

pour the solid directly from the original bottle, because spills are more likely. Carefully transfer the solid to your reaction flask or other container. You may also weigh the solid directly into the reaction vessel by first taring the flask or conical vial. *Clean any spills promptly.*

## 7 MELTING-POINT METHODS AND APPARATUS



See video on *Melting Point Methods*

### Capillary Tubes and Sample Preparation

The laboratory practices and apparatus used to determine **melting points** of solids are discussed in this section, and the theory and use of melting points are described in Section 3.3. The task of determining the melting point of a compound simply involves heating a small amount of a solid and determining the temperature at which it melts. Many different types of heating devices can be used, but most utilize a capillary tube to contain the sample so that only a small amount of the sample is required.

The first step in determining a melting point is transferring the sample into a melting-point capillary tube. Such tubes have one sealed end and are commercially available. The proper method for loading the sample into the capillary tube is as follows. Place a small amount of the solid on a clean watchglass and press the open end of the tube into the solid to force a small amount of solid (about 2–3 mm in height) into the tube (Fig. 16a); this operation should *not* be performed on filter paper, because fibers of paper as well as the solid may be forced into the tube. Then take a piece of 6–8-mm tubing about 1 m long, hold it vertically on a hard surface such as the bench top or floor, and drop the capillary tube down the larger tubing several times with the sealed end *down* (Fig. 16b). This packs the solid sample at the closed end of the capillary tube.

### Melting-Point Determination

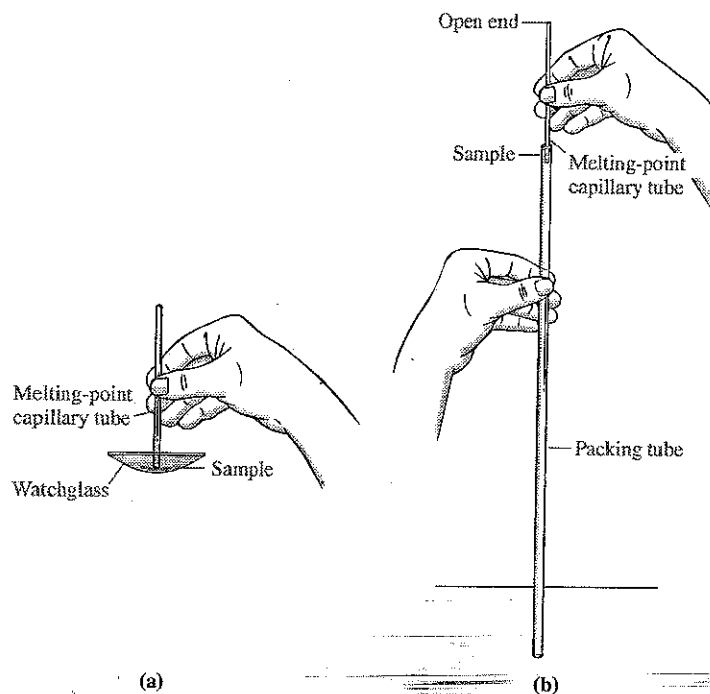
The melting point of the crystalline solid is determined by heating the packed capillary tube until the solid melts. Some representative devices for measuring melting points are presented in Figures 17–19. The most reproducible and accurate results are obtained by heating the sample at the rate of about 1–2 °C/min to ensure that heat is transferred to the sample at the same rate as the temperature increases and that the mercury in the thermometer and the sample in the capillary tube are in thermal equilibrium.

Many organic compounds undergo a change in crystalline structure just before melting, perhaps as a consequence of release of the solvent of crystallization. The solid takes on a softer, “wet” appearance, which may also be accompanied by shrinkage of the sample in the capillary tube. These changes in the sample should *not* be interpreted as the beginning of the melting process. Wait for the first tiny drop of liquid to appear.

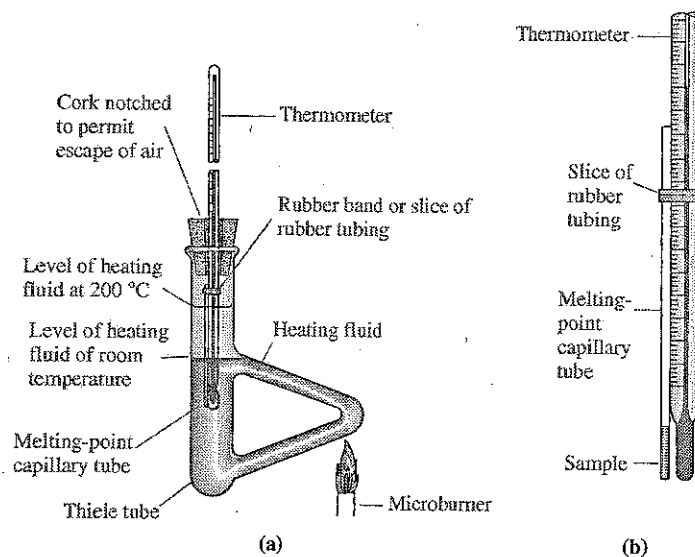
Melting usually occurs over a range of a degree, perhaps slightly more. Accordingly, a **melting-point range** of a compound is typically reported with the lower temperature being that at which the first tiny drop of liquid appears and the higher temperature is that at which the solid has completely melted.

### Melting-Point Apparatus

A simple type of melting-point apparatus is the **Thiele tube**, shown in Figure 17a. This tube is shaped such that the heat applied to a heating liquid in the sidearm by a burner is distributed evenly to all parts of the vessel by convection currents, so

**Figure 16**

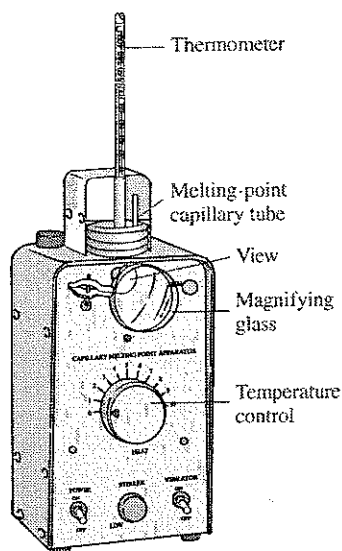
(a) Filling a melting-point capillary tube. (b) Packing the sample at the bottom of the tube.

