# 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 <u>first begin to liquefy</u> to the point at which <u>the entire sample is liquid</u>.  Most pure organics melt over a narrow temperature range of 1-2ºC, <u>if heated slowly enough</u>.  Impure samples will normally have melting ranges that are both larger (>1ºC) and begin lower.

**Taking the melting range of a sample is useful for two reasons:**
1. <u>Identification</u> of an <u>unknown</u> sample (compare it's observed melting range with that of known compounds)
2. Assessment of <u>sample purity</u> for a <u>known</u> 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:**
1. Melting range <u>depression</u> (lower end of the range drops)
2. Melting range <u>broadening</u> (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 5º 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**?
1. The disruption weakens the lattice, so that the lattice can be broken down more easily; the weakened structure melts more easily at reduced temperature (<u>depression</u>).
2. Disruption of the lattice makes it non-uniform.  At the molecular level, the molecules closest to the impurities melt fastest.  Further away from the impurities, the crystal lattice is relatively undisturbed and therefore melts at or nearer the normal temperature.

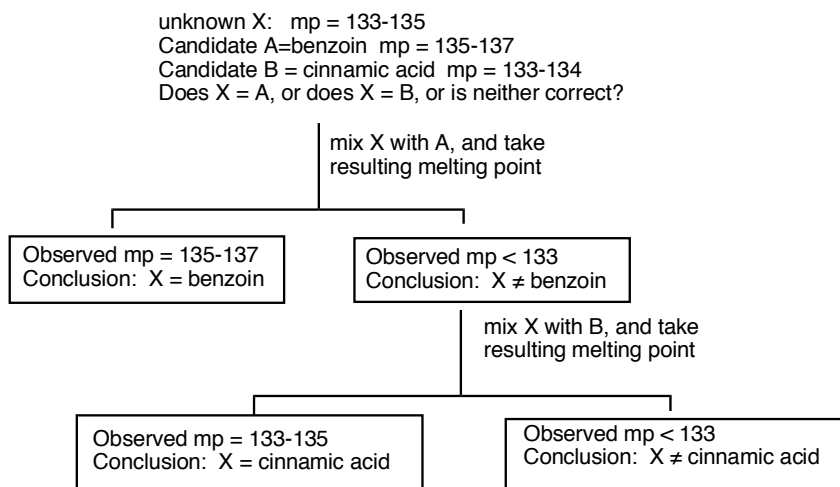**Miscellaneous notes on melting range depression/broadening:**
1. Only "soluble" impurities, which are incorporated into the crystal structure at the molecular level, cause depression and broadening.  An insoluble piece of metal or wood ionic salt crystal has negligible effect, because only a few organic molecules will be in contact and will be affected.
2. At the chemical level, <u>it is impossible to "raise" the melting point of an already pure substance</u>.  It's 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 mp's 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.  <u>For example</u>:  suppose an unknown sample X melts at 148-152º, and is thought to be either candidate A (known

range is 141-142º) or B (known range is 161-162º).  <u>Sample X cannot be candidate A</u>, but it can be an impure and thus depressed version of candidate B.

3.  Often contaminated solids are purified by <u>recrystallization</u>.  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.

4.  When crystals are isolated by filtration from a <u>solvent</u>, it is important to allow complete <u>drying/evaporation</u> 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.

5.  When two chemicals are <u>mixed</u>, the resulting melting point is **not** the average of the two mp's.  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 130º is contaminated by a small amount of material that when pure melts at 200º, the resulting mixture will not melt between 130º and 200º.  Rather, the melting point of the major component will be depressed, and the observed melting range will begin lower than 130º.

6.  Even when two chemicals with exactly the same melting point when pure 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 <u>not be depressed</u>.  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 ≠ A or B.

unknown X:  mp = 133-135
Candidate A=benzoin  mp = 135-137
Candidate B = cinnamic acid  mp = 133-134
Does X = A, or does X = B, or is neither correct?

mix X with A, and take
resulting melting point

Observed mp = 135-137
Conclusion:  X = benzoin

Observed mp < 133
Conclusion:  X ≠ benzoin

mix X with B, and take
resulting melting point

Observed mp = 133-135
Conclusion:  X = cinnamic acid

Observed mp < 133
Conclusion:  X ≠ cinnamic acid

**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 >0º, it doesn't melt instantly.  To get maximal accuracy in taking a melting range, heating should proceed at only 1º/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: <u>What happens</u> **if I heat too fast**?  A:  Your <u>melting range will be too broad</u>, but this time you will see **inflation on the high end**!  If a sample should melt at 130-131º, but you are heating fast, it will still probable begin to melt at about 130º, but the full sample won't have time to absorb heat and finish melting by 131º.  Instead, the heating device may have warmed well above 131º before the interior liquefies, so the observed range may appear to be 130-136º.  <u>Both the magnitude of the range and **the high end** of the range may be misleading</u>.

- For doing <u>routine samples</u>, it is appropriate to be warming at 5 degrees 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.

