

3. Melting Points

A. Background

The melting point of a pure compound is one of several methods that can be used to characterize and help identify a substance. For example pure water has a melting point of 0 °C. If water is free of all impurities, you will find that it completely melts or freezes at exactly 0 °C. The presence of impurities in the water cause the melting point (and freezing point) to be **depressed**. For this reason, salt is distributed onto icy roads in the wintertime, which causes the ice to melt.

For organic compounds, the melting point is actually recorded as a **melting range**. The melting range recorded by taking the temperature at which the first crystal just begins to melt followed by the temperature at which the last crystal disappears. A pure crystalline compound will always have the same melting point. If however the sample is not pure, two phenomena will be observed. First, the presence of impurities will result in a lowering of the melting point. Second, an impure compound will exhibit a wider melting point range. For example, pure benzoic acid has a melting point range of 121-123 °C. If benzoic were contaminated with an impurity, the melting point range might decrease and broaden to 117-120 °C. The specific change in melting point resulting from an impurity is a factor of both the structure and amount of impurity contaminating the sample.

There are three main reasons to record the melting point of a sample.

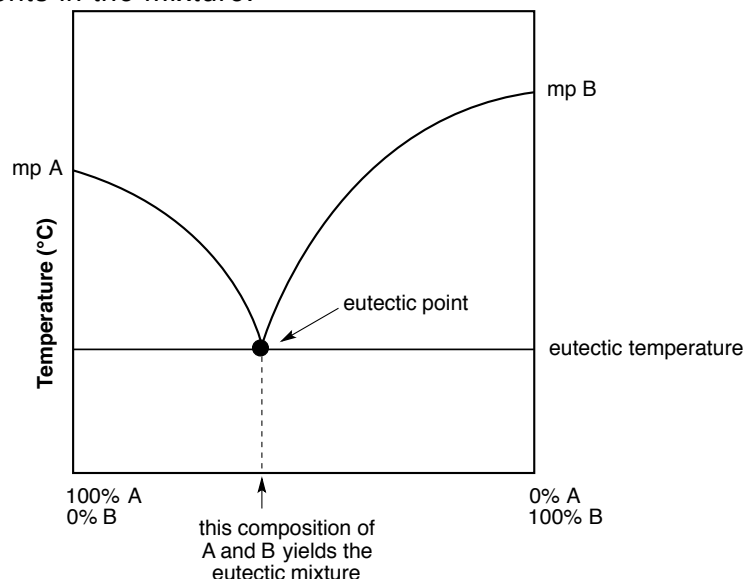
1. **Assessment of Purity** – As a rule of thumb, if your compound has a melting range that is greater than 2 °C, the compound is likely impure.
2. **Characterization of a New Compound** – When a new compound is prepared, the chemist who synthesized it must collect characterization data for the new compound. Characterization data includes, but is not limited to: melting point, boiling point, density, and spectroscopic characterization (covered later on). This characterization data not only help the chemist determine the structure of the new compound, but it also provides reference data for anyone else who prepares the same compound in the future.
3. **Identification of an Unknown** – If you have a solid unknown, you can take a melting point and compare your obtained value to known values in tables or online databases. If your unknown is confined to a small set of possible compounds, this technique is relatively useful. If, however, you have a substantial number of possible compounds to choose from, you will likely only be able to narrow down the possibilities by comparison of melting point values. This technique can, however, be expanded upon by taking a *mixed melting point*.

Mixed Melting Points

Suppose you have an unknown that melts at 131-132 °C. Based on comparison to literature values for known compounds you conclude that your unknown is likely urea (mp, 132 °C). In order to confirm or disprove your suspicion, you can prepare a mixture containing your unknown as well as some authentic urea. If the mixture melts at the same temperature, it is reasonable to confirm the identity of your unknown as urea. If, however,

the mixture melts at a lower temperature over a broad range, then the urea is in effect an impurity introduced into your sample. Thus, in this case, your unknown is not urea.

On occasion, a mixed melting point experiment might result in a lower melting point with a very sharp range. This type of mixture is referred to as a **eutectic mixture**. The eutectic point (or temperature) of a mixture is the temperature at which a particular ratio of the two components gives a sharp melting point that is lower than the melting point of either of the two pure components in the mixture.



For confirmation of an unknown, it is advisable to prepare at least two mixed melting point samples, varying the ratios of known to unknown in each. If the melting point remains constant for both samples, the compounds in question are identical. Although there are some exceptions to the rule, the probability of having an exception is very low. To confirm the conclusion based on melting points, spectroscopic methods are necessary.

B. Melting Point Determination

When doing a melting point determination, be careful to avoid contamination with impurities. Ensure you are using a new melting point capillary and a clean spatula and watch glass.

