Background:

The melting point of an organic solid is probably the most widely used physical constant. If you want a quick, easy, and cheap way to characterize an unknown solid, determining the melting point is your ticket to success. A melting point of a solid is the temperature at which the first crystal just starts to melt until the temperature at which the last crystal just disappears. Thus, the melting point (m.p.) is actually a melting range.

For a pure compound the melting point is quite sharp (occurs over a 0.5 -1°C temperature range). A melting point range of greater than 5° C usually indicates an impure compound or poor technique. The melting points are characteristic of a compound but the melting point itself is not a unique characteristic of the compound. That is, two different compounds could have the same melting point, but two substances of differing melting point are unlikely to be the same compounds.

Mixed Melting Points

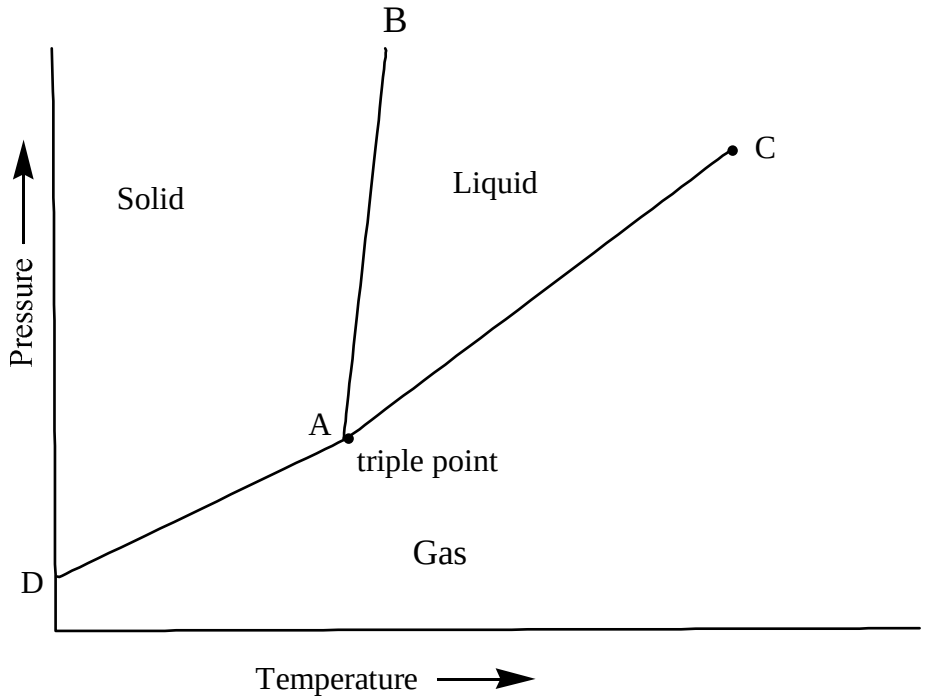
You can compare an unknown compound with a known compound by thoroughly mixing the two and taking the melting point. If the mixture melts at a lower temperature than the known compound or over a broad range, your unknown is not the same compound. If the mixture melts at the same temperature and same range as the known compound it's a good bet that it is the same compound.

Thermodynamics:

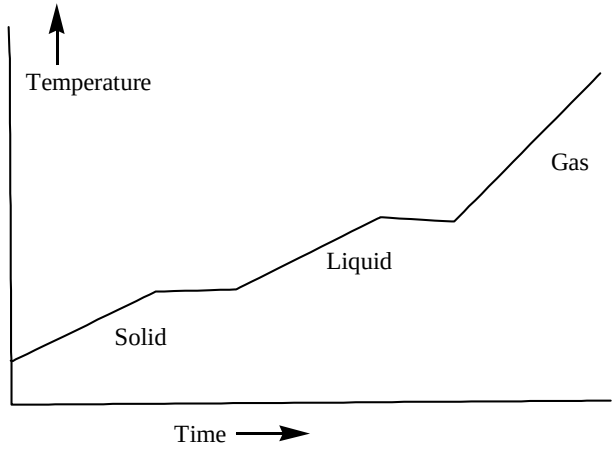
In melting, energy to disrupt the crystal lattice is supplied in the form of heat. As heat is applied, the vibrational energy of the molecules increases until it reaches a level where it exceeds the lattice energy and, in effect, the crystal lattice falls apart. The highly ordered molecules in the solid are thus converted to a more random array of molecules in the liquid state.

