital thermometer has been introduced.

Many of the Techniques chapters have been updated. New problems have been added to the chapters on infrared and NMR spectroscopy (Techniques 25, 26, and 27). Many of the old 60 MHz NMR spectra have been replaced by more modern 300 MHz spectra. As in previous editions, the techniques chapters include both microscale and macroscale methods.

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INSTRUCTOR RESOURCES

Instructor's Manual

We would like to call your attention to the Instructor's Manual that accompanies our textbook and is available as a digital download for qualified instructors. The manual contains complete instructions for the preparation of reagents and equipment for each experiment, as well as answers to each of the questions in this textbook. In some cases, additional optional experiments are included. Instructors will also find helpful the estimated time to complete each experiment and notes regarding special equipment or reagent handling. We strongly recommend that qualified adopters obtain a copy of this manual at **login.cengage.com** by searching for this book using the ISBN on the back cover. You may also contact your local Cengage Learning, Brooks/Cole representative for assistance. Contact information for your representative is available at **www.cengagelearning.com** through the "Find Your Rep" link at the top of the page.

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In preparing this new edition, we have also attempted to incorporate the many improvements and suggestions that have been forwarded to us by the many instructors who have used our materials over the past several years.

We thank all who contributed, with special thanks to our developmental editor, Peter McGahey; acquiring sponsoring editor, Christopher Simpson; assistant editor, Krista Mastroianni; editorial assistant, Alicia Landsberg; senior content project manager, Matthew Ballantyne; and associate media editor, Stephanie Van Camp.

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November 2011

How To Use This Book

OVERALL STRUCTURE OF THE BOOK

This textbook is divided into two major sections (see Table of Contents). The first section, which includes Part One through Part Five, contains all of the experiments in this book. The second major section includes only Part Six, which contains all of the important techniques you will use in performing the experiments in this book. Interspersed among the experiments in Part One through Part Three is a series of essays. The essays provide a context for many of the experiments and often relate the experiment to real world applications. When your instructor assigns an experiment, he or she will often assign an essay and/or several techniques chapters along with the experiment. Before you come to lab, you should read all of these. In addition, it is likely that you will need to prepare some sections in your laboratory notebook (see Technique 2) before you come to the lab.

STRUCTURE OF THE EXPERIMENTS

In this section we discuss how each experiment is organized in the textbook. To follow this discussion, you may want to refer to a specific experiment, such as Experiment 13.

Multiple Parts Experiments

Some experiments, such as Experiment 13, are divided into two or more individual parts that are designated by the experiment number and the letters A, B, etc. In some experiments, like Experiment 13, each part is a separate but related experiment, and you will most likely perform only one part. In Experiment 13, you would do Experiment 13A (Isolation of Caffeine from Tea Leaves) or Experiment 13B (Isolation of Caffeine from a Tea Bag). In other experiments, for example Experiment 32, the various parts can be linked together to form a multistep synthesis. In a few experiments, such as Experiment 22, the last part describes how you should analyze your final product.

Featured Topics and Techniques Lists

Directly under the title of each experiment (see Experiment 13), there will be a list of topics. These topics may explain what kind of experiment it is, such as isolation of a natural product or Green Chemistry. The topics may also include major techniques that are required to perform the experiment, such as crystallization or extraction.

Required Reading

In the introduction to each experiment, there will be a section labeled Required Reading. Within this section, some of the required readings are labeled Review and some are labeled New. You should always read the chapters listed in the New section. Sometimes it will also be helpful to do the readings in the Review section.

Special Instructions

You should always read this section since it may include instructions that are essential to the success of the experiment.

Suggested Waste Disposal

This very important section gives instructions on how to dispose of the waste generated in an experiment. Often your instructor will provide you with additional instructions on how to handle the waste.

Notes to Instructor

It will usually not be necessary to read this section. This section provides special advice for the instructor that will help to make the experiment successful.

Procedure

This section provides detailed instructions on how to carry out the experiments. Within the procedure, there will be many references to the techniques chapters, which you may need to consult in order to perform an experiment.

Report

In some experiments, specific suggestions for what should be included in the laboratory report will be given. Your instructor may refer to these recommendations or may have other directions for you to follow.

Questions

At the end of most experiments will be a list of questions related to the experiment. It is likely that your instructor will assign at least some of these questions along with the laboratory report.

Contents

PART 1

Introduction to Basic Laboratory Techniques

1 EXPERIMENT 1

Introduction to Microscale Laboratory

This textbook discusses the important laboratory techniques of organic chemistry and illustrates many important reactions and concepts. In the traditional approach to teaching this subject, the quantities of chemicals used were on the order of 5–100 grams, and glassware was designed to contain up to 500 mL of liquid. This scale of experiment we might call a **macroscale** experiment. The approach used here, a **microscale** approach, differs from the traditional laboratory course in that nearly all the experiments use small amounts of chemicals. Quantities of chemicals used range from about 50 to 1000 *milli*grams (0.050–1.000 g), and glassware is designed to contain less than 25 mL of liquid. The advantages include improved safety in the laboratory, reduced risk of fire and explosion, and reduced exposure to hazardous vapors. This approach decreases the need for hazardous waste disposal, leading to reduced contamination of the environment. You will learn to work with the same level of care and neatness that has previously been confined to courses in analytical chemistry.

This experiment introduces the equipment and shows how to construct some of the apparatus needed to carry out further experiments. Detailed discussion of how to assemble apparatus and how to practice the techniques is found in Part Six ("The Techniques") of this textbook. This experiment provides only a brief introduction, sufficient to allow you to begin working. You will need to read the techniques chapters for more complete discussions.

Microscale organic experiments require you to develop careful laboratory techniques and to become familiar with apparatus that is somewhat unusual, compared with traditional glassware. We strongly recommend that each student do Laboratory Exercises 1 and 2. These exercises will acquaint you with the most basic microscale techniques. To provide a strong foundation, we further recommend that each student complete most of Experiments 2 through 18 in Part One of this textbook before attempting any other experiments in the textbook.

READ Technique 1 "Laboratory Safety."

HEATING METHODS

Aluminum Block

The most convenient means of heating chemical reactions on a small scale is to use an **aluminum block.** An aluminum block consists of a square of aluminum that has holes drilled into it. The holes are sized to correspond to the diameters of the most common vials and flasks that are likely to be heated. Often there is also a hole intended to accept the bulb of a thermometer, so that the temperature of the block can be monitored. However, this practice is not recommended. The aluminum block is heated by placing it on a hot plate. An aluminum block is shown in Figure 1. Note that the thermometer in this figure is not used to monitor the temperature of the block.

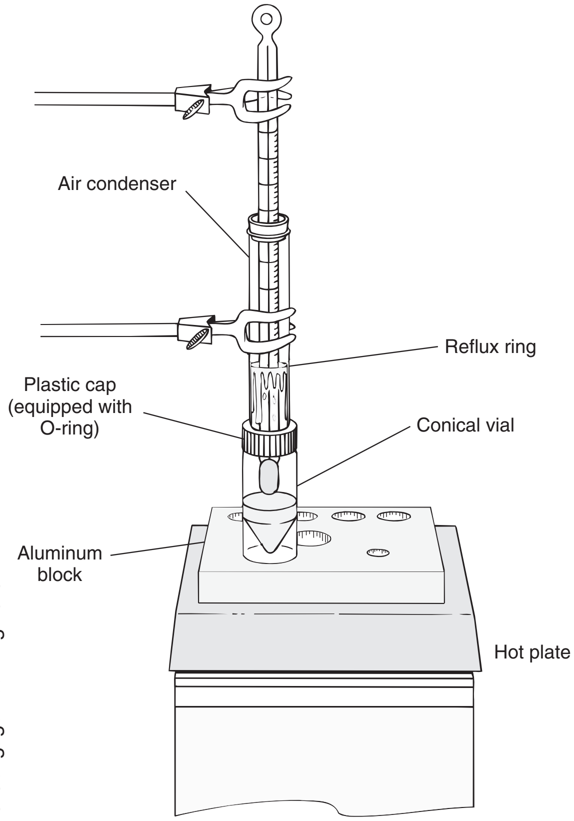

Figure 1
Aluminum block with hot plate and reflux apparatus.