**Figure 17**

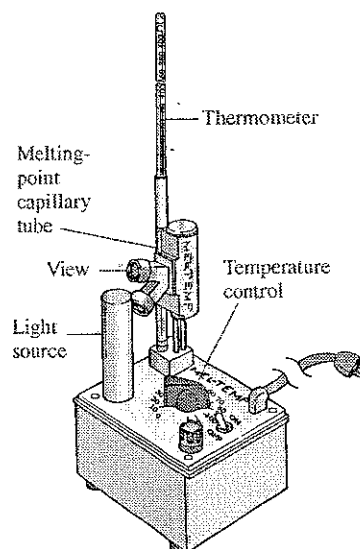
(a) Thiele melting-point apparatus. (b) Arrangement of sample and thermometer for determining melting point.

stirring is not required. Temperature control is accomplished by adjusting the flame produced by the microburner; this may seem difficult at first but can be mastered with practice.

Proper use of the Thiele tube is required to obtain reliable melting points. Secure the capillary tube to the thermometer at the position indicated in Figure 17b using either a rubber band or a small segment of rubber tubing. Be sure that the



**Figure 18**  
Thomas-Hoover© melting-point apparatus (courtesy of Arthur H. Thomas Company).



**Figure 19**  
Mel-Temp© melting-point apparatus (courtesy of Laboratory Devices).

band holding the capillary tube on the thermometer is as close to the top of the tube as possible. Now support the thermometer and the attached capillary tube containing the sample in the apparatus either with a rubber stopper cork, as shown in Figure 17a, or by carefully clamping the thermometer so that it is immersed in the oil. The thermometer and capillary tube must *not* contact the glass of the Thiele tube. Since the oil will expand on heating, make sure that the height of the heating fluid is approximately at the level indicated in Figure 17a and that the rubber band is in the position indicated. Otherwise, the hot oil will come in contact with the rubber, causing the band to expand and loosen; the sample tube may then fall into the oil. Heat the Thiele tube at the rate of  $1\text{--}2\text{ }^{\circ}\text{C}/\text{min}$  in order to determine the melting point. The maximum temperature to which the apparatus can be heated is dictated by the nature of the heating fluid, a topic that is discussed in Section 2.9.

The Thiele tube has been replaced in modern laboratories by various **electric melting-point devices**, which are much more convenient to use. One common type of electric melting-point apparatus is the Thomas-Hoover melting-point unit shown in Figure 18. This particular unit has a built-in vibrating device to pack the sample in the capillary tube, and it also allows for the determination of the melting points of up to five samples simultaneously. The oil bath in this unit is electrically heated and stirred. An electrical resistance heater is immersed in a container of silicone oil. The voltage across the heating element is varied by turning the large knob in the front of the apparatus so that the oil is heated at a slow, controlled rate. A motor drives a stirrer in the oil bath to ensure even heating; the rate of stirring is controlled by a knob at the bottom of the unit. Some models are equipped with a movable magnifying lens system that gives the user a better view of the thermometer

and the sample in the capillary tube. The capillary tube containing the sample is inserted into the apparatus as illustrated in Figure 18.

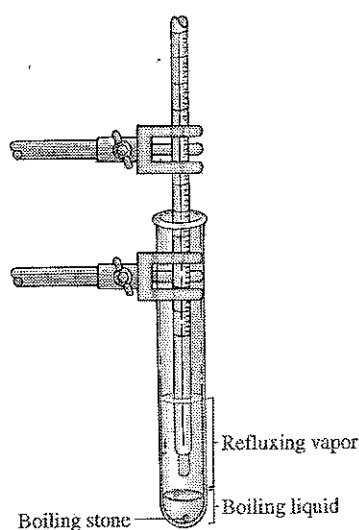
The Mel-Temp<sup>®</sup> apparatus shown in Figure 19 is another electrical unit that utilizes a heated metal block rather than a liquid for transferring the heat to the capillary tube. A thermometer is inserted into a hole bored into the block, and the thermometer gives the temperature of the block and the capillary tube. Heating is accomplished by controlling the voltage applied to the heating element contained within the block.

## 8 BOILING-POINT METHODS AND APPARATUS

There are several techniques that may be used to determine the **boiling point** of a liquid, depending upon the amount of material available. When multigram quantities are available, the boiling point is typically determined by reading the thermometer during a simple distillation, which is described in Section 2.13. However, for smaller amounts of liquid there is sometimes not enough sample to distill, so other techniques have been developed. Two of these are described here.

### Miniscale Method

An accurate boiling point may be determined with as little as 0.5–1.0 mL of liquid using the method illustrated in Figure 20. Working at a hood, place the liquid in a long, narrow Pyrex<sup>®</sup> test tube, and add a small, black carborundum boiling stone; do not use a white marble chip, as bumping is more likely. Clamp the test tube and position the thermometer about 2 cm above the level of the liquid using a second clamp. Bring the liquid rapidly to a vigorous boil using a suitable heating device suggested by your instructor. You should see a reflux ring move up the test tube, and drops of the liquid should condense on the walls of the test tube. Control the amount of heating so the liquid does not boil out of the test tube. Be sure the bulb of the thermometer is fully immersed in the vapor of the boiling liquid long enough to allow the equilibration required for a good temperature reading to be obtained.



