EXPERIMENT 1 (Organic Chemistry I)

Melting Point Determination

Purpose

a) Determine the purity of a substance using melting point as physical property
b) Identify an unknown compound using its melting point
c) Identify an unknown compound using mixture melting point
d) Learn how to obtain an accurate melting point using a Mel-Temp apparatus

Discussion

Identifying an unknown compound can be a tedious and exacting task. In identifying a compound, a chemist often measures several physical properties (melting point, boiling point, density, etc.) and observes a few chemical properties (reactivity, acidity, basicity, etc.) of the compound. The reason for determining several chemical and physical properties of the compound is that it is quite possible for two different compounds to have a few physical and or chemical properties in common; but it is highly unlikely for the two compounds to have very many identical physical and chemical properties.

Useful physical properties that are often utilized by chemists in identifying an organic compound include color, odor, physical state, melting point (M.P.), boiling point (B.P.), density (d), infrared (IR) spectrum, nuclear magnetic (NMR) spectrum and ultraviolet (UV) spectrum.
Physical constants are numerical values measured at the time certain physical properties are observed. As long as the physical constants are determined under standard conditions (temperature, pressure, etc.), they are invariant and, therefore, useful in helping to determine the identity of unknown substances.

Chemists regard a table of physical properties and physical constants to be extremely helpful in identifying unknown compounds. There are a number of reference books that contain tables of physical properties and physical constants of compounds. One of the most common is the *Handbook of Chemistry and Physics* published by the Chemical Rubber Company (CRC). If the physical properties of an unknown compound are identical to the physical properties of a compound listed in the tables, the two compounds are probably the same. Thus, a colorless, liquid compound with a melting point of 5.5 ^{o}C, a boiling point (at 760 mm) of 80.1^{o}C, is likely to be benzene, although we might want to make a few more observations to be sure.

It should be pointed out, however, that it is not possible to accurately predict the physical properties of newly synthesized or isolated compounds. Therefore, tables of physical properties are only useful in identifying previously known compounds. However, useful information as to the compound's identity and its purity can often be obtained from its melting point.

The **melting point of a solid** is defined as the **temperature** at which the liquid and solid phases are in equilibrium.

The **freezing point of a liquid** is the same **temperature** as the melting point of its solid. However, freezing points are rarely measured in practice because they are more difficult to determine. One reason for this is that solidification may not occur at the correct temperature due to the phenomenon of **supercooling.** Supercooling occurs when a liquid is cooled below its freezing point does not solidify.

Determination of the temperature at which the solid and liquid phases of a substance are in equilibrium is tedious and time consuming; it is also quite difficult with a small amount of sample. Thus, in practice, most melting points are determined as capillary melting points, which can be done quickly with a small amount of sample in a capillary tube. A **capillary melting point** is defined as the temperature range over which a small amount of solid in a thin walled capillary tube first visibly softens (first drop of liquid) and then completely liquefies.

A solid is said to melt **sharply** if the melting point range is 0.5 - 1.0 ^{o}C (narrow melting point range). A pure solid will generally melt sharply because the forces of attraction between its particles are the same. However, the presence of a foreign particle in a crystal lattice interrupts its uniform structure and the forces of attraction are weakened.

An impure solid melts at a lower temperature and over a wider range. Thus, a solid's melting point is useful not only as an aid in identification but also as an indication of purity.
Suppose two compounds X and Y have identical melting points of 131- 132 ^{o}C and appear to be identical. We can easily determine whether or not X and Y really are the same compound by mixing a small amount of Y with X (or vice versa) and taking the melting point of the mixture. (The melting point of a mixture is called the **mixture melting point**). **If X and Y are the same compound**, the mixture melting point will be the same as the melting point of pure X or pure Y. **If X and Y are not the same compound**, one will act as an impurity in the other and the mixture melting point will be lower and more spread out (wide range 120-125 ^{o}C in this case) than the individual melting points of pure X or pure Y.