CAUTION

You should not use a *mercury* thermometer in direct contact with an aluminum block. If it breaks, the mercury will vaporize on the hot surface. Instead, use a nonmercury thermometer, a metal dial thermometer, or a digital electronic temperature-measuring device. See Technique 6, Section 6.1.

It is recommended that an equipment kit contain two aluminum blocks, one drilled with small holes and able to accept the conical vials found in the glassware kit and another drilled with larger holes and able to accept small round-bottom flasks. The aluminum blocks can be made from inexpensive materials in a small mechanical shop, or they can be purchased from a glassware supplier.

Sand Baths

Another commonly used means of heating chemical reactions on a small scale is to use a **sand bath.** The sand bath consists of a Petri dish or a small crystallizing dish that has been filled to a depth of about 1 cm with sand. The sand bath is also heated by placing it on a hot plate. The temperature of the sand bath may be monitored by clamping a thermometer in position so that the bulb of the thermometer is buried in the sand. A sand bath, with thermometer, is shown in Figure 2.

We recommend that an aluminum block, rather than a sand bath, be used as a heating source whenever possible. The aluminum block can be heated and cooled quickly, it is indestructible, and there are no problems with spillage of sand.

Water Bath

When precise control at lower temperatures (below about 80°C) is desired, a suitable alternative is to prepare a **water bath.** The water bath consists of a beaker filled to the required depth with water. The hot plate is used to heat the water bath to the desired temperature. The water in the water bath can evaporate during heating. It is useful to cover the top of the beaker with aluminum foil to diminish this problem.

CONICAL REACTION VIALS

One of the most versatile pieces of glassware contained in the microscale organic glassware kit is the **conical reaction vial.** This vial is used as a vessel in which organic reactions are performed. It may serve as a storage container. It is also used for extractions (see Technique 12). A reaction vial is shown in Figure 3.

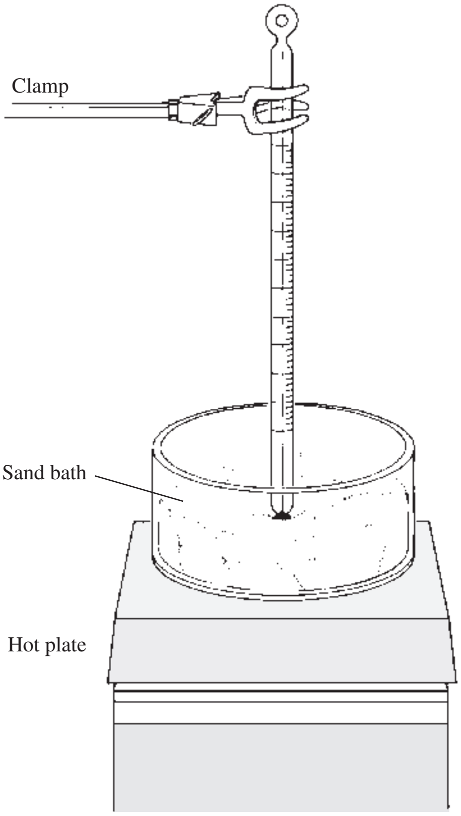

Figure 2
Sand bath with hot plate and thermometer.

The flat base of the vial allows it to stand upright on the laboratory bench. The interior of the vial tapers to a narrow bottom. This shape makes it possible to withdraw liquids completely from the vial, using a disposable Pasteur pipette. The vial has a screw cap, which tightens by means of threads cast into the top of the vial. The top also has a ground-glass inner surface. This ground-glass joint allows you to assemble components of glassware tightly.

The plastic cap that fits the top of the conical vial has a hole in the top. This hole is large enough to permit the cap to fit over the inner joints of other components of the glassware kit (see Figure 4). A Teflon insert, or liner, fits inside the cap to cover the hole when the cap is used to seal a vial tightly. Notice that only one side of the liner is coated with Teflon; the other side is coated with a silicone rubber. The Teflon side generally is the harder side of the insert, and it will feel more slippery. The Teflon side should always face toward the inside of the vial. An O-ring fits inside the cap when the cap is used to fasten pieces of glassware together. The cap and its Teflon insert are shown in the expanded view in Figure 3.

NOTE: Do not use the O-ring when the cap is used to seal the vial.

You can assemble the components of the glassware kit into one unit that holds together firmly and clamps easily to a ring stand. Slip the cap from the conical vial over the inner (male) joint of the upper piece of glassware and fit a rubber O-ring over the inner joint. Then assemble the apparatus by fitting the inner ground-glass joint into the outer (female) joint of the reaction vial and tighten the screw cap to attach the entire apparatus firmly together. The assembly is illustrated in Figure 4.

The walls of the conical vials are made of thick glass. Heat does not transfer through these walls very quickly. This means that if the vial is subjected to rapid changes in temperature, strain building up within the glass walls of the vial may cause the glass to crack. For this reason, do not attempt to cool these vials quickly by running cold water on them. It is safer to allow them to cool naturally by allowing them to stand.

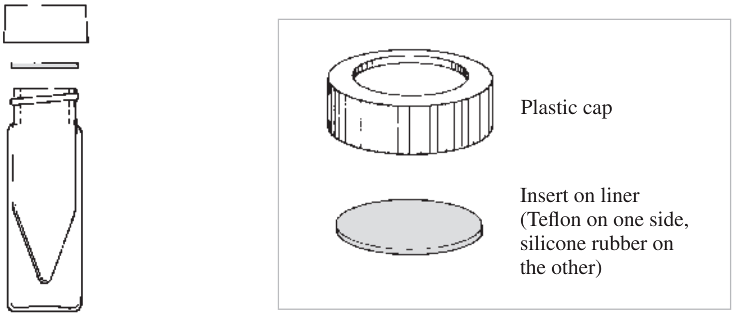

Figure 3
A conical reaction vial. (The inset shows an expanded view of the cap with its Teflon insert.)

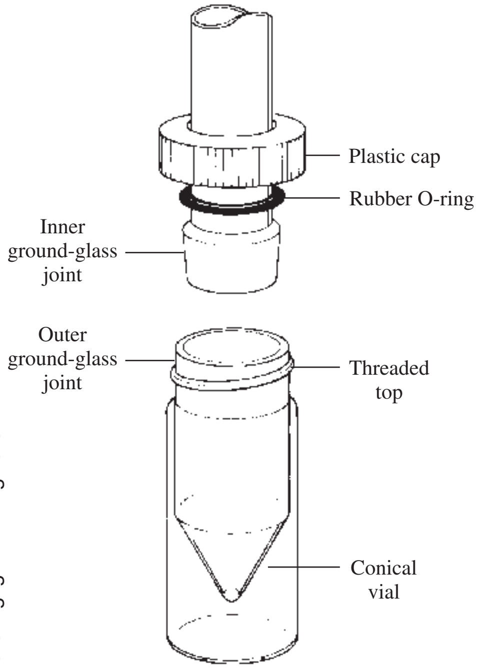

Figure 4
Assembling glassware components.

Although the conical vials have flat bottoms intended to allow them to stand up on the laboratory bench, this does not prevent them from falling over.

NOTE: It is good practice to store the vials standing upright inside small beakers.

The vials are somewhat top-heavy, and it is easy to upset them. The beaker will prevent the vial from falling over onto its side.

MEASUREMENT OF SOLIDS

Weighing substances to the nearest milligram requires that the weighings be done on a sensitive **top-loading balance** or an **analytical balance.**

NOTE: You must not weigh chemicals directly on balance pans.

