

CH 2020

Melting Point Determination (adapted from *Organic Chemistry: A Short Course*, H. Hart, L. E. Craine, D. J. Hart, and T.K. Vinod 13th ed. Houghton-Mifflin, Boston, 2012)

Materials

From the Chemicals Hood:	From the Stockroom (Blue Bin):
Unknowns A – F	Succinimide (123-125 °C)
Urea (132-133 °C)	Benzamide (128-129 °C)
Cinnamic acid (132-133 °C)	Benzilic acid (150-152 °C)
Fluorene (116-117 °C)	Adipic acid (151-153 °C)
Acetanilide (113-114 °C)	N-phenylsuccinimide (155-156 °C)
Benzoic acid (121-122 °C)	Salicylic acid (156-158 °C)

Melting Range

Background Information: The melting range of a pure solid organic is the temperature range at which the solid is in equilibrium with its liquid. As heat is added to a solid, the solid eventually changes to a liquid. This occurs as molecules acquire enough energy to overcome the intermolecular forces previously binding them together in an orderly crystalline lattice. Melting does not occur instantaneously, because molecules must absorb the energy and then physically break the binding forces. Typically the outside of a crystal will melt faster than the inside, because it takes time for heat to penetrate. (Imagine an ice cube melting from the outside in, and not doing so instantly...)

The melting range of a compound is one of the characteristic properties of a pure solid. The melting range is defined as the span of temperature from the point at which the crystals first begin to liquefy to the point at which the entire sample is liquid. Most pure organics melt over a narrow temperature range of 1-2 °C, if heated slowly enough. Impure samples will normally have melting ranges that are both larger (>1 °C) and begin lower.

Taking the melting range of a sample is useful for two reasons:

It allows identification of an unknown sample (compare its observed melting range with that of known compounds).

Assessment of sample purity for a known substance

By comparing observed range for an actual sample to the known range for a pure sample, you can tell whether your actual sample is pure or contaminated (the range is depressed and broadened).

The presence of impurity has two effects on a substance's melting range

Melting range depression (lower end of the range drops)

Melting range broadening (the range simply increases. Often the low end drops a lot, the high end less so or sometimes not much at all.) A melting range of 5 °C or more indicates that a compound is impure.

Why? The reason for this depression/broadening is that contaminants disrupt the consistency and organization of the crystal lattice at the molecular level. Contaminants don't "fit" correctly into what would be the normal pure lattice.

How does this manifest itself? The disruption weakens the lattice, so that the lattice can be broken down more easily; the weakened structure melts more easily at reduced temperature (depression). Disruption of the lattice makes it non-uniform. At the molecular level, the molecules closest to the impurities melt fastest. Farther away from the impurities, the crystal lattice is relatively undisturbed and therefore melts at or nearer the normal temperature.

Miscellaneous notes on melting range depression/broadening:

Only "soluble" impurities, which are incorporated into the crystal structure at the molecular level, cause depression and broadening. An insoluble piece of metal or wood ionic salt crystal has negligible effect, because only a few organic molecules will be in contact and will be affected.

At the chemical level, it is impossible to "raise" the melting point of an already pure substance. Its melting point can be depressed by contamination, but not raised.

Practical: If the melting point for an unknown sample is observed to be in between that of two candidates whose pure melting points are known, the unknown can't actually be equal to the lower-melting candidate. (Short of the rapid-heating effect, see later.) Most likely the unknown sample is an impure version of the higher melting candidate. For example: suppose an

unknown sample X melts at 148-152 °C, and is thought to be either candidate A (known range is 141-142 °C) or B (known range is 161-162 °C). Sample X cannot be candidate A, but it can be an impure and thus depressed version of candidate B. Often, contaminated solids are purified by recrystallization. If the resulting melting range is unchanged, the original sample probably was pure to begin with. But if the resulting melting point gets higher, the original sample was obviously impure. When crystals are isolated by filtration from a solvent, it is important to allow complete drying/evaporation of the solvent in order to get a good melting range. Residual solvent functions as a contaminant and will depress/broaden the melting range for a crystal.

When two chemicals are mixed, the resulting melting point is **not** the average of the two melting points. It is always depressed from the melting point of the major component in the mixture. This is true even if the impurity is higher melting (when pure) than the major component. For example, if a chemical that normally melts at 130 °C is contaminated by a small amount of material that when pure melts at 200 °C, the resulting mixture will not melt between 130 °C and 200 °C. Rather, the melting point of the major component will be depressed, and the observed melting range will begin lower than 130 °C. When two different pure chemicals with exactly the same melting point are mixed, the resulting melting point is depressed.

