INSTRUCTOR'S MANUAL FOR

Selected Experiments in Organic Chemistry

Third Edition

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W.H. Freeman and Company
New York San Francisco

REAGENTS NEEDED

Several reagents and solutions are used so frequently in carrying out the experiments in this manual that they should be available at all times on the side shelf. No amounts of such reagents are specified in this listing or under the descriptions of the individual experiments because it is assumed that all teaching laboratories have ample supplies. It is assumed that crushed ice is available in or near the laboratory.

SOLVENTS

- Acetone
- Cyclohexane
- Dichloromethane
- Ethyl alcohol (95%)
- Ethyl ether (solvent grade)
- Ethyl ether (Grignard quality)
- Isopropyl alcohol
- Methyl alcohol
- Petroleum ether (bp range, about 30-60°
- Petroleum ether (bp range, about 60-90°
- Toluene

ACIDS AND BASES

- Acetic acid (glacial)
- Ammonium hydroxide (conc)
- Hydrochloric acid (6 M)
- Hydrochloric acid (conc)
- Nitric acid (6 M)
- Nitric acid (conc)
- Sulfuric acid (6 M)
- Sulfuric acid (conc)

SOLID REAGENTS

- Ammonium chloride
- Calcium chloride (8 mesh)
- Decolorizing charcoal
- Diatomaceous earth
- Potassium carbonate (anhydrous powder)
- Potassium hydroxide (pellets)
- Potassium hydroxide (technical flakes)
- Potassium permanganate
- Sodium bisulfite
- Sodium bromide
- Sodium chloride
- Sodium hydroxide (pellets)
- Sodium sulfate (anhyd powder)

DESK EQUIPMENT

A standard set of standard taper desk equipment is listed that will accommodate most of the experiments in the manual. If standard taper ware is not available, minor changes in the distillation set will provide a satisfactory alternate list. Furthermore, at the discretion of the instructor or by the ommission of certain experiments, this list can be reduced by limiting the variation in sizes of items such as flasks, beakers and separatory funnels. Following the listing of standard desk items, there is given a description of apparatus that is convenient but unessential.

Desk List

1 Adapter, distillation, standard taper (see Fig. 2-10)
2 Adapters, for filter flasks
1 Beaker, 50 mL
1 Beaker, 150 mL
1 Beaker, 250 mL
1 Beaker, 600 mL
1 Burner, micro
1 Burner, standard
2 Clamps, three-fingered
1 Clamp, pinch or screw type
2 Clamps, universal
4 Clamp holders
1 Condenser, West type, standard taper
1 Cylinder, graduated, 10 mL
1 Cylinder, graduated, 100 mL
1 Distillation head, standard taper, for thermometer (see Fig. 2-10)
1 Dropper, medicine type
1 Drying tube
1 File, triangular
1 File, round
1 Flask, conical, 25 mL
2 Flasks, conical, 50 mL
3 Flasks, conical, 125 mL
2 Flasks, conical, 250 mL
1 Flask, conical, 500 mL
1 Flask, filter, 125 mL
1 Flask, filter, 500 mL
1 Flask, round-bottomed, 100 mL, standard taper
1 Flask, round-bottomed, 200 mL, standard taper
1 Flask, round-bottomed, 500 mL, standard taper
1 Forceps
1 Funnel, Büchner, size 0
1 Funnel, Büchner, medium size
1 Funnel, 60°, no stem
1 Funnel, 60°, with stem
1 Funnel, Hirsch
1 Funnel, separatory, 250 mL
1 Funnel, separatory, 500 mL
1 Ring, iron, 3"
1 Rod, soft glass, 3 mm, 1 ft
1 Rod, soft glass, 5 mm, 1 ft
1 Spatula, small
1 Steam bath, 6-8"
1 Stirring rod
4 Test tubes, Pyrex, 4"
8 Test tubes, Pyrex, 6"
1 Test tube, Pyrex, 8"
1 Thermometer, 110° (optional)
1 Thermometer, 360°, to fit distillation head

DESK EQUIPMENT

1 Tubing, Pyrex, 5 mm, 4 ft
3 Tubing, rubber, standard, 3-ft lengths
1 Tubing, rubber, vacuum, 3 ft
1 Tubing, soft glass, 5 mm, 2 ft
1 Tubing, soft glass, 6 mm, 1 ft
1 Tubing, soft glass, 10 mm, 4 ft (if melting point capillaries are to be prepared)
10 Vials, glass
1 Watch glass, 3"
1 Wire gauze

