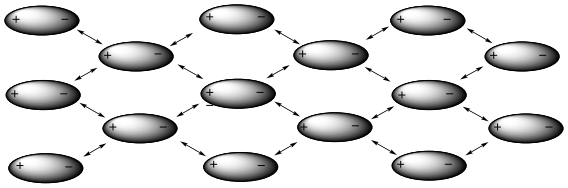
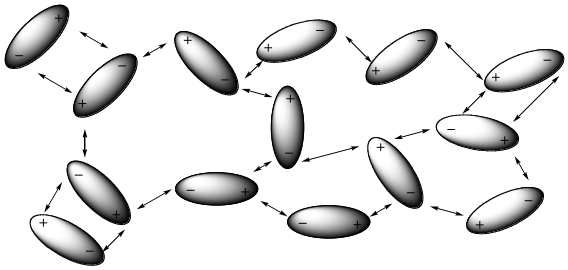
Melting: the change of a solid to the liquid state.

For a solid to melt, the forces holding the structural units in the lattice sites must be broken, at least partially. In a molecular solid (organic compound), these forces are weak intermolecular attractions. None of the covalent bonds inside the molecules themselves break.

Alignment of polar molecules in a crystalline lattice with regularly repeating intermolecular forces:



Random motion of molecules in a liquid with only partial disruption of the alignment:



Complete breakage of all intermolecular forces would result in complete dissociation and resultant gas formation.

The regularly repeating intermolecular forces require a specific amount of heat to loosen and break. That corresponds to a specific temperature – a temperature called "**the melting point**".

Melting Point Analysis:

The term "melting point" is a misnomer because it implies a single temperature. It is more correct to say "melting point range" because **you must record the temperature at which the crystals begin to melt and the temperature when they are finished melting**. Since this cannot occur simultaneously, you must record a RANGE of temperatures.

Wrong: 123° Right: 123.0-123.5°C

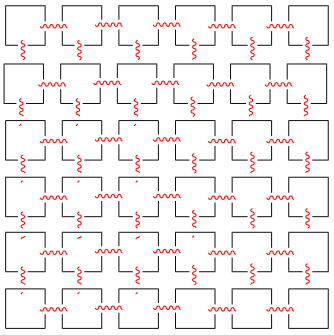
There are two reasons to do a melting point analysis:

1. To Evaluate Purity:

A pure compound will always melt in a temperature range that spans no more than 2°C AND must match or fall within the range of the known melting point if, in fact, there is one.

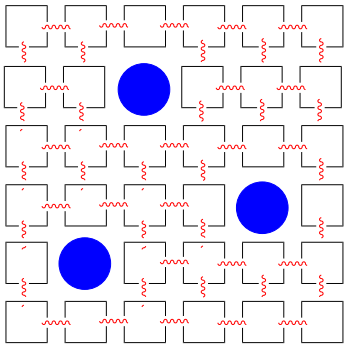
If the range is larger than 2°C, and/or it melts too soon (i.e. lower than the expected melting point), then the compound is determined to be impure.

Solids are vibrating particles in a lattice arrangement held together by intermolecular forces (Van der Waals or hydrogen bonds). Regular, repeating intermolecular forces means the same amount of energy will uniformly break the bonds to cause the crystal to become "fluid" or to melt.



Why do impurities cause the melting point temperature to be lower?

Impurities in the lattice disrupt the regularity of the linkages, causing weak spots in the lattice. The weak spots require less energy to break the lattice at those points, thus the crystal melts earlier than expected, referred to as a "depressed melting point" (lower than normal)



If the Unknown compound is supposed to melt 96-98°C and your compound melted at 91-97°C, is it pure?

No, the range is greater than 2°C.

If the Unknown compound is supposed to melt 96-98°C and your compound melted at 93-94°C, is it pure?

While close in range (1° difference between start and stop), the range is **still below that of what was expected** for this particular compound so the compound is not entirely pure.

Note that even though its "**CLOSE**" to being correct, close doesn't matter. Even though its only 2° below the expected value, that doesn't matter. It's still **BELOW**, so "close" doesn't count!

If the Unknown compound is supposed to melt 96-98°C and your compound melted at 96.1-97.3°C, is it pure?

Yes, the melting point start and stop fell within the expected range value of the compound's expected melting point. The goal is to be WITHIN the range, not necessarily

cover the entire range (i.e. it doesn't have to be exactly 96-98°, just WITHIN 96-98°). You have a defined set of values and your result must be somewhere IN BETWEEN, IN THE MIDDLE, NOT OUTSIDE OF those values.