Let God arise, let his enemies be scattered:
let them also that hate him flee before him.
As smoke is driven away,
so drive them away:
as wax melteth before the fire,
so let the wicked perish at the presence of God.
Bible, Psalms 68:1

In thermodynamic terms, the melting point of a solid is defined as that temperature at which the liquid and solid phase exist in equilibrium at an external pressure of one atmosphere. Since the two phases are in equilibrium, we can say that the vapor pressures of solid and liquid phase are equal. Line DA represents and equilibrium between solid and gas. Line AB represents and equilibrium between solid and liquid. The melting temperature at a given pressure is represented by line AB.



While the solid is melting the temperature remains the same. When all the solid is melted, the heat put in begins to raise the temperature of the liquid.



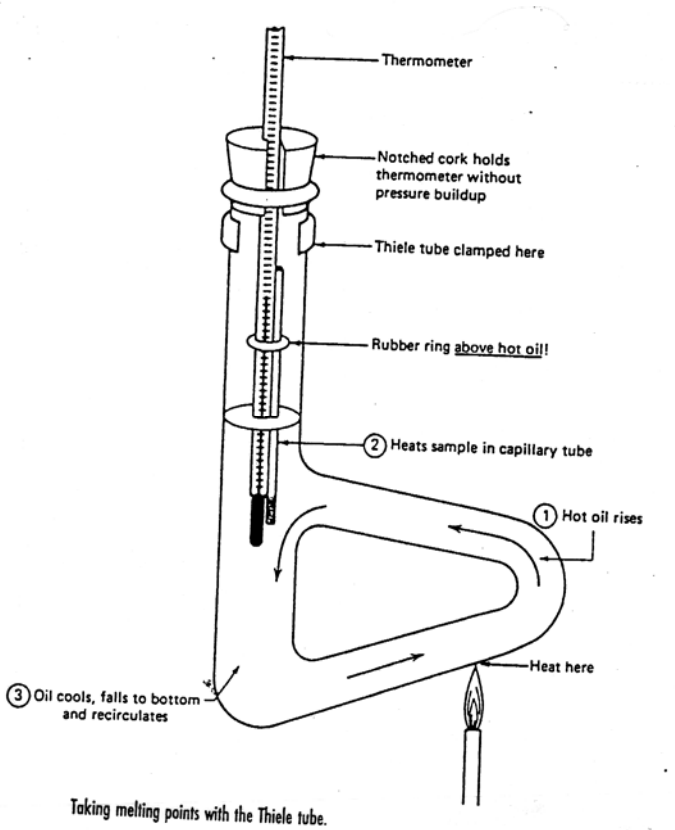
The Melting Point Apparatus

The apparatus most commonly used in the student laboratory for melting point determinations is the Thiele tube. It is a glass vessel filled with oil and so designed that the oil is efficiently circulated by convection currents when the vessel is heated at the point shown in the diagram. Heating is generally done with the small flame from a micro-burner.

The thermometer is held in the place indicated by a split stopper. The stopper has a v-shaped groove cut in the side to allow for air and oil expansion when the vessel is heated and also to expose that portion of the thermometer scale which would otherwise be covered by the stopper. The capillary tube is held in place by a rubber band cut from a small piece of rubber tubing. The bottom of the capillary containing the sample is placed as close to the center of the thermometer bulb as possible. The capillary tube is left in place until the new one is slipped under the rubber band.

Since the oil expands considerably when heated, be certain to keep the rubber band and the open end of the capillary tube well above the oil level. Also be sure that the bottom of the capillary is effectively sealed.

The bath oil is a stable, high boiling liquid. It should not be heated much above 200°C.



Taking melting points with the Thiele tube.