Special Items (Optional)

1 Adapter, vacuum, standard taper (see Fig. 5-4)
25 Capillary tubes, for melting points
1 Heating mantle, for 100-mL flask
1 Heating mantle, for 200-mL flask
1 Thiele tube (optional)

LABORATORY APPARATUS AND SUPPLIES FOR GENERAL USE

Aluminum foil
Balance, triple-beam, 500 g
Barometer
Boiling chips, carborundum, about 4 mesh
Copper wire
Cotton
Distilling tube, more than 2 theor. plates
Dropping pipet, disposable
Filter paper, Hirsch
Filter paper, No. 0, for Büchner, 4.5 cm
Filter paper, for medium Büchner
Glass wool
Heating mantles, 500 mL (one per station
Labels, gummed
Litmus paper, red and blue
Magnetic stirrers and bars
Ring stands or support bars, two per station
Stopcock grease, for burets and standard taper apparatus
Stoppers, cork, miscellaneous
Stoppers, rubber, solid, 1-hole, 2-hole
Variable transformer, one per station
Water traps (see Fig. 5-2), one per station

EXPERIMENTS

Certain experiments in the laboratory manual require the use of specialized pieces of apparatus and chemicals. In the following section, each experiment will be described with regard to reagents, apparatus, precautions, general comments, answers to questions, and coordination with other experiments.

All reagents are given in the approximate quantity needed per student (unless indicated otherwise).

One laboratory period is assumed to involve three hours of work.

EXPERIMENT 1-B

Special Chemicals:
Cinnamic acid, 0.5 g Urea, 0.5 g
Comments: Experiment to be concurrent with 1-A and 1-C. The mixed melting point data is most satisfactory when the components are ground together intimately.

EXPERIMENT 1-C

Special Chemicals:
About 0.1 g each of the following materials:
Acetanilide Succinimide Urea
Cinnamic acid Hippuric acid Thiourea
Comments: Experiment to be concurrent with 1-A and 1-B. It is advisable that all of the above materials are ground finely enough that they cannot be recognized by comparison of the appearance of the crystals.
Answers to Questions:

1. Compare with another (calibrated) thermometer.
2. The heat capacity and the rate of heat transfer of a large quantity of glass can cause the sample temperature to lag behind the bath temperature.
3. The basicity of the two glasses are different and this might induce different interactions with the compounds; or, the glasses might have different solubilities in the compound.
4. In both the solid and liquid phases of a substance the volumes are only slightly affected by changes in pressure (compare gases, for example). Hence, since the effect is small, and particularly since it is similar, the temperature of transition from one phase to the other should not be highly dependent on pressure.
5. As a substance melts heat is absorbed (heat of fusion). If a large quantity of material is present, so much heat must be transferred through the walls of the capillary that the bath temperature will have risen to an excessively high degree before melting is complete.
6. Crystal structure, refractive index, density, diffration patterns (X-ray or electron), infrared spectra.

EXPERIMENT 2-A

Time: 3 hours if boiling points of known samples are run and/or capillary tubes are hand-drawn. Otherwise, the experiment should be concurrent with 2-B.
Special Chemicals: Each student will require about one ml of a liquid that is listed in Table 2-4, p. 16.
Comments: The most common error in this experiment is the failure to heat the test apparatus to the point

EXPERIMENT 2-A

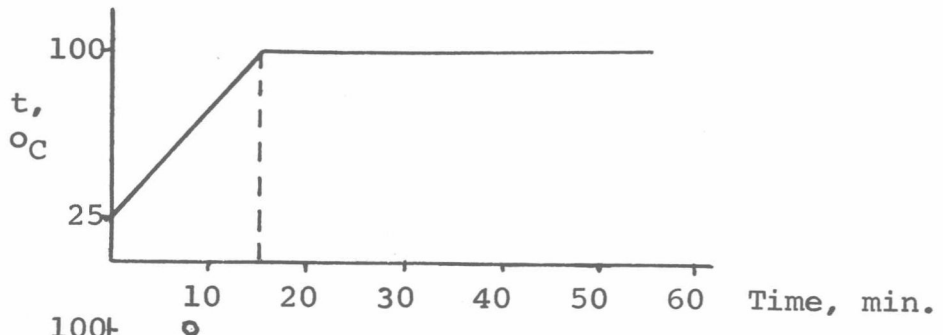
at which the liquid is boiling vigorously. If all air is not expelled from the capillary tube, the apparent boiling point will be low.