**Figure 20**  
*Miniscale technique to determine the boiling point of a liquid.*

## Crystallization

When a solid organic compound is prepared in the laboratory or isolated from a natural source, it is almost always impure. A simple technique for the purification of such a solid compound is **crystallization**. To carry out a crystallization, dissolve the compound in a minimum amount of hot solvent. If insoluble impurities are present, the hot solution is filtered. If the solution is contaminated with colored impurities, it may be treated with decolorizing charcoal and filtered. The hot, saturated solution is finally allowed to cool slowly so that the desired compound crystallizes at a moderate rate. When the crystals are fully formed, they are isolated from the **mother liquor** (the solution) by filtration.

If an extremely pure compound is desired, the filtered crystals may be crystallized again, often referred to as **recrystallization**. Of course, each crystallization results in some loss of the desired compound, which remains dissolved in the mother liquor along with the impurities.

Crystallization is the *slow* formation of a crystalline solid, as opposed to precipitation, which is the *rapid* formation of an amorphous solid. If a hot, saturated solution is cooled too quickly, the compound may precipitate instead of crystallizing. A precipitated solute may contain many impurities trapped in the rapidly formed amorphous mass by entrainment. On the other hand, when a solution is allowed to crystallize slowly, impurities tend to be excluded from the growing crystal structure because the molecules in the crystal lattice are in equilibrium with the molecules in solution. Molecules unsuitable for the crystal lattice are likely to remain in the solution, and only the most suitable molecules are retained in the crystal structure. Because impurities are usually present in low concentration, they remain in solution even when the solution cools.

To understand why a slow and careful crystallization is preferable to a rapid precipitation, consider the mechanism of crystallization. Crystallization occurs in stages. As the hot, saturated solution cools, it becomes supersaturated; then crystal nuclei form. These nuclei often form on the walls of the container, at the liquid surface, or on a foreign body (such as a dust particle), because there is a greater probability of proper molecular association at these locations.

Once the crystal nuclei have been formed, additional molecules migrate to their surfaces by diffusion and join the crystal lattice. Because the molecules must migrate from the bulk of the solution to the growing crystal surface, the solution surrounding the crystal becomes less concentrated than the bulk of the solution. Also, crystal growth is usually exothermic. So the heat released from the growing crystal increases the solubility of the compound near the surface. For crystallization to continue, the concentration of solute at the crystal site must be increased and the

heat must be dissipated. These processes occur by diffusion and take time. Premature chilling or agitation can increase the rate of crystal growth to the point at which a precipitate (an amorphous solid) forms. The purest crystals are obtained when crystallization occurs slowly from an undisturbed solution.

## 1.1 Solvents for Crystallization

The ideal solvent for the crystallization of a particular compound is one that

- does not react with the compound
- boils at a temperature below the compound's melting point
- dissolves a moderately large amount of the compound when hot
- dissolves only a small amount of the compound when cool
- is moderately volatile so that the final crystals can be dried readily
- is nontoxic, nonflammable, and inexpensive
- does not dissolve impurities when hot
- does dissolve impurities when cold

As you might guess, a solvent possessing *all* of these attributes does not exist. The primary consideration in choosing a solvent for crystallizing a compound is that the compound be moderately soluble in the hot solvent and less so in the cold solvent. Unfortunately, the solubility of a compound in a solvent cannot be predicted with accuracy. Most commonly, in the selection of a specific solvent for a specific compound, the solubility of the compound in various solvents is determined by trial and error. If the best solvent for crystallizing a compound is not known, small portions of the compound can be tested with a variety of likely solvents (see Section 1.3B, p. 35).

General guidelines for predicting solubilities based on the structures of organic compounds do exist. For example, an *alcohol*, a compound containing the hydroxyl ( $-\text{OH}$ ) group as its functional group, may be soluble in water because it can form hydrogen bonds with water molecules. *Carboxylic acids* (compounds containing  $-\text{CO}_2\text{H}$  groups) and *amines* (compounds containing  $-\text{NH}_2$ ,  $-\text{NHR}$ , or  $-\text{NR}_2$  groups) also can form hydrogen bonds and are also generally soluble in polar solvents such as water or alcohols.

As the amount of hydrocarbon in the compound increases, the compound's solubility in water will decrease, but it still may be soluble in an alcohol, such as ethanol. Compounds that are largely hydrocarbon in structure are not soluble in polar solvents because  $\text{C}-\text{C}$  and  $\text{C}-\text{H}$  bonds are not polar. For these compounds, we would choose a nonpolar solvent—for example, petroleum ether, which is a mixture of alkanes such as pentane,  $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$ , and hexane,  $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$ . Thus, in choosing crystallization solvents, chemists generally follow the rule of the thumb that like dissolves like. Table 1.1 lists some common crystallization solvents, arranged according to their polarities.

For well-known compounds, suitable crystallization solvents have already been determined. Procedures for experiments in laboratory textbooks and chemical journals usually designate the optimal crystallization solvent.

Ideally, a compound to be crystallized should be soluble in the hot solvent but insoluble in the cold solvent. When such a solvent cannot be found, a chemist may use a *solvent pair*. A solvent pair is simply two miscible liquids chosen so that one

**Table 1.1** Some common crystallization solvents, listed in order of decreasing polarity.

Name	Formula	Dielectric constant*	bp (°C)	Comments
water	H <sub>2</sub> O	78.5	100	—
methanol	CH <sub>3</sub> OH	32.6	65	flammable, toxic
ethanol (95%)	CH <sub>3</sub> CH <sub>2</sub> OH	24.3	78	flammable
acetone	(CH <sub>3</sub> ) <sub>2</sub> C=O	20.7	56	flammable
methylene chloride†	CH <sub>2</sub> Cl <sub>2</sub>	9.1	40	toxic
ethyl acetate	CH <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	6.0	77	flammable
chloroform	CHCl <sub>3</sub>	4.8	61	toxic
diethyl ether	(CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> O	4.3	35	highly flammable
toluene	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	2.4	111	flammable
cyclohexane	C <sub>6</sub> H <sub>12</sub>	2.0	81	flammable
hexanes	C <sub>6</sub> H <sub>14</sub>	2.0	67–69	flammable
petroleum ether‡	C <sub>n</sub> H <sub>2n+2</sub>	~1.8	~30–60	flammable

\* Dielectric constant (a measure of polarity) at about 20°–25°.

