Experiment

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Determination of Melting and Boiling Points

Objectives

1) To determine melting point and boiling point of unknown compounds.
2) To identify a solid unknown by measuring mixed melting points.
3) To properly use general apparatus in organic chemistry laboratory.

Introduction

The melting point of a compound is the temperature at which the solid phase is in equilibrium with the liquid phase. 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](image_url)
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 $C$-$B$ 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 compound $X$ 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-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 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 $Y$ also melts (20 µg $X$ x 60/40 ratio = 30 µg $Y$). At this point, the remaining 50 µg of solid $Y$ 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 $B$-$C$.

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 at which the entire mixture liquefies is 142 °C, 6 degrees lower than the melting point of pure $Y$. Also, the melting point range 130-142 °C is quite broad.

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 $B$-$A$ or $B$-$C$, respectively. Observing this melting point increase indicates that the original sample is not pure.

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 compound may be the same. However, many different compounds have the same melting point.
A mixed melting point can be 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 may be identical. A decrease in the melting point of the mixture and a broadening of the melting point range indicates that the compounds are likely to be different.

Melting points can also be used to assess compound purity. Generally, 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.

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 the melting point apparatus.

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.

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 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 occur. 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 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 phase without going through the liquid phase, a process 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*.

**Boiling points** are also useful physical properties for indicating the purity of an organic compound. Boiling point is the temperature at which the vapor pressure of a liquid equals atmospheric pressure or some other applied pressure. A boiling point is commonly measured during a distillation, in which a liquid is heated to form vapor, and then the vapor is condensed and collected in another container. The boiling temperature is measured as distillation vapor covers the bulb of a thermometer suspended above the boiling liquid. Typically, the most accurate boiling point measurement is the relatively constant temperature achieved during a distillation.

**Experimental Procedure for Melting Point Determination**

1) Obtain a sample from your instructor. Record sample ID.
2) Put the sample into a capillary tube (about 2-3 mm in height).
3) Measure the melting point using the apparatus as shown in Figure 2. Attach the capillary tube to a thermometer with sewing thread. Place 25-30 mL of paraffin oil or glycerol in a 50 mL beaker.
4) Turn on the hotplate and observe the melting point. Use a clean glass rod to stir the oil to ensure a uniform heat distribution.
5) Record the melting point range (for example 70-73°C). Repeat the experiment one more time.
6) Put the sample into another capillary tube, and measure the melting point of the sample again using the electrothermal melting point apparatus, e.g. as shown in Figure 3. Record the melting point range. (Hint: In Discussion, describe whether the obtained result is similar to that recorded earlier. Which methods are easier to obtain data? Why?)

![Apparatus set-up for melting-point determination](image2)

**Figure 2. Apparatus set-up for melting-point determination**

![Example of an electrothermal melting point apparatus](image3)

**Figure 3\(^1\). Example of an electrothermal melting point apparatus**

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\(^1\) Diagram taken from “Instructions for use” of Stuart Scientific melting point apparatus SMP11
7) Based on the observed melting points, select 2 compounds in the table below that are most likely to be your unknown.

<table>
<thead>
<tr>
<th>Compound</th>
<th>mp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resorcinol</td>
<td>110-112</td>
</tr>
<tr>
<td>Acetanilide</td>
<td>113-116</td>
</tr>
<tr>
<td>Citric acid</td>
<td>153-159</td>
</tr>
<tr>
<td>Salicylic acid</td>
<td>158-161</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>99-101</td>
</tr>
<tr>
<td>4-tert-Butyl phenol</td>
<td>96-101</td>
</tr>
</tbody>
</table>

8) Verify the identity of your unknown by measuring the mixed melting point with each of the selected known compounds using either of the methods mentioned earlier. The mixture can be made by putting together an equal quantity of the unknown and the known compounds on a watch glass. Use a spatula to thoroughly blend the mixture. Record the melting point range and identify the unknown compounds.

**Laboratory Safety Precaution**

1) Wear safety goggles and lab coat at all times while working in the laboratory.

2) Many chemicals are potentially harmful. Prevent contact with your eyes, skin, and clothing. Avoid ingesting any of the reagents.

3) Unknowns may be flammable, toxic, and irritating.

4) Capillary tubes are fragile and easily broken.

5) Wash your hands thoroughly with soap or detergent before leaving the laboratory.

6) Take care to avoid burning yourself when using hot chemicals and equipments.