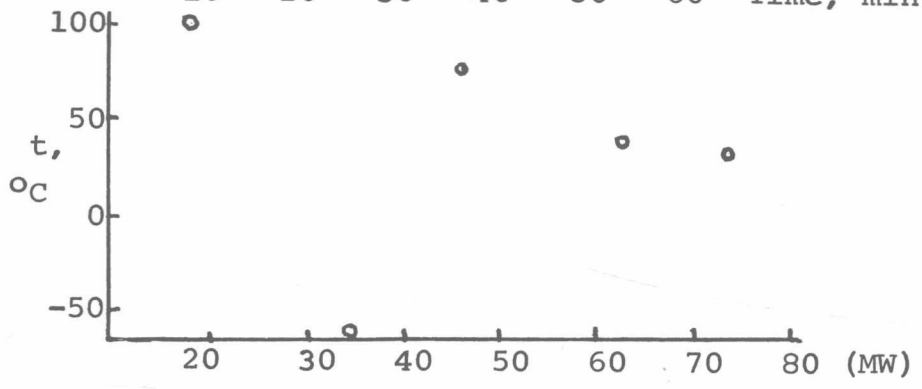
EXPERIMENT 2-B

Special Chemicals: 2-propanol, 25 mL

Comments: May be concurrent with 2-A.
In this and subsequent distillation experiments, it is most appropriate for the student to record data directly on a graph. The temperature transitions become immediately apparent from the curve. This is the first experiment in which the heating mantle is introduced.

Answers to Questions:

1. Literature boiling point: 83°.
2. (Answer to be determined by the plateau on the student's graph). A discrepancy can be due to a faulty thermometer (+ or - error), placement of the thermometer at too high a level (low reading), or superheating because of too rapid a rate of distillation (high reading).
3. (The percent recovery should be around 95%, even if the flask is heated to dryness).
4. a. The density of 2-propanol at 20° is 0.785; hence 20 g were present to start with.
   b. The amount present at the end is to be approximated from the perfect gas law. About 2.0 g remains if the amount of liquid adhering to the walls of the vessel is ignored. About 10% of the product would have been lost.
5. 

6. 

a. Hydrogen bonding causes a major deviation from the curve.
b. The forces between ions should be so great that for a given "molecular weight" the boiling point would be exceedingly high.

7. The molecular weights versus boiling points that should appear on the graph are as follows:

Inert Gas	At. Wt.	Boiling Point, ^{o}C
He	4	-269
Ne	20	-246
Ar	40	-186
Kr	84	-152
Xe	131	-109
Rn	222	-62

8. If the heat supplied to a boiling liquid at a constant temperature is increased, the liquid will boil faster without a significant increase in temperature. However, if heat is applied to its vapor, there is no particular limit to the temperature that can be reached. Hot spots from the mantle or burner heat the portion of the flask that contains the vapor, and the phenomenon of superheating occurs.

EXPERIMENT 3-A

Special Chemicals: Biphenyl, 5 g Methyl Orange, 0.1 g
Comments: The impure material to be crystallized should be ground up thoroughly in a mortar. Students often use too little solvent for the crystallization or lose solvent by evaporation from the hot solution. With good technique and fast filter paper, 50 mL of methyl alcohol is adequate.

The melting point of pure biphenyl is 70.5^{o}.

EXPERIMENT 3-B

Special Chemicals: Biphenyl, 1 g
Benzoic acid, 2 g
Anthranilic acid, 1 g
Special Apparatus: 2 50-mL Conical flasks per mixture
Comments: If the anthranilic acid/benzoic acid mixture must be filtered to remove insoluble material, the funnel should be heated on the steam bath.

Metling points are as follows: Benzoic acid, 122^{o}; biphenyl, 71^{o}; anthranilic acid, 146^{o} (sublimes).