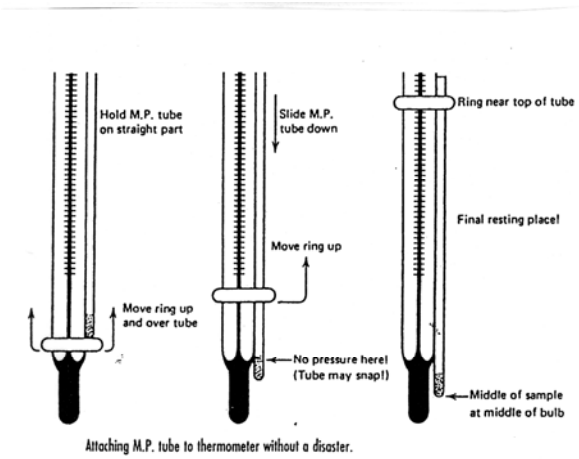
Taking the Melting Point

When the tube is in position, adjust the heating rate to give a convenient rate of temperature increase. If the approximate melting temperature is known, the bath can be heated rapidly until it is about 10° below the melting point. The temperature rise during the last several degrees should be no more rapid than; 1-2° per minute, to allow the sample to be well equilibrated at the melting point. If the melting temperature is unknown, it is convenient to prepare two tubes of the sample and to determine an approximate melting point with one tube, using a rapid heating rate. The bath is then cooled to about 10° below this temperature, and the accurate value determined with the second tube.

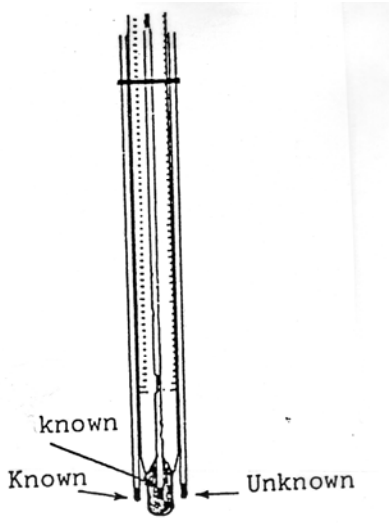
If the sample is very pure, it will change from a solid to a liquid over a very narrow temperature range. In a less pure sample, liquid and solid may exist in equilibrium over a considerably wider range of temperature. An initial softening and shrinking of the sample is sometimes observed at the onset of melting. The lowest temperature at which liquid is visible in the capillary is defined as the lower bound of the melting range. The upper limit is the temperature at which, the last crystal in the tube melts to give a completely transparent liquid. This is the melting point range and is reported as such, for example, 79.0-80.5°.

Filling the Capillary Tube

The tube itself is a thin walled capillary of about 1mm. internal diameter, sealed at one end. It is important that the sample be dry. Any solvent remaining on the crystals is an impurity that will affect the melting behavior. Several milligrams of the dry, finely powdered solid are placed on a glazed paper or clean glass surface and the open end of the tube is pushed onto the mound. The solid that sticks inside is then shaken to the bottom either by gently stroking the tube with a file (to create vibrations), or by tapping the bottom of the tube on a hard surface. The capillary may also be dropped through a long vertical glass tube onto a hard surface. A firm packing is necessary for the efficient heat transfer to the sample. More solid is then taken up until the height of the sample in the tube is 1-2 mm.; if a larger quantity is present, the problem of heat conduction to the bulk of the sample may seriously impair the accuracy of the melting point.



Attaching M.P. tube to thermometer without a disaster.



Procedure:

In this experiment you will identify your unknown by matching its melting point with that of a known compound.

Obtain the mass of your recovered crystals in Lab #3.

Compounds for Melting Point Determination

benzoic acid
trans-cinnamic acid (cinnamic acid)
4-methoxyphenol (p-methoxyphenol)
2-naphthol (β-naphthol)
4-chloroaniline (p-chloroaniline)
acetanilide
1,4-dibromobenzene (p-dibromobenzene)
2-methoxynaphthalene (β-methoxynaphthalene)
1-naphthylamine

1. Set up your Thiele tube, 200º + C thermometer and micro-burner.
2. Obtain three melting point capillary tubes.
3. Load the 3 tubes with one of your unknowns (1-2 mm in height)
4. Do a rapid melting point estimation with one tube. Record the m.p with your 200º C thermometer.
5. With that information perform a slower melting point determination run with a second tube. Record the melting point range.
6. Compare your melting point with the (book value) melting points of the known compounds. Chose a known compound that has a melting point close to that of your unknown. In case of uncertainty, get advice from your instructor.
7. Load a tube with the known compound.
8. Run the known compound at the same time as your third unknown tube. Record the two melting points.
9. How do they compare? Is it a match or do you need to compare your unknown with another known?

Repeat steps 2 through 8 with your other unknown.

