Experiment 1
Check-in/Melting Points/ Unknowns

In the first experiment you will do three things: (A) check-in (B) take melting points of a series of known mixtures and (C) identify an unknown compound on the basis of its melting point using the mixed melting point technique.

The purpose of the first experiment is to learn the technique of taking a melting point and to learn how to identify an unknown compound using the melting point technique.

A. Check-in

Be sure that all of your glassware is present in your locker at check-in time. Once you have checked-in you will be held responsible for missing glassware items. Pay particular attention to the glassware that has ground glass joints. These joints have been ground by hand to fit in a secure manner so that no liquids or gases will escape. This glassware is very expensive. Treat it with respect.

When you are checking–in, it is a good idea to clean all of the glassware before putting it away the first time, so that it will be clean, dry and ready for you to use in the next experiment.

Store your safety glasses and labcoat in your locker for the semester. No one else has access to your locker and your safety glasses will be safe and ready for you to use each week.

B. Melting Points. Background and Theory:

The melting point is a quick method for the identification of a compound and for the determination of the purity of a compound. The melting point of a pure solid organic substance is one of its characteristic physical properties, along with the molecular weight, boiling point, refractive index, density, etc.

Molecules in a crystalline solid are arranged in a regular pattern in which there are intermolecular forces holding the molecules together in this pattern. Melting occurs when this fixed array of molecules rearranges to the more random, freely moving liquid state. Energy in the form of heat is required to break down the intermolecular forces that hold the crystal lattice together. As heat is added to the solid, the molecules will vibrate and perhaps rotate and suddenly acquire enough energy to overcome the forces that hold them together in the crystal lattice. The melting of a solid is the temperature at which the transition from the solid state to the liquid state occurs (or *vice versa)*.

The forces that attract one molecule to another include ionic interactions between positive and negative ions. These forces tend to be very strong and are often found in inorganic compounds. In organic compounds, the forces are generally the weaker ones of dipole-dipole interactions, hydrogen bonding and van der Waals interactions. Most simple organic molecules are covalent in nature and melt at temperatures below 300 °C. Typical inorganic salts melt at much higher temperatures. For example, sodium chloride melts at 800 °C.

In general, larger molecules melt at higher temperatures than smaller ones. Among structural isomers, the more symmetrical isomers will have the higher melting points because they pack together more tightly. Molecules that can form hydrogen bonds will usually have higher melting points than compounds of similar molecular weight that cannot form hydrogen bonds.

The melting point is always given as a **RANGE** of two numbers. The first number is the temperature at which the crystals just start to melt (i.e. when you first see a drop of liquid) and the final temperature is the point when all of the crystals in the sample have melted. Pure compounds generally have a sharp, well-defined melting point usually over a range of 1-2 degrees but impure compounds have a very broad melting point range. The melting point is always **lowered** by any impurity and the melting point range is **broadened**.

We can understand how this happens by looking at the melting point behavior of a simple mixture of two compounds X and Y. The diagram in Figure 1.1 shows the behavior of melting point as a function of