EXPERIMENT 4-A

EXPERIMENT 4-A

Special Chemicals: 1-Butanol, 15 mL
Comments: This experiment can be run concurrently with 4-B if fractional distillation columns are already set up in the laboratory. Three distillations (two with simple apparatus) must then be run in one period. If fractional distillation is to be carried out concurrently or otherwise, the 2-propanol/1-butanol distillate from the simple distillation may be reused for the fractionation.
Answers to Questions

1. The boiling points are: 2-propanol, 83°; 1-butanol, 116°.
2. (The answer should relate to flatness of the plateaus and sharpness of the transition between the two components.)
3. Even though the difference in boiling points between acetone and 2-propanol is smaller, the separation is better. This is related primarily to the larger difference in heats of vaporization: acetone, 134.7 cal/g; 2-propanol, 159.4 cal/g; 1-butanol, 141.3 cal/g.
4. Use the midpoint of the acetone plateau and correct this temperature for atmospheric pressure (see p. 10) and thermometer error.

EXPERIMENT 4-B

Special Chemicals: 1-Butanol, 15 mL (however, see comments).
Special Apparatus: Fractional distilling tubes with at least two theoretical plates.
Comments: This experiment can be run concurrently with 4-A if fractional distillation columns are already set up in the laboratory. Three distillations (one with a fractionating column) must then be run in one period, and one column per three people will suffice. If 4-A and 4-B are combined, the 2-propanol/1-butanol distillate and residue from the simple distillation can be combined and reused for fractionation.
Answers to Questions

1. At equilibrium the vapor above a mixture is richer than the liquid in the more volatile component. A simple distillation, at best, can approach one theoretical equilibration; a fractionating column can have more than one, with successive enrichment of the more volatile component in the distillate.
2. The plateaus are more nearly flat and the temperature transition is more abrupt.
3. By using a longer column, using more-efficient packing, protecting the column from heat loss, and slowing down the distillation.
4. a. (760 torr)(0.90) = 684 torr
   (where 0.90 = mol fraction of N)

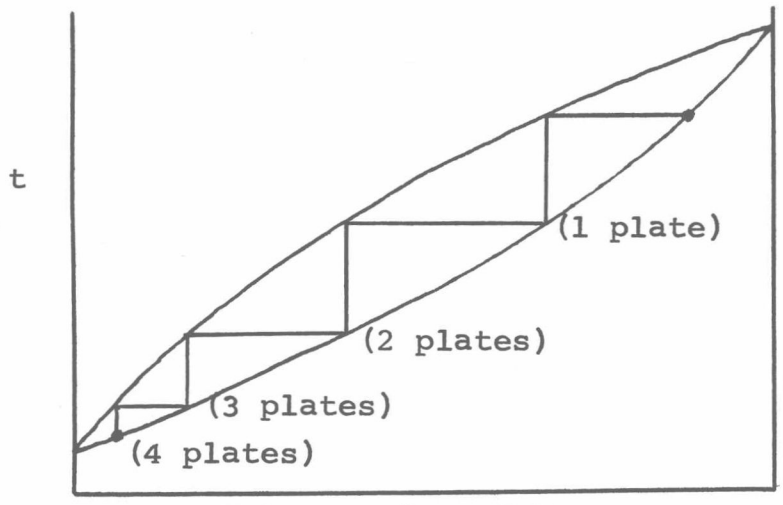
b. The temperature is 100° and the material is pure N.
c. A straight line with zero slope.
d. It would start above 100° and rise as the distillation proceeded.

5. a. 2-Propanol: $(30/60)/[(30/60) + 37/74)] = 0.50$
b. $(0.50)(250 \text{ torr}) = 125 \text{ torr}$.
c. At 100°, $P_{tot} = (0.50)(1260) + (0.50)(320)$
$= 790 \text{ torr}$
At 90°, $P_{tot} = (0.50)(870) + (0.50)(215)$
$= 542 \text{ torr}$
Although a plot of vapor pressure vs temperature is not linear (see Fig. 2-1, p. 10), over a small range of temperature for the purpose of our calculation, we can make such an approximation.

$(10^{\circ})(760 - 542)/(790 - 542) + 90^{\circ} = 99^{\circ}$

d. 2-Propanol:
$[(1260 - 870)(0.9) + 870](0.50) = 610 \text{ torr}$
1-Butanol:
$[(320 - 215)(0.9) + 215](0.50) = \underline{155 \text{ torr}}$
Total $= 765 \text{ torr}$

6.