Place your unknowns in two clearly labeled vials. Your name, date, m.p. & sample name should appear on the label tag.

Disposal: Put melting point capillaries in the solid disposal container.

Checklist for completing the "Prelab" section: (refer to Laboratory Syllabus for complete directions)

____ *Title*.
____ *Purpose*. Refer to procedure

Physical constants. Create a table of physical constants, solubility and safety data for:

____ benzoic acid -- experiment #1
____ *trans*-cinnamic acid -- experiment #3
____ 4-methoxyphenol (*p*-methoxyphenol)
____ 2-naphthol (β-naphthol) -- experiment #1
____ 4-chloroaniline (p-chloroaniline) -- experiment #1
____ acetanilide -- experiment #3
____ 1,4-dibromobenzene (*p*-dibromobenzene)
____ 2-methoxynaphthalene (β-methoxynaphthalene) -- experiment #1
____ 1-naphthamine

____ References

Structures and equations. NONE

___ *Flowchart.* Refer to "Procedure"

Calculations.

Obtain the melting points of the 8 solids from 2 different sources such as the Aldrich catalog, chemfinder.com, the Merck Index and/or the CRC Handbook.

____ benzoic acid
____ *trans*-cinnamic acid
____ 4-methoxyphenol (p-methoxyphenol or p-hydroxyanisole)
____ 2-naphthol (β-naphthol)
____ 4-chloroaniline (p-chloroaniline)
____ acetanilide
____ 1,4-dibromobenzene (p-dibromobenzene)
____ 2-methoxynaphthalene (β-methoxynaphthalene)
____ 1-naphthamine

____ references

Why do you think that there are sometimes discrepancies between melting points recorded in the literature (2 reasons)?

Safety Question: What are two 1st aide procedures to treat a burn (like you would get from getting hot oil splattered on your hand)? Cite your sources.

Experimental Observations and Data: Experiment #4

Hand in a copy of your experimental observations and data before you leave lab.

Experimental Observations.

___ Describe the physical appearance of each of the standard compounds.

___ Are your melting points recorded as "ranges" and not "points?"

___ Describe the melting process as you observed it.

___ About how long does it take to do a melting point determination?

___ What happened to the compound in the melt tubes after they were re-cooled?

___ Any blunders to report?

___ Did you record interesting sights and smells?

Data:

Be sure to record all the relevant data that made it possible to identify your unknowns.

I'll stop the world and melt with you
You've seen the difference and it's getting better all the time
And there's nothing you and I won't do
I'll stop the world and melt with you

MEST "I Melt With You" http://www.azlyrics.com/lyrics/mest/imeltwithyou.html

Lab Report Checklist: Experiment #4

___ Look at your corrected experiments 1, 2 and 3 lab reports. What did you do well? What can you improve on?

Results.

___ Create a table to organize your raw data. For example:

Sample	Rapid heat	Slow heat 1	Slow heat 2	Slow heat 3	comments
Unknown 1					
Candidate 1a					
Candidate 1b					
Unknown 2					
Candidate 2a					
Candidate 2b					

____ Submit samples of your unknowns in labeled vials.

Discussion and Conclusion.

____ Comment on the melting point technique. What are 2 advantages of using melting point to characterize a substance compared with TLC (experiment #1)?
_____ What are 2 disadvantages of using melting point to characterize a substance compared with TLC (experiment #1)?
_____ Why does the size (quantity) of your solid in the capillary tube make a difference?

_____ Why does it make a difference in the observed melting point if you heat your sample rapidly or slowly?

_____ Would it work to take the melting point by using the same capillary tube for all three trials? Solid → melt(1) → solidify → melt(2) → solidify → melt(3)
____ What is the relationship between pressure and melting point? Will different atmospheric pressures affect the measured melting point of a compound?
____ What were your conclusions from the m.p. experiment (as to the identity of your unknowns)?

____ How do your conclusions connect with your findings in experiments 1, 2 and 3? Are they consistent? Describe 2 or 3 specific examples to support your opinions.

____ How well did experiments 1,2,3 and 4 hang together for you? Did they offer you a logical progression towards the separation, purification and identification of a mixture of unknowns? Describe 2 or 3 specific examples to support your opinions.

_____ Green question. What is the chemical composition of “mineral oil?” How would you (or would you) dispose of it?