1. The Determination of Melting Point

Objective

The melting point of a pure substance is a characteristic property of the substance. In this experiment you will determine the melting point of an unknown sample, and will then confirm the identity of the uknown by a "mixed" melting point determination.

Introduction

The melting point of a pure substance is a *characteristic* property for a given substance. That is, under the same laboratory conditions, a given substance will always have the *same* melting point. Characteristic physical properties (such as the melting point of a pure substance) are of immense help in the identification of unknown substances. Such properties are routinely reported in scientific papers when new substances are isolated or synthesized, and are compiled in tables in the various handbooks of chemical data that are available in science libraries. When an unknown substance is isolated from a chemical system, its melting point may be measured (along with certain other characteristic properties) and then *compared* with tabulated data. If the experimentally determined physical properties of the unknown *match* those found in the literature, you can typically assume that you have identified the unknown substance.

When a pure solid substance melts during heating, the melting usually occurs quickly at one specific, characteristic temperature. For certain substances, especially more complicated organic substances or biological substances that tend to decompose slightly when heated, the melting may occur over a span of a few degrees, called the **melting range**. Melting ranges are also commonly observed if the substance being determined is not completely pure. The presence of an impurity will *broaden* the melting point of the major component and will also *lower* the temperature at which melting begins. Melting points of solid substances are routinely reported in the scientific literature and are tabulated in handbooks for use in identification of unknown substances. Melting point determinations are very common and will be used as an aid in identification of substances in several later experiments in this manual.

The apparatus used for heating samples in this experiment is called a **Thiele tube**. The Thiele tube contains oil (typically mineral oil) as a fluid, which permits the determination of temperatures up to about 200°C. The Thiele tube is constructed in such a way that when the side arm is heated, the warm oil will rise and enter the main chamber of the tube, which provides for circulation of the oil and for a more uniform temperature. Samples to be placed in the Thiele tube are ordinarily positioned so that the sample is aligned with the top branch of the side arm. When using a Thiele tube, remember that it contains hot oil, which can be dangerous if caution is not exercised.

In today's experiment, you will first make duplicate determinations of the melting point of an unknown pure substance provided by your instructor. Your instructor will then list for you on the chalkboard the names of the substances from which the unknowns were prepared, along with the literature values for the melting points of these substances. Based on your experimental data, you will choose one of the substances listed on the chalkboard as the most likely candidate for the identity of your unknown. You will then perform a “mixed” melting point determination of a combination of a small amount of your unknown substance and an authentic sample of the substance you believe the unknown to be. If the two substances (unknown and authentic sample) are the *same substance,* the mixture should melt at the same temperature as in your previous melting point determinations of the unknown alone. If you choose the identity of your unknown *incorrectly,* then the mixture of your unknown and the authentic sample will not be a pure substance, and will demonstrate a much lower and broader melting range than did the pure unknown alone.

SAFETY PRECAUTIONS

- **Wear safety glasses at all times while in the laboratory.**
- **Thermometers are often fitted with rubber stoppers as an aid in supporting the thermometer with a clamp. Inserting a thermometer through a stopper must be done carefully to prevent breaking of the thermometer, which would release mercury and possibly cut you. Your instructor will demonstrate the proper technique for inserting your thermometer through the hole of a rubber stopper. Glycerine is used to lubricate the thermometer and stopper. Protect your hands with a towel during this procedure.**
- **The red liquid used as the temperature-sensing liquid in some lab thermometers is flammable. If a red-liquid thermometer breaks, extinguish all flames in the vicinity. Mercury may be used as the temperature-sensing fluid in other types of thermometers. Mercury is poisonous and is absorbed through the skin. Its vapor is toxic. If mercury is spilled from a broken thermometer, inform the instructor immediately so that the mercury can be removed. Do not attempt to handle spilled mercury.**
- **The solid samples used in this experiment may be toxic if ingested or if absorbed through the skin. Wash immediately if spilled on skin and consult with the instructor.**
- ***Caution:* Oil is used as the heating fluid in the Thiele tube used for the boiling/melting point determinations that follow. Hot oil may spatter if it is heated too strongly, especially if any moisture is introduced into the oil from glassware that is not completely dry. The oil may smoke or ignite if heated above 200°C.**

Apparatus/Reagents Required

Thermometer and clamp, several beakers, Thiele tube, melting point capillaries, 5–6-mm-diameter glass tubing, burner and rubber tubing, file, scissors, medicine dropper, unknown sample for melting point determination

Procedure

Record all data and observations directly in your notebook in ink.