Many chemicals can react with the metal surface of the balance pan and thus ruin it. All weighings must be made into a container that has been weighed previously (**tared**). This tare weight is subtracted from the total weight of container plus sample to give the weight of the sample. Some balances have a built-in compensating feature, the tare button, that allows you to subtract the tare weight of the container automatically, thus giving the weight of the sample directly. A top-loading and an analytical balance are shown in Figure 5.

Balances of this type are quite sensitive and expensive. Take care not to spill chemicals on the balance. It is also important to make certain that any spilled materials are cleaned up immediately.

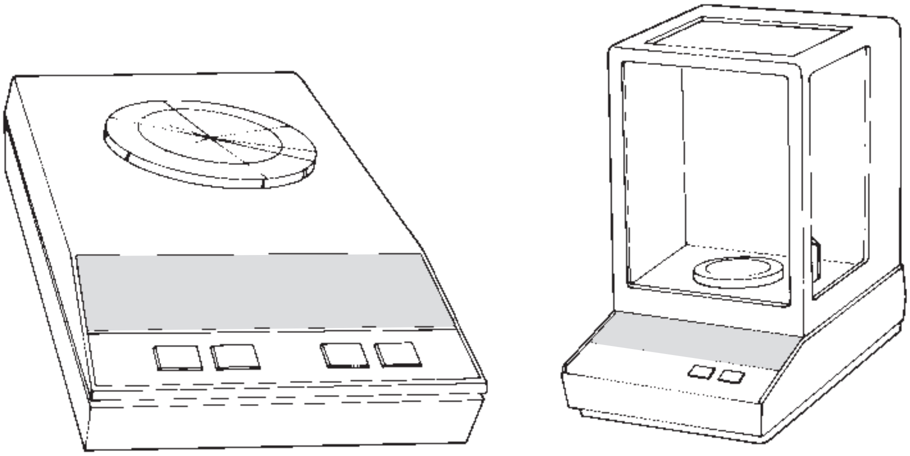
A. Top-loading balance
B. Analytical balance

Figure 5
Laboratory balances.

MEASUREMENT OF LIQUIDS

In microscale experiments, liquid samples are measured using a pipette. When small quantities are used, graduated cylinders do not provide the accuracy needed to give good results. There are two common methods of delivering known amounts of liquid samples, **automatic pipettes** and **graduated pipettes.** When accurate quantities of liquid reagents are required, the best technique is to deliver the desired amount of liquid reagent from the pipette into a container whose tare weight has been determined previously. The container, with sample, is then weighed a second time in order to obtain a precise value of the amount of reagent.

Automatic Pipettes

Automatic pipettes may vary in design, according to the manufacturer. The following description, however, should apply to most models. The automatic pipette consists of a handle that contains a spring-loaded plunger and a micrometer dial. The dial controls the travel of the plunger and is the means used to select the amount of liquid that the pipette is intended to dispense. Automatic pipettes are designed to deliver liquids within a particular range of volumes. For example, a pipette may be designed to cover the range from 10 to 100 μL (0.010 to 0.100 mL) or from 100 to 1000 μL (0.100 to 1.000 mL).

Automatic pipettes must never be dipped directly into the liquid sample without a plastic tip. The pipette is designed so that the liquid is drawn only into the tip. The liquids are never allowed to come in contact with the internal parts of the pipette. The plunger has two **detent,** or "stop," positions used to control the filling and dispensing steps. Most automatic pipettes have a stiffer spring that controls the movement of the plunger from the first to the second detent position. You will find a greater resistance as you press the plunger past the first detent.

To use the automatic pipette, follow the steps as outlined here. These steps are also illustrated in Figure 6.

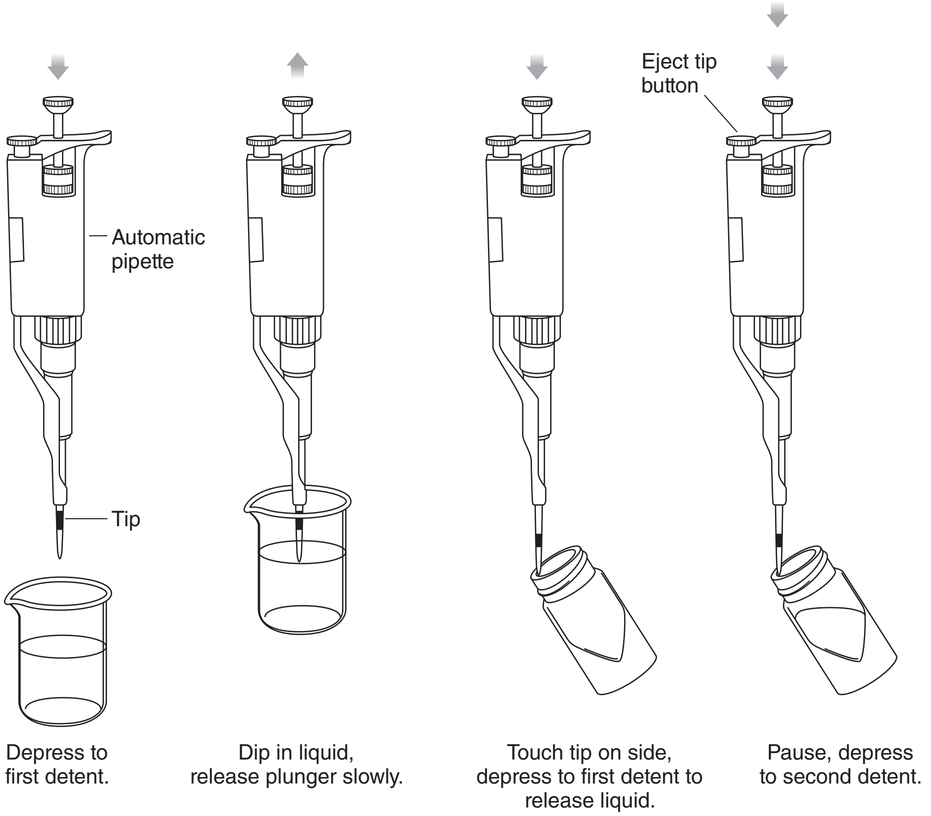

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Figure 6
Use of an automatic pipette.

1. Select the desired volume by adjusting the micrometer control on the pipette handle.
2. Place a plastic tip on the pipette. Be certain that the tip is attached securely.
3. Push the plunger down to the first detent position. Do not press the plunger to the second position. If you press the plunger to the second detent, an incorrect volume of liquid will be delivered.
4. Dip the tip of the pipette into the liquid sample. Do not immerse the entire length of the plastic tip in the liquid. It is best to dip the tip only to a depth of about 1 cm.
5. Release the plunger *slowly*. Do not allow the plunger to snap back, or liquid may splash up into the plunger mechanism and ruin the pipette. Furthermore, rapid release of the plunger may cause air bubbles to be drawn into the pipette. At this point, the pipette has been filled.
6. Move the pipette to the receiving vessel. Touch the tip of the pipette to an interior wall of the container.
7. Slowly push the plunger down to the first detent. This action dispenses the liquid into the container.
8. Pause 1–2 seconds and then depress the plunger to its second detent position to expel the last drop of liquid. The action of the plunger may be stiffer in this range than it was up to the first detent.
9. Withdraw the pipette from the receiver. If the pipette is to be used with a different liquid, remove the pipette tip and discard it.

Automatic pipettes are designed to deliver aqueous solutions with an accuracy of within a few percentage points. The amount of liquid actually dispensed varies, however, depending on the viscosity, surface tension, and vapor pressure of the liquid. The typical automatic pipette is very accurate with aqueous solutions but is not always as accurate with other liquids.

