CER · Modular · Laboratory · Program · in · Chemistry
editor: Joe Jeffers
TECH 701

Measuring the Melting Points of Compounds and Mixtures

prepared by **Joseph W. LeFevre,** SUNY, Oswego

PURPOSE OF THE EXPERIMENT

Measure the melting points of pure benzoic acid and pure mandelic acid. Determine the eutectic composition and the eutectic temperature of benzoic acid–mandelic acid mixtures. Identify an unknown compound using mixture melting points.

BACKGROUND REQUIRED

None

BACKGROUND INFORMATION

The **melting point** of a compound is the temperature at which the solid is in equilibrium with its liquid. A solid compound changes to a liquid when the molecules acquire enough energy to overcome the forces holding them together in an orderly crystalline lattice. For most organic compounds, these intermolecular forces are relatively weak.

The **melting point range** is defined as the span of temperature from the point at which the crystals first begin to liquefy to the point at which the entire sample is liquid. Most pure organic compounds melt over a narrow temperature range of 1–2 °C.

The presence of a soluble impurity almost always causes a decrease in the melting point expected for the pure compound and a broadening of the melting point range. In order to understand the effects of impurities on melting point behavior, consider the melting point–mass percent composition diagram for two different fictitious organic compounds, *X* and *Y*, shown in Figure 1. The vertical axis represents temperature and the horizontal axis represents varying mass percent compositions of *X* and *Y*.

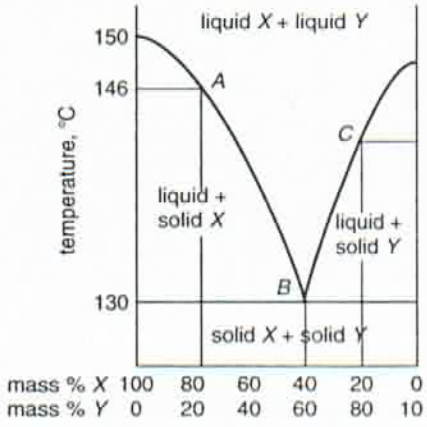

Figure 1 Melting point–mass percent composition diagram for a two-component mixture

Both compounds have sharp melting points. Compound *X* melts at 150 °C, as shown on the left vertical axis, and *Y* melts at 148 °C, as shown on the right vertical axis. As compound *X* is added to pure *Y*, the melting point of the mixture decreases along curve *CB* until a minimum temperature of 130 °C is reached. Point *B* corresponds to 40 mass percent *X* and 60 mass percent *Y* and is called the **eutectic composition** for compounds *X* and *Y*. Here, both solid *X* and solid *Y* are in equilibrium with the liquid. The **eutectic temperature** of 130 °C is the lowest possible melting point for a mixture of *X* and *Y*. At temperatures below 130 °C, mixtures of *X* and *Y* exist together only in solid form.

Consider a 100-microgram (µg) mixture composed of 20 µg of *X* and 80 µg of *Y*. In this mixture, *X* acts as an impurity in *Y*. As the mixture is heated, the temperature rises to the eutectic temperature of 130 °C. At this temperature, *X* and *Y* begin to melt together at point *B*, the eutectic composition of 40 mass percent *X* and 60 mass percent *Y*. The temperature remains constant at 130 °C until all 20 µg of *X* melts. At the eutectic temperature, *X* and *Y* will melt in the ratio of 40 parts *X* to 60 parts *Y*. If 20 µg of *X* melts, then 30 µg of *Y* (20 µg *X* × 60/40 ratio = 30 µg *Y*) also melts. At this point, the remaining 50 µg of solid *Y* (80 µg − 30 µg = 50 µg) is in equilibrium with a molten mixture of the eutectic composition.

As more heat is applied to the mixture, the temperature begins to rise, and the remaining *Y* begins to melt. *Y* continues to melt as the temperature increases, shown by curve *BC*.

Finally, at 142 °C, point *C*, where the liquid composition is 20 mass percent *X* and 80 mass percent *Y*, all of *Y* is melted. At temperatures higher than 142 °C, liquid *X* and liquid *Y* exist together with a composition of 20 mass percent *X* and 80 mass percent *Y*. Thus, the melting point at which the entire mixture liquefies is 142 °C, six degrees lower than the melting point of pure *Y*. Also, the melting point range 130–142 °C is quite broad.

