

# Determination of Melting Points

This experiment consists of three parts. In the first part, you will determine the melting point range of three known compounds. This part is mostly for practice, to make sure you know how to use the Mel-Temp apparatus to obtain melting point ranges that are close to the literature values (that is, the values in this manual) of fairly pure samples.

In the second part, you will determine the melting point range of an unknown compound and tentatively identify the compound.

In the last part, you will confirm the identity of your unknown by doing what is known as a mixed melting point determination. Since the actual melting point determination procedure is the same for all of your samples, the procedure will be described at the beginning and not repeated. Determining the melting point range of a compound is a procedure that you will perform many times during this course.

## PRE-EXPERIMENT ASSIGNMENT

Study this chapter of the manual and the lecture notes on the Organic Chemistry departmental web site. Complete the first six sections of your notebook write up. (Instructions on completing these sections may be found in the laboratory notebook chapter of the lab manual.)

**A student who has prepared for the Melting Point experiment should be able to:**

1. Define or explain: melting point, melting point range, phase transitions, and eutectics.
2. Explain why chemists determine the melting point ranges of samples. (To identify unknown compounds, to determine the purity of the samples, and to characterize new compounds.)
3. Draw the structure given the name, or give the name from the structure, of any of the compounds used in the day's experiment.
4. Explain how soluble and insoluble impurities will alter a melting point range.
5. Explain how a melting point capillary is filled and how an accurate melting point range is obtained.
6. Identify and explain safety considerations for the day's experiment.
7. Perform the day's experiment safely and successfully.

Quizzes given after the experiment has been performed may also include:

8. Give procedures for identifying unknowns from melting point data, and use melting point range data to identify unknowns (note: students are not required to memorize literature melting points).
9. Recognize and explain the behavior of samples when they are melted, including both pure and impure samples. Note: Impure samples may contain either soluble or insoluble impurities.

### **Procedure for determining melting point ranges with the Mel-Temp apparatus:**

#### ***Safety Precautions***

You will be using a Mel-Temp apparatus and the thermometer from your equipment drawer. The bulb end of the thermometer will fit into the round chimney shaped opening in the Mel-Temp apparatus. It should fit easily. *Do not force it.* If it does not fit easily, change either the thermometer or the Mel-Temp.

Do not put a room-temperature thermometer into a hot Mel-Temp. Never cool a hot thermometer by running cold water over it or by placing it in an ice bath. Do not place a hot thermometer on a cold bench top. If you do any of these things, it will often shatter. When waiting for the Mel-Temp to cool, it does not help to remove the thermometer and wave it around; the Mel-Temp apparatus takes longer to cool.

Do not leave a Mel-Temp on when you are not actually using it. Do not leave one running unattended. Do not heat it beyond the capacity of the thermometer (210°C). Do not touch either the hot metal block of the Mel-Temp or the hot (blue) end of your thermometer.

Once the desired compounds have melted, turn the Mel-Temp off to start the cooling process.

The compounds you will be using in this experiment are not harmless. Most of them have some toxicity. Do not place any into mouth. For details of the hazards involved, consult the Material Safety Data Sheet for each substance. These are available in the laboratory, and you can find them on the web.

#### **Filling the Capillary Tube**

Obtain a melting point capillary from the lab supply. Place a tiny sample of the compound whose melting point is to be determined on a piece of weighing paper or a watch glass. If the sample is in chunks, grind the sample to a fine powder using the flat portion of your clean spatula.

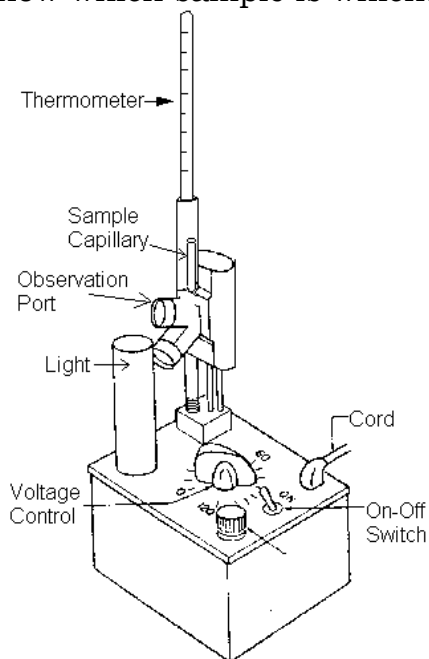
Push the open end of the capillary down into the pile. A small amount of the sample will go into the open end. Rap the closed end of the capillary sharply on the bench top two or three times. The sample should fall to the closed end. The amount should be enough to fill the tube to a depth of about one millimeters. (This is close to the thickness, not the diameter, of a quarter.)

More than 2 mm or so of sample in the capillary may give you bad results, as it may not heat uniformly.

If the substance does not fall to the bottom, drop the capillary, closed end down, onto the bench top through a piece of glass tubing about 2 or 3 ft. long. Repeat this if necessary. If the sample does not fall to the bottom of the capillary after the treatment described above, it may be wet. Dry the sample further and attempt the procedure again. (You probably won't encounter this problem in this experiment, but you may in later experiments.)

### Measuring the Melting Point Range

Make sure that the Mel-Temp is cooler than the expected melting point of your sample by at least ten degrees. It is not necessary to cool the Mel-Temp to room temperature between runs. Insert the capillary tube, closed end down, into the slot between the observation port and the thermometer chimney on the Mel-Temp. Three samples can be placed in the Mel-Temp at one time, provided that their melting points are not too close to each other. (How close together they can be depends on your skill at using the Mel-Temp.) Make sure that you know which sample is which.