2. To Identify a Compound:

A pure compound will always have the same melting point, if you do the analysis correctly.

So, how do you use this to identify a compound using melting point analysis?

Consider the following: Compound A melts at 55-56°C and Compound B melts at 101-102°C. Let's assume you took the melting point of an unknown, Compound X, and found that it melted at 55-56°C. Which Compound is it? A or B?

With only two possible choices, you can see that it matches Compound A. In general, if you know the melting point of a pure compound, you can open up reference books and start matching up melting point values to help identify which compound is which. Unfortunately, you may find MANY possible compounds in the temperature ranges that your compound should be melting at.

Today you have only two choices, but they are two compounds with a relatively small difference between melting point values. Benzamide melts between 125-128°C and 2-Ethoxybenzamide melts at 132-134°C. While those may seem significantly different, any impurity will lower the melting point and will be enough to mislead you. With only a couple degrees difference, merely taking the melting point will not enable you to tell them apart.

Mixed Melting Point Analysis: In this technique, an unknown compound is mixed with other known compounds that have a similar melting point.

The correct compound will perfectly blend, the crystalline lattice will not change, and thus the melting point will not change.

The incorrect compound will act as an impurity, changing the regularity of the intermolecular forces and causing weak spots in the lattice of the crystals you analyze. The melting point will then be lower and will often have a broader range.

Factors to consider for a melting point analysis:

1. The Capillary tube: sealed on one end, open on the other. Place 1-2 mm of compound in the end and pack until crystals reach bottom of tube. THE SMALLEST AMOUNT YOU CAN STILL SEE. If you have to ask "Did I use too much?" the answer is typically "YES!"

- Too much compound – Zubrick says "***heats unevenly***" or "***poor heat transfer***" will occur. More sample means more intermolecular forces that need to be broken and that will result in more heat being needed to break them apart. Heating it more will result in a rising temperature. This will falsely inflate the melting point higher than it ought to be.
- Not packed correctly – Again, Zubrick says "***heats unevenly***" or "***poor heat transfer***" will occur. If you do not pack down your sample of crystals, pockets of air will result between the crystals. While this doesn't sound like a big deal, in a melting point analysis, it is. It means that there are air pockets between the crystals that must also be heated to continue the melting process throughout the entire sample. Having to heat air pockets will result in needing more heat to do so. This will also falsely inflate the melting point higher than it ought to be.
- You cannot re-use a sample once it has been heated. Heating in the presence of air (oxygen!) can result in chemical changes to your sample. The composition of the compound may have been changed upon heating so a fresh sample must be used each time.

Dispose of used capillary tubes in designated beakers found in the wooden boxes around the lab near the DigiMelts or in the glass waste box, found by the door in the back of our lab, near the safety shower.

2. Rate of Heating:

Heat too slow – the temperature rises at a rate of 1-2°/minute

Positive – very accurate results

Negative - may result in a melting point taking **HOURS.** Consider taking a melting point on a compound whose melting point is 130-132°C. If room temperature is 20°C, then you must wait for a rise of 110°, if it is pure. At 1-2 degrees per minute, that could take you 1-2 hours. Not time efficient for a lab that ends at 4:20.

Heat too fast – the temperature rises at a rate of 20°/min

Positive - very time efficient

Negative - not often very accurate as you are watching the sample melting and having to record the temperature data (eye-finger coordination!). If you are heating and you are unable to see a RANGE because it appears to melt too quickly, you are definitely heating too fast.

How can compromise the two so we save some time and still be accurate in our results?

Take a "Ball-Park Run" – This is a melting point analysis intentionally taken too fast, intended to melt your crystals quickly without giving you accurate data but giving a better idea of approximately at what temperature your compound will melt.

To take a "Ball-Park Run", set the DigiMelt at a high rate of heating (20°C per minute). Your compound will melt in the approximate temperature range and will give you a better idea of approximately what temperature to begin your slow and accurate run.

As a rule, we always begin a slow, accurate run at a temperature **10°C below the starting melting temperature of the ball park run**. For instance, if your ballpark run had a melting point range of 187.1-189.2°, then set your slow run START TEMP at 10° below 187, which would be 177°.

If your ballpark run results were 123.1-127.2°C, where would you reset the Digimelt for the slow run?
113°!

