

EXPERIMENT #1 - MELTING POINT

Definition

When a solid substance is heated, typically it will melt; that is to say, at some temperature the solid will begin to liquify and by some slightly higher temperature all of the solid will have become liquid. The melting point (actually melting point range) of a compound is then defined as the temperature at which an observer can first see liquid forming from the solid to the temperature where the last particle of solid has become liquid. For example, the melting point of pure sucrose (table sugar) is 185^o-186^oC. This means that as a small sample of sucrose is slowly heated some of the crystals begin to liquefy at 185^o and all of the crystals have become liquid by 186^oC. Sometimes only the second number (completely melted) is reported as the melting point. In general, this is not a good idea and should be avoided.

Purpose

There are several purposes for doing this experiment. The first is to learn how to determine the melting range of a solid substance accurately. When a solid substance is prepared its melting point is usually determined to aid in its identification and to get some idea of its purity. The second is to observe the effect of the purity of a substance on its melting behavior. Pure substances usually have melting point ranges of a degree or two; impure substances (which are mixtures of two or more substances) often have wider ranges. Thus, a sharp melting point is often taken as *prima facie* evidence that a substance is pure, while a wide range suggests that it is not. It is often, but not always, true that an impure substance will have a lower melting point than the same substance when it is pure. Thus, pure benzoic acid has a melting point of 122-123^oC, while an impure sample might have a melting point of, say, 115-120^oC. The third is to use a physical constant of an unknown substance – its melting point – to identify it from among several possibilities. In most cases, the melting point alone will not enable you to identify a compound. Millions of solid organic compounds, and their melting points, are known. Perhaps 10,000 of these will have the same melting point as your unknown compound. You don't know what the compound is yet, but you have narrowed the field. In this experiment you will attempt to determine the identity of a compound, from among ten contenders, based on its melting point.

Determination of Melting Points – Practical Aspects

First, the term “melting point” is a misnomer; what we really mean is melting range, the temperature *from* which you first observe liquid in the sample *to* the temperature at which all of the solid has just melted. ***Whenever – now and in the future – you are asked to take a "melting point", you must determine and record the melting range.*** [Remember – the two reasons for determining melting point are compound identification and estimation of purity. If you do not report the range, you have provided no information about the latter and the former is compromised since the melting point of an impure substance is usually different from the pure substance.] Melting points are usually determined by placing one or two milligrams of the material to be tested into a *melting point capillary*, and heating the capillary and a thermometer together, and observing over what temperature range the material melts. The melting point capillary is a thin-walled glass tube, about 100 mm in length and not more than 2 mm in outside diameter, sealed at one end.

Filling the Capillary Tube

Make sure the sample is dry. [This is not an issue in this experiment, but in the future you will want to determine the melting point of a solid you have just separated from a liquid by filtration. If you try to do this while the solid is damp it is impure and the melting point will reflect this.] Place a small spatula tip full of the sample on a watch glass and pulverize it with the spatula until it is a powder. Form the powder into a mound and push the open end of the capillary into the mound several times to force some of the powder into it. You want between 1 and 2 millimeters of sample, lengthwise, in the capillary. Holding the melting point tube between your thumb and forefinger, strike the closed end against the benchtop perpendicularly until the material is firmly packed against that end of the tube. Repeat this process if you do not have enough sample (1-2 mm) in the tube. If it is difficult for you to force the sample from the open end to the closed end, try dropping the capillary onto a hard surface (closed end down) through a 4 foot section of glass tubing. It is surprising how well this works. The sample should be well packed or it will not melt evenly.

Insert your (dry) thermometer into one of the small rubber bands you will find on the side bench. Push the rubber band up the thermometer so it will be able to hold the capillary, near its open end, to the thermometer with the closed end next to the thermometer bulb (see Fig. 1). Pinch the rubber band and slide the top of the melting point tube under it; then adjust the position of the capillary.