In the previous example, *X* acts as an impurity in *Y*. Compound *Y* can also act as an impurity in *X*, as indicated in Figure 1 earlier in this experiment. For example, in a mixture composed of 80 µg of *X* and 20 µg of *Y*, the mixture begins to melt at the eutectic temperature of 130 °C. As before, at this temperature, the eutectic composition is 40 mass percent *X* and 60 mass percent *Y*. The temperature remains at 130 °C until all 20 µg of *Y* melts. At the eutectic temperature, *X* and *Y* will melt in the ratio of 40 parts *X* to 60 parts *Y*. Thus, if 20 µg of *Y* melts, 13 µg of *X* (20 µg *Y* × 40/60 ratio = 13 µg *X*) also melts.

The remaining 67 µg of *X* (80 µg − 13 µg = 67 µg) melts over the range of 130–146 °C, shown by curve *BA*. At 146 °C, the last traces of *X* melt. This melting range is larger than the range over which 20 mass percent *X* and 80 mass percent *Y* melts.

If a mixture has exactly the eutectic composition of 40 mass percent X and 60 mass percent *Y*, the mixture shows a sharp melting point at 130 °C. Observing this melting point could lead to the false conclusion that the mixture is a pure compound. Addition of either pure *X* or pure *Y* to the mixture causes an increase in the melting point, as indicated by curve *BA* or *BC*, respectively. Observing this melting point increase indicates that the original sample is not pure.

The initial melting that occurs at the eutectic temperature is sometimes very difficult to observe. This difficulty is especially true if only a small amount of an impurity is present, because the quantity of liquid produced at the eutectic temperature is very small. However, the temperature at which the last trace of solid melts can be accurately measured. Hence, a sample with a small amount of impurity will have an observed melting point much higher than the eutectic temperature, but lower than that of the pure compound.

Because the melting point of a compound is a physical constant, the melting point can be helpful in determining the identity of an unknown compound. A good correlation between the experimentally measured melting point of an unknown compound and the accepted melting point

of a known compound suggests that the compounds may be the same. However, many different compounds have the same melting point.

A **mixture melting point** is useful in confirming the identity of an unknown compound. A small portion of a known compound, whose melting point is known from the chemical literature, is mixed with the unknown compound. If the melting point of the mixture is the same as that of the known compound, then the known and the unknown compounds are most likely identical. A decrease in the melting point of the mixture and a broadening of the melting point range indicates that the compounds are different. A flowchart for using a mixture melting point to identify an unknown compound is shown in Figure 2.