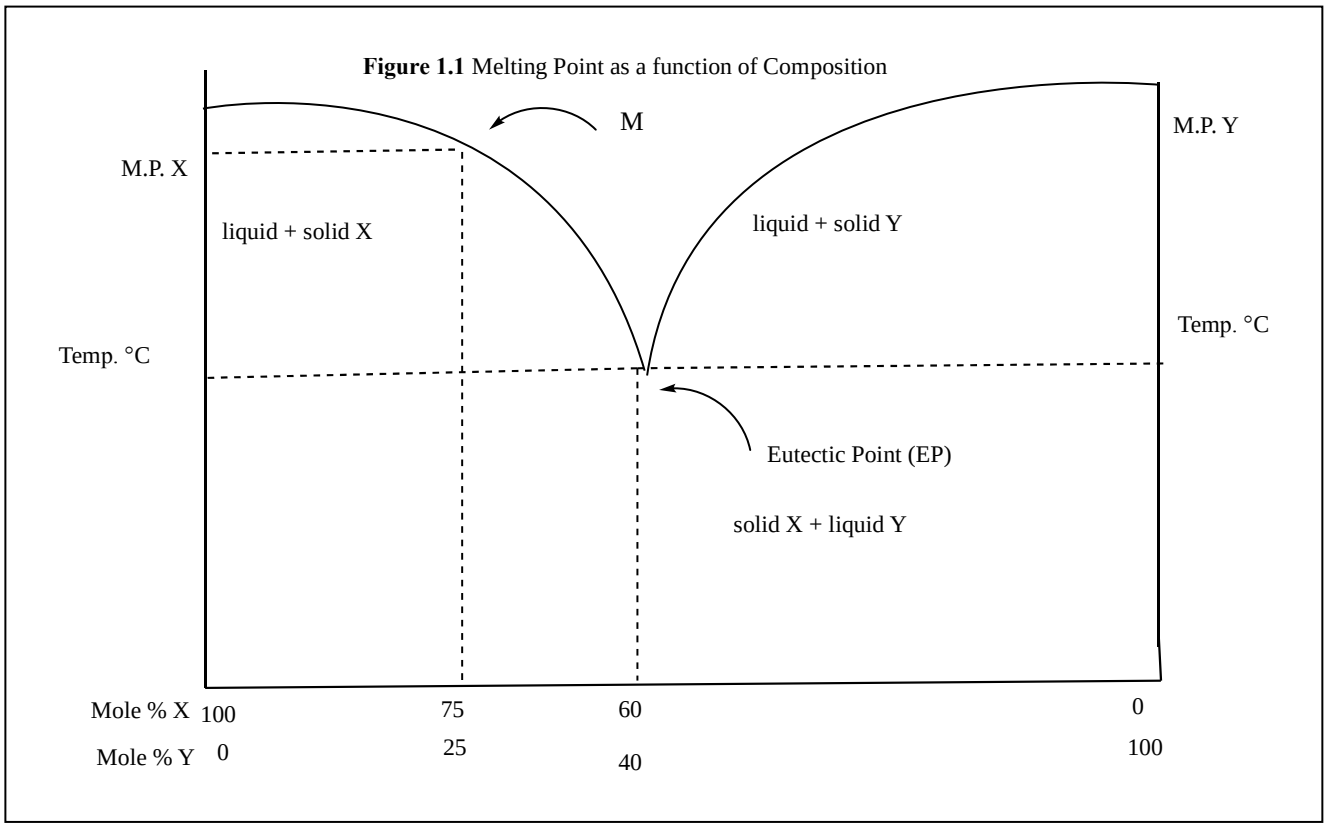


Figure 1.1 Melting Point as a function of Composition

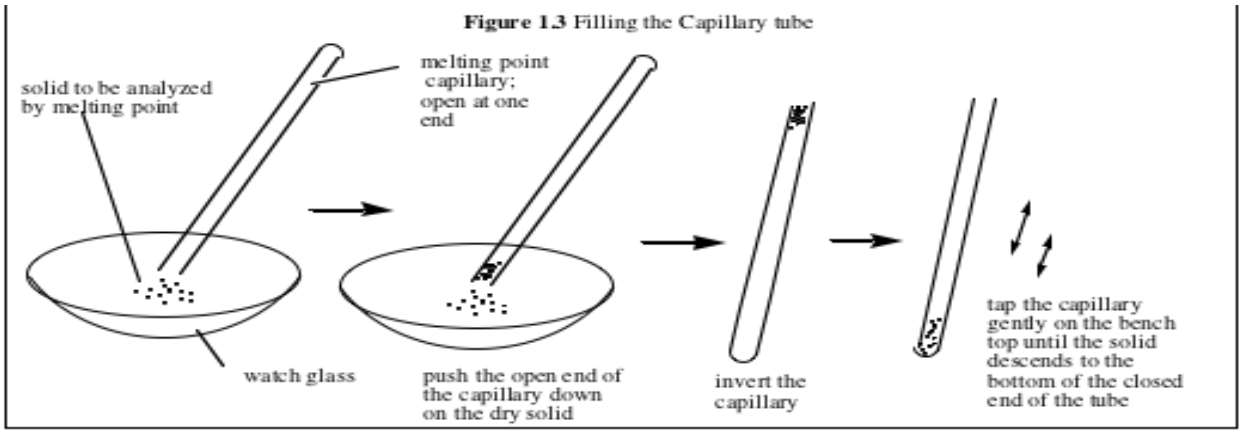
composition. The melting point of a pure compound is the temperature at which the vapor pressures of the solid and liquid are equal. But when we have a mixture of two compounds, the situation is different. For example, consider the case of a mixture of 75% X and 25% Y. At a temperature below EP, the eutectic point, the mixture is solid Y and solid X. At the eutectic point the solid begins to melt. The melt is a solution of Y dissolved in liquid X. According to Raoult's Law, the vapor pressure of the solution of X and Y together is less than that of the vapor pressure of pure X at the melting point. Therefore, the melting point of the mixture is lowered. As the temperature is raised, more and more of solid X melts until at point M (temperature m) all of solid X is gone. The melting point range therefore is from the eutectic point EP to M. In the example above, this point is reached when there is a mixture of 60% X and 40% Y. The melting point at the eutectic point should be sharp.

In actual practice, it is very difficult to find the eutectic point because it represents the point when an infinitesimal amount of liquid has started to melt and this is very hard to detect when using capillary tubes.

C. Apparatus and Determining Melting Ranges:

We will use the Reach Device shown in Figure 1.2. This consists of an electrically heated aluminum block that has space for six capillary tubes. The capillary tube is a small glass tube that is open at one end.