† Also known as dichloromethane.

‡ A mixture of alkanes boiling at various ranges as specified by the manufacturer. Ranges of 30°–60° are usually designated “low-boiling petroleum ether” and ranges of 60°–90° are generally designated “high-boiling petroleum ether.” High-boiling petroleum ether is sometimes called “ligroin.” Note that petroleum ether is a mixture of alkanes and not a true ether.

liquid dissolves the compound readily and the other does not. For example, many polar organic compounds are very soluble in ethanol but insoluble in water. To crystallize such a compound, dissolve it in a moderate amount of hot ethanol; then add water drop by drop until the solution becomes turbid (cloudy). Finally, add a few drops of ethanol to redissolve the precipitating compound. The resulting ethanol–water solution is a saturated solution and is allowed to cool slowly so that crystallization will occur. Table 1.2 lists some common solvent pairs.

**Table 1.2** Some common solvent pairs for crystallization.

methanol–water	diethyl ether–methanol
ethanol–water	diethyl ether–acetone
acetone–water	diethyl ether–petroleum ether
benzene–hexanes	methanol–methylene chloride

## 1.2 Steps in Crystallization

Note: The steps discussed in the following paragraphs are summarized in chart form in Figure 1.3, p. 33.

### (1) Dissolving the Compound

The first step in crystallization is dissolving the compound in a minimum amount of the appropriate hot solvent in an Erlenmeyer flask. Be sure to add boiling chips to the flask before you bring the solvent to a boil (see Technique 14, p. 155). An Erlenmeyer flask is used instead of a beaker or other container for several reasons. The solution is less likely to splash out and dust is less likely to get in. The sloping sides allow boiling solvent to condense and return to the solution and allow easy removal of crystals. Also, an Erlenmeyer flask can be corked and stored in your locker.

Pulverize a lumpy solid with a spatula or glass rod to dissolve it more rapidly. To ensure that a minimum amount of solvent is used, add the solvent a few milliliters at a time and heat the mixture with constant stirring or swirling. When almost all of the solid has dissolved, examine the solution and the bottom of the flask for insoluble impurities. If impurities are visible, do not add excess solvent in an attempt to dissolve them, but filter the hot solution (step 2, below). This hot filtration is not necessary and is, in fact, undesirable if the solution looks clear and clean. If the solution appears to be contaminated with colored impurities, decolorizing charcoal may be added at this time. The use of decolorizing charcoal is discussed in Section 1.3C, p. 36.

If impurities are not visible and if the solution is not contaminated with colored impurities, skip the next step and go directly to step 3, Crystallizing the Compound.

### (2) Filtering Insoluble Impurities

Filtering a hot, saturated solution inevitably results in cooling and in evaporation of some of the solvent. Therefore, a premature crystallization of the compound on the filter and in the funnel may occur. A few precautions can minimize this premature crystallization.

To help prevent clogging in the funnel, choose a stemless funnel, a short-stemmed funnel, or a powder funnel. Preheat the funnel by placing boiling chips and a small amount of solvent in the receiving Erlenmeyer flask, resting the funnel on top, and heating. Alternatively, warm the funnel on the flask containing the hot solution to be filtered.

Before filtering, add a little extra solvent (about 5–10% of the total volume) to the solution, and keep the solution hot while preparing the filtration apparatus. Filter the hot solution through either filter paper or a plug of glass wool. If you are using filter paper, choose a porous paper. Filter paper is rated by its porosity, with higher numbers corresponding to lower porosity. For hot filtration, use Whatman's No. 1 or 2; do not use No. 5 or 6, which have slower filter speeds.

Fluted filter paper is preferred to folded filter paper, because the increased surface area of the fluted paper allows the filtration to proceed more rapidly. Figure 1.1 shows how to prepare a piece of fluted filter paper. Place the fluted filter paper

in the warm funnel in the neck of the receiving flask. The funnel must be supported slightly away from the lip of the flask in order to prevent a liquid seal from blocking the flow of air and solvent fumes.

To pour the hot solution, wrap the hot flask in a towel or hold it in a clamp. Do not use a test tube clamp or tongs, because they do not have enough strength to hold the flask. Alternatively, use a pair of inexpensive cotton gloves.

During the filtration, keep both flasks hot on a steam bath or hot plate. To keep the solution hot, pour only small amounts into the filter paper (instead of filling the filter paper to the brim). If a flammable solvent and a hot plate are used, move the flasks away from the hot plate when pouring so that solvent vapors do not flow over the heating element.

If crystallization occurs in the funnel, you can often remove the crystals by heating the receiving flask to boiling with the funnel still on it. Solvent condensing in the funnel may dissolve the crystals and carry them back to the filtered solution. Alternatively, wash the solid into the flask with a little hot solvent.

After all of the hot solution has been filtered, wash the original flask with a small amount of hot solvent. Pour this solvent through the filter paper into the receiving flask to transfer the final traces of the desired compound. Two washings may be necessary; however, use a minimum amount of solvent.