It should be noted, however, that there is one unique mixture of two compounds, X and Y, which has a lower melting point than any other mixture of the two compounds. This particular mixture is called the **eutectic mixture**. The melting point of the eutectic mixture is called the **eutectic point**. A mixture whose composition corresponds exactly to its eutectic mixture will have a relatively sharp melting point. Thus, there is a possibility that a eutectic mixture could be mistaken for a pure compound. However, if a small amount of either X or Y (assuming they are both known) is added to the mixture, the melting point of the resulting mixture will be **higher** and more spread out than the melting point of the eutectic mixture.
Some solids pass directly from the solid state to the gaseous state without first liquefying; this phenomenon is called **sublimation.** The temperature at which sublimation occurs is called the **sublimation point**. Other solids decompose rather than melt. The temperature at which a solid decomposes is the **decomposition point**. While both sublimation points and decomposition points are useful helping to identify compounds, neither is very helpful in establishing the purity of a compound.

Some solids begin to "sweat" a few degrees below their true melting points. Other solids suddenly shrink just before melting. Such shrinkage of a solid being heated is called **sintering**.
Soluble impurities (that is, impurities that are included within the crystal matrix) tend to lower the observed melting point and broaden the melting point range. Insoluble impurities have no effect on the melting point.

MEL-TEMP OPERATING INSTRUCTIONS

CAUTION: Never assume the unit is cold! Wait for the heating block to cool if the temperature is not <20°C below the melting point (MP) of your compound. Allow the block to cool to room temperature if you have no idea what the approximate melting point of your compound is.

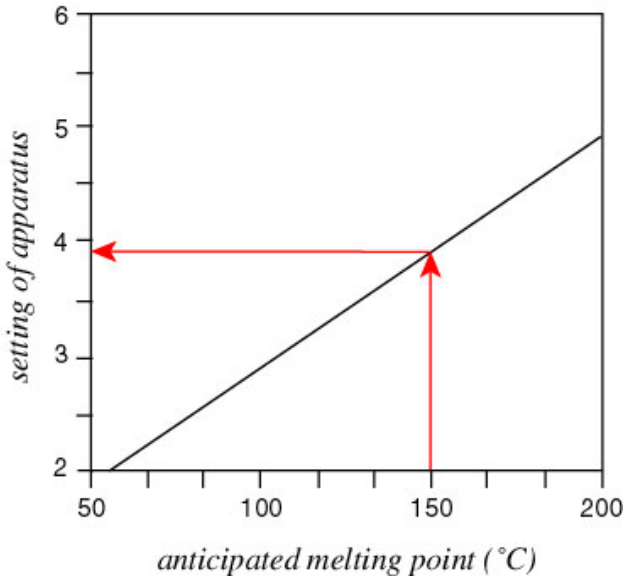
1. Set voltage to obtain the desired heating rate at the anticipated melting point range***. The voltage control controls the rate of heating, not the temperature!*** The higher the setting, the faster the temperature rise. Use the heating rate charts below to select the correct voltage and estimate the amount of time to obtain a temperature within 20°C of the melting point.

   NOTE: It is always a good idea to determine the approximate value for the MP in a literature source prior to lab. If the approximate value is impossible to obtain, save time by first obtaining a quick melting range, then repeat slowly with another sample.

2. Obtain a sample or prepare a sample by packing capillary tube 3-4mm high with thoroughly dried, finely powdered, densely packed sample. Larger, loose samples will heat unevenly! Insert the loaded MP tube in one of the (three) channels in the opening at the top of the unit.
3. Insert thermometer into thermometer well of instrument (bulb first).
4. Turn on power switch, making sure that apparatus is plugged in. Set the power according to the heating rate chart (below).
5. Observe samples with the eye about 6" from lens. Turn down the voltage control to get a 2°C per minute rise when you are within 20°C of the melting range (see example below right). Be patient!
6. Record the temperatures of the melting *range*.
   T_1: Temperature at which 1st drop of liquid appears.
   T_2: Temperature at which the last crystal *just* disappears.