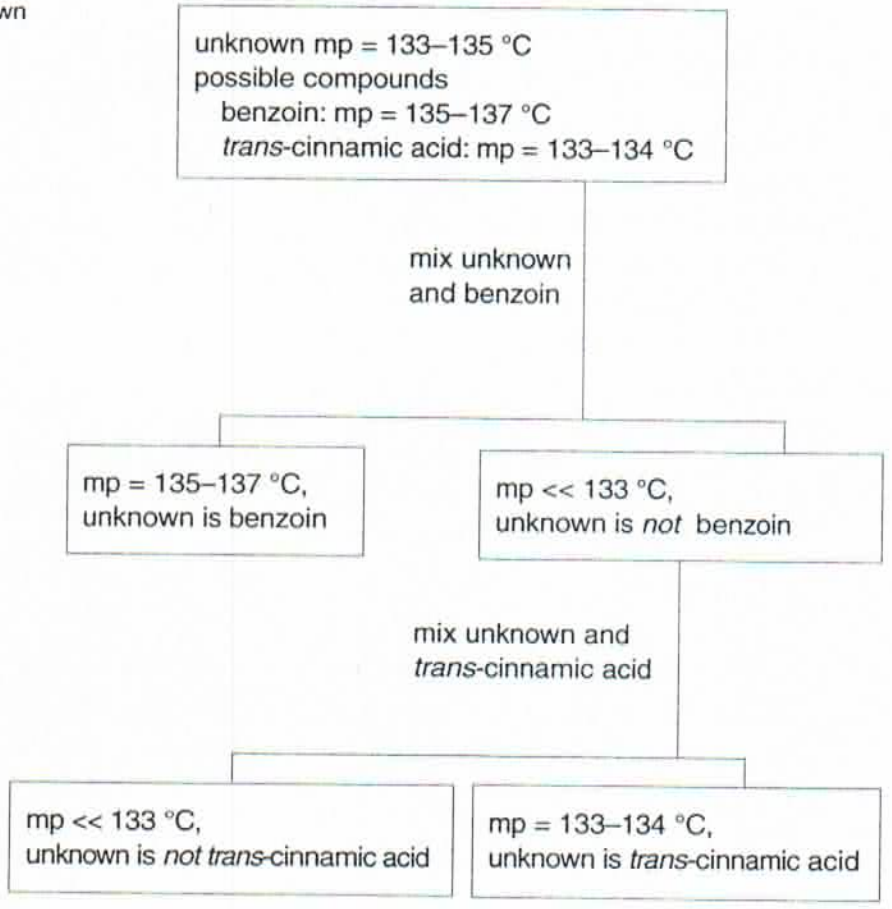

Figure 2 Flowchart for mixture melting point determination of an unknown

Melting points can also be used to assess compound purity. A melting point range of 5 °C or more indicates that a compound is impure. Purification of the compound causes the melting point range to narrow and the melting point to increase. Repeated purification may be necessary before the melting point range narrows to 1–2 °C and reaches its maximum value, indicating that the compound is pure.

Measuring Melting Points

In practice, measuring the melting point of a crystalline compound involves several steps. First, a finely powdered compound is packed into a melting point capillary tube to a depth of 1–2 mm. Then the capillary tube containing the sample compound is inserted into one of several devices used to measure melting points.

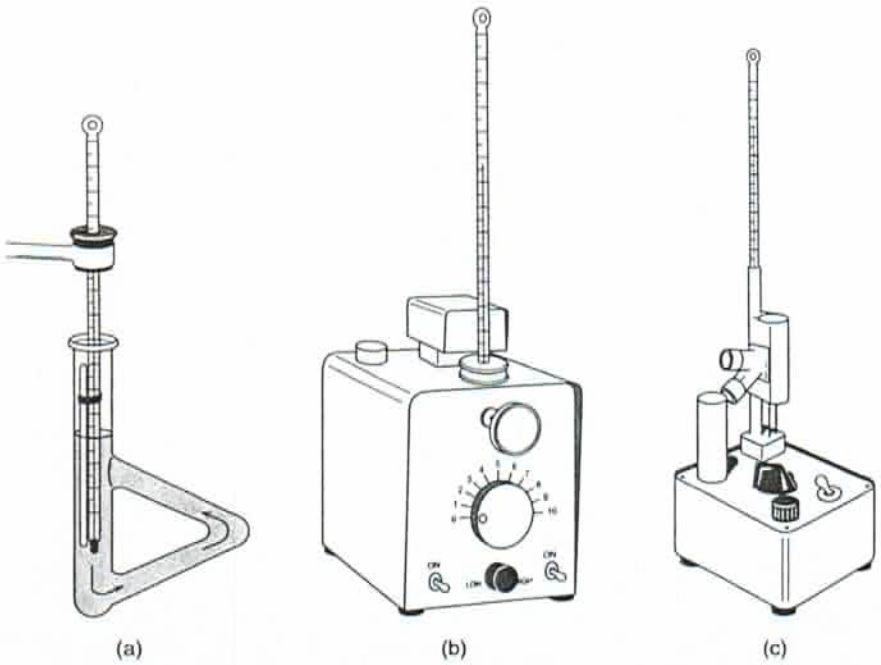

Figure 3 Different types of melting point apparatus: (a) Thiele tube; (b) Thomas–Hoover; (c) Mel-Temp

Figure 3(a) shows the Thiele tube apparatus, filled to the base of the neck with silicone oil or mineral oil. The capillary tube is attached to a thermometer so that the sample is located next to the middle of the thermometer bulb. The thermometer is inserted into the oil and then the side arm of the Thiele tube is heated with a Bunsen burner flame.

The Thomas–Hoover Uni-Melt device, shown in Figure 3(b), contains silicone oil that is stirred and heated electrically. Silicone oil can be heated to temperatures up to 250 °C. With this device, up to seven samples can be analyzed at one time.

The Mel-Temp apparatus, shown in Figure 3(c), consists of an aluminum block that is heated electrically. The aluminum block can be heated easily to temperatures up to 400 °C, and can tolerate temperatures up to 500 °C for brief time periods. A thermometer and up to three samples can be inserted into the block at one time. A light and magnifier permit easy viewing of the sample(s).

If the melting point of the compound is unknown, it is convenient to first measure the approximate melting point of the compound, called the **orientation melting point.** The sample is heated at a rate of 10–15 °C per minute until it melts. Then the melting point apparatus is cooled to approximately 15 °C below the orientation melting point. A new sample is heated, increasing the temperature at a much slower rate of 1–2 °C per minute, to accurately measure the melting point. A slow heating rate is necessary because heating a sample too rapidly may cause the thermometer reading to differ from the actual temperature of the heat source. The result would be an observed temperature reading that differs from the actual melting point temperature.