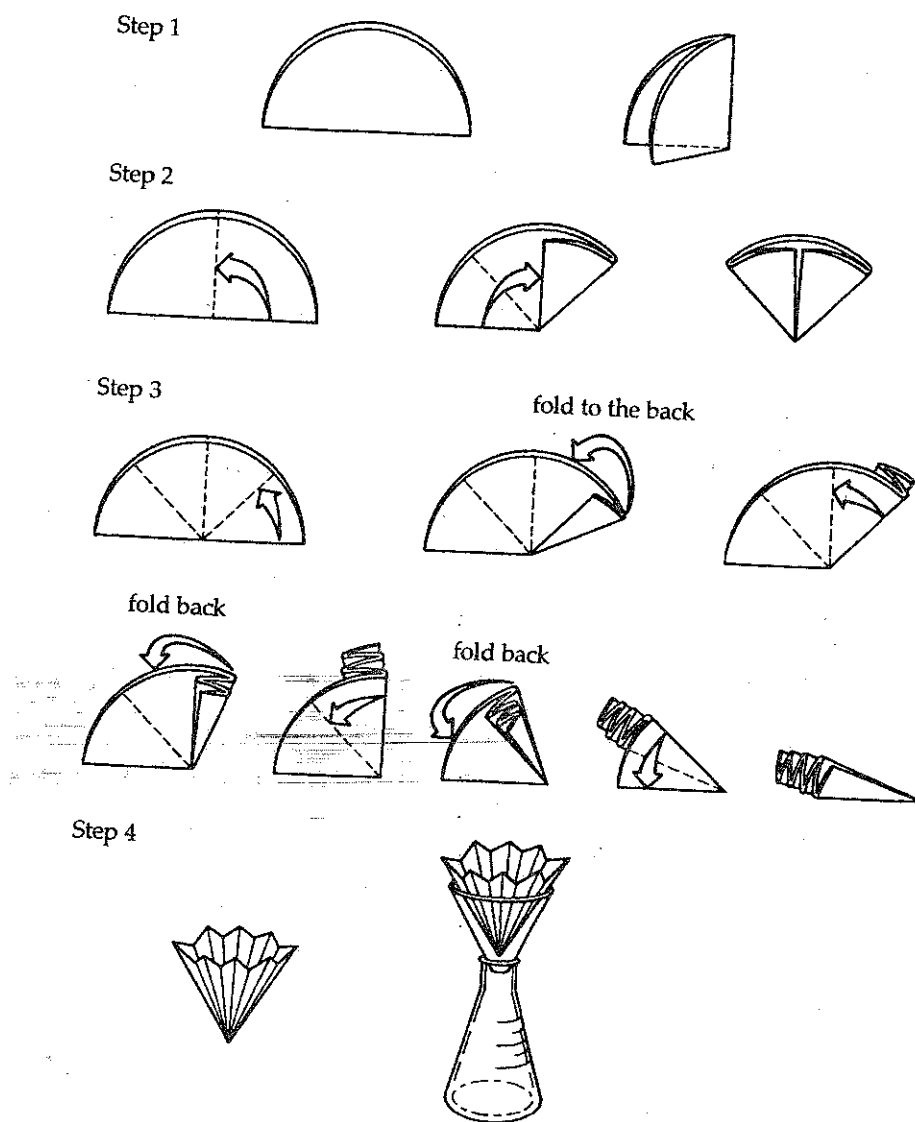
The crystallization flask should contain a hot, clear, saturated solution of the compound. Boil away excess solvent at this time using boiling chips or a boiling stick to prevent bumping. (Remember to use the hood for a toxic or flammable solvent.) If the hot solution starts to crystallize, reheat it to dissolve the crystals. If so much solvent has evaporated that these crystals will not redissolve, add a small additional amount of solvent to the flask and bring the mixture to a boil.

### (3) Crystallizing the Compound

Cover the flask containing the hot, saturated solution with a watch glass or inverted beaker to prevent solvent evaporation and dust contamination. Then set the flask aside where it can remain undisturbed (no jostling or bumping, which will induce precipitation rather than crystallization) for an hour or several hours. If the flask must sit for several days, allow it to cool to room temperature. Then stopper it with a cork (not a rubber stopper if an organic solvent was used) to prevent solvent evaporation.

Chilling the mixture in an ice-water bath after crystallization appears complete will increase the yield of crystals. Be sure to allow ample time for the final crystal growth to occur before chilling.

Sometimes a hot solution cools to room temperature with no crystallization occurring. In such a case, your first question should be, "Is the solution *supersaturated*?" Often, crystallization can be induced in a supersaturated solution by scratching the inside of the flask up and down at the surface of the solution with a glass rod. The scratching of the glass is thought to release microcrystals of glass, which serve as a template, or seeds, for crystal growth. If scratching the flask does not start the crystallization, a seed crystal may be added. A seed crystal is a small crystal of the original material set aside to provide a nucleus upon which other crystals can grow. Sometimes seed crystals can be obtained from the glass rod used for scratching, after the solvent has evaporated from it. Allowing a few drops of solution to



**Figure 1.1** How to prepare fluted filter paper.

evaporate on a watch glass may also produce seed crystals. After addition of the seed crystal, set the flask aside to allow for crystallization to proceed.

If scratching and seeding do not produce crystals, your next question should be, "Did I use *too much* solvent?" If more than the minimum amount of solvent was used in the earlier steps, the excess must be boiled away (reduce the volume by about one-third) and the flask again set aside to crystallize.

Another problem encountered in crystallization is **oiling out**: Instead of crystals appearing, an oily liquid separates from solution. A compound may oil out if its melting point is lower than the boiling point of the solvent. A very impure compound may oil out because the impurities depress its melting point. The formation

of an oil is not selective, as is crystallization; therefore, the oil (even if it solidifies) is probably not a pure compound.

Reheat a mixture that has oiled out in order to dissolve the oil (add more solvent if necessary). Then allow the solution to cool slowly, perhaps adding a seed crystal or scratching with a glass rod. If the substance has a low melting point, a lower-boiling solvent may be necessary. Alternatively, use more solvent and keep the temperature of the solvent below the melting point of the solute.

If these techniques do not prevent oiling out, allow the oil to solidify (a seed crystal or chilling may be necessary), filter the solid or decant (pour off) the solvent, and crystallize the solid using fresh or a different solvent. Enough impurities may have been removed in the attempted crystallization that the second one will proceed smoothly.