Use caution when working with the Mel-Temp apparatus as it can become very hot!

Melting points are obtained on very small samples of material, by placing the material in a melting point capillary tube, which is then placed in an instrument known as a Mel-Temp apparatus. The Mel-Temp has a voltage control knob that allows you to adjust the heating rate. A thermocouple (digital temperature sensor) is connected to the Mel-Temp. This will allow you to monitor the temperature over time. The Mel-Temp apparatus has a viewing window that will allow you to observe your sample as it melts.

Procedure for Standard Melting Point Determination

1. Crush your solid sample so that you have a very fine powder. Load the sample into the melting point tube such that there is 2-3 mm of sample in the bottom of the tube. Gentle tapping on the bench top may be required in order to get your sample down to the bottom of the tube.
2. Ensure that the Mel-Temp apparatus is relatively cool (should be at least 20 °C below the melting point of your sample). Load the capillary containing your sample into the Mel-Temp apparatus.
3. Turn on the Mel-Temp and be sure the light is illuminated.
4. Set the voltage such that the temperature rises 5-10 °C per minute. This is considered a “fast run” and will give you an approximate melting point. Once your sample melts, note the temperature and throw away the sample.
5. Now you are ready for the “slow run.” Once the Mel-Temp has cooled, insert a fresh sample (never re-melt a sample) and ramp the temperature to about 20 °C below the estimated melting point from step 4. Then, cut back the voltage such that you have ~2 °C/min temperature rise.
6. When you observe melting of the first crystal, write down this temperature. Continue to watch the sample melt. When the very last crystal melts, write down this temperature value. The two recorded temperature values represent the melting point range.
7. Turn off the Mel-Temp and thermocouple and discard your samples.

Mixed Melting Point Determination

When a mixed melting point is desired, prepare two equal sized portions of the components to be mixed. Grind these substances together thoroughly on a watch glass. Once the samples are mixed, load the capillary and determine the melting point as described above.

Occasionally you will have unexpected results such as impurities that don't appear to melt or complete decomposition of the material. Regardless of the results, be sure to record what you observe in your lab notebook.

C. Experimental Procedure

In this lab experiment you will be doing the following:

- Determine the melting point of a benzoic acid sample.
- Determine the melting point of a 2-naphthol sample.
- Determine the mixed melting point of a 1:1 mixture of benzoic acid and 2-naphthol.
- Determine the identity of an unknown based on melting point data.

First, determine the melting point of both benzoic acid (mp 122 °C) and 2-naphthol (mp 123 °C). Determine how close your measured values come to the literature values. Record your results in your lab notebook.

Next, you will explore how an impurity affects the melting point of a sample. Prepare a 1:1 mixture of benzoic acid and 2-naphthol and determine the mixed melting point. How does the mixed melting point compare to the melting points of pure benzoic acid and pure 2-naphthol? Record your results in your lab notebook.

Finally, you will determine the identity of an unknown using melting point data. Your TA will assign you an unknown. Your unknown is one of the compounds listed in the table below. First, determine the melting point of the unknown to narrow down the possibilities to two or three potential compounds. Next, prepare mixed melting point samples of your unknown with each of the possible compounds (pure samples of each compound is available in the lab). Determine the mixed melting point for each sample. The mixture that does not exhibit a melting point depression will allow you to deduce the identity of your unknown. Record all observations in your lab notebook.

Potential Unknowns

Compound	mp, °C	Compound	mp, °C
Fluoranthene	110	Urea	132
<i>Meta</i> -Toluic Acid	114	Acetyl Salicylic Acid	140
Mandelic Acid	120	Salicylic Acid	159
Benzoic Acid	122	Benzanilide	163
Succinimide	126	Triphenylmethanol	163

Dispose of all chemical waste in the properly labeled containers. Glass waste should be placed in the broken glass container.

D. Pre-Lab Questions

1. Define the “melting point” of a substance.
2. Why should you always use a new capillary tube when performing a second melting point determination on your sample?
3. Why is it necessary to allow the Mel-Temp to cool before performing a second melting point determination?
4. Given a sample of a eutectic mixture containing 60.6 mol % naphthalene and 39.5 mol % 1-naphthol, which melts sharply at 61.0 °C, how could you prove that it is not a pure substance? What would you do and what would you observe?

E. Post-Lab Questions

1. In the experiment you used only 2-3 mm of sample in the melting point tube. What disadvantage is associated with using too much material?
2. Why should you use the same melting point apparatus for all melting point measurements?
3. What happens if you heat your sample in the Mel-Temp at too fast of a rate?
4. Why is the Mel-Temp capillary tube method generally not useful for determining the melting points of inorganic compounds?