Mixed Melting Points

That mixtures have depressed melting points, even when both components have comparable melting points when each is pure, provides a useful laboratory technique. Consider the following situation and flow chart. If an unknown candidate X melts at a temperature close to that of two potential candidates A and B, you can identify it by taking X+A mixed melting point, and X+B mixed melting point. If X is equal to either candidate, one of these mixed melting points will not be depressed. If the mixture with X+A is not depressed, X = A. If the mixture with X+B is not depressed, X = B. If both mixtures are depressed, then $X \neq A$ or B.

The Rate of Heating and Some Practical Tips

It takes time for a crystal to absorb heat and to melt, from the outside in. Just as when you place an ice-cube into a liquid that is >0 °C, it doesn't melt instantly. To get maximal accuracy in taking a melting range, heating should proceed at only 1 °C/minute! This is the standard heating rate when publishing melting ranges in scientific journals. This is also inconveniently slow, especially if you don't know where your sample is likely to melt (as when examining an unknown).

Q: What happens if I heat too fast? **A:** Your melting range will be too broad, but this time on the high end! If a sample should melt at 130-131 °C, but you are heating fast, it will still probably begin to melt at about 130 °C, but the full sample won't have time to absorb heat and finish melting by 131 °C. Instead, the heating device may have warmed well above 131° before the interior liquefies, so the observed range may appear to be 130-136 °C. Both the magnitude of the range and the high end of the range may be misleading.

For doing routine samples, it is appropriate to be warming at 5 °C per minute around the temperature at which melting occurs. This broadens the range somewhat, but not badly. And it keeps the melting point experiment from taking forever. Practical tip 1: If the approximate temperature at which your sample should melt is known, the sample can be quickly heated to within 10-15 °C of its melting point. Then the heating rate can be slowed to 2-4 °C per minute until the sample melts. For example, if you know your material should melt around 180 °C, but you are just trying to check the purity, you can heat rapidly until you are up to 165 °C or so, and only when you are getting close turn the heating rate down.

Practical tip 2: If you have no clue where your sample will melt, it's common to heat rapidly to get a ballpark estimate of where melting will occur. 60 °C? 140 °C? 240 °C? If it turns out to be 240 °C and you heated only cautiously from the beginning, it will take a loooooong time to get to the measurement. By heating rapidly, you can get an "orientation melting point" quickly, and then repeat with more care for a more precise reading.

Practical tip 3: Heat transfer problems are minimized if the sample is ground finely. If the particles are too coarse, they do not pack as well, causing air pockets that slow heat transfer. Because the thermometer keeps heating while the sample is melting rather slowly, the high end of your range will be inflated.

Practical tip 4: Loading too much sample makes it harder for the interior to get heated and melted. Because the thermometer keeps heating while the sample is melting rather slowly, the high end of your range will be inflated.

"Sagging"

Sometimes slight changes, such as shrinking and sagging, occur in the crystalline structure of the sample before melting occurs. The temperature at the bottom end of the melting range corresponds to the first appearance of **liquid** within the sample mixture; if the crystals are changing their appearance, but you don't yet see any actual liquid, you should **NOT** record this as the lower end of the melting range yet.

Goals:

Learn how to run a melting point device and measure melting range.

The Experiment:

Pulverize 50-100 mg of urea by crushing it with a spatula against either a clean, dry watch glass, the walls of a small (50 mL) dry beaker, or on a piece of weighing paper (place your sample in the middle of a piece of weighing paper, fold the weighing paper over the sample and roll your glass stirring rod over the weighing paper several times). Fill a melting point tube with a sample of urea by thrusting the open end into the beaker several times. (When we say “fill” we mean put enough sample into the capillary tube just so you can see it.) To work the plug of solid material down to the sealed end of the tube, vigorously tap the sealed end on the bench top, drop the capillary (sealed end down!) down a length of tubing, or use the vibrator on the small black melting point apparatus. Repeat the procedure until the tube contains a 1-2 mm column of densely packed powder at the bottom.

Prepare a melting point sample of cinnamic acid similarly and insert both samples into the melting point apparatus. If you are using one of the small black apparatus, the instructions are contained on the front of the apparatus. Urea melts at approximately 130 °C, and cinnamic acid also melts at approximately 130 °C.