Now: DAY TWO, Finish Experiment 1:
1. Obtain a mass of your pure crystals:
a. Find a clean dry sample vial from your drawer, with a white cap. Weigh these two together.
b. Using your wide-mouth plastic funnel, slide the crystals in the vial.

c. Reweigh to get total weight. Be sure to **record both weights in that data table** in your notebook. The difference in weights is the weight of your crystals. You can include this value also in your data table if you wish.

2. **Observe** what the final crystals appear to look like (it should be distinctly different from what you started with!) and record info in notebook. Be specific – avoid writing "white crystals" as that doesn't describe them very distinctly.

3. In your Calculations section of your notebook, be sure to calculate your percent recovery:

$$\frac{\text{(Amount of pure compound isolated)}}{\text{(Amount of impure compound used)}} \times 100$$

4. Obtain a melting point (range) on your crystals:
You will perform two runs for your unknown compound analysis, one fast "ballpark" run and one slow run.
The SLOW run will tell us how **pure** your compound is. You have to record both the **Start** and **STOP** melting temperatures for EACH run, regardless.

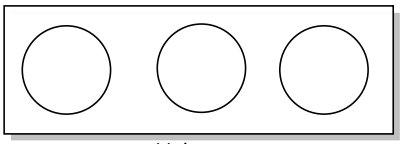
Parameters for the Digimelt:
Ball Park Run:

Start Temp: 60°C
Ramp Rate: 20°C/min
End Temp: 140°C

Slow Run (and Mixed Melting Point Runs)
Start Temp: (Beginning of Ball Park Melting Temperature minus 10°C)
Ramp Rate: 1 or 2°C/min
End Temp: 140°C

FINALLY: You need to do your mixed melting point analysis to determine the name of your unknown compound.

Place a SMALL amount of your unknown compound in one of the wells of the porcelain tray provided and then add an equal small amount of benzamide to the first and then repeat again with a second portion of your compound in a second well with an equal portion of 2-ethoxybenzamide. Use a clean spatula when reaching into each of the vials (no cross contamination, please).



Be sure to mix well with the end of a clean glass stirring rod or you may find yourself not taking the melting point of an actual mixture. Using large amounts of crystals will make this mixing part difficult so keep the amounts you use small. Then pack one capillary tube with one mixture and pack another with the other mixture. Feel free to label with sticker flags after packing, if you need help keeping track of which is which. Then you are going to melt both mixtures at the same time, **using same parameters as the slow run.**

SIMULTANEOUSLY melt both mixtures, **using same parameters as the slow run.** Check that the Digimelt has cooled back to the appropriate starting temperature (10° below the Ballpark start). Watch your capillary tubes as soon as you place them in your instrument. You may see one of your mixed melting point mixtures melt IMMEDIATELY! If so, simply record the temperature on the Digimelt in your notebook along with the fact that it melted immediately ("Melted immediately at 109.1°C), then finish taking the other melting point, as required.

NOTE: This is not a melting point analysis for purity nor will it be accurate in any way. If "immediate melting" occurs, it signifies that the melting point temperature is somewhere BELOW what the Digimelt is currently pre-heated to. Instead of resetting the Digimelt for a lower temperature, we can make the conclusion that this mixture is a mixture of major impurities.

So, the mixed melting point analysis will tell us **which** compound, benzamide or 2-ethoxybenzamide, is **your** compound. When mixed together, the melting point of one of the compounds will closely (but not necessarily exactly) match the melting point of your unknown and the other mixture melting point will not match that of your compound.

Each melting point run, ballpark, slow, mixtures (and every other one this semester) **should be recorded in your data table**, and the data table must include the START temp, the RAMP rate and the STOP temp used for each Digimelt analysis, as well as the beginning of the melting point range and the end of the melting point range.

Oh – and Melting Points are never averaged together so don't bother doing that math…

Data Table						
			Melting Point Information			
	Weight (g)	**Volume (mL)**	**Start (ºC)**	**Ramp (ºC/min)**	**Stop (ºC)**	**MP Range (ºC)**
ID# JD001.345						
Impure Cmpd	1.12					
Empty Vial/cap	7.56					
Vial/Cmpd/cap	7.99					
Ballpark Run			60	20	140	119.0-125.1
Slow Run			109	2	140	121.4-123.1
Mixed/Benzamide			109	2	140	melted @ 109
Mixed/2-Ethoxybenzamide			109	2	140	121.2-123.4