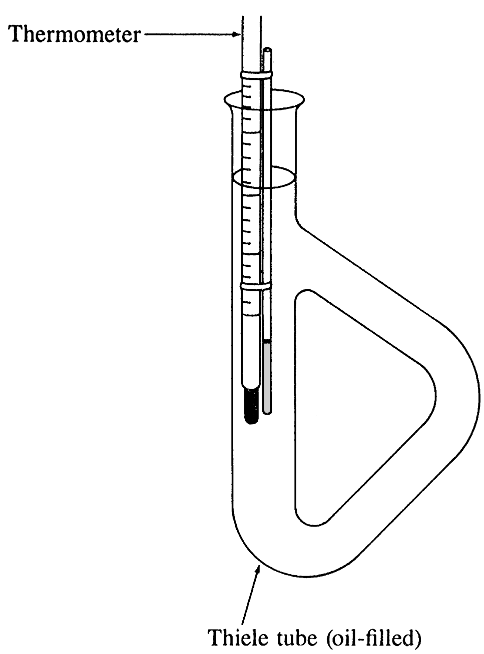
A. Melting Point of Unkown

Obtain a solid unknown sample for melting point determination from your instructor. Record the identification code number in your notebook and on the lab report form. If the solid is not finely powdered, grind some of the crystals on a watchglass or flat glass plate with the bottom of a clean beaker. Set aside part of this unknown sample for use in Part B.

Pick up a few crystals of the unknown solid in the open mouth of a melting point capillary tube. Tap the sealed end of the capillary tube on the lab bench to pack the crystals into a tight column at the sealed end of the tube. Repeat this process until you have a column of crystals approximately 2–3 mm high at the sealed end of the capillary.

Set up the Thiele tube apparatus as indicated in Figure 1-1. Attach the capillary tube containing the crystals to the thermometer with one or two small rubber bands, and position the capillary so that the crystals are *next to* the temperature-sensing bulb of the thermometer.

FIGURE 1-1
Thiele tube oil bath for boiling/melting determinations. Exercise caution when dealing with heated oil.



Lower the thermometer into the oil bath, and begin heating the side arm of the Thiele tube with a very small flame. Adjust the flame as necessary so that the temperature rises by one or two degrees per minute.

Watch the crystals in the capillary tube, and record the exact temperature at which the crystals first *begin* to melt, and the exact temperature at which the last portion *finishes* melting. Record these two temperatures as the melting range of the unknown.

Allow the oil bath to cool by *at least* 20°C.

Prepare another sample of the unknown crystals in a fresh capillary tube, and repeat the determination of the melting point. If this second determination differs significantly from the first determination, repeat the experiment a third time. Calculate the average value of your melting point determinations.

B. Mixed Melting Point

Your instructor will have listed on the chalkboard the names and melting points of the pure substances from which the unknown samples were prepared. By comparing the experimental value for the melting point of your unknown with the melting points of the pure substances listed on the chalkboard, choose the most likely candidate for the identity of your unknown. Obtain an authentic sample of this substance from your instructor or the stockroom.

Mix a small amout of the authentic sample with a small amount of the unknown sample (saved from Part A). Use approximately equal amounts of the two materials to give a total volume about the size of a pea. Use a stirring rod to mix together the two components of the mixture.

Pick up a few crystals of the mixture in the open mouth of a melting point capillary tube. Tap the sealed end of the capillary tube on the lab bench to pack the crystals into a tight column at the sealed end of the tube. Repeat this process until you have a column of crystals approximately 1 cm high at the sealed end of the capillary.

Attach the capillary tube containing the crystals to the thermometer of the Thiele tube apparatus with one or two small rubber bands, and position the capillary so that the crystals are *next to* the temperature-sensing bulb of the thermometer.

Lower the thermometer into the oil bath, and begin heating the side arm of the Thiele tube with a very small flame. Adjust the flame as necessary so that the temperature rises by only one or two degrees per minute.

Watch the crystals in the capillary tube, and record the exact temperature at which the crystals first *begin* to melt, and the exact temperature at which the last portion *finishes* melting. Record these two temperatures as the melting range of the mixture.

Allow the oil bath to cool by *at least* 20°C.

Prepare another sample of the crystals in a fresh capillary tube, and repeat the determination of the melting point. If this second determination differs significantly from the first determination, repeat the experiment a third time. Calculate the average value of your melting point determinations.

If the average melting temperature range for the *mixture* of unknown and authentic sample does not differ from the melting point of the unknown *itself* (Part A) by more than 1°C, you may assume that you have identified the unknown correctly.

If the melting range of the mixture differs significantly from the melting point of the unknown itself, consult with the instructor about performing additional melting point determinations of the unknown.

The Determination of Melting Point

Date: .... Student name: ....

Course: .... Team members: ....

Section: ....

Instructor: ....

Prelaboratory Questions

1. What does it mean to say that the melting point of a pure substance is a *characteristic* property of the substance?

2. What effect does the presence of an *impurity* have on the melting point of a substance?

3. What is meant by a *mixed melting point* determination?

The Determination of Melting Point

Date: ....
Course: ....
Section: ....
Instructor: ....

Student name: ....
Team members: ....
....
....

Results/Observations

A. Melting Point of Unknown

Identification number of unknown solid sample ....

First determination of melting point ....

Second determination of melting point ....

Mean value for melting point of unknown ....

B. Mixed Melting Point

Substance taken for mixed melting point determination ....

First determination of melting point ....

Second determination of melting point ....

Mean value for melting point of mixture ....

Questions

1. Suggest a *reason* why the melting point of a binary mixture is lowered and broadened, compared to the melting point of either component of the mixture.

2. Using a handbook, look up the normal melting points of each of the following substances:

   NaCl ....

   Biphenyl ....

   Naphthalene ....