If the melting point of the sample is known, the sample can be quickly heated to within 10–15 °C of its melting point. Then the heating rate can be slowed to increase 1–2 °C per minute until the sample melts.

Errors in observed melting points often occur due to a poor heat transfer rate from the heat source to the compound. One cause of a poor heat transfer rate is the placement of too much sample into the capillary tube. Finely ground particles of the compound are also necessary for good heat transfer. If the particles are too coarse, they do not pack well, causing air pockets that slow heat transfer.

Sometimes slight changes, such as shrinking and sagging, occur in the crystalline structure of the sample before melting occurs. Also, traces of solvent may be present due to insufficient drying and may appear as droplets on the outside surface of the sample. This phenomenon is called **sweating** and should not be mistaken for melting. The initial melting point temperature always corresponds to the first appearance of liquid within the bulk of the sample itself.

Some compounds decompose at or near their melting points. This decomposition is usually characterized by a darkening in the color of the compound as it melts. If the decomposition and melting occur over a narrow temperature range of 1–2 °C, the melting point is used for identification and as an indication of sample purity. The melting point of such a compound is listed in the literature accompanied by *d* or *decomp*. If the sample melts over a large temperature range with decomposition, the data cannot be used for identification purposes.

Some compounds pass directly from solid to vapor without going through the liquid phase, a behavior called **sublimation.** When sublimation occurs, the sample at the bottom of the capillary tube vaporizes and recrystallizes higher up in the capillary tube. A sealed capillary tube is used to take the melting point of a compound that sublimes at or below its melting point. The literature reports the melting point for these compounds accompanied by *s*, *sub*, or *subl*.

In this experiment you will measure the melting points of benzoic acid, mandelic acid, and mixtures of these two compounds. Both compounds melt near 122 °C. You will use these data to construct a melting point–mass percent composition diagram. From this diagram, you will estimate the eutectic temperature and eutectic composition for benzoic acid and mandelic acid. Finally, using the mixture melting point method, you will identify an unknown compound.

Measuring the Melting Points of Compounds and Mixtures

Equipment

graph paper	metric ruler (mm)
marking pen	microspatula
melting point capillary tubes	2 watch glasses

Reagents and Properties

substance	*quantity*	*molar mass (g/mol)*	*mp (°C)*	*bp (°C)*
benzoic acid	10 mg	122.12	122–123	249
mandelic acid	10 mg	152.15	120–122	

Preview

- Measure the melting point of benzoic acid
- Measure the melting point of mandelic acid
- Measure the melting point range of four mixtures containing various amounts of benzoic acid and mandelic acid
- Obtain a sample of an unknown compound
- Measure an orientation melting point and an accurate melting point of your unknown compound
- Obtain a sample of each of two substances appearing in Table 1 that have melting points similar to your unknown
- Prepare a mixture of your unknown compound and each of your selected compounds
- Measure the melting point of each mixture
- Identify your unknown compound

PROCEDURE

Caution: Wear departmentally approved safety goggles at all times while in the chemistry laboratory.

Always use caution in the laboratory. Many chemicals are potentially harmful. Prevent contact with your eyes, skin, and clothing. Avoid ingesting any of the reagents.

1. Measuring Melting Points of Benzoic Acid and Mandelic Acid

Caution: Benzoic acid is an irritant.

Place 2–3 mg of benzoic acid on a clean, dry watch glass. If the compound is not a fine powder, pulverize it using a microspatula.

Caution: Capillary tubes are fragile and easily broken.

Load a melting point capillary tube by pressing the open end of the tube into the powder. Pack the powder into the closed end of the tube by tapping the closed end against the bench top. Repeat the cycle of loading and packing until you can see 1–2 mm of benzoic acid through the tube. [NOTE 1]

NOTE 1: Make certain that no more than 1–2 mm of compound is placed in the capillary tube. A larger amount will give a melting point range that is too large.

To ensure good packing, drop the capillary tube with the open end up through a 1-m-long piece of glass tubing onto the bench top. Repeat several times. Place the capillary tube in the melting point apparatus provided by your laboratory instructor.

Because pure benzoic acid melts at 122–123 °C, heat the capillary tube rapidly to 110 °C. Then slow the heating rate to 1–2 °C per min. [NOTE 2] Record the temperature at which liquid first appears in the bulk of the sample and the temperature at which the entire sample becomes liquid.

NOTE 2: Heating the capillary tube too quickly near the melting point will result in an inaccurate melting point measurement.