Turn the Mel-Temp on and view the sample through the magnifier observation port. Begin heating the sample by turning the voltage control dial to a setting that causes the temperature to rise rapidly to about ten degrees under the expected melting point. Do not turn the dial to a full 100% and leave it there. When the sample reaches that temperature, turn the dial down so that the temperature increases at a rate of about one degree per minute through the expected melting point range.

Record the temperature when you see the first signs of liquid droplets in the sample. Do not mistake settling of the sample for melting. Keep observing

the sample and record the temperature at which the entire sample becomes liquid. Report the melting point range of the sample as the first temperature to the second temperature. ***Always report a melting point range. Mel-Temps will not give you a single melting point.***

The amount of sample that you use and the heating rate through the melting range are critical. If you use too much sample or heat too rapidly you will not get accurate results. Be patient and do it right the first time.

Once the sample in the capillary melts, don't use it again. If you have to repeat a measurement for any reason, you must start with a fresh sample in a new capillary.

This procedure requires some idea of the expected melting point of the sample. If this is not given to you in the manual or text, then you must look it up in a handbook or other sources. If the sample is unknown, then you need to do two runs. First do a rapid measurement (about 15 to 20°C per minute) to determine an approximate melting point. Then do the normal measurement on a fresh sample using the approximate melting point as your expected melting point.

The Mel-Temp takes a non-negligible amount of time to cool. If you are doing more than one sample, be sure to start with the material with the lowest melting point. As soon as the desired samples have finished melting, turn the Mel-Temp off and allow to cool. A significant amount of time can be wasted while waiting for a hot Mel-Temp to cool to a useable temperature.

Up to three samples can be run at the same time. This takes some organization, but saves much of time.

### **Comparison of Reported and Observed Melting Points**

Determine the melting point ranges of the following three compounds: naphthalene, acetanilide, and urea. Read the thermometer to one decimal place. You should be able to obtain melting point ranges of four degrees or less with the upper temperature of the range within two degrees of the literature values given above. If you do not come this close, repeat the measurement. Common mistakes are using too large a sample, heating too rapidly, and mistaking the onset of melting. If you do not come close enough after repeating the measurement once, consult your instructor. *Record all melting point ranges directly into your lab notebook.*

### **Melting Point of an Unknown**

Obtain an unknown and record its number in your lab notebook. The following table lists the melting points for possible identities for the unknown<sup>1</sup>. Your unknown will be one of these 11 compounds. Note, the Mel-Temps do not allow for a single melting point to be determined. Only ranges of melting points are possible when using a Mel-Temp.

Compound	Literature Melting Point
4-nitrotoluene	54.5°C
Naphthalene	80.5°C
glutaric acid	99°C
2-methylbenzoic acid	107°C
Acetanilide	114.3°C
benzoic acid	122.1°C
Urea	135°C
salicylic acid	158°C
Sulfanilamide	165°C
succinic acid	188°C
3,5-dinitrobenzoic acid	205°C

Determine the melting point range of the unknown. Compare your observed m.p. to those in the table and tentatively identify your unknown. Remember that any soluble impurities will lower the melting point. Therefore, if you did the procedure correctly, you are more likely to be under the actual melting point than over it. *Record all melting point ranges directly into your lab notebook.*

### **Mixed Melting Point Determination**

Select the three compounds closest in temperature to your unknown. Obtain a small sample of each of these compounds. Mix an equal amount of your unknown with each of the three known compounds. Grind the samples together so that they are thoroughly mixed. These can be mixed using a spatula against a watch glass or by rolling the materials together in a piece of weigh paper. Load a separate capillary with each mixture. Place all three into the Mel-temp and simultaneously observe and record the melting points of each. Be sure to record the location of each mixture in the Mel-temp in your notebook.

If the melting point range of the mixture differs substantially from that of the pure compound or if the range is too wide, then the compound and the unknown are different materials. If the melting point behavior of the mixture is the same or very similar to that of the pure compound, you have confirmed the identity of your unknown.

*Record all melting point ranges directly into your lab notebook.*

### **CLEANUP**

Used capillaries and broken ones should be put into the broken glass container. Excess chemicals from this experiment should be placed in the non-halogenated organic solid waste bottle in the hood. Wash all used glassware, replace in drawer.

## **POST-EXPERIMENT ASSIGNMENT**

Complete the datasheet and turn in before leaving class. Turn in the white notebook pages from your lab notebook. Staple multiple sheets together. Tear off rough edges.

Prepare for the melting point portion of the next quiz. Remember that you may be asked questions on anything you should have learned from assigned readings, pre-experiment lecture, or doing the experiment.

## **REFERENCES**

<sup>i</sup> *CRC Handbook of Chemistry and Physics*, 65<sup>th</sup> ed, CRC press, 1984, p c-65-c-575

Mel-Temp image

[http://www.scottsmithonline.com/interests/medicalschoo/chemistry/104a/file\\_storage/CourseWebSite/ww.vanderbilt.edu/AnS/Chemistry/general\\_chem/104atest/measurement\\_of\\_melting\\_point.htm](http://www.scottsmithonline.com/interests/medicalschoo/chemistry/104a/file_storage/CourseWebSite/ww.vanderbilt.edu/AnS/Chemistry/general_chem/104atest/measurement_of_melting_point.htm) (December 10, 2010)

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<sup>i</sup> *CRC Handbook of Chemistry and Physics*, 65<sup>th</sup> ed, CRC press, 1984, p C-65-C-575