Now you need to insert the bulb end of the thermometer, along with the attached capillary tube, into oil that is contained in an apparatus known as a Thiele tube. You will need to clamp the Thiele tube and the top of the thermometer to a ring stand with clamps. Both the Thiele tube and thermometer should be vertical. The thermometer should be centered in the Thiele tube with its bulb below the side-arm of the Thiele tube. The thermometer and capillary tube must not touch the Thiele tube (see Fig. 1). (If your clamp will not hold your thermometer, you can attach the thermometer adapter and clamp to the rubber piece of that. **Safety tip: Be sure to lubricate the top of the thermometer with a small amount of stopcock grease before attempting to slide the adapter onto the thermometer. Do not force the adapter or you may wind up breaking the thermometer and inserting its stub into your hand.**)

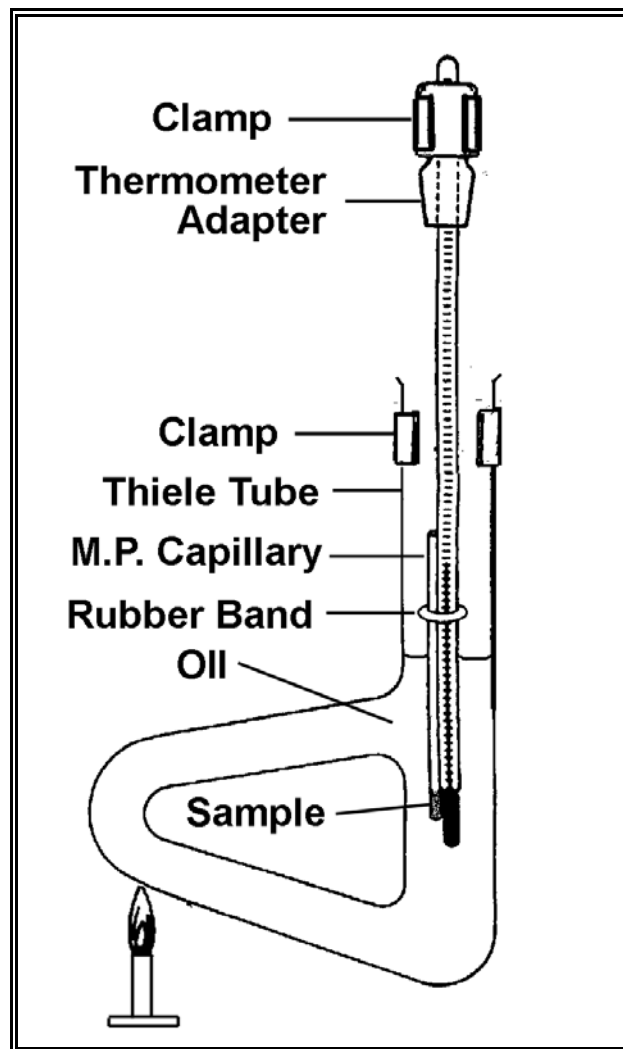


Figure 1 - Melting Point Using Thiele Tube

The Thiele tube is warmed using a microburner which heats the sidearm elbow (see Fig. 1). This causes the oil to flow around the tube and past the sample and thermometer bulb by convection, thus warming the sample and thermometer.

To obtain an accurate melting point you must heat the oil at a rate of 1 to 2 degrees per minute as you approach and go through the melting range of the sample. If you heat faster your result will be in error because the bulb of the thermometer will not warm up as quickly as the oil, but your sample will; consequently, the thermometer and sample would be at different temperatures – not a good situation. If you have no idea what the melting point of your sample is, you have two choices at this point. (1) You could start at room temperature and warm at the recommended rate until the solid melts. This could take more than an hour. (2) You could start at room temperature and warm at about 10 degrees a minute and obtain an approximate melting point. Then, after the apparatus has cooled below the sample's melting point, replace the sample (and capillary) with a new one, and heat slowly until the sample has melted, thus getting an accurate melting point. [Sometimes materials decompose as they melt, so you should use a new sample.] Neither of these options may thrill you, but the second is better, unless you have happen to have a low melting solid.

