# Melting Point[1]

The temperature at which a solid melts is known as the melting point (MP) of that substance. The melting point is a physical property of a solid and can be used to help identify a substance. In practice, a solid usually melts over a range of temperatures rather than at one specific temperature. For this reason, it is more useful to speak of a melting point range. Although the term "melting point" is usually used, what is meant by this term is "melting point range." If the compound melts over a very narrow range, it can usually be assumed that the compound is relatively pure. Conversely, compounds that melt over a wide range are assumed to be relatively impure.

Besides melting over a wide range, impure solids also melt at a temperature lower than that of the pure compound. For our purposes, a range greater than 2 °C is considered to be wide. For example, if an unknown solid melts at 102 – 106 °C, the 4 °C range suggests that the sample is impure. If the unknown is one of four possible compounds which melt at 102, 104, 106, and 108 °C, it is most likely that which melts at 108 °C. To summarize, an impure solid melts over a wide range and at a temperature lower than that of the pure solid. It should be noted that "insoluble" impurities such as bits of filter paper or dust have no effect on the MP of a substance. To impact the MP the impurity must be soluble in the solid.

Several devices are available for measuring melting points. The lab is equipped with a computer-controlled digital instrument. Your TA will demonstrate how to use it. There is also a handout posted on the course website, as well as directions printed on each melting point apparatus.

Sample is added to a small glass capillary tube that is closed at one end. It is important to use as small amount of sample as possible so that sufficient heat is present to melt the sample rapidly. The temperature of the sample is measured via digital thermometer. The sample is heated slowly as the temperature approaches the MP, while the sample is carefully observed. The temperature at which the first drop of liquid is observed is recorded as the beginning of the melting point range. The temperature at which all solid has melted is recorded as the end of the melting point range. Upon heating, the solid may expand and move slightly in the tube. This movement should not be interpreted as the beginning of the MP range. The melting point (MP) is recorded in the ELN as, for example, MP (compound A) 102.5-104.0 °C.

To determine the MP of an unknown solid, to save time, an approximate MP is first determined by heating the sample fairly rapidly. Once the approximate MP is known, a more careful determination is made on a fresh sample. There is more detail on this in the second section below. Note that once a sample has been melted, it may have decomposed slightly. Contamination with decomposition product will change the MP of the sample, so a fresh sample must always be used for each determination.

The effect of impurities on the MP can actually be used to help identify a compound. For example, if an unknown solid is known to be one of two possible known compounds, both having the same MP, the unknown can be mixed with one of the known compounds and a MP taken of the mixture. If the MP range is lowered and widened, it means that the two are different compounds. If the MP

[1] Revised 3/2020

stays the same it means that the two compounds are likely identical. This technique is known as a mixed melting point.

To summarize, melting points can provide information about the identity and the purity of a solid sample, however, in no way is a melting point unique to a specific compound.

**Prelab: You may either print out your prelab and bring it with you to lab, or bring your computer. Your TA will grade it on the spot before you begin the experiment. For the in lab observations, you may use scratch paper and record later in your ELN, or bring your computer and record directly in your ELN.**

**Postlab Report: Make sure to use the non-formal postlab report template on the course website!**

## Experimental Procedure.[2]

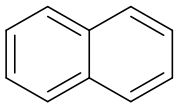
The purpose of this experiment is to learn to determine melting points (MPs) accurately. This is an important technique that will be used in many of the experiments in the organic lab. Always record a MP range—the temperature at which the first drop of liquid appears, to the temperature at which all sample has melted. Be sure to distinguish between melting and movement of the solid due to expansion. The MP range begins when the first tiny drop of liquid is observed. Remember that an impure sample melts over a wide range and at a temperature lower than that of the pure material. For the purposes of this course, a compound with a MP range of 2 °C or less will be considered to be sufficiently pure.

a. Fill the capillary tube:
    a. Adding sample is accomplished by pushing the open end of the capillary down into the powdered sample, then tapping the sample down into the closed end of the capillary tube by dropping the tube, closed end first, down into a 2' length of glass tubing so the sample bounces and allows the solid to pack into the closed end.
    b. This can also be done by tapping the closed end gently on the desktop but care must be taken to not break the fragile tube.
    c. The height of sample in the capillary should be about 2-3 mm (thickness of two quarters). Too much sample will yield poor results.