#### (4) Isolating the Crystals

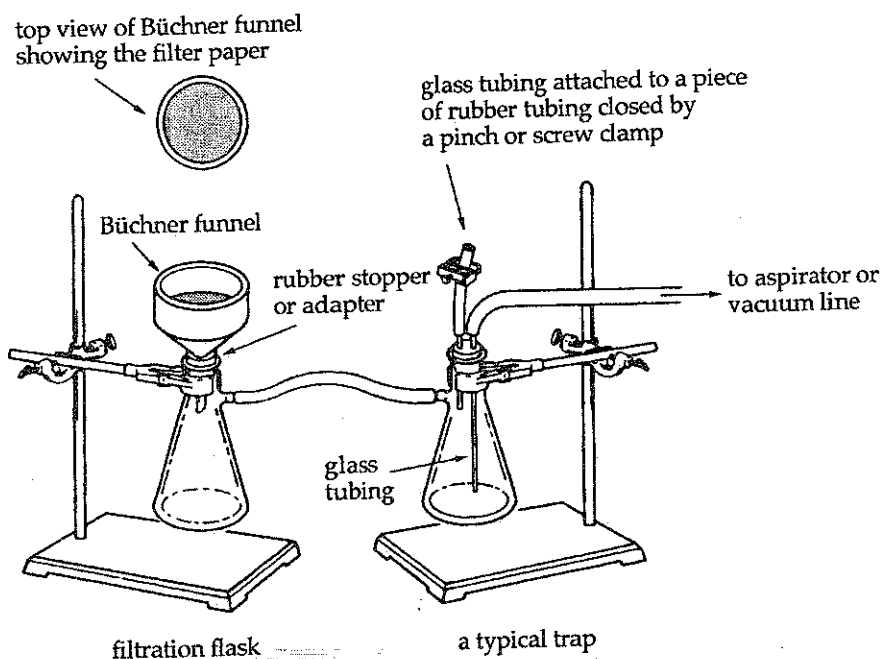
Crystals are separated from their mother liquor by filtration. **Vacuum filtration** is the procedure of choice in all situations unless a very low-boiling crystallization solvent has been used. If a low-boiling solvent is used, the crystals are separated by gravity filtration.

**Vacuum filtration apparatus.** If water or a high-boiling organic solvent (such as the alcohols and most hydrocarbon solvents) has been used, then vacuum or suction filtration is used. Vacuum filtration has the advantage of being much faster than gravity filtration. It has the disadvantage of requiring more equipment. Figure 1.2 shows the physical setup required for vacuum filtration. The trap is necessary regardless of whether a water aspirator or a centralized vacuum system is used. The purpose of this trap is to (1) prevent any solution from being accidentally sucked into the vacuum line and (2) prevent any water from an aspirator from backing up into the filter flask. With a trap, this water will be caught before it contaminates the mother liquor.

Heavy-walled vacuum tubing must be used for vacuum connections, because ordinary tubing collapses when vacuum is applied. All flasks should be clamped to ring stands. The filter flask, especially, should be firmly clamped, because it usually becomes top-heavy when a Büchner funnel and vacuum line are connected to it.

Attach a Büchner funnel or Hirsch funnel to the filter flask with a rubber adapter or a one-holed rubber stopper (best) so that the connection will be airtight when vacuum is applied. Place a medium- or slow-speed filter paper (such as Whatman's No. 2, 5, or 6) on the perforated surface of the funnel. (A fast-speed, porous filter paper allows finely divided solids to pass through under vacuum.) The filter paper must lie flat and not curl up at the sides, yet it must cover all the holes. When the vacuum is applied, the filter paper is pulled snugly to the flat surface of the funnel by suction. To ensure no leakage around the edges, moisten the filter paper with the solvent before applying vacuum.

**Water aspirator.** Many laboratories are equipped with **water aspirators**, devices that attach to faucets and develop a vacuum through a side tube when water flows through the main tube. Place a large beaker in the sink under the water outlet to minimize splashing. Because aspirators are easily plugged, they should be checked before each use. Turn the water on *full force* and hold your finger on the



**Figure 1.2** A vacuum filtration apparatus. *Note:* The flasks and tubing are heavy-walled.

vacuum hole to feel the suction before attaching the rubber tube of your filtration apparatus.

As previously mentioned, an aspirator can "back up." A slight decrease in water pressure can result in a greater vacuum in your filtration apparatus, causing it to suck water back into the apparatus. If you see water entering the trap, break the vacuum by opening the stopcock or pinch clamp on the trap, and then turn off the water.

**The actual filtration.** For nonvolatile solvents like water, apply the vacuum and pour the crystallization mixture into the Büchner funnel at such a rate that the bottom of the funnel is always covered with some solution. For high-boiling organic solvents, pour an initial portion of the mixture into the funnel; then apply the vacuum. In both cases, when the vacuum is applied, the mother liquor is literally sucked through the filter paper into the filter flask while the crystals remain on the filter paper. When the mother liquor ceases to flow from the funnel stem, release the vacuum by opening the stopcock on the trap. Then turn off the aspirator or vacuum line.

**Washing.** To wash the contaminating mother liquor from the crystals, transfer the crystal mass, or *filter cake*, to a small beaker, using a spatula to loosen, remove, and scrape the filter paper. Place fresh filter paper in the Büchner funnel, stir the crystals with a small amount of *chilled* solvent, and then immediately refilter. Small amounts of crystals may be washed right in the funnel on the original filter paper. This procedure is not recommended, because the wet filter paper may tear when you stir the wash solvent into the crystals and because this type of washing is not as thorough as a beaker washing.

Remove excess solvent from the crystals by putting a fresh piece of filter paper *on top of the crystals* still in the funnel and pressing this filter paper down firmly and all over with a cork. Keep the vacuum on during this pressing. When as much solvent has been pressed out of the filter cake as possible, leave the vacuum running for another minute or so. The air pulled through the filter cake will remove even more solvent. Then, open the trap clamp, turn off the vacuum, remove the Büchner funnel, and disconnect the filter flask assembly from the vacuum line. Using a spatula, pry the filter cake from the funnel for drying. The filter cake will often adhere to wet filter paper. Scrape the crystals from the paper only after it has dried.