Procedures

Calibration of Thermometer

Actually this section should be called, "Finding Defective Thermometers." Fill a beaker with crushed ice to a depth of about 10 cm (4 in). Add just enough cold water to completely fill the voids between the pieces of ice and barely float the mass of ice off the bottom of the beaker. Immerse the bottom of your thermometer into the ice-water mixture to a depth of 7 or 8 cm. Using the thermometer, stir the ice gently, and observe the drop in temperature as shown by the thermometer. When the temperature stops decreasing and has stabilized for 10 or 15 seconds, observe the temperature displayed by the thermometer without removing it from the ice-water bath. Record this temperature on your report sheet. If the reading is within one Celsius degree of 0° C, the thermometer is a keeper; if the reading differs from 0° C by more than one Celsius degree, return the thermometer to your instructor for a replacement. Should you get a replacement, test it at 0°, also.

Dry the thermometer with a paper towel.

Determination of Melting Points of Biphenyl, Naphthalene, and Biphenyl-Naphthalene Mixtures

If your thermometer is wet, dry it. If there is water on your thermometer the oil in the Thiele tube will become cloudy because oil and water are not miscible.

Using a Thiele tube, determine the melting points (*actually* melting **ranges**) of pure biphenyl (Sample #1), pure naphthalene (#8), and the following mixtures of biphenyl and naphthalene: 90% biphenyl/10% naphthalene (#2), 60% biphenyl/40% naphthalene (#4), 45% biphenyl/55% naphthalene (#5), and 15% biphenyl/85% naphthalene (#7). The various mixtures have already been prepared for you and can be found in bottles on the side bench near the balances, along with the pure naphthalene and biphenyl. You will not need more than a small spatula tip full of each sample since each melting point requires only a couple of milligrams of material. Record your data on

the report sheet. Follow the instructions above for using the Thiele tube. Remember that you should not allow the temperature to rise faster than 1 to 2° per minute as a sample is melting. If you go faster than this the thermal lag of the more massive thermometer will be greater than that of the capillary and they will not be at the same temperature! Too rapid heating is the most common melting point mistake made by neophyte chemists. Your setup should look like Figure 4, above, with one exception –

There should be two (or three) capillary tubes attached to the thermometer, each containing a *different* sample. This will greatly speed up your work, provided you remember which capillary contains which sample! Rather than trust your memory, you should write this information down.

N. B. Do not try to cool down a hot thermometer or Thiele tube using water. The thermometer *will* crack and the Thiele tube might.

Run samples 4 and 5 first. These materials should not begin melting below 30° C. We'll skip samples 3 and 6. Then run samples 2 and 7. These materials will not begin melting below about 50° C. Then run the pure compounds, 1 and 8, together. Neither should melt below 60° C.

Identification of an Unknown Compound by Melting Point Determination

Determine the melting point of your unknown compound. You should first get an approximate melting point by heating the oil in the Thiele tube rapidly, say about 10° per minute. Then, using a *fresh sample*, heat rapidly until you get within about 15° of the melting point; at that point slow down to a rise of 1-2° per minute. Record the melting point of your unknown on your report sheet. Try to ascertain the identity of your compound from among the candidates below and record your guess on your report sheet.

Compound	MP, °C	Compound	MP, °C
benzophenone	49-51	<i>o</i> -nitrobenzoic acid	143-145
naphthalene	80-82	salicylic acid	158-159
acetanilide	113-114	sulfanilamide	165-166
benzoic acid	121-122	succinic acid	184-185
urea	132-133	phthalic acid	230-231

Cleanup

There should not be much to clean up if you took samples of appropriate size. You should dispose of used capillary tubes in a box on the side bench or in the broken glass garbage can in the front of the lab. You should never put glass you are disposing of in the wastepaper baskets at the ends of the benches near the sinks; always dispose of glass in the garbage can in the front of the room. You should dispose of the biphenyl/naphthalene samples in a jar labeled "Used Biphenyl/Naphthalene," which you will find in a fume hood. Wash the remainder of your unknown sample down the drain with water.