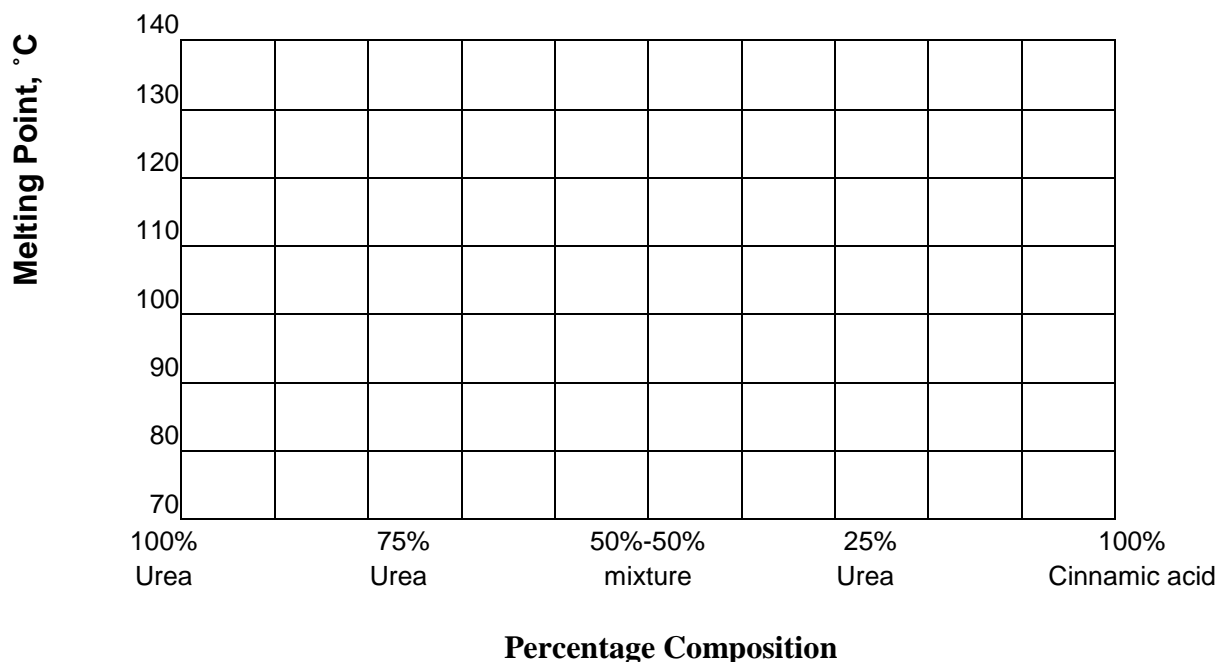
1. Set the start temperature at the lowest melting point of the compounds' possibilities and then raise the temperature at 20 °C/min. Note where the samples begin to melt.
2. Take your second set of samples and set the start temperature 5 °C below the previous samples' lowest melting point, then raise the temperature at 1 °C/min.

Record the melting point ranges of urea and cinnamic acid in your notebook.

To demonstrate the effect of impurities on the melting point of a pure substance, determine the melting point range of a 50-50 mixture by weight (use about 50 mg of each compound) of urea and cinnamic acid. Simultaneously, determine the melting point ranges of 75-25 and 25-75 mixtures.

1. Set the start temperature to 70 °C and then raise the temperature at 20 °C/min. Note where the samples begin to melt.
2. Take your second set of samples and set the start temperature 10 °C below the previous samples' lowest melting point, then raise the temperature at 1 °C/min.

Using the ranges of the melting points, plot the data in your notebook. The graph should look like the graph below.



Unknown Analysis

Goals:

Learn how to run a melting point device and measure melting range

By comparing results for the two mixtures, see how not all mixtures depress/broaden to the same extent.

Identify your unknown from the list shown below.

Unknown Candidates

Fluorene; Acetanilide; Benzoic Acid; Succinimide; Benzamide; Cinnamic Acid; Urea; Benzilic Acid; Adipic Acid; *N*-Phenylsuccinimide; Salicylic Acid

Obtain an unknown sample from your instructor. Write the unknown letter in your notebook. Fill two melting point tubes with samples of the unknown. Use one tube to determine the approximate melting point.

3. Set the start temperature at the lowest melting point of the unknowns' possibilities and then raise the temperature at 20 °C/min. Note where that sample begins to melt.
4. Take your second sample and set the start temperature 5 °C below the previous sample's lowest melting point, then raise the temperature at 1 °C/min.

Use the melting points to make a preliminary identification of your unknown. Then confirm its identity by the mixture melting point technique: Mix about 50 mg of the unknown with an equal weight of the substance you suspect it to be and determine the mixture melting point. Record your results and conclusion in your notebook. Confirm the identity of your unknown with your TA before you leave.

Waste

Discard your used melting point tubes in the waste glass container at the end of each bench. Place extra

Disposal

solids from the mixture melting point in the solid organic waste container provided.