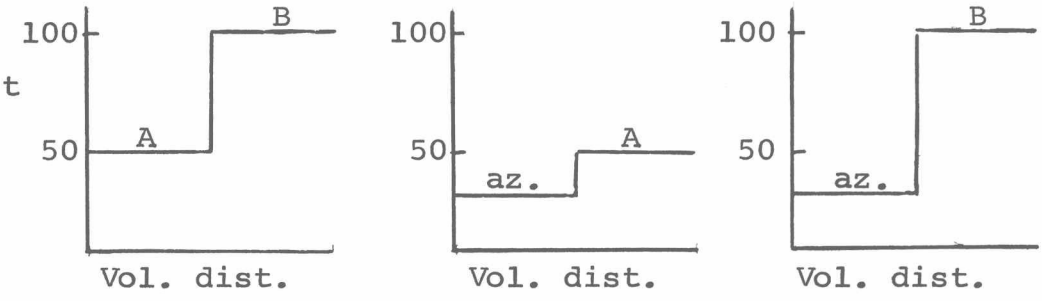


EXPERIMENT 4-C

Special Chemicals: Absolute ethanol, 20 mL
Comments: The composition of the constant-boiling mixture is 30.5% ethanol and 69.5% cyclohexane. It boils at 64.9°.
Answers to Questions
1. The lower phase is water-ethanol.
2. (To be calculated from data.)

EXPERIMENT 4-C

3. The plateaus would have been flatter and the temperature break sharper, but the temperatures would have been about the same and the break-point at the same percentage.
4. a. b. c.



5. Partial pressure of X: (500 torr)(0.5) = 250 torr
Partial pressure of Y:(1000 torr)(0.5) = 500 torr
Total vapor pressure = 750 torr

EXPERIMENT 4-D

Special Chemicals: Acetonitrile 50 mL per 7 students
1-Butanol 75 mL per 7 students
Special Apparatus: Fractional distillation columns with more than two theoretical plates.
Comments: Data from a laboratory section is to be posted by the end of the laboratory period. These data must be available to students for later interpretation by answering the questions.

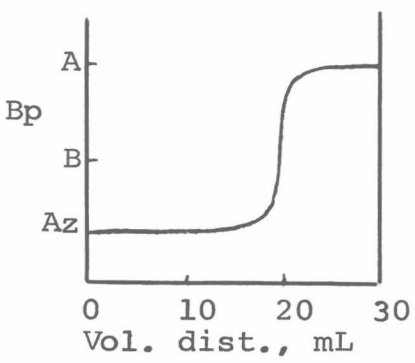
Students run three distillations, two with their desk apparatus and one with special fractionating columns. With proper timing, one-third as many columns as students will suffice.

The mixtures distil as follows:

Acetone/water: reasonably separable.
Ethanol/cyclohexane: azeotrope, bp 64.9°, 70% cyclohexane.
Ethanol/2-propanol: non-azeotrope, bp's 78° (ethanol) and 82°; hard to separate.
Cyclohexane/acetonitrile: Azeotrope, bp 62.2°, 67% cyclohexane.
Cyclohexane/2-propanol: Azeotrope, bp 68.6°, 67% cyclohexane.
2-Propanol/1-butanol: non-azeotrope, bp's 82° 2-propanol) and 117°; fair separation.
Water/1-butanol: Azeotrope, bp 93°, 52% water.

Answers to Questions:
1. (See the systems described under Comments.)

2. The following is a typical situation.



All of B (15 mL) appears in the azeotrope. Total volume of azeotrope = 20 mL, therefore 5 mL of A are in the azeotrope. The azeotrope has 25% of A and 75% of B.

3. a. (Best shown by comparing the boiling point of water with that of compounds 1-4.)
   b. (Best shown by noting that boiling point increases with molecular weight, as in acetone vs cyclohexane.)
   c. (Best shown by noting that acetonitrile has a relatively high boiling point as compared with cyclohexane, even though its molecular weight is much lower.)
   d. (Best shown by comparing primary alcohols.)
4. (See data under Comments.)