To fill the capillary tube (see Figure 1.3), you can insert the **open** of a capillary tube directly into a vial containing the compound whose melting point you want to take. Be careful to **NOT** contaminate the vial. A better method is to place a spatula tip of the compound on a watch glass. You can also use a small piece of weighing paper. Push the open-end of the capillary tube down over a small amount of the compound. Some material will be forced up into the open end of the tube. Turn the tube upside down and tap gently against the bench top. The material that was at the top open end of the capillary will now fall down to the closed bottom end of the capillary tube. **CAUTION.** Be careful not to break the capillary tube. The tubes are fragile and they are sharp when broken. Another method is to drop the capillary tube, with the closed end pointing



down, into your long-stemmed funnel. The capillary will bounce up and down in the stem of the funnel, causing the compound to sink to the bottom of the tube.

You do NOT need to fill up the whole capillary. You need just enough compound so that you can see it. The melting point is **NOT** function of the amount of material present. About 1 mm of sample is a good amount. If your compound is wet then it may be difficult to get it to fall to the bottom of the capillary but if it is wet then it is contaminated with solvent and therefore impure. The melting point of a wet compound is not going to be accurate and is useless.

Fig. 1.2

Instructions for Reach Melting Point Devices

1. Plug in the power cord directly into the **WALL** outlet. This is usually on the **RIGHT** side of your "monkey bars) at your bench. (Do **NOT** use the Rheostat).
2. Press the "On" button on the front of the device. The sample holder light, the front display light and fans will turn on.
3. Insert your sample(s) into the lighted sample holder section on the left top of the device. You can insert up to **six** samples at a time. Take care not to break the fragile capillaries and be sure the **CLOSED END** of the capillary tube is pointing **DOWN**.
4. Press "Run" to start the measurement. The "idle" message on the front will change to "running", one fan will stop and the temperature will rise.
5. There are four heating rates (1.5, 3, 6, 12°C/min). These can be selected using the "Faster" or "Slower" buttons on the front of the device. The display on the front indicates that heating rate.
6. To stop the run at any time press "Run" again. The front display will switch to "idle" mode and the rapid cool-off fan will turn on. If the user does not press "Run" a second time, the temperature will continue to rise to 250°C. At this temperature the device shuts off automatically.
Usually about 10 min in the idle/cooling mode at room temperature are enough to cool the device from 250°C to 45°C.
7. To begin a new run, press "Run" again. If "Run" is not pressed again, the device will shut off automatically after 10 min in "idle" mode.
8. When you are finished taking the melting point(s), unplug the device, secure the cord with the attached Velcro strap and return it to the storage shelves.

Always prepare a new sample if you are repeating a melting point since many organic compounds decompose when heated.

D. Melting Points of Mixtures

A series of mixtures of urea and cinnamic acid have been prepared and you will use these to make your own melting-point/composition diagram like the one shown in Figure 1.1. In this part you will take **7** melting points, doing four and three at a time for a total of two runs.

You will take the melting points of the following compounds:

(1) pure urea
(2) pure *trans*-cinnamic acid
(3) 20% urea, 80% *trans*-cinnamic acid
(4) 40% urea, 60% *trans*-cinnamic acid
(5) 50% urea, 50% *trans*-cinnamic acid
(6) 60% urea, 40% *trans*-cinnamic acid
(7) 80% urea, 20% *trans*-cinnamic acid

When you finish the 7 melting points make a graph of melting point versus percent urea. See if you can locate (approximately) the eutectic point.

E. Identification of an Unknown using Mixed Melting Points

Get an unknown compound from the Teaching Assistant. Record the number of your unknown in your notebook and also on your "Unknown Report" sheet that you will turn in at the end of the experiment.

Take a melting point of your unknown. Then, from the list given below, pick the compound (or compounds) which most closely has the same melting point. Mix and grind together thoroughly equal amounts of samples from each on a clean watch glass (a spatula tip of each is enough) and take a new melting point. If the compound with which you mixed your unknown is the same as the unknown, then the m.p. of the mixture will be the same as that of the pure compound. If your unknown is not this compound, then the melting point of the mixture will be lower and broader than that of the pure unknown.

Repeat this process of taking mixed melting points until a match is found. Record on your "Unknown Report" sheet the actual m.p. of your compound, the unknown number and the identity of your unknown. Also record all of the compounds with which you mixed your unknown and the melting points of the mixtures.

Table 1.1 Possible Unknowns

COMPOUND	MELTING POINT (°C)
Urea	133 – 134
trans-Cinnamic Acid	133 – 134
Mandelic Acid	121 – 123
Benzoin	133 – 134
Benzoic Acid	121 – 122
Biphenyl	69 – 71
β-Naphthol	123 – 124
Salicyclic Acid	159 – 160
Naphthalene	80 – 81
Acetanilide	114 – 116

DISCARD ALL USED MELTING POINT CAPILLARIES IN THE BROKEN GLASS CONTAINER PLEASE MAKE SURE YOUR BENCH AND SINK ARE CLEAN FOR THE NEXT CLASS COMING IN.