Do not discard the mother liquor (in the filter flask), but place it in a corked Erlenmeyer flask until the completion of the experiment. The reason for saving the mother liquor is that it may still contain a substantial amount of the desired compound. Until you can determine a percent recovery of yield, you will not know if it is worthwhile to attempt to recover more material.

**Gravity filtration.** Gravity filtration is used if the crystallization solvent is low-boiling, for instance, diethyl ether or methylene chloride. Vacuum filtration should not be used for these solvents, because the solvent will evaporate during the filtration process and contaminate the crystals with the impurities that have just been removed.

Also called "simple filtration," gravity filtration employs a stemmed or stemless funnel and fluted filter paper. Select the size of filter paper that, when folded, will be a few millimeters below the rim of the funnel. Support the funnel in a ring or place it in the neck of an Erlenmeyer flask (use a paper clip to keep the funnel slightly away from the flask). Wet the filter paper with a few milliliters of cold solvent. Pour the mixture to be filtered through the funnel, in portions if necessary. Rinse the crystals on the filter paper with a small amount of chilled solvent, or use the beaker washing method described above.

### (5) Drying the Crystals

The filter cake removed from the Büchner funnel or the gravity filtration filter paper still contains an appreciable amount of solvent. The crystals must be dried thoroughly before they can be weighed or before a melting point can be taken.

There are many methods of drying crystals. The simplest is *air-drying*, in which the crystals (with any lumps crushed) are spread out on a watch glass or large piece of filter paper and allowed to dry. Air-drying is sometimes slow, especially if water or some other high-boiling solvent was used. Unless the crystals are partially covered, they can collect dust. Another watch glass or a beaker, propped on corks to allow air to get to the crystals, may be used as a cover. For a melting-point determination, a few crystals may be removed from the mass and allowed to air-dry on a separate, uncovered watch glass. If a compound is hygroscopic (attracts water from the air), it cannot be air-dried.

In some laboratories, particularly in large student laboratories, drying chemicals on watch glasses in an open room that has a static atmosphere is discouraged for health reasons. Before air-drying your product, check the policy in force in your laboratory.

A desiccator may be used for drying a water-crystallized or hygroscopic compound. A desiccant (drying agent) such as anhydrous calcium chloride is placed in

# Acetylsalicylic Acid

Prepared by Donald L. Pavia, Gary M. Lampman, George S. Kriz, Randall G. Engel  
Western Washington University; North Seattle Community College

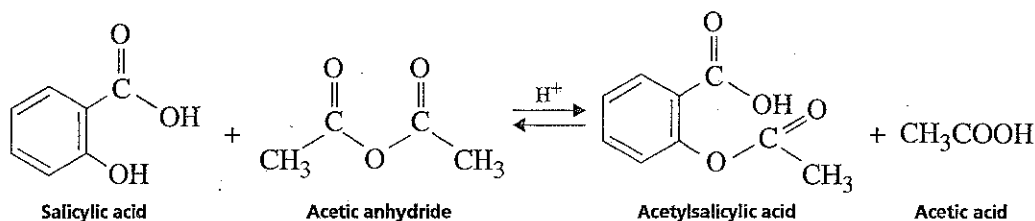
## Crystallization

## Vacuum filtration

## Melting point

## Esterification

Aspirin (acetylsalicylic acid) can be prepared by the reaction between salicylic acid and acetic anhydride:



In this reaction, the hydroxyl group ( $-OH$ ) on the benzene ring in salicylic acid reacts with acetic anhydride to form an ester functional group. Thus, the formation of acetylsalicylic acid is referred to as an **esterification** reaction. This reaction requires the presence of an acid catalyst, indicated by the  $H^+$  above the equilibrium arrows.

When the reaction is complete, some unreacted salicylic acid and acetic anhydride will be present along with acetylsalicylic acid, acetic acid, and the catalyst. The technique used to purify the acetylsalicylic acid from the other substances is called **crystallization**. The basic principle is quite simple. At the end of this reaction, the reaction mixture will be hot, and all substances will be in solution. As the solution is allowed to cool, the solubility of acetylsalicylic acid will decrease, and it will gradually come out of solution, or crystallize. Because the other substances are either liquids at room temperature or are present in much smaller amounts, the crystals formed will be composed mainly of acetylsalicylic acid. Thus, a separation of acetylsalicylic acid from the other materials will have largely been accomplished. The purification process is facilitated by the addition of water after the crystals have formed. The water decreases the solubility of acetylsalicylic acid and dissolves some of the impurities.

To purify the product even more, a recrystallization procedure will also be performed. In order to prevent the decomposition of acetylsalicylic acid, ethyl acetate, rather than water, will be used as the solvent for recrystallization.

## Acetylsalicylic Acid

The most likely impurity in the product after purification is salicylic acid itself, which can arise from incomplete reaction of the starting materials or from hydrolysis (reaction with water) of the product during the isolation steps. The hydrolysis reaction of acetylsalicylic acid produces salicylic acid. Salicylic acid and other compounds that contain a hydroxyl group on the benzene ring are referred to as **phenols**. Phenols form a highly colored complex with ferric chloride ( $\text{Fe}^{3+}$  ion). Aspirin is not a phenol, because it does not possess a hydroxyl group directly attached to the benzene ring. Because aspirin will not give the color reaction with ferric chloride, the presence of salicylic acid in the final product is easily detected. The purity of your product will also be determined by obtaining the melting point.

## REQUIRED READING



Sign in at [www.cengage.com](http://www.cengage.com) to access Pre-Lab Video Exercises for techniques marked with an asterisk.

**Review:** \*Technique 8

\*Technique 9

**New:** Technique 5

Technique 6

\*Technique 7

\*Technique 11

Essay

Filtration, Sections 8.1–8.6

Physical Constants of Solids: The Melting Point

Measurement of Volume and Weight

Heating and Cooling Methods

Reaction Methods, Sections 7.1, 7.4–7.6

Crystallization: Purification of Solids

Aspirin

## SPECIAL INSTRUCTIONS

This experiment involves concentrated sulfuric acid, which is highly corrosive. It will cause burns if it is spilled on the skin. Exercise care in handling it.