Dispensing Pumps

Some scientific supply catalogs offer a series of dispensing pumps. These pumps are useful in a microscale organic laboratory because they are simple to operate, easy to clean, chemically inert, and quite accurate. The interior parts of dispensing pumps are made of Teflon, which renders them inert to most organic solvents and reagents. A dispensing pump is illustrated in Figure 7.

The first step in using a dispensing pump is to adjust the pump so that it dispenses the desired volume of liquid. Normally, the instructor will make this adjustment. Once the pump is adjusted correctly, it is a simple matter to dispense a liquid. Simply lift the head of the pump as far as it will travel. When you release the head, it will fall, and the liquid will issue from the spout. With viscous liquids, the head of the pump may not fall by itself. In such an instance, gently guide the head downward. After the liquid has been dispensed, you should touch the tip of the dispensing tube to an interior wall of the container in order to remove the last drop of liquid.

As with automatic pipettes, dispensing pumps are designed to deliver aqueous solutions with an accuracy of within a few percentage points. The amount of liquid actually dispensed will vary, however, depending on

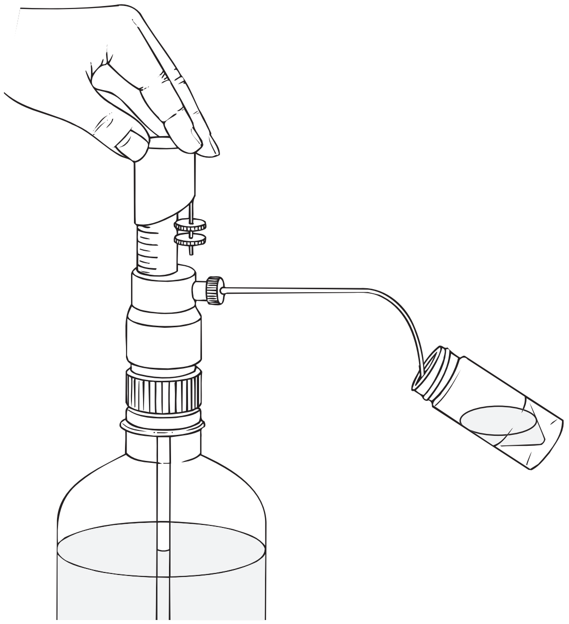

Figure 7
Use of a dispensing pump.

the viscosity, surface tension, and vapor pressure of the liquid. You should always weigh the liquid to determine the amount accurately.

Graduated Pipettes

A less-expensive means of delivering known quantities of liquid is to use a graduated pipette. Graduated pipettes should be familiar to those of you who have taken general chemistry or quantitative analysis courses. Because they are made of glass, they are inert to most organic solvents and reagents. Disposable serological pipettes may be an attractive alternative to standard graduated pipettes. The 2-mL size of a disposable pipette represents a convenient size for the organic laboratory.

Never draw liquids into the pipettes using mouth suction. A pipette bulb or a pipette pump, not a rubber dropper bulb, must be used to fill pipettes. We recommend the use of a pipette pump. A pipette fits snugly into the pipette pump, and the pump can be controlled to deliver precise volumes of liquids. Control of the pipette pump is accomplished by rotating a knob on the pump. Suction created when the knob is turned draws the liquid into the pipette. Liquid is expelled from the pipette by turning the knob in the opposite direction. The pump works satisfactorily with organic, as well as aqueous, solutions.

An alternative, and less expensive, approach is to use a rubber pipette bulb. Use of the pipette bulb is made more convenient by inserting a plastic automatic pipette tip into a rubber pipette bulb.[1] The tapered end of the pipette tip fits snugly into the end of a pipette. Drawing the liquid into the pipette is made easy, and it is also convenient to remove the pipette bulb and place a finger over the pipette opening to control the flow of liquid.

The calibrations printed on graduated pipettes are reasonably accurate, but you should practice using the pipettes in order to achieve this accuracy. When accurate quantities of liquids are required, the best technique is to weigh the reagent that has been delivered from the pipette.

LABORATORY EXERCISE 1

Option A, Automatic Pipette

Accurately weigh a 3-mL conical vial, with screw cap and Teflon insert, on a balance. Determine its weight to the nearest milligram (nearest 0.001 g). Using the automatic pipette, dispense 0.500 mL of water into the vial, replace the cap assembly (with the insert arranged Teflon side down), and weigh the vial a second time. Determine the weight of water dispensed. Calculate the density of water from your results. Repeat the experiment using 0.500 mL of hexane. Dispose of any excess hexane in a designated waste container. Calculate the density of hexane from your data. Record the results in your notebook, along with your comments on any deviations from literature values that you may have noticed. At room temperature, the density of water is 0.997 g/mL, and the density of hexane is 0.660 g/mL.

Option B, Dispensing Pump

Accurately weigh a 3-mL conical vial, with screw cap and Teflon insert, on a balance. Determine its weight to the nearest milligram (nearest 0.001 g). Using a dispensing pump that has been adjusted to deliver 0.500 mL, dispense 0.500 mL of water into the vial, replace the cap assembly, and weigh the vial a second time. Determine the weight of water dispensed. Calculate the density of water from your results. Repeat the experiment using 0.500 mL of hexane. Dispose of any excess hexane in a designated waste container. Calculate the density of hexane from your data.

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[1] This technique was described in Deckey, G. A Versatile and Inexpensive Pipet Bulb. *Journal of Chemical Education,* 57 (July 1980): 526.

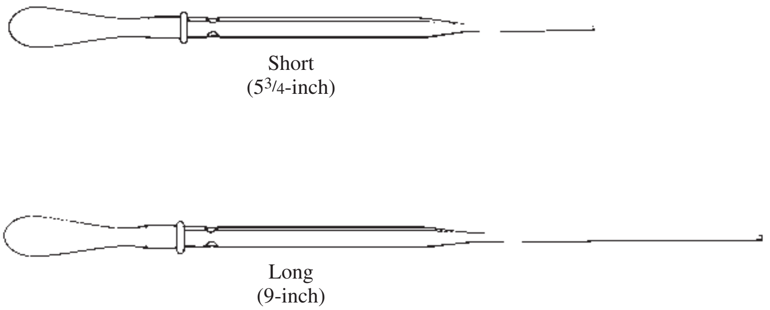


Figure 8
Disposable Pasteur pipettes.

Record the results in your notebook, along with your comments on any deviations from literature values that you may have noticed. See Option A for the density of water and of hexane.

Option C, Graduated Pipette

Accurately weigh a 3-mL conical vial, with screw cap and Teflon insert, on a balance. Determine its weight to the nearest milligram (nearest 0.001 g). Using a 1.0-mL graduated pipette, dispense 0.50 mL of water into the vial, replace the cap assembly, and weigh the vial a second time. Determine the weight of water dispensed. Calculate the density of water from your results. Repeat the experiment using 0.50 mL of hexane. Dispose of any excess hexane in a designated waste container. Calculate the density of hexane from your data. Record the results in your notebook along with your comments on any deviations from literature values that you may have noticed. See Option A for the density of water and of hexane

Disposable (Pasteur) Pipettes

A convenient way of dispensing liquids when a great deal of accuracy is not required is to use a disposable pipette, or Pasteur pipette. Two sizes of Pasteur pipettes are shown in Figure 8. Even though accurate calibration may not be required when these pipettes are used, it is nevertheless handy to have some idea of the volume contained in the pipette. A crude calibration is, therefore, recommended.

LABORATORY EXERCISE 2

Pipette Calibration

On a balance, weigh 0.5 grams (0.5 mL) of water into a 3-mL conical vial. Select a short (5¾-inch) Pasteur pipette and attach a rubber bulb. Squeeze the rubber bulb before inserting the tip of the pipette into the water. Try to control how much you depress the bulb, so that when the pipette is placed into the water and the bulb is completely released, only the desired amount of liquid is drawn into the pipette. (This skill may take some time to acquire, but it will facilitate your use of a Pasteur pipette.) When the water has been drawn up, place a mark with an indelible marking pen at the position of the meniscus. A more durable mark can be made by scoring the pipette with a file. Repeat this procedure with 1.0 gram of water, and make a 1-mL mark on the same pipette.

