There are a variety of methods by which a sample’s melting point can be measured, with the newest being electrical probes (e.g. Vernier MeltStation). Presented in this section are traditional methods that use an electrical melting point apparatus and Thiele tube. Both methods use capillary samples that are prepared in the same manner.

### Sample Preparation

1. Obtain a glass capillary melting point tube, which has one end sealed and the other end open. Jab the open end of the tube into a pile of the solid to be analyzed (Figure 6.10a). The solid must be dry or the results will be affected as solvent can act as an impurity and affect the melting range. If the solid is granular, pulverize the solid somewhat before packing.

2. Invert the capillary tube and gently tap the tube on the benchtop to cause the solid to fall to the closed end (Figure 6.10b). Then, drop the capillary tube closed side down several times through a long narrow tube (glass tube or cut PVC pipe, Figure 6.10c). The capillary tube will bounce as it hits the benchtop, and pack the solid into the bottom of the tube. Failure to pack the solid well may cause it to shrink when heating, which can cause confusion as to the correct melting temperature.

3. If needed, repeat the previous steps to load sample until it is a height of \(2\text{–}3 \text{ mm}\) in the tube (when packed, Figure 6.10d). It is important that the sample be no higher than \(3 \text{ mm}\) or the melting range will be artificially broad.

### Melting Point Apparatus

1. Insert the capillary tube containing the sample into a slot behind the viewfinder of a melting point apparatus (Figure 6.11a). There are usually three slots in each apparatus, and multiple melting points can be taken simultaneously after gaining experience with the technique.

2. Turn on the apparatus and adjust the setting to an appropriate heating rate (Figure 6.11b). The rate of heating is often experimental and should be adjusted by careful monitoring of the thermometer on the apparatus.

3. Look through the viewfinder (Figure 6.11c) to see a magnified view of the sample in the apparatus, which should be illuminated.
4. If the expected melting point of the compound is known, heat at a medium rate to \(20^\circ\text{C}\) below the expected melting point, then slow the rate of heating such that the temperature increases no more than \(1^\circ\text{C}\) every 30 seconds (i.e., very slowly). The temperature must be incremental as the melting point is approached so the system can reach equilibrium, making the thermometer temperature an accurate gauge of the solid’s true temperature.

5. If the expected melting point of the compound is NOT known, heat the sample at a medium rate the entire time and determine an approximate melting point. Repeat the process with a fresh sample after allowing the apparatus to cool and use the recommendations in prompt 4 to perform a more careful assessment of the melting point. A fresh sample is necessary for a second melting point trial; even if the first sample solidifies after cooling it should not be used again. Differences in crystal structure between the original solid and the previously melted solid could lead to different melting ranges.

Figure 6.12: a) Monitoring the sample by looking through the viewfinder, b) Initial melting of a sample, c) Midway, d) Mostly melted sample.

6. The solid may be approaching its melting point if the solid is seen pulling away from the walls of the tube to form a cone of solid (Figure 6.12b), which is called "sintering." Melting will normally occur within a few degrees of this point. The solid may also shrink or compact before melting.

Figure 6.13: Melting of benzoic acid: a) Well below the melting point, b) Glistening, c) First liquid droplet seen, d) Sample is completely melted. Additional pictures for the melting of this sample can be seen in Figure 6.2.

7. Record the first temperature of the melting range with the appearance of the first visible drop of liquid. At first it may seem as if the sides of the solid glisten (Figure 6.13b), and the temperature should be recorded when a droplet is seen on the side or bottom of the tube (a hint of movement will be noticed in the tube, Figure 6.13c). Record the temperature reading to the nearest degree. Although some thermometers may read to greater precision, the imperfect heat transfer between the metal block and sample leaves the error larger than \(0.1^\circ\text{C}\).

8. Record the second temperature of the melting range when the entire sample has just melted (Figure 6.13d), which occurs when all portions of the opaque solid have turned to a transparent liquid.

9. The following unusual situations may occur in the process:
   a. The sample may begin to darken, which indicates decomposition is occurring before the sample is melting. Take note of the decomposition temperature, as it is sometimes as reliable a reference point as a compound’s melting point. Use the letter "d" after a melting point to indicate decomposition (e.g. \(251^\circ\text{C} d\)).
   b. The sample may sublime instead of melting. Sublimation may be noticed by a ring of solid above where the sample is heated. Take note of this behavior in your lab notebook.

10. If another melting point trial is to be performed directly after the first, the metal block should be rapidly cooled to at least \(20^\circ\text{C}\) below the next melting point by touching it with wet paper towels (Figure 6.11d) or cooling it with a jet of air.
1. Obtain a Thiele tube and clamp it to a ring stand or latticework (Figure 6.15b). The tube is normally filled with clear mineral oil, but it may have darkened from oxidation or spilled compounds. If the oil is quite dark, it should be replaced. The oil should be filled to at least $1 \text{ cm}$ higher than the top triangular arm (an appropriate oil level is pointed to in Figure 6.15c), and if too low the oil will not circulate as needed (Figure 6.15d).