EXPERIMENT 5-A

Special Chemicals: Tea leaves, 25 g
Saturated aqueous NaCl, 300 mL
Anhydrous, powdered sodium sulfate, 1 g

Answers to Questions:

1. a. Among the solid remains.
   b. In the aqueous phase.
   c. In the dichloromethane.
   d. In the aqueous phase.
2. Advantages of chloroform: Easier to separate from the aqueous phase because of higher density; easier to handle in a separatory funnel because of lower vapor pressure.
   Disadvantages of chloroform: Higher toxicity; harder to remove by distillation because of higher boiling point.
3. The water vapor pressure over $CaCl_2 \cdot 2H_2O$ is 1 torr; it must be the same over the organic solution because they are at equilibrium.
   Mol fraction of water in organic phase, N_{water}:
   $$P^{o}_{water} N_{water} = 1 \text{ torr} \quad N_{water} = 1/25 = 0.04$$
4. Remains unchanged.
5. (1) Not completely removed from the leaves.
   (2) Not completely removed from aqueous phase by CH_2Cl_2.

EXPERIMENT 5-A

(3) Some remains in the crystallizing solvent.
(4) All losses due to spills and solvents wetting glass surfaces.

EXPERIMENT 5-B

Special Chemicals: Salicylic acid, 0.2 g
Caffeine, 0.2 g (if none is available from Experiment 5-A)

EXPERIMENT 5-C

Special Chemicals: Cola syrup, 50 mL
Salicylic acid, 0.2 g

EXPERIMENT 5-D

Special Chemicals: Ground nutmeg, 50 g
Answers to Questions:

1. Water would not have served as a crystallization solvent because of insolubility due to the long alkyl groups. The presence of three functional groups raises a question about the suitability of the highly non-polar hydrocarbon solvent. Acetone is a reasonable compromise.
2. Ethanol boils above the melting point of trimyristin (49^{o} or 57^{o}, depending on the crystal modification). The product would tend to oil out of the hot ethanolic solution unless a large excess of solvent was present.
3. It has a highly polar (ionic) end and a highly non-polar end. Each has an affinity for a different kind of solvent.

EXPERIMENT 6-A

Special Chemicals: Benzophenone, 0.1 g
Benzhydrol, 0.1 g (see also Comments)
Special Apparatus: Chromatography column; six 50-mL flasks.
Comments: The melting point of benzophenone is 48^{o}; that of benzhydrol is 69^{o}.

A wide variety of materials may be separated by column chromatography. Naphthalene and biphenyl separate well. With a longer (20 cm) column cis- and trans-stilbenes can be separated after the trans-stilbene has been irradiated to promote isomerization. Chlorophyll-carotene mixtures from plants can be separated.

For this experiment we used Merck Chromatographic Grade Alumina, though others are equally satisfactory.

EXPERIMENT 6-B

Special Chemicals: Iodine, 1 g Benzophenone, 0.1 g
Benzhydrol, 0.1 g
Special Apparatus: Two 2-L beakers per station
Thin-layer plates
Comments: We used Mallinckrodt SilicAR TLC-7GF thin layer chromatographic adsorbent. The experiment is most successful if the instructor prepares the plates and distributes them to the class. Mallinckrodt makes a a special tape which can be afixed to the sides of plates; the adsorbent slurry is poured on the plate, and a glass rod is passed over the plates using the tape as a thickness spacer. For a few plates in an emergency, the slurry can be poured on a plate and simply caused to fill the available area by tilting the plate. Eastman Chromatogram Sheets 6060 is silica gel; 6062 is an alumina sheet.

Several other TLC experiments might be of interest. Two or three commercial tablets containing caffeine, phenacetin and acetylsalicylic acid are powdered, extracted with 7 mL of methanol, and the suspension filtered. The mixture is spotted on a silica gel plate along with knowns. Develop with benzene/ether/acetic acid/methanol (120/60/18/1). Detect spots with iodine or with spray reagents (1 part aqueous 5% potassium ferricyanide, 2 parts 10% ferric chloride and 8 parts distilled water); must be freshly prepared; acetylsalicylic acid, brown; phenacetin, blue.

In another option, some leaves from plants are ground up in a mortar with methanol for a few minutes then with petroleum ether/methanol (50/50). The last extraction is mixed with an equal volume of water and the aqueous methanol layer is discarded. The petroleum ether layer is filtered and evaporated to about 10% of its original volume. The petroleum ether layer is spotted on a silica get plate and developed with 1:1 petroleum ether/benzene.