Additional Pasteur pipettes can be calibrated easily by holding them next to the pipette calibrated in Laboratory Exercise 2 and scoring a new mark on each pipette at the same level as the mark placed on the calibrated pipette. We recommend that several Pasteur pipettes be calibrated at one time for use in future experiments.

Extraction

A technique frequently applied in purifying organic reaction products is **extraction.** In this method, a solution is mixed thoroughly with a second solvent. The second solvent is not miscible with the first solvent. When the two solvents are mixed, the dissolved substances (solutes) distribute themselves between the two solvents until an equilibrium is established. When the mixing is stopped, the two immiscible solvents separate into two distinct layers. The solutes are distributed between the two solvents so that each solute is found in greater concentration in that solvent in which it is more soluble. Separation of the two immiscible solvent layers thus becomes a means of separating solutes from one another based on their relative solubilities in the two solvents.

In a common application, an aqueous solution may contain both inorganic and organic products. An organic solvent that is immiscible with water is added, and the mixture is shaken thoroughly. When the two solvent layers are allowed to form again, on standing, the organic solutes are transferred to the organic solvent while the inorganic solutes remain in the aqueous layer. When the two layers separate, the organic and inorganic products also separate from one another. The separation, as described here, may not be complete. The inorganic materials may be somewhat soluble in the organic solvent, and the organic products may retain some water solubility. Nevertheless, reasonably complete separations of reaction products can be achieved by the extraction method.

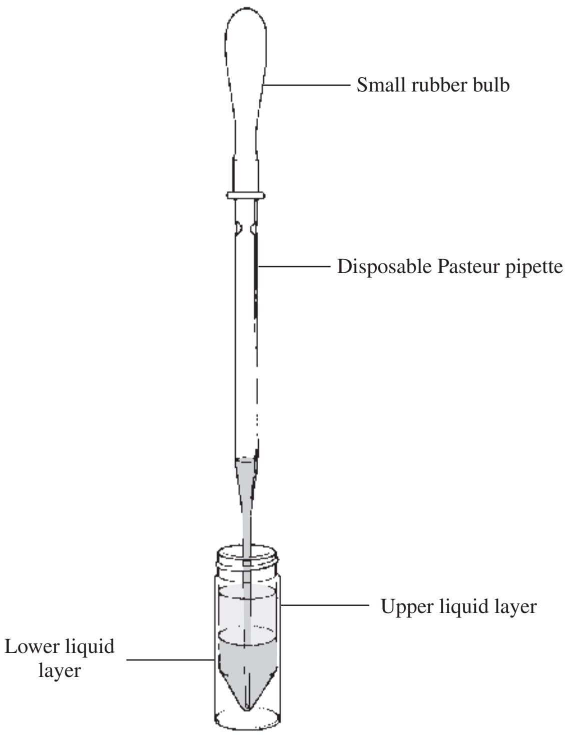


Figure 9
Separation of immiscible liquid layers in a conical vial.

For microscale experiments, the conical reaction vial is the glassware item used for extractions. Place the two immiscible liquid layers in the vial, and seal the top with a screw cap and a Teflon insert (Teflon side toward the inside of the vial). Shake the vial to provide thorough mixing between the two liquid phases. As the shaking continues, vent the vial periodically by loosening the cap and then tightening it again. After about 5 or 10 seconds of shaking, loosen the cap to vent the vial, retighten it, and allow the vial to stand upright in a beaker until the two liquid layers separate completely.

The two liquid layers are separated by withdrawing the *lower* layer using a disposable Pasteur pipette. This separation technique is illustrated in Figure 9. Take care not to disturb the liquid layers by allowing bubbles to issue from the pipette. Squeeze the pipette bulb to the required amount before introducing the pipette into the vial. Also take care not to allow any of the upper liquid layer to enter the pipette. The pointed shape of the interior of the conical vial makes it easy to remove all the lower layer without allowing it be contaminated by some of the upper liquid layer. More precise control in the separation can be achieved by using a filter-tip pipette (see Technique 8, Section 8.6).

Other Useful Techniques

The practice of organic chemistry requires you to master many more techniques than the ones described in this experiment. Those techniques included here are only the most elementary ones, those needed to get you started in the laboratory. Additional techniques are described fully in Part Six of this textbook, and Experiments 2 through 18 expose you to the most important of them.

Some other practical hints need to be introduced at this point. The first of these involves manipulating small amounts of solid substances. The efficient transfer of solids requires a small spatula. We recommend that you have two **microspatulas,** similar to those shown in Figure 10, as part of your standard desk stock. The design

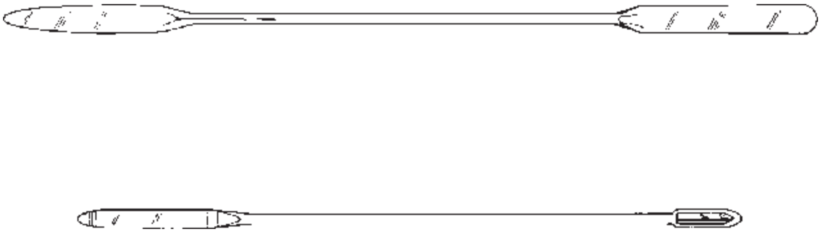


Figure 10
Microspatulas.

of these spatulas permits the handling of milligram quantities of substances without undue spillage or waste. The larger style (see Figure 10) is more useful when relatively large quantities of solid must be dispensed.

A clean work area is of utmost importance when working in the laboratory. The need for cleanliness is particularly great when working with the small amounts of materials characteristic of microscale laboratory experiments.

NOTE: You must read Technique 1 "Laboratory Safety." In preventing accidents, there is no substitute for preparation and care.

With this final word of caution and advice, we hope you enjoy the learning experience you are about to begin. Learning the care and precision that microscale experiments require may seem difficult at first, but before long you will be comfortable with the scale of the experiments. You will develop much better laboratory technique as a result of microscale practice, and this added skill will serve you well.

Solubility

Solubility
Polarity
Acid-base chemistry
Critical thinking application
Nanotechnology

Having a good comprehension of solubility behavior is essential for understanding many procedures and techniques in the organic chemistry laboratory. For a thorough discussion of solubility, read the chapter on this concept (Technique 10) before proceeding because an understanding of this material is assumed in this experiment.

In Parts A and B of this experiment, you will investigate the solubility of various substances in different solvents. As you are performing these tests, it is helpful to pay attention to the polarities of the solutes and solvents and to even make predictions based on this (see "Guidelines for Predicting Polarity and Solubility," Technique 10, Section 10.4). The goal of Part C is similar to that of Parts A and B, except that you will be looking at miscible and immiscible pairs of liquids. In Part D, you will investigate the solubility of organic acids and bases. Technique 10, Section 10.2B will help you understand and explain these results.

In Part E, you will perform several exercises that involve the application of the solubility principles learned in Parts A–D of this experiment. Part F is a unique nanotechnology experiment that also relates to solubility.

REQUIRED READING

New:	Technique 5	Measurement of Volume and Weight
	Technique 10	Solubility

SUGGESTED WASTE DISPOSAL

Dispose of all wastes containing methylene chloride into the container marked for halogenated waste. Place all other organic wastes into the nonhalogenated organic waste container.

NOTES TO THE INSTRUCTOR

In Part A of the procedure, it is important that students follow the instructions carefully. Otherwise, the results may be difficult to interpret. It is particularly important that consistent stirring be done for each solubility test. This can be done most easily by using the larger-style microspatula shown in Figure 10 in Experiment 1, Introduction to Microscale Laboratory.