- <u>Practical tip 1</u>:  If the approximate temperature at which your sample should melt is known, the sample can be quickly heated to within 10-15º of its melting point.  Then the heating rate can be slowed to 2-4º per minute until the sample melts. For example, if you know your material should melt around 180º, but you are just trying to check the purity, you can heat rapidly until you are up to 165º or so, and only when you are getting close turn the heating rate down.

- <u>Practical tip 2</u>:  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. 60º? 140º? 240º? If it turns out to be 240º and you heated only cautiously from the beginning, it will take a looooong time to get to the measurement.  By heating rapidly, you can get an "<u>orientation melting point</u>" quickly, and then repeat with more care for a more precise reading.  Often you don't even need to prepare a fresh sample, because after cooling the melted sample often recrystallizes.

- <u>Practical tip 3</u>:  **Course versus finely ground**.  Heat transfer problems are minimized if the sample is <u>ground finely</u>.  **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**.

- <u>Practical tip 4</u>:  **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**.

- <u>Practical tip 5</u>:  **Sometimes it's hard to recognize the initiation of a melt.** When some liquid first appears, against a backdrop of solid, it's not always easy to recognize, especially for an inexperienced user.  This may someti

**"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 <u>first appearance of **liquid**</u> 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.

**The Experiment:**                     **(**Work alone or with One Partner)
**Overview, if working with a partner:  You will run three samples.**
1. One will be either pure urea (mp = 132-133) or pure cinnamic acid (mp = 133-134). Whichever you run should be the opposite of what your partner runs. <u>Record your range, and share your observed results with your partner</u>
2. The second will be mixture of the two, either 4:1 cinnamic acid:urea or 1:4 cinnamic acid:urea.  Whichever mixture you run should be the opposite of the mixture that your partner runs.  <u>Record your range, and share your observed results with your partner</u>.
3. The third will be an unknown.  Record your range and identify which of the unknown candidates is really yours.  (You and partner must run different unknowns.  You do not need to share this result with your partner.)

**Unknown Candidates**
Acetanilide     112-115
Benzoic Acid  118-123
Cinnamic acid 131-134
Salicylic acid  155-160
Sulfanilamide  163-166
Succinic acid  184-185

**Learning 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.

**If working alone:  You will run five samples.**
1. Run <u>both</u> pure urea (mp = 132-133) and pure cinnamic acid (mp = 133-134).
2. Run both the 4:1 cinnamic acid:urea and the 1:4 cinnamic acid:urea mixtures.
3. Run one unknown.  (You and partner must run different unknowns.)

**Lab Report Requirements**
No introduction or procedure write-up is required.

Fill in the data section on the report hand in (next page in manual), and answer the questions.

Melting Point Lab Report.  Chem 355                          Name:

> Partner's Name (if you shared data with a partner:

> <u>Experimental Data</u>                                                    <u>melting range</u>

- My Known:  (U or C or both)

- My mixture:  (4:1 C:U or 4:1 U:C or both)

- Partner's mixture (4:1 C:U or 4:1 U:C)

- My Unknown:  (1, 2, 3, or 4…)

- Which compound is your unknown? (from the list on previous page)


- Any doubts, discussion, or logic on your identification of unknown.   (Not necessary, but if you have a tricky one or one that for whatever reason you get wrong, if your discussion shows some reasonable analysis or logic, it may help you get partial credit!  ☺)



<u>Discussion questions:</u>
1.  Compare the ranges observed with the two mixtures.
    a.  Did they depress and broaden about the same, or different?


    b.  What does that say about the degree of depression and broadening that occurs when mixtures are used?  Do all impurities depress to the same degree, or by some predictable formula?  Or do you think it's more of a case-by-case deal?




2.  Strictly speaking, why is it incorrect to speak of a melting "point"?




3.  How will your melting range be perturbed if you haven't completely dried your sample? (For example, after you've filtered crystals away from a solvent, and/or have washed the crystals with solvent…)   (Be specific, for example, "low end depressed" or "high end inflated")

4. What's the advantage of a finely powdered sample over a coarser sample?  How will your melting range be perturbed with coarse sample?  (Be specific, for example, "low end depressed" or "high end inflated")

5. What's the advantage of putting in a relatively small amount of sample as opposed to putting in lots and lots of sample? How will your melting range be perturbed with huge sample?  (Be specific, for example, "low end depressed" or "high end inflated")

6. Why is it desirable to heat the sample relatively slowly? How will your melting range be perturbed by heating too fast? (Be specific:  "low end depressed" or "high end inflated")

7. You have a sample that you are sure is Jaspersium, which has a list melting range of 145-146.
   - Suppose you run your sample and observe a melting range of 145-151.  Is your sample impure, or did you heat too fast?

   - Suppose you run your sample and observe a melting range of 139-145.  Is your sample impure, or did you heat too fast?

8. You have isolated an unknown compound that shows an observed melting range of 90-94. Which is it more likely to be, candidate X (list mp 97-98) or candidate Y (list mp 80-83).  Why might your sample not have the same melting range as either of the known compounds, given that it must be one of them?

9. Three test tubes labeled A, B, and C contain substances with approximately the same melting points.  How could you prove the test tubes contained three different chemical compounds?