EXPERIMENT 6-C

Special Chemicals: Unknowns consisting of gaseous mixtures of 1-butene, cis-2-butene and trans-2-butene; or, of liquid cyclohexane, cyclohexene and hexane.
Special Apparatus: Gas chromatographs; 2-ml syringes for injecting gas samples; 10-microliter syringes for liquid samples.
Comments: Isobutylene and 1-butene will not separate with the suggested column. Many other mixtures can be used: Benzene/cyclohexane/cyclohexene will separate with a 10-ft column of silicone rubber at about 65°. Acetone and methanol are another pair.

EXPERIMENT 6-C

The instructor should check to see that the filament current is turned off when the column is not in use; should the helium fail while the filaments are heated, the filaments will burn out.

Answers to Questions:

1. The usual process is one of solubility in the column material. The more soluble material is held back relative to the less soluble material.
2. The distilling column is better for large quantities of materials; the GLC works best for analytical uses or separation of small amounts of materials. Better separation occurs in the latter.
3. 122.
4. Silver ion complexes with the olefin and selectively retards olefins relative to alkanes.
5. This corrects for the dead space in the column; you are assuming that the air moves with the gas front throughout the column.

EXPERIMENT 6-D

Special Chemicals:
- 2% Ammonium hydroxide, 10 mL
- 0.05 M solutions of each of the following in 1.5% hydrochloric acid: Glycine, tyrosine, leucine, asparatic acid.
- Unknowns, containing one or more of the above amino acids in 1.5% hydrochloric acid. Each component should be present to the extent of 0.05 M
- Ninhydrin, 2% in ethanol, 5-10 mL

Special Apparatus:
- Whatman No. 1 filter paper cut into 12 x 22 cm pieces
- 1000-mL beaker
- Aluminum foil, to cover beaker
- Rulers or straight edges
- Stapler
- Oven, 100-115^{o}
- Ninhydrin sprayer (perfume type with rubber bulb, or commercial sprayer for use with bulb or compressed air).

EXPERIMENT 7-A

Time: The time for obtaining spectra is very short, but the availability of instruments will determine the total time needed by laboratory sections. As an option, copies of prerecorded spectra may be used as a substitute.

Special Chemicals: It will be necessary to provide about 1 g of each of the listed compounds for every ten students in a laboratory section.

Special Apparatus: Thin-film cells for infrared spectra.
Comments: The student should be expected to note at least the following features about each compound:

Acetophenone. Aromatic and aliphatic C-H stretch; mono-conjugated carbonyl; C-methyl; aromatic bands in the 1500-1600 region; monosubstituted phenyl.

Cyclohexanone. Absence of evidence of aromatic ring; unconjugated ketone-type carbonyl.

Benzyl Alcohol. Hydroxyl stretch, mostly without hydrogen bonding; both aliphatic and aromatic C-H stretch; aromatic bands in the 1500-1600 region; monosubstituted phenyl.

Cyclohexanol. Hydroxyl stretch, mostly without hydrogen bonding; absence of evidence of aromatic ring.

Toluene. Aliphatic and aromatic C-H stretch; aromatic bands in the 1500-1600 region; monosubstituted phenyl; C-methyl; absence of absorption in the carbonyl or hydroxyl region.

Benzaldehyde. Aromatic and aldehydic C-H stretch; aromatic bands in the 1500-1600 region; monosubstituted phenyl; conjugated carbonyl.

Benzonitrile. Aromatic C-H stretch; aromatic bands in the 1500-1600 region; monosubstituted phenyl; nitrile band.

Styrene. Aromatic and vinyl C-H stretch; aromatic bands in the 1500-1600 region; conjugated olefin stretch; terminal methylene; monosubstituted phenyl; absence of carbonyl stretch.

Cyclohexane. Absence of C-H stretch above 3000; absence of hydroxyl or carbonyl stretch; no aromatic bands at 1500-1600 or in the monosbustituted phenyl region; absence of C-methyl.

Methylcyclohexane. Same as cyclohexane except for the presence of C-methyl.