## SUGGESTED WASTE DISPOSAL

Dispose of the aqueous filtrate in the container for aqueous waste. The filtrate from the recrystallization in ethyl acetate should be disposed of in the container for non-halogenated organic waste.

## PROCEDURE

**Preparation of Acetylsalicylic Acid (Aspirin).** Weigh 2.0 g of salicylic acid ( $MW = 138.1$ ) and place this in a 125-mL Erlenmeyer flask. Add 5.0 mL of acetic anhydride ( $MW = 102.1$ ,  $d = 1.08 \text{ g/mL}$ ), followed by 5 drops of concentrated sulfuric acid, and swirl the flask gently until

## CAUTION



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the salicylic acid dissolves. Heat the flask gently on the steam bath or in a hot-water bath at about  $50^\circ\text{C}$  (see Technique 6, Figure 6.4) for at least 10 minutes. Allow the flask to cool to room temperature, during which time the acetylsalicylic acid should begin to crystallize from

the reaction mixture. If it does not, scratch the walls of the flask with a glass rod and cool the mixture slightly in an ice bath until crystallization has occurred. After crystal formation is complete (usually when the product appears as a solid mass), add 50 mL of water and cool the mixture in an ice bath.

**Vacuum Filtration.** Collect the product by vacuum filtration on a Büchner funnel (see Technique 8, Section 8.3, and Figure 5). A small amount of additional cold water can be used to aid in the transfer of crystals to the funnel. Rinse the crystals several times with small portions of cold water. Continue drawing air through the crystals on the Büchner funnel by suction until the crystals are free of solvent (5–10 minutes). Remove the crystals for air drying. Weigh the crude product, which may contain some unreacted salicylic acid, and calculate the percentage yield of crude acetylsalicylic acid ( $MW = 180.2$ ).

**Ferric-Chloride Test for Purity.** You can perform this test on a sample of your product that is not completely dry. To determine if there is any salicylic acid remaining in your product, carry out the following procedure. Obtain three small test tubes. Add 0.5 mL of water to each test tube. Dissolve a small amount of salicylic acid in the first tube. Add a similar amount of your product to the second tube. The third test tube, which contains only solvent, will serve as the control. Add 1 drop of 1% ferric chloride solution to each tube and note the color after shaking. Formation of an iron-phenol complex with  $Fe(III)$  gives a definite color ranging from red to violet, depending on the particular phenol present.

**Optional Exercise: Recrystallization.**<sup>1</sup> Water is not a suitable solvent for crystallization because aspirin will partially decompose when heated in water. Follow the general instructions described in Technique 11, Section 11.3, and Figure 11.4. Dissolve the product in a minimum amount of hot ethyl acetate (no more than 2–3 mL) in a 25-mL Erlenmeyer flask, while gently and continuously heating the mixture on a steam bath or a hot plate.<sup>2</sup>

When the mixture cools to room temperature, the aspirin should crystallize. If it does not, evaporate some of the ethyl acetate solvent to concentrate the solution and cool the solution in ice water while scratching the inside of the flask with a glass rod (not a fire-polished one). Collect the product by vacuum filtration, using a Büchner funnel. Any remaining material can be rinsed out of the flask with a few milliliters of cold petroleum ether. Dispose of the residual solvents in the waste container for non-halogenated organic waste. Test the aspirin for purity with ferric chloride as described above. Determine the melting point of your product (see Technique 9, Sections 9.5–9.8). The melting point must be obtained with a completely dried sample. Pure aspirin has a melting point of 135–136°C.

Place your product in a small vial, label it properly Technique 2, Section 2.4, and submit it to your instructor.

## ASPIRIN TABLETS

Aspirin tablets consist of acetylsalicylic acid pressed together with a small amount of inert binding material. Common binding substances include starch, methylcellulose, and microcrystalline cellulose. You can test for the presence of starch by boiling approximately one-

<sup>1</sup>Crystallization is not necessary. The crude product is quite pure and is sometimes degraded by the crystallization (as judged by  $FeCl_3$ ).

<sup>2</sup>It will usually not be necessary to filter the hot mixture. If an appreciable amount of solid material remains, add 5 mL of additional ethyl acetate, heat the solution to boiling, and filter the hot solution by gravity into an Erlenmeyer flask through a fluted filter. Be sure to preheat the short-stemmed funnel by pouring hot ethyl acetate through it (see Technique 8, Section 8.1, and Technique 11, Section 11.3). Reduce the volume until crystals appear. Add a minimum additional amount of hot ethyl acetate until the crystals dissolve. Let the filtered solution stand.

## Acetylsalicylic Acid

fourth of an aspirin tablet with 2 mL of water. Cool the liquid and add a drop of iodine solution. If starch is present, it will form a complex with the iodine. The starch-iodine complex is a deep blue-violet. Repeat this test with a commercial aspirin tablet and with the acetylsalicylic acid prepared in this experiment.

## QUESTIONS

1. What is the purpose of the concentrated sulfuric acid used in the first step?
2. What would happen if the sulfuric acid were left out?
3. If you used 5.0 g of salicylic acid and excess acetic anhydride in the preceding synthesis of aspirin, what would be the theoretical yield of acetylsalicylic acid in moles? in grams?
4. What is the equation for the decomposition reaction that can occur with aspirin?
5. Most aspirin tablets contain five grains of acetylsalicylic acid. How many milligrams is this?
6. A student performed the reaction in this experiment using a water bath at 90°C instead of 50°C. The final product was tested for the presence of phenols with ferric chloride. This test was negative (no color observed); however, the melting point of the dry product was 122–125°C. Explain these results as completely as possible.
7. If the aspirin crystals were not completely dried before the melting point was determined, what effect would this have on the observed melting point?