Caution: The capillary tubes are hot. Allow them to cool enough to avoid burning your fingers.

When finished, remove the capillary tube. Place all used capillary tubes in the container labeled "Discarded Capillary Tubes", provided by your laboratory instructor.

Obtain 2–3 mg of mandelic acid and measure the melting point following the procedure described for benzoic acid. Pure mandelic acid melts at 120–122 °C.

2. Determining the Eutectic Temperature and Composition of a Benzoic Acid–Mandelic Acid Mixture

From your laboratory instructor, obtain four benzoic acid–mandelic acid mixtures of the following compositions:

	percent benzoic acid	*percent mandelic acid*
mixture 1	80	20
mixture 2	60	40
mixture 3	40	60
mixture 4	20	80

Using a marking pen, carefully label a capillary tube for each mixture. For example, near the top of the tube, mark the tube that will contain mixture 1 with one horizontal line. Similarly, mark the tubes for mixtures 2–4 with two, three, and four lines, respectively. Load each mixture into its capillary tube as previously described.

Place the capillaries containing mixtures 1 and 2 into the melting point apparatus. [NOTE 3] Heat the samples rapidly to 80 °C. Then slow the rate of increase to 1–2 °C per min. *Carefully* observe and record the temperature at which the crystals first begin to melt and the temperature at which the last trace of crystals melts. [NOTE 4]

Allow the apparatus to cool to 80 °C and repeat the melting point measurements, using the capillaries containing mixtures 3 and 4.

NOTE 3: If you are using a Thiele tube, place the samples to the left and right of the thermometer bulb. Secure them in place with a small ring of rubber tubing, as shown in Figure 4. Make certain the bottom of the capillary tube is positioned vertically near the midpoint of the thermometer bulb. Also, be certain the rubber tubing and pen marks are 2–3 cm above the oil surface because the oil expands when heated.

NOTE 4: If you are using a Mel-Temp apparatus, you will need to lift the samples a few millimeters above the base and slowly rotate the samples to see the last trace of crystals melt. Be careful not to break the capillary tubes.

3. Identifying an Unknown Compound by Mixture Melting Point

Caution: Unknowns may be flammable, toxic, and irritating.

Obtain 10 mg of an unknown compound from your laboratory instructor and record its identification code. Pulverize the sample, label and load a capillary tube, and take an orientation melting point. Cool the apparatus to 15 °C below its orientation melting point. Prepare a new sample, and accurately measure the melting point.

From Table 1 (on the next page), identify the two compounds that have melting points closest to the melting point of your unknown compound. Obtain a few milligrams of each of these compounds. Place one known compound on a clean, dry, labeled watch glass. Add an approximately equal amount of your unknown compound.

Similarly, place the other known compound on a second watch glass and add an approximately equal amount of your unknown. Pulverize and mix each sample thoroughly, using a clean microspatula each time. Load the samples into separate, labeled capillary tubes. Also, load two capillary tubes with pure unknown.

Take the melting point of one of the mixtures and the pure unknown *simultaneously*. Quickly heat the samples to within 30 °C of the pure compound's melting point. Then slow the heating rate increase to 1–2 °C per min.

Repeat the procedure using the other mixture. Compare your data and identify your unknown.

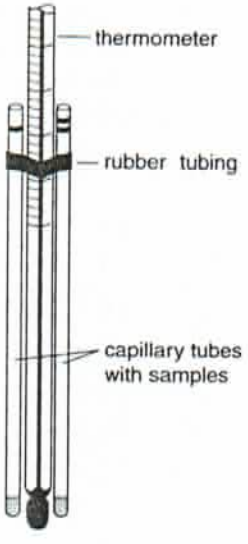

Figure 4 Attachment of two capillary tubes to a thermometer

Table 1 Melting points of compounds used as unknowns

compound	*mp (°C)*	*compound*	*mp (°C)*
benzhydrol	65–67	*trans*-cinnamic acid	133–134
biphenyl	69–72	benzoin	135–137
phenanthrene	99–101	benzilic acid	150–153
o-toluic acid	103–105	adipic acid	152–154
acetanilide	113–115	benzanilide	164–166
fluorene	114–116	4-bromoacetanilide	167–169
(*R,S*)-mandelic acid	120–122	4-hydroxybenzoic acid	215–217
benzoic acid	122–123	anthracene	216–218

4. Cleaning Up Use the labeled collection containers provided by your laboratory instructor. Wash your glassware with soap or detergent.

Caution: Wash your hands thoroughly with soap or detergent before leaving the laboratory.