Set the voltage control to zero and turn off the power switch when finished. Leave apparatus on lab bench until cool. Discard the sample in the glass disposal box.

Chart for setting the Mel-Temp melting point apparatus



Experimental Procedures

A. Preparing the Sample

Place a pea-size mound of one of the listed compounds on a piece of paper and grind it to a fine powder using a spatula. Use the spatula to push a small amount of the solid into the open end of a capillary tube. Then drop the capillary down several times to fill and pack the sample well to cause the solid to fall to the bottom. Repeat this step until you have accumulated a sample 2-4 mm (≈ 0.5 cm) high in the bottom of the tube (see Fig. 1).

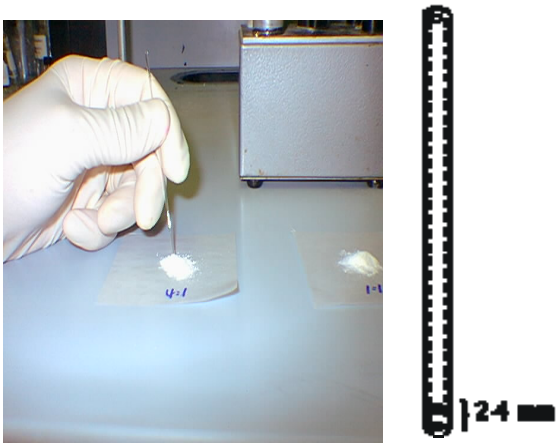
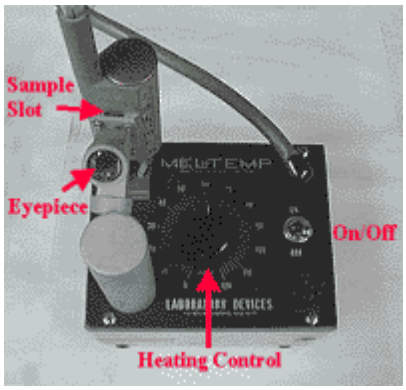


Fig. 1 – Preparing the sample



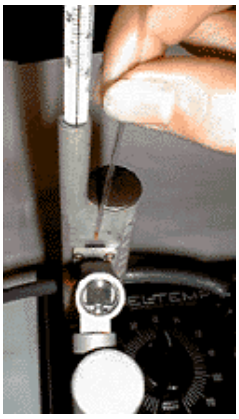


Fig. 2 - Taking a Melting Point

B. Taking a Melting Point

To record the melting point range of a compound fill two capillary tubes each to a depth of 2-4 millimeters with the compound of interest. First, get a rough idea of the approximate melting point range (see Fig. 2). Place one of the tubes in the Mel-Tem apparatus and raise the temperature a relatively fast rate, about 10 °C/minute. Record the range of temperature from the first visible evidence of liquid (the sample appears moist, or a tiny drop of liquid is observed) to the complete liquefaction of the sample.

Note the temperature at which the compound first begins to melt. Allow the melting point apparatus to cool to about 20 °C below that temperature, and then insert the second tube. Raise the temperature more slowly this time, at the rate of about 2 °C/min.

Note the temperatures at which: I. the first crystals melt, and; II. at which the sample has completely melted. This is the melting point range. For example, a mp range of 164-168 °C average of 166 °C indicates the sample softened or began to melt at 164 °C and that transition to a liquid was complete at 168 °C.

C. Mixture Melting Point

Take approximately equal amounts of the two compounds for which you have already determined melting points and grind them together very thoroughly. Prepare a capillary containing a sample of this mixture as described in Part B and determine its melting point.