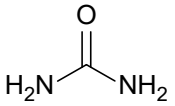
b. Using the digital device: Two capillaries can be heated at the same time, although when learning to use the apparatus it is less confusing to do one at a time.
    a. Heating is accomplished by turning on the unit and setting the plateau temperature. Start at a setting about ten degrees Celsius below the known melting temperature.
    b. When the unit reaches this plateau temperature, press "Start". The computer controls the rate increase at about 1 °C/min. Note that the internal thermometers used here are accurate only to about ± 2 ° C. **WHEN FINISHED, ALWAYS TURN OFF THE TOGGLE SWITCH ON THE BACK OF THE UNIT.**

[2] Revised 3/2020

c. Knowns: Determine the MPs of naphthalene and urea.
    a. Note that the MPs of samples used in the lab may differ slightly from those given in a handbook. Therefore, use the MP values given below.
    b. Samples will be dispensed in labeled recrystallization dishes on the center bench. Do not move the dishes. Fill the capillaries right there.
    c. Determine the MPs of these known compounds in order of increasing MP. This will obviate the need to allow the apparatus to cool between determinations. The values that you find should agree with those listed and the range should be narrow. If you find a wide range (> about 2 °C) or a value different from that expected (within ± 2 °C - remember that the thermometers used here are good only to about ± 2 °C), so do a second determination on a fresh sample.
    d. It is important to use a small sample size (height in capillary tube 2-3 mm). If a MP must be re-determined always use a fresh sample. Once a sample has melted, it is now known as an amorphous solid, and therefore has no well-defined crystal structure. This can cause the MP to become depressed and the range widened.
    e. Never dispose of used capillaries or any glass in the regular trash. The person who empties the trash could be injured by broken glass. Place the used capillaries in the dishes provided at your lab bench.



Naphthalene
MP 79 - 80 °C




Urea
MP 132 - 134 °C

d. Unknown: Determine the MP of one unknown compound. Your TA will assign your unknown to you.
    a. To save time, when you determine the MP of a sample with an unknown melting point, first **find a crude MP**. To do this, set the temperature to the value of the lowest melting point in the list of unknowns. Observe the sample. If it doesn't melt, set for ten degrees higher (same sample) and observe. Repeat this until you see that the sample is starting to melt. Record this crude temperature.
    b. Prepare a fresh sample, set the unit at 10-15 °C below the crude temperature you just found. Once the unit reaches this goal temp, it will automatically increase at a rate of about 1 °C/min. Observe and record the melting point. Using the MP, identify your compound using the table of possible compounds at the end of this document.

**BEFORE LEAVING THE LAB: Turn off the melting point apparatus. Clean up your work area and ask your TA for their signature after they check your area for cleanliness.**

**WASTE DISPOSAL**: Place used MP capillary tubes in the evaporating dishes on the side benches. Never place any glass into the trash. The custodian could become injured due to broken glass.

**SAFETY**: The heating device can become very HOT. Burned tissue caused by hot surfaces or flames should be immediately placed under cold tap water and as soon as possible into ice/water. This will minimize the pain and tissue damage. Keep all lab chemicals off of your skin. Gloves are always available if you want to use them.

## Postlab Questions

1.) A solid sample has a MP of 133 - 137°C. What can one conclude about the sample?

2.) For question 1, if the sample is one of four possible compounds the melting points of which are 133°, 135°, 137°, and 139°C, which is it most likely to be? Why?

3.) Two test tubes contain compounds having the same MP. Using MPs, how could you determine whether the two test tubes contain the same or different compounds?

4.) In a recrystallization (a technique that you will encounter later in the semester), a solid is dissolved in a solvent and later the solvent is removed. If a MP of the sample is taken while the sample is still moist with solvent, what effect would that have on the MP of the sample?

5.) What two pieces of information can a MP determination provide?

Possible Unknown Compounds

| Compound | Melting Point ( °C) |
|---|---|
| 4-Methylphenol | 35 |
| Benzophenone | 48-50 |
| Maleic anhydride | 54-56 |
| 4-Bromophenol | 64-66 |
| 4-Aminobenzaldehyde | 71 |
| Naphthalene | 79-80 |
| 3,4-Diaminotoluene | 89-90 |
| Acenaphthene | 94-96 |
| Isobutyranilide | 106-107 |
| Acetanilide | 113-115 |
| Benzoic acid | 122-123 |
| Urea | 132-134 |
| d,l-Glyceraldehyde | 145 |
| Adipic acid | 152-154 |
| Sulfanilamide | 165-167 |
| 2-Aminophenol | 174 |
| 4-Toluic acid | 180-182 |

| | |
|---|---|
| Succinic acid | 187-189 |

The melting points listed here vary slightly from those found in reference texts. These are closer to what you will observe because our compounds are not ultra-pure as ultra-pure compounds are ultra-expensive!!