We have found that some students have difficulty performing Critical Thinking Application 2 in Part E on the same day that they complete the rest of this experiment. Many students need time to assimilate the material in this experiment before they can complete this exercise successfully. One approach is to assign Critical Thinking Applications from several technique experiments (for example, Experiments 2–4) to a laboratory period after students complete the individual technique experiments. This provides an effective way of reviewing some of the basic techniques.

PROCEDURE

NOTE: It is very important that you follow these instructions carefully and that consistent stirring be done for each solubility test.

Part A. Solubility of Solid Compounds

Place about 40 mg (0.040 g) of benzophenone into each of four *dry* test tubes.[1] (Don't try to be exact: You can be 1–2 mg off and the experiment will still work.) Label the test tubes and then add 1 mL of water to the first tube, 1 mL of methyl alcohol to the second tube, and 1 mL of hexane to the third tube. The fourth tube will serve as a control. Determine the solubility of each sample in the following way: Using the rounded end of a microspatula (the larger style, in Figure 10 in Experiment 1, Introduction to Microscale Laboratory), stir each sample continuously for 60 seconds by twirling the spatula rapidly. If a solid dissolves completely, note how long it takes for the solid to dissolve. *After 60 seconds* (do not stir longer), note whether the compound is soluble (dissolves completely), insoluble (none of it dissolves), or partially soluble. You should compare each tube with the control in making these determinations. You should state that a sample is partially soluble only if a significant amount (at least 50%) of the solid has dissolved. If it is not clear that a significant amount of solid has dissolved, then state that the sample is insoluble. If all but a couple of granules have dissolved, state that the sample is soluble. An additional hint for determining partial solubility is given in the next paragraph. Record these results in your notebook in the form of a table, as shown on this page. For those substances that dissolve completely, note how long it took for the solid to dissolve.

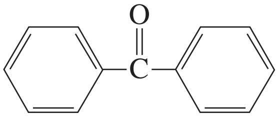
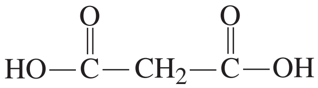
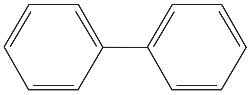
Although the instructions just given should enable you to determine whether a substance is partially soluble, you may use the following procedure to confirm this. Using a Pasteur pipette, carefully remove most of the solvent from the test tube *while leaving the solid behind.* Transfer the liquid to another test tube and then evaporate the solvent by heating the tube in a hot water bath. Directing a stream of air or nitrogen gas into the tube will speed up the evaporation (see Technique 7, Section 7.10). When the solvent has completely evaporated, examine the test tube for any remaining solid. If there is solid in the test tube, the compound is partially soluble. If there is no, or very little, solid remaining, you can assume that the compound is insoluble.

Now repeat the directions just given, substituting malonic acid and biphenyl for benzophenone. Record these results in your notebook.

---

[1] *Note to the instructor:* Grind up the benzophenone flakes into a powder.

Solvents

Organic Compounds	*Water (highly polar)*	*Methyl Alcohol (intermediate polarity)*	*Hexane (nonpolar)*
Benzophenone 			
Malonic acid  $\mathrm{HO{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}OH}$			
Biphenyl 			

Part B. Solubility of Different Alcohols

For each solubility test (see table below), add 1 mL of solvent (water or hexane) to a test tube. Then add one of the alcohols, *dropwise*. Carefully observe what happens as you add each drop. If the liquid solute is soluble in the solvent, you may see tiny horizontal lines in the solvent. These mixing lines indicate that solution is taking place. *Shake the tube after adding each drop*. While you shake the tube, the liquid that was added may break up into small balls that disappear in a few seconds. This also indicates that solution is taking place. Continue adding the alcohol with shaking until you have added a total of 20 drops. If an alcohol is partially soluble, you will observe that at first the drops will dissolve, but eventually a second layer of liquid (undissolved alcohol) will form in the test tube. Record your results (soluble, insoluble, or partially soluble) in your notebook in table form.

Solvents

Alcohols	*Water*	*Hexane*
1-Octanol $CH_3(CH_2)_6CH_2OH$		
1-Butanol $CH_3CH_2CH_2CH_2OH$		
Methyl alcohol CH_3OH		

Part C. Miscible or Immiscible Pairs

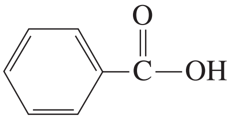
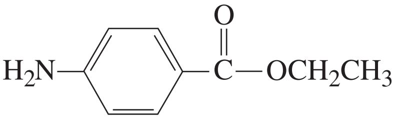
For each of the following pairs of compounds, add 1 mL of each liquid to the same test tube. Use a different test tube for each pair. Shake the test tube for 10–20 seconds to determine whether the two liquids are miscible (form one layer) or immiscible (form two layers). Record your results in your notebook.

Water and ethyl alcohol
Water and diethyl ether
Water and methylene chloride
Water and hexane
Hexane and methylene chloride

Part D. Solubility of Organic Acids and Bases

Place about 30 mg (0.030 g) of benzoic acid into each of three *dry* test tubes. Label the test tubes and then add 1 mL of water to the first tube, 1 mL of 1.0 *M* NaOH to the second tube, and 1 mL of 1.0 *M* HCl to the third tube. Stir the mixture in each test tube with a microspatula for 10–20 seconds. Note whether the compound is soluble (dissolves completely) or is insoluble (none of it dissolves). Record these results in the table. Now take the second tube containing benzoic acid and 1.0 *M* NaOH. With stirring add 6 *M* HCl dropwise until the mixture is acidic. Test the mixture with litmus or pH paper to determine when it is acidic.[2] When it is acidic, stir the mixture for 10–20 seconds and note the result (soluble or insoluble) in the table.

Repeat this experiment using ethyl 4-aminobenzoate and the same three solvents. Record the results. Now take the third tube containing ethyl 4-aminobenzoate and 1.0 *M* HCl. With stirring, add 6 *M* NaOH dropwise until the mixture is basic. Test the mixture with litmus or pH paper to determine when it is basic. Stir the mixture for 10–20 seconds and note the result.

	Solvents		
Compounds	*Water*	*1.0* M *NaOH*	*1.0* M *HCl*
Benzoic acid 			
		Add 6.0 *M* HCl	
Ethyl 4-aminobenzoate 			
			Add 6.0 *M* NaOH

Part E. Critical Thinking Applications

1. Determine by experiment whether each of the following pairs of liquids is miscible or immiscible.

   Acetone and water

   Acetone and hexane

   How can you explain these results, given that water and hexane are immiscible?

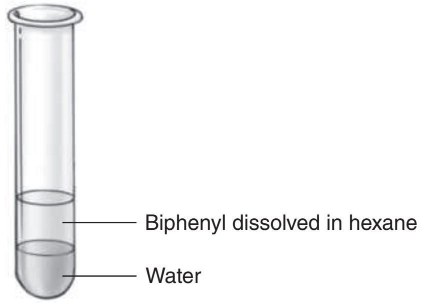
2. You will be given a test tube containing two immiscible liquids and a solid organic compound that is dissolved in one of the liquids.[3] You will be told the identity of the two liquids and the solid compound, but you will not know the relative positions of the two liquids or in which liquid the solid is dissolved.

---

[2] Do not place the litmus or pH paper into the sample; the dye will dissolve. Instead, place a drop of solution from your spatula onto the test paper. With this method, several tests can be performed using a single strip of paper.

[3] The sample you are given may contain one of the following combinations of solid and liquids (the solid is listed first): fluorene, methylene chloride, water; triphenylmethanol, diethyl ether, water; salicylic acid, methylene chloride, 1 *M* NaOH; ethyl 4-aminobenzoate, diethyl ether, 1 *M* HCl; naphthalene, hexane, water; benzoic acid, diethyl ether, 1 *M* NaOH; *p*-aminoacetophenone, methylene chloride, 1 *M* HCl.

