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 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 for 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 affect the MP the impurity must be soluble in the solid.

Several devices are available for measuring melting points. A Mel-Temp device is used in this lab (note that there are a few different models in the lab but that all work the same way). Below is a photo of a Mel-Temp device along with a close-up.

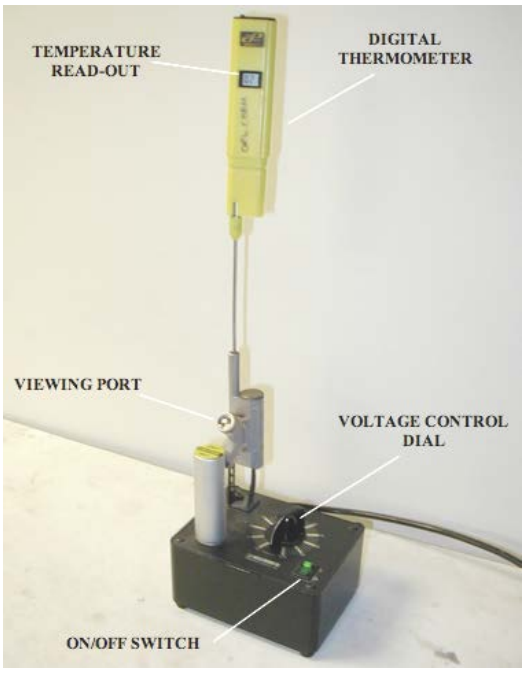

Figure 1. The mel-Temp device.

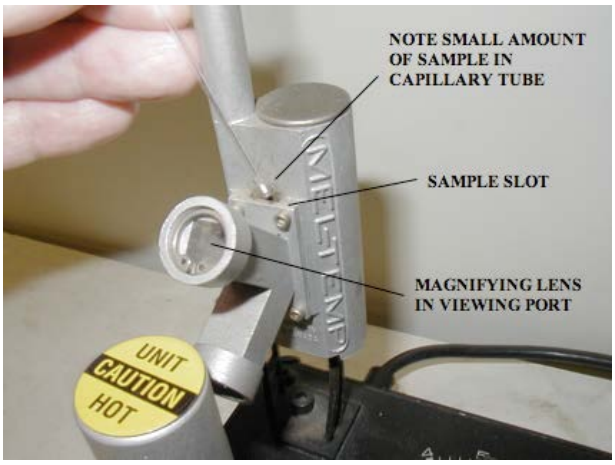

Figure 2. A close-up of the "business end" of the Mel-Temp apparatus.

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Sample is added to a small glass capillary tube, which 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 with a 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 lab notebook 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. 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 stays the same it means that the two compounds are likely identical. This technique is known as a mixed melting point determination.

To summarize, melting points can provide information about the identity and the purity of a solid sample.

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.

Filling the capillary tube: 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. 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. The height of sample in the capillary should be about 2-3 mm (thickness of two 25 cent coins). Too much sample will result in poor results.

Using the Mel-Temp device. Three 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. Heating is accomplished by adjusting the voltage control - note that the settings are not temperature settings. Settings are given either in volts or in units of 0 to 10, where 0 means zero voltage and 10 means full voltage. A higher setting results in a faster rate of heating. Start at a low setting, observe the temperature for several minutes to get a feel for use of the apparatus, then adjust the setting so that the temperature rises at a reasonable rate to about 10 °C below the expected MP range. (reasonable rate = rapidly enough so that time is not wasted but slowly enough so that the temperature does not increase past the expected MP range) The setting is then adjusted to achieve the desired temperature rise of 1°/minute near the MP of the sample. Note the settings and temperatures for future reference. A lag time exists between changing the voltage and observing a temperature change on the thermometer. When a voltage change is made therefore, allow time for the temperature to equilibrate. Note that the digital thermometers used here are accurate only to about ± 2 ° C. **Caution**: the heating block in which the thermometer and sample tube reside gets very hot! **WHEN FINISHED USING A MEL-TEMP, ALWAYS TURN THE VOLTAGE TO ZERO, TURN THE SWITCH TO OFF, AND TURN THE DIGITAL THERMOMETER OFF.**

(1.) Knowns. Determine the MPs of naphthalene, urea, and sulfanilamide. 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. Samples will be dispensed in labeled crystal dishes on the side bench. Do not move the dishes. Fill the capillaries right there. 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 well 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), do a second determination on a fresh sample. It is important to use a small sample and to raise the temperature

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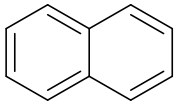
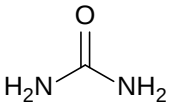
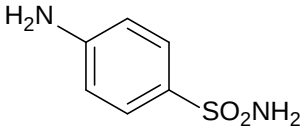
very slowly (about 1°C/minute) when you are near the MP of the sample. If a MP must be redetermined always use a fresh sample - once a sample has melted, you must assume that it may have decomposed, and therefore become contaminated with impurities, causing the MP to become depressed and the range widened. 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. ALWAYS turn the device and digital thermometer off when finished.



Naphthalene
MP 79 - 80 °C



Urea
MP 132 - 134 °C



Sulfanilamide
MP 165 - 167 °C

(2.) Determine the MP of two unknown compounds. Your TA will assign your unknowns to you. To save time, when you determine the MP of an unknown sample, first find an approximate MP by raising the temperature much more rapidly than you normally would to get the approximate MP, and then redo it using a fresh sample, raising the temperature at about 1 °C/minute when you get near the MP. Using the MP, identify your compounds using the table of possible compounds at end of this document.

BEFORE LEAVING THE LAB: TURN THE VOLTAGE ON THE MEL-TEMP TO ZERO, TURN THE SWITCH TO OFF, AND TURN THE DIGITAL THERMOMETER OFF. Clean up your work area, lock up and ask your TA for her or his signature.

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 with 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.

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!!