Chapter 10: Melting Point

The melting point of a compound is the temperature or the range of temperature at which it melts. For an organic compound, the melting point is well defined and used both to identify and to assess the purity of a solid compound.

10.1 Compound Identification

An organic compound's melting point is one of several physical properties by which it is identified. A physical property is a property that is intrinsic to a compound when it is pure, such as its color, boiling point, density, refractive index, optical rotation, and spectra (IR, NMR, UV-VIS, and MS). A chemist must measure several physical properties of a compound to determine its identity. Since melting points are relatively easy and inexpensive to determine, they are handy identification tools to the organic chemist.

The graph in Figure 10-1 illustrates the ideal melting behavior of a solid compound. At a temperature below the melting point, only solid is present. As heat is applied, the temperature of the solid initially rises and the intermolecular vibrations in the crystal increase. When the melting point is reached, additional heat input goes into separating molecules from the crystal rather than raising the temperature of the solid: the temperature remains constant with heat input at the melting point. When all of the solid has been changed to liquid, heat input raises the temperature of the liquid and molecular motion within the liquid increases.

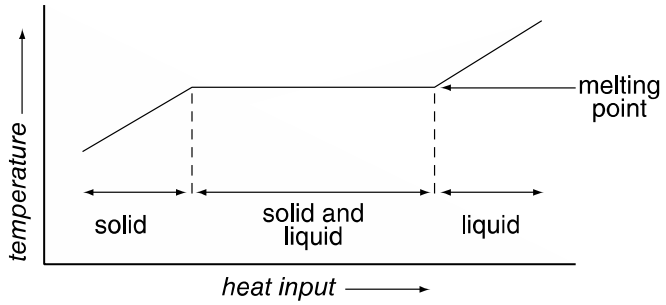

Figure 10-1: Melting behavior of solid compounds.

Because the temperature of the solid remains constant with heat input at the transition between solid and liquid phases, the observer sees a sharp melting point. Each pure compound has a particular temperature – the melting point – at which this phase change occurs.

The atmospheric pressure in Colorado is lower than the atmospheric pressure at sea level. Physical data in the literature, including melting points, are measured at standard conditions, or 760 torr. Are melting points different because of the decreased atmospheric vapor pressure in Boulder? The answer is no, because the vapor pressure of solids is low, so the melting points or the temperature at which the vapor pressure of the solid equals that of the liquid are not influenced by normal atmospheric pressure changes.

Once the melting point of the compound is determined, the value is compared with those of known compounds. More information about where to find literature values for melting points is given in Chapter 2 of this Handbook. However, determination of a melting point – even a mixed melting point (see section 10.4) – does not absolutely identify a compound because more than one compound could have the same melting point.

10.2 Visual Observation of Melting Point

There are several points of interest that occur when a substance melts, based on the varying amounts of liquid and solid that are present. These are shown in Figure 10-2.

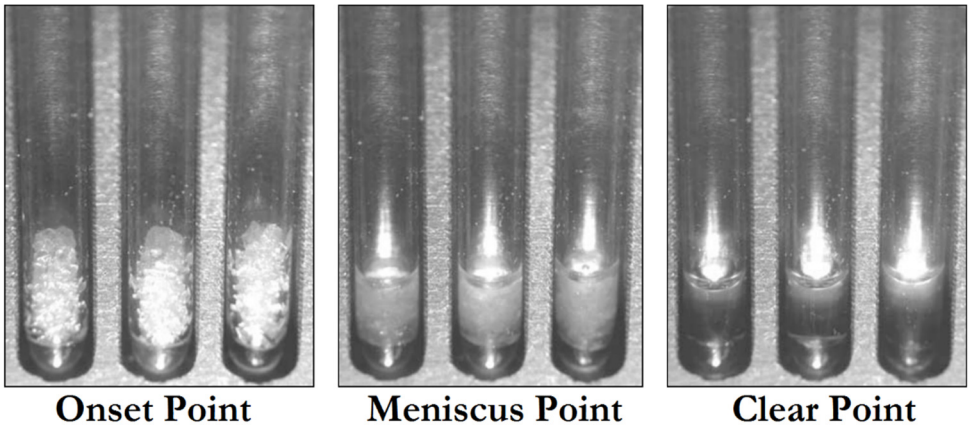

Figure 10-2: The onset point, meniscus point, and clear point are the three most important visual observations.

The onset point, or collapse point, is considered the point at which the melt officially begins. This is the lowest temperature at which a small amount of liquid is clearly visible. The meniscus point is the lowest temperature at which enough liquid is present to form a meniscus (a curve where the liquid adheres to the walls of the tube). The clear point is the lowest temperature at which all the solid has melted and there is only liquid remaining in the tube.

The clear point is more dependent on the speed of heating than the other two points are. For this reason, the more slowly you heat the sample, the more accurate your results will be. In most US-based literature sources, if a single temperature is listed, it will be for the clearing point. (By contrast, many European sources typically list the meniscus point, so they may differ by a degree or two from US sources for the same compound.) However, for the purpose of writing lab reports, it is more useful to report the range between the onset point and the clear point.