List of Melting Points for Standard Compounds

Compound	M.P. degrees C
o-toluic acid	103-105
Acetanilide	113-114
Fluorene	114 -115
dl-Mandelic Acid	117-118
Benzoic Acid	121-122
2-Naphthol	121-122
Urea	132-133
trans-Cinnamic Acid	132-133
Benzoin	136-137
Maleic Acid	136-137
Vanilin	81-82
Cholesterol	148-150
Biphenyl	70-71
Phenylbenzoate	69-70
Benzhydrol	68 –69
Benzophenone	48- 49

D. Determination of the Identity of an Unknown

Obtain an unknown compound from your instructor. Prepare two capillaries containing the unknown. Determine an approximate melting point for it using the first tube and a heating rate of 15-20 degrees per minute. Then let the thermometer and Mel-Temp apparatus cool to at least 20 degrees below this approximate melting point and use the second tube to obtain an accurate melting point with a heating rate of no more than 3 degrees per minute.

From the found melting point of your unknown, decide which of the listed compounds it might possibly be. There may well be more than one reasonable possibility. Prepare a mixture of your compound with the compound that is the most likely of the possible choices and take a melting point of t his mixture. If its melting point is the same as that of the unknown, it is likely that your unknown and the compound with which you mixed it are the same. If the melting point of the mixture is lower than that of the unknown, you should prepare a mixture of your unknown with the next most likely choice. You must continue to experiment until you have found a substance that does not lower the melting point of your unknown. When you have confirmed the identity of your unknown, record your findings to report sheet.

EXPERIMENT 1 – Melting Point Determination

REPORT FORM

Name _____

Instructor _____

Date _____

I. Melting Points of Pure compounds

Name of compound	M.P.,^{o}C (Experimental)	M.P.,^{o}C (Literature)
(a) _____		
(b) _____		

II. Melting Point of an Impure Substance

Melting Point of a Mixture of (a) and (b) _____^{o}C

III. Identification of an Unknown Solid from its Melting Point

Unknown Number = _____

M.P. of PURE unknown = _____^{o}C

Trial 1: M.P.of unknown when mixed with _____ = _____^{o}C
(name of compound)

Trial 2: M.P. of unknown when mixed with _____ = _____^{o}C
(name of compound)

Trial 3: M.P. of unknown when mixed with _____ = _____^{o}C
(name of compound)

My unknown compound is _____
(name of compound)

Pre-Laboratory Questions–EXP 1 Name:

Due before lab begins. Answer in space provided.

1. List six physical properties of organic compounds that are often measured by organic chemists in attempting to identify a compound.

2. Melting point determination can be used for several purposes. What are those purposes?

3. Define the following terms:

   a) melting point –

   b) sublimation –

   c) sintering –

   d) eutectic mixture –

4. What is the effect of a small amount of impurity on the melting point of an organic compound?

5. What is the difference between the capillary melting point and true melting point?

Post-Laboratory Questions–EXP 1 Name:

Due after completing the lab.

1. What would be the effect on the observed melting point if sample were:

   a) too small –

   b) too large –

   c) poorly packed –

   d) heated too rapidly –

2. Some compounds sublime in the capillary and some decompose before melting. How do you determine melting point of these compounds?

3. A student was given a white solid for an unknown. Its melting point range was 119 – 121 ^{o}C. The student has previously worked with benzoic acid, and had observed that it was a white crystalline solid with a melting point of 122 ^{o}C.
   (a) Can the student conclude that the unknown is benzoic acid on the basis of her work to this? Why or why not?

   (b) What additional experimental work should be done to verify this compound?

4. You and your lab partner take melting points of the same sample. You observe a melting point of 101-107°C, while your partner observes a value of 110-112°C. Explain how you can get two different values with exactly the same sample.

5. An unidentified compound is observed to melt sharply at 111 °C with the vigorous evolution of a gas. The sample then solidifies and does not melt until the temperature reaches 155 °C, at which time it again melts sharply. Briefly explain these observations.