Consider the following example, in which the liquids are water and hexane and the solid compound is biphenyl.



a. Without doing any experimental work, predict where each liquid is (top or bottom) and in which liquid the solid is dissolved. Justify your prediction. You may want to consult a handbook such as *The Merck Index* or the *CRC Handbook of Chemistry and Physics* to determine the molecular structure of a compound or to find any other relevant information. Note that dilute solutions such as 1 *M* HCl are composed mainly of water, and the density will be close to 1.0 g/mL. Furthermore, you should assume that the density of a solvent is not altered significantly when a solid dissolves in the solvent.

b. Now try to prove your prediction experimentally. That is, demonstrate which liquid the solid compound is dissolved in and the relative positions of the two liquids. You may use any experimental technique discussed in this experiment or any other technique that your instructor will let you try. In order to perform this part of the experiment, it may be helpful to separate the two layers in the test tube. This can be done easily and effectively with a Pasteur pipette. Squeeze the bulb on the Pasteur pipette and then place the tip of the pipette on the bottom of the test tube. Now withdraw only the bottom layer and transfer it to another test tube. Note that evaporating the water from an aqueous sample takes a very long time; therefore, this may not be a good way to show that an aqueous solution contains a dissolved compound. However, other solvents may be evaporated more easily. Explain what you did and whether or not the results of your experimental work were consistent with your prediction.

3. Add 0.025 g of tetraphenylcyclopentadienone to a dry test tube. Add 1 mL of methyl alcohol to the tube and shake for 60 seconds. Is the solid soluble, partially soluble, or insoluble? Explain your answer.

Part F. Nanotechnology Demonstration[4]

In this exercise, you will react a thiol (R-SH) with a gold surface to form a **self-assembled monolayer (SAM)** of thiol molecules on the gold. The thickness of this layer is about 2 nm (nanometer). A molecular system like this with dimensions at the nanometer level is an example of **nanotechnology.** Molecular self-assembly is also the key mechanism used in nature for the creation of complex structures such as the DNA double helix, proteins, enzymes, and the lipid bilayer of cell walls.

The thiol that is used in this experiment is 11-mercaptoundecan-1-ol, $HS(CH_2)_{11}OH$. The self-assembly of this thiol onto gold is caused by an interplay between the attraction of sulfur and gold and the drive to minimize the energy of the system by packing the alkane chain of the thiols into an optimal

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[4] This experiment is based on the Self-Assembled Monolayer Demonstration Kit, produced by Asemblon, Inc., 15340 NE 92nd St., Suite B, Redmond, WA 98052; phone: 425–558–5100. Dr. Daniel Graham, a principal scientist and founder of Asemblon, suggested this demonstration for inclusion in this book and helped to write the experiment.

arrangement (see figure). The bond energy of the sulfur–gold bond is about 45 kcal/mol, the strength of a partial covalent bond. As more thiols come to the surface of the gold, the interaction between the alkane chains becomes increasingly important. This is caused by the van der Waals attraction between the methylene groups (CH_2), which packs the chains close together in a crystalline-like monolayer. The process of self-assembly occurs quickly (within seconds) and results in the formation of an ordered surface that is only one molecule thick. This surface is referred to as a self-assembled monolayer.

The thiol used in this experiment consists of a terminal mercapto group (-SH), a spacer group (chain of CH_2 units), and a head group (-OH). Different head groups can be used, which makes thiol SAMs powerful surface engineering tools. Because a hydroxyl group attracts water, it is said to be hydrophilic. Since the hydroxyl group is positioned on the outer surface of the SAM, the outer surface takes on the properties of the head group and is also hydrophilic.

The first step in this experiment is to use a butane torch to clean the gold slide (glass plate coated with gold). The purpose of this step is to remove hydrocarbons from the air that have deposited on the gold surface over time. If the slide is dipped into water immediately after being cleaned, the gold surface should be coated with water. This occurs because the pure gold surface is a high-energy surface, which attracts the water molecules. Within a few minutes, the gold surface will be covered with hydrocarbons. In this experiment, you will wait a few minutes after the slide has been cleaned with the butane torch. The slide will then be dipped into water and wiped dry with tissue paper. You will print a word on the gold slide using a specially prepared pen containing the thiol. After rinsing the slide in water again, you will observe what has occurred on the surface of the slide.

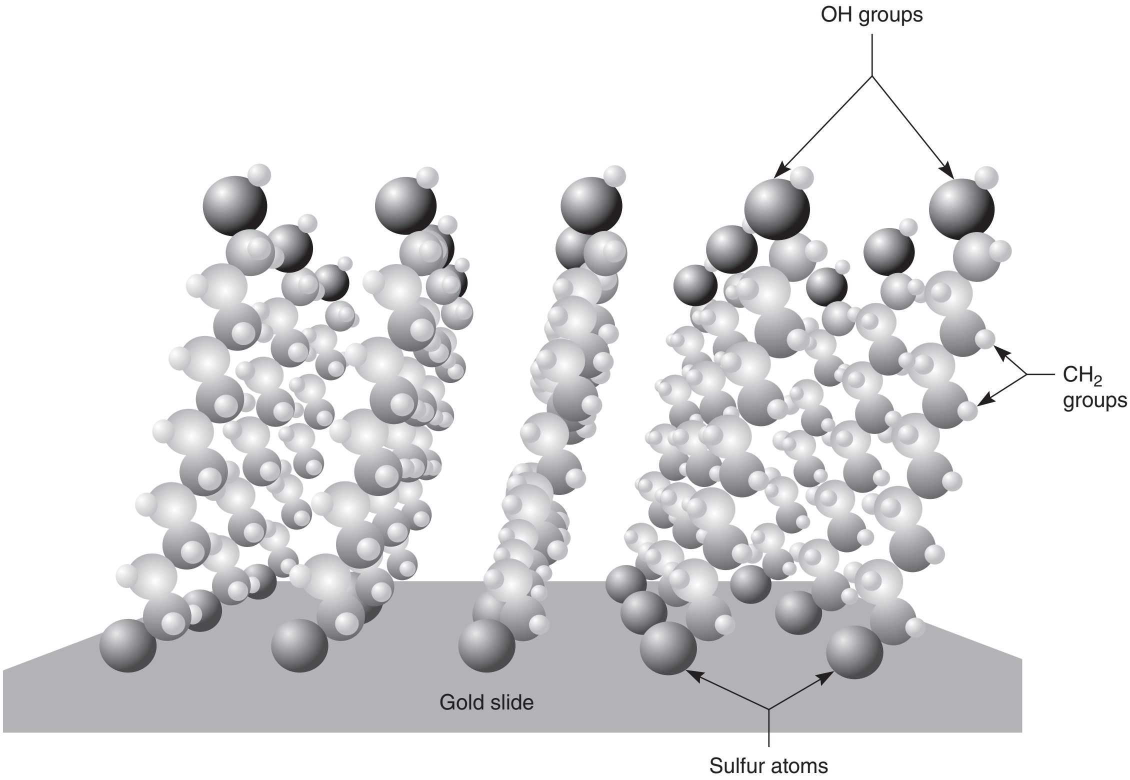
PROCEDURE

NOTE: Your instructor will first “erase” the gold using a butane torch.

CAUTION

When handling the gold slide, it is important to avoid touching the surface. Touching the surface can transfer contaminants from your fingers *or* gloves that can interface with the experiment. If you inadvertently touch the surface and leave fingerprints or other contaminants on it, you can clean the slide by rinsing it with methanol and then acetone until the slide is clean.