10.3 Determination of Purity

A pure organic solid compound melts at a specific temperature or within a narrow temperature range (0.5 to 2°C). A melting range of 1–2°C indicates an organic compound is pure enough for most purposes. If a compound is contaminated with even small amounts of an impurity, the melting range will be wider and lower. As a rule of thumb, each 1% of the sample that is impurities will result in a 0.5°C depression of melting point.

Why do impurities lower melting point? A review of some of the principles learned in general chemistry will help in your understanding of melting point behavior.

The melting point of a compound is identical to its freezing point. The melting point/freezing point is the temperature at which the liquid and solid phases coexist in equilibrium; the molecules move from liquid to solid and solid to liquid at the same rate. At the melting temperature, the vapor pressure of the solid equals the vapor pressure of the liquid.

Recall from general chemistry the colligative properties of ideal solutions: freezing-point depression, boiling-point elevation, and osmotic pressure. Colligative properties of solutions depend only on the

number – not on the identity – of the solute particles in the solution. The presence of nonvolatile solute molecules in a solution causes freezing point depression because they lower the vapor pressure of the liquid. Impurities do not affect the vapor pressure of the solid.

Since at any given temperature the vapor pressure of a liquid mixture is lower than the vapor pressure of the pure liquid, the mixture's vapor pressure will match the vapor pressure of the solid at a lower temperature. Thus, the mixture will freeze at a lower temperature: freezing point depression. The greater the number of solute molecules in the mixture, the larger the depression.

A classic illustration of freezing point depression is the addition of salt to water. Salt water freezes at a temperature below 0°C, the exact freezing temperature depending on the amount of salt in the water.'

How does freezing point depression apply to the melting point depression of a contaminated solid? Consider a mixture of a solid, called for convenience the "primary" solid, and a small amount of another solid compound, called the "impurity." The temperature of the mixture is raised slowly, and eventually the primary solid starts to "soften." (This phenomenon is not really visible – it happens before any liquid is actually seen.) As soon as this happens, the impurity dissolves in the soft or melted parts of the primary solid, thus becoming a "solute" in the liquid. This liquid has a lower freezing/melting point than the pure compound, and an observer sees the compound melt at a temperature lower than the literature value reported for the pure compound.

A hypothetical melting point-composition curve for various molar compositions of a mixture of two compounds A and B is illustrated in the graph in Figure 10-3. Pure A melts sharply at the melting point of A; as B is added to A, the melting range will become wider and the entire melting range will be lowered. Consider a mixture of composition x. As heat is applied to the mixture, it will start to melt at temperature y, and continue melting until temperature z, at which point the entire mixture will be a liquid.

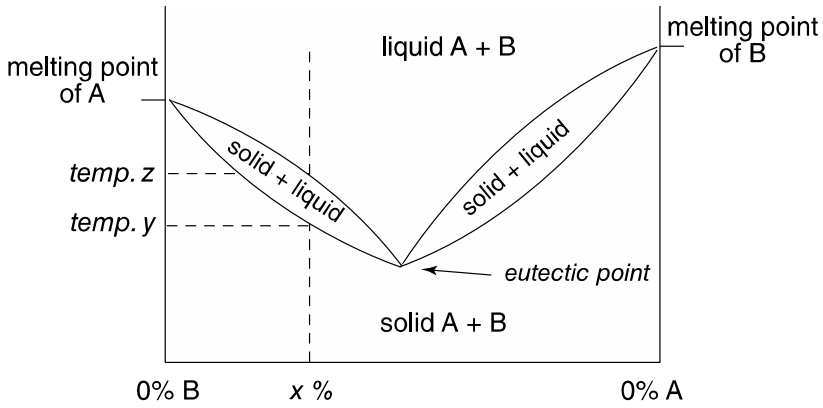

Figure 10-3: Melting point-composition curve for a mixture of Compounds A and B.

At the minimum point of the melting point-composition curves, the mixture can form a eutectic, which is the temperature and composition at which a mixture melts sharply. Not all mixtures form a eutectic, while some mixtures form more than one such point.

10.4 Mixed Melting Points

A mixed melting point is a special procedure that is performed to support the identification of a compound. This procedure is based on the principles of colligative properties. If one compound is contaminated with another compound, its melting point will be depressed. This principle holds true even if the compounds have the exact same melting point.

A mixed melting point requires that you have available an authentic sample of the compound you think you have isolated. Mix equal amounts of the compound you isolated and of the authentic sample and pulverize the mixture into a fine powder. Take a melting point of the mixture and compare it with the melting point of the unmixed samples. If they are the same compound, the melting point of the mixture will not differ from that of the pure sample. If they are not the same compound, they will melt at a lower temperature.

Suppose that you have isolated a compound in lab that you think is benzalacetophenone, which the literature reports as melting at 58°C. Sure enough, the compound you isolated melts at 58°C. Obtain a sample that is known to be benzalacetophenone, and mix it with your compound in a mortar and pestle. Take a melting point of the mixed compounds: is it 58°C? If so, you have most likely isolated benzalacetophenone. However, if the melting point range is wide and low, for example, 45–52°C, you have isolated a compound other than benzalacetophenone. For example, you could have isolated indanone, which the literature reports melts at 58°C. The addition of authentic indanone to the isolated benzalacetophenone would cause the melting point to be depressed and be a wide range, even though both compounds have identical melting points.