2. Insert a thermometer into a one-holed rubber stopper with a slit down one side. Attach the capillary sample to the thermometer with a tiny rubber band (as indicated in Figure 6.15a). These tiny rubber bands are often made by cutting pieces of small rubber tubing.

3. Position the capillary tube so that the solid sample is lined up with the middle of the thermometer bulb (Figure 6.15a).

4. Place the rubber stopper and thermometer assembly into the Thiele tube, adjusting the height so that the sample is midway inside the tube (Figure 6.15c). The rubber band should be adjusted so it is not submerged in the mineral oil, keeping in mind that the oil may expand somewhat during heating. The thermometer should not touch the sides of the glass, and if it does it should be clamped in such a way that it no longer touches.

5. Heat the apparatus gently on the side arm of the Thiele tube with a microburner if available or Bunsen burner using a back and forth motion (Figure 6.15d). As the oil warms and becomes less dense, it will rise and travel up the triangular portion of the tube. The cooler, denser oil will sink, thereby creating an oil current as shown in Figure 6.15d. This method is an excellent way to indirectly and slowly heat the sample.

6. Although bubbles should not be seen in the Thiele tube as it warms, they commonly are seen if the tube is used for other purposes (bubbles are seen in Figure 6.15d). For example, Thiele tubes can be used for boiling point determinations, and on occasion a sample falls into the oil and contaminates it. If the oil is not subsequently changed, the sample may boil when heated in the tube. If bubbles are seen upon heating a Thiele tube, the entire setup should be conducted in the fume hood.

7. If the expected melting point of the compound is known, heat at a medium rate to $20^\text{oC}$ below the expected melting point, then slow the rate of heating such that the temperature increases no more than $1^\text{oC}$ every 30 seconds (i.e., very slowly). The temperature must be incremental as the melting point is approached so the system can reach equilibrium, making the thermometer temperature an accurate gauge of the solid’s true temperature.

8. If the expected melting point of the compound is NOT known, heat the sample at a medium rate the entire time and
determine an approximate melting point. Repeat the process with a fresh sample after allowing the oil to cool to at least \(20^\text{o} \text{C}\) below the previous melting point, and use the recommendations in prompt 7 to perform a more careful assessment of the melting point.

A fresh sample is necessary for a second melting point trial; even if the first sample solidifies after cooling it should not be used again. Differences in crystal structure between the original solid and the previously melted solid could lead to different melting ranges.

Figure 6.16: a) Solid sample inside a Thiele Tube, as indicated with an arrow, b) Initial melting of the sample, c) Midway, d) Melted sample.

9. Record the first temperature of the melting range with the appearance of the first visible drop of liquid. At first it may seem as if the sides of the solid glisten (Figure 6.13b), and the temperature should be recorded when a droplet is seen on the side or bottom of the tube (a hint of movement will be noticed in the tube, Figure 6.16b). Record the temperature reading to the nearest degree. Although some thermometers may read to greater precision, the imperfect heat transfer between the oil and sample leaves the error larger than \(0.1^\text{o} \text{C}\).

10. Record the second temperature of the melting range when the entire sample has just melted (Figure 6.16d), which occurs when all portions of the opaque solid have turned to a transparent liquid.

11. Take note if darkening or sublimation occur.

12. If another melting point trial is to be performed directly after the first, be sure to allow the oil to cool to at least \(20^\text{o} \text{C}\) below the next melting point beforehand.

13. Cleanup note: drops of mineral oil on the benchtop do not easily wipe away, but can be cleaned by a paper towel soaked with either window cleaner or hexanes.
Table 6.2: Procedural summary for obtaining a melting point.

Load the sample by jabbing the open end of a capillary tube into a pile of the sample.

With closed end down, drop the tube down a long hollow tube so that it hits the benchtop and packs the sample into the closed end of the tube.

Load the sample to a height of \((2\text{--}3\text{ mm})\).

Place the sample into a slot in the MelTemp.

Turn the dial to begin heating.

Heat at a medium rate to \((20\degree \text{C})\) below the expected melting point.

Then heat very slowly \((1\degree \text{C} \text{ every 30 seconds})\).

Record the temperature where the first droplet of liquid is seen (there is movement in the tube).

Record the second temperature when the entire sample liquefies (the entire sample changes from opaque to transparent).

Record a melting range, e.g. \((120\degree \text{C})\).
**Thiele Tube Variation:**

Attach the sample to a thermometer with a tiny rubber band, positioning the sample flush with the bottom of the thermometer.

Insert the sample into a Thiele tube, so that the sample is near the middle of the tube.

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