EXPERIMENT 7-B

Special Chemicals: 1 mL each of o-cresol, p-cresol, 2,6-diisopropylphenol, 2,6-di-tert-butylphenol
tert-Butyl alcohol, 2 mL
2-Nitrophenol, 0.5 g
Special Apparatus: 0.05-mm infrared cell
1-mm or 0.5-mm infrared cell (optional)

EXPERIMENT 7-C

Special Apparatus: 1-cm Cells for uv-spectrophotometer
Comments: May be combined with 7B for one period total. Solutions should be prepared before the class meets.
Answers to Questions:

1. Wavelengths (or difference) should be converted to energy units. One factor is E = 28,600/nm.

EXPERIMENT 7-C

279 nm (hexane) = 102.5 and 272 (ethanol) = 105.1 Kcal/mol. 105.1 - 102.5 = 2.6 Kcan/mol.

2. Ground state has high dipole, H-bonds better.
3. Measure abs. max. of acetone in $CHCl_3$ and cyclohexane.

EXPERIMENT 7-D

Time: The procedure is purely a paper experiment unless nmr instrumentation is available.

Special Chemicals: About 1-g amount of the chemicals listed in Experiment 7-A will be necessary if nmr spectra are to be run.

Comments: Since it is highly unlikely that nmr spectra will be run for individual students, it is most convenient to provide spectra for the listed compounds.

Answers to Questions:

1. At 50% transmission, log I_o/I will be equal to log 2.

$$\log 2 = 0.30 = (10{,}000)(1)\underline{c}$$

$$\underline{c} = 3 \times 10^{-5} \text{ mol/liter}$$

2. If we use about a 20% solution of a compound with a molecular weight of 100 and density of about 1.0, the concentration will be approximately 200 g/L or 2 mols/L.
3. Ultraviolet spectrophotometry can be adapted most readily to quantitative measurements; nmr is also useful; but infrared instrumentation is such that quantitative measurements are very difficult. In contrast, ultraviolet spectrophotometry provides the least useful specific information about functional groups of unknown compounds; nmr is the most useful for this purpose because it provides relative numbers of protons responsible for signals, information about general molecular environment through chemical shifts, and details about immediate neighbors of protons through spin-spin splitting; infrared provides information about specific functional groups and gives a profile spectrum of compounds for convenient comparison. Finally, infrared instrumentation is very generally available and infrared spectra are quite easy to obtain; nmr spectra require much more expensive equipment and considerably more skill on the part of the operator; ultraviolet spectra are easily obtained with recording instruments, but the specific data restriction limits the usefulness.
4. First, a decrease in stretching frequency indicates a lower energy for the particular transition. When a carbon-carbon or carbon-oxygen double bond is conjugated, the double bond character decreases (as

shown for example by providing the canonical forms in the resonance structures). A double bond is stronger than a single bond, and the larger force constant of the former will demand greater energy input for excitation of the stretching mode.

EXPERIMENT 8-A

Special Chemicals: Propionic acid, 5 mL
Phenolphthalein indicator solution
0.5 M Sodium hydroxide (see Comments)
Special Apparatus: Buret, 50 mL or 100 mL (see Comments)
Comments: It has been found satisfactory to provide one buret for each three or four students. In this case, it is necessary to make up, or have a group of students make up, about 500 mL of 0.5 M sodium hydroxide for each buret. There is no need for taking pains in making up the solution. Simply dissolve about 12 g of sodium hydroxide pellets in about 500 mL of distilled water.

The distribution coefficient is very close to 0.5.

EXPERIMENT 8-B

Special Chemicals: Formic acid, 3 mL per 10 students
Propionic acid, 15 mL per 10 students
Caproic acid, 3 mL per 10 students
Special Apparatus: See Experiment 8-A
Interpretation of Results:

1. Saturate the water with sodium chloride and extract with the solvent showing the largest value of K.
2. Extract with water (preferably sodium hydroxide solution).
3. In a series of organic acids with one functional group, the distribution coefficient decreases as the molecular weight of the acid increases.
4. Wash the mixture successively with a water solution of sodium hydroxide (to remove the acids as their salts) and water (to remove the impurities left with traces of the aqueous base); dry over calcium chloride; distil.

EXPERIMENT 8-C

Special Chemicals: 1 g Each of 2-butanone, cyclohexanone and acetophenone per laboratory section.
Special Apparatus: 50-Microliter and 1-microliter micropipets (Hamilton syringes are satisfactory).
1-cm Ultraviolet cells
1 50mL Conical flask per compound per students.