10.5 Determination of Melting Point

The melting point apparatuses used in the organic labs are called DigiMelts (Figure 10-4).

Figure 10-4: A DigiMelt apparatus.

These instruments hold a glass melting point capillary tube which is closed at the bottom end. Each DigiMelt can hold up to three tubes at once, which means you can run up to three samples simultaneously. To use the DigiMelt, follow these steps.

1. Load the sample.

Pack the capillary tube by pressing the open end gently into a sample of the compound to be analyzed, then scooping up the compound. The solid should fill the tube to a depth of 2–3 mm.

You will need to pack the sample down into the bottom of the tube. Tap the bottom of the capillary on a hard surface so that the sample packs down into the bottom of the tube. Alternatively, drop the capillary tube down a long length of glass tubing to pack the sample into the bottom of the tube. The

DigiMelts also have a "Tube Tapper" located in the front right corner of the device; if you insert your tube into here and hold down the Tube Tapper button, it will vibrate the sample and pack it down into the bottom of the capillary.

Once the compound is packed into the bottom of the tube, place the tube into the slot behind the eyepiece. Plug the DigiMelt in and turn it on, using the switch on the back of the unit.

2. Measure the heating point.

Instructions for use are printed on the front of the DigiMelt. If you do not know the expected melting point of your compound, a ramp rate of 10°C per minute should give you a rough first guess. You can then cool back down to about 20°C below your estimate of the melting point, and start heating again with a ramp rate of 0.5 or 1°C per minute to refine your estimate.

While the temperature on the DigiMelt is ramping up, you should be observing your sample through the illuminated viewing lens. When you notice any visual signs of melting (see section 10.2), you can record the temperature by pressing the button corresponding to whichever of the three samples has exhibited that sign. The DigiMelt will record the temperature when the button is pressed, so that you can read the data out later. This allows you to keep your eyes on the sample.

10.6 Common Problems Encountered in Melting Point Determinations

1. The melting point apparatus is heated too fast.

The apparatus must be heated slowly for the sample, the heating plate, and the thermometer to come into thermal equilibrium. If it is heated too fast, a false-low melting point will be recorded.

2. The sample decomposes as it melts.

Some organic compounds decompose as they are heated and therefore do not show a "typical" melting point. Decomposition is indicated by color changes, darkening, effervescence, or other changes in appearance as the compound is heated. Certain types of organic compounds are more likely to decompose on heating, such as amino acids, salts of amines, salts of carboxylic acids, and carbohydrates. Organic compounds that undergo decarboxylation or anhydride formation when heated will show decomposition rather than a true melting point.

When decomposition occurs during a melting point determination, the decomposition products formed act as impurities to lower and broaden the observed melting point of the substance. If you observe decomposition, record the melting range as the temperature range followed by a lower case "d" to indicate "decomposition." This is the same convention used by those who compile tables of physical data: a "dec" or "d" after the melting point of a compound denotes decomposition.

Note: Sometimes a student heats a sample too fast in the melting point apparatus, or looks away just as the sample melts. In most cases, the sample could simply be cooled and re-melted, without preparing a new sample. However, if the sample has decomposed, this will not be possible, because the sample is no longer the same compound.

3. The compound sublimes.

Sublimation is when a compound goes directly from the solid phase to the gas phase and it occurs when a solid compound has a very high vapor pressure. If sublimation occurs, you will observe disappearance of the solid concurrent with no appearance of liquid. If a sample is prone to sublimation, you must determine the melting point of the compound in a sealed capillary tube.

10.7 Study Questions

1. You have isolated the following compounds in lab and observed the melting points in the table below. For each compound, look up the literature melting point and judge the purity of the compound.

Compound	Observed melting point (°C)
Naphthalene	79–80°
Benzophenone	45–47°
p-Anisic acid	178–182°
Salicylic acid acetate	135°
3-Chlorobenzoic acid	157–158°
Sulfanilamide	165–166°
Ferrocene	157.5–161.5°

2. You think that you have isolated ibuprofen in the lab. It melts at 75–77°C. Since you don't totally trust your own laboratory techniques, you want to prove to yourself that you have ibuprofen before you ingest it. Using only melting point techniques, explain how you can prove that you actually have ibuprofen. Assume the stockroom is able to supply you with any compound you need.

3. The melting point of a pure compound is known to be 110–111°C. Describe the melting behavior expected if this compound is contaminated with 5% of an impurity.

4. You are taking a melting point of a compound, get distracted, and look away. By the time you look back it has already melted. You note that it has changed to a dark color. Should you cool the sample and re-melt it, or start over with a fresh sample?

5. You melt a compound and it disappears. What should you do?

6. You and your lab partner take melting points of the same sample. You observe a melting point of 101–107°C, while your partner observes a value of 110–112°C. Explain how you can get two different values with exactly the same sample.