Select a gold-coated slide that has been flamed by your instructor. You should wait several minutes after the slide has been cleaned before proceeding with the next step. Holding the gold-coated slide in one hand **by the outer edges,** rinse the slide by completely dipping it in a beaker filled with de-ionized water. The water should roll off the slide when tilted. If the water droplets stick, gently wipe the slide off with a tissue paper and dip the slide in water again. Repeat this process until the slide comes out mostly dry. Gently wipe the slide completely dry with tissue paper. Breathe gently across the slide as if you were trying to fog up a window. Immediately after breathing on the slide, look at it before the moisture from your breath has evaporated. No writing should appear on the slide. If it does, your instructor should repeat the “erasing” step with the butane torch. Then repeat the rinsing procedure described above until the slide comes out mostly dry. Gently wipe it completely dry with tissue paper.



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Self-assembled monolayer of 11-mercaptoundecan-1-ol.

Place the slide with the gold side up on a flat surface. Take the Asemblon thiol pen and print a word of your choice. For best results, you should use gentle constant pressure and write in large block letters. The ink should wet the surface, and the lines in each letter should be continuous. The thiol assembly happens almost instantaneously, but to get good letter shapes the ink must completely wet all parts of each letter. If the ink does not adhere to a given part of a letter as you write it, go over it again with the pen. Let the ink sit on the gold surface for 30 seconds. Carefully pick up the slide by the edges at one end without touching the gold surface. Dip the slide into the beaker filled with de-ionized water and pull it out. Repeat this rinsing procedure four or five times.

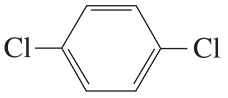
Look at the slide and record what you see. Water should adhere to the letters that were written, and the rest of the slide should remain dry. Letters that have a closed loop often trap water within the loop due to the high surface tension of water. If this occurs, try shaking off the excess water. If water still remains in the loops, take a piece of wet tissue paper and gently wipe across the surface. This should remove the water within the loops, but not the water that adheres to the letters.

REPORT

Part A

1. Summarize your results in table form.
2. Explain the results for all the tests done. In explaining these results, you should consider the polarities of the compound and the solvent and the potential for hydrogen bonding. For example, consider a similar solubility test for *p*-dichlorobenzene in hexane. The test indicates that *p*-dichlorobenzene is soluble in hexane. This result can be explained by stating that hexane is nonpolar, whereas

p-dichlorobenzene is slightly polar. Because the polarities of the solvent and solute are similar, the solid is soluble. (Remember that the presence of a halogen does not significantly increase the polarity of a compound.)



***p*-Dichlorobenzene**

3. There should be a difference in your results between the solubilities of biphenyl and benzophenone in methyl alcohol. Explain this difference.
4. There should be a difference in your results between the solubilities of benzophenone in methyl alcohol and benzophenone in hexane. Explain this difference.

Part B

1. Summarize your results in table form.
2. Explain the results for the tests done in water. In explaining these results, you should consider the polarities of the alcohols and water.
3. Explain, in terms of polarities, the results for the tests done in hexane.

Part C

1. Summarize your results in table form.
2. Explain the results in terms of polarities and/or hydrogen bonding.

Part D

1. Summarize your results in table form.
2. Explain the results for the tube in which 1.0 *M* NaOH was added to benzoic acid. Write an equation for this, using complete structures for all organic substances. Now describe what happened when 6.0 *M* HCl was added to this same tube and explain this result.
3. Explain the results for the tube in which 1.0 *M* HCl was added to ethyl 4-aminobenzoate. Write an equation for this. Now describe what happened when 6.0 *M* NaOH was added to this same tube and explain.

Part E

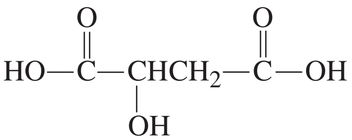
Give the results for any Critical Thinking Applications completed and answer all questions given in the Procedure for these exercises.

Part F

Record what you see after writing on the plate and dipping the plate into deionized water.

QUESTIONS

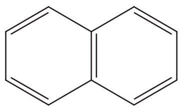
1. For each of the following pairs of solutes and solvent, predict whether the solute would be soluble or insoluble. After making your predictions, you can check your answers by looking up the compounds in *The Merck Index* or the *CRC Handbook of Chemistry and Physics*. Generally, *The Merck Index* is the easier reference book to use. If the substance has a solubility greater than 40 mg/mL, you may conclude that it is soluble.
   a. Malic acid in water



$$\mathrm{HO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle OH}{|}}{C}HCH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH}$$

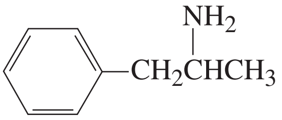
Malic acid

b. Naphthalene in water



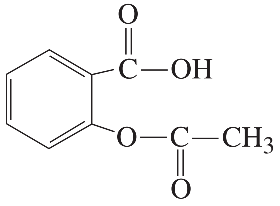
Naphthalene

c. Amphetamine in ethyl alcohol



Amphetamine

d. Aspirin in water



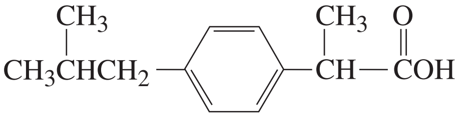
Aspirin

e. Succinic acid in hexane (*Note:* The polarity of hexane is similar to that of petroleum ether.)

$$\mathrm{HO{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_2CH_2{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OH}$$

Succinic acid

f. Ibuprofen in diethyl ether



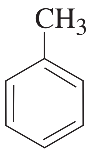
Ibuprofen

g. 1-Decanol (*n*-decyl alcohol) in water

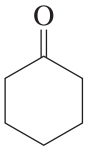
$CH_3(CH_2)_8CH_2OH$

1-Decanol

2. Predict whether the following pairs of liquids would be miscible or immiscible:
   - **a.** Water and methyl alcohol
   - **b.** Hexane and benzene
   - **c.** Methylene chloride and benzene
   - **d.** Water and toluene
   - **e.** Cyclohexanone and water

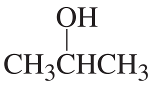


Toluene



Cyclohexanone

f. Ethyl alcohol and isopropyl alcohol

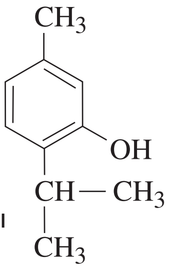


$CH_3\overset{OH}{\overset{|}{C}}HCH_3$

Isopropyl alcohol

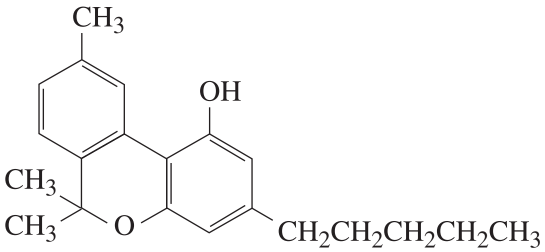
3. Would you expect ibuprofen (see 1f) to be soluble or insoluble in 1.0 *M* NaOH? Explain.

4. Thymol is very slightly soluble in water and very soluble in 1.0 *M* NaOH. Explain.



Thymol

5. Although cannabinol and methyl alcohol are both alcohols, cannabinol is very slightly soluble in methyl alcohol at room temperature. Explain.



Cannabinol

Questions 6–11 relate to Part F. Nanotechnology Demonstration

6. Why do the letters stay wet while the rest of the surface is dry?

7. Immediately after flame-cleaning the gold surface, water will adhere to the surface when the slide is dipped in water. If this water is cleaned off the slide and the slide is allowed to sit in the air for several minutes, water will no longer adhere to the surface when the slide is rinsed in water. Explain why.

8. A hydroxyl group on the end of the molecule makes the surface of the gold hydrophilic. How would a methyl group affect the surface? What is this effect called?

9. Why does heating the slide with a butane torch “erase” the writing?

10. How is this exercise different than writing on a glass surface with a crayon or wax pencil?

11. Why does water sometimes stick in the middle of some letters like P, O, or B, where there should not be any thiol?