# *CHEM 008 Experiment 2*

# MELTING POINTS

## Text Topics and New Techniques

Physical properties, melting points, freezing point depressions

## Discussion

Synthesis, separation and purification, identification and characterization: You will find as you progress through this course that the laboratory experiments usually contain one or more of these procedures. This experiment will focus on one very important identification technique, the determination of the melting point of a solid. Anytime a compound is obtained from a natural or synthetic source or even the stockroom, its identity must be determined and/or verified. Intensive physical properties such as melting point, boiling point, density and refractive index are extremely useful for verification purposes because they involve inexpensive instrumentation and accurate procedures.

Melting points also provide a simple method of obtaining a rough indication of purity. A 5 Celsius degree difference between an experimental and an expected melting point, for example, indicates that the sample is approximately 95% pure. Each 1% (up to about 10%), very roughly, depresses the melting point 1 Celsius degree. Impurities not only depress melting points but also broaden them. Thus, if compound *A* is supposed to melt at 65-66°C but experimentally it is found that heating causes it to begin softening at 57°C and totally liquefy at 62°C, we report that the sample has a melting range of 57 - 62°C and is impure. Note that counter intuitively, even if the impurity (<10%) has a higher melting point than the melting point of the major compound, the melting point observed will be lower (and broadened) than the melting point of the major compound. It is good technique to experimentally determine the melting points of chemicals obtained directly from stockroom bottles for both identity verification and for purity. Commercially supplied chemicals are supplied in several grades of purity varying from below 90% to about 99.99%.

The fact that contaminants tend to depress melting points enables us to distinguish between two compounds with the same melting points. Suppose you have two labeled bottles, *A* and *B*, and a third unlabeled bottle. Assume the solids in all three bottles have the same melting point (say 65-66°C) within experimental error. If some of the unlabeled compound is mixed with *A* and with *B*, melting ranges of 64 - 65°C and 53 - 57°C respectively are observed. This strongly indicates that the unlabeled bottle is compound *A*. Why?

**Chemistry History Capsule**

Now, lets journey back in time to the 1820's. Organic chemistry was defined differently than it is today. Instead of the current definition, **the chemistry of compounds that contain carbon**, organic chemistry was considered to be the study of compounds derived from living species. It was believed that compounds derived from plants and animals had a special quality called "vitalism" and it was believed that vitalism would not be present in compounds synthesized from "inorganic" substances. Frederich Wöhler's serendipitously prepared urea from compounds (silver cyanate and ammonium chloride) obtained from non-living sources. Wöhler demonstrated that the urea he prepared and urea obtained from animals have the same properties. This was the first reported demonstration that the concept of vitalism was not valid. Even so, it took about 50 years after Wöhler's experiment and additional supporting evidence for vitalism to disappear from science literature and for today's definition of organic chemistry to be accepted. Although the scientific community discarded vitalism over 100 years ago, there are many people today who demonstrate their belief in vitalism by purchasing the higher priced natural Vitamin C rather than the lower priced but identical synthetic Vitamin C.

Besides invalidating the vitalism concept, Wöhler's synthesis of urea from ammonium cyanate was one of the first if not the first demonstration of another extremely important concept in organic chemistry. Both the ammonium cyanate and urea have the same molecular formula [$CH_4N_2O$] but distinctly different properties.

$$NH_4OCN(aq) \quad -\Delta\rightarrow \quad CO(NH_2)_2(aq)$$

For example, ammonium cyanate is ionic and therefore a strong electrolyte. Urea has only covalent bonds and although it is very soluble in water, urea is a non-electrolyte. Compounds with the same formula but different properties are called isomers. As you progress through this course you will study two major classes of isomers called structural (or constitutional) and stereoisomers. There are many subdivisions to both of the major classes of isomers.

In last week's experiment, you attempted to purify a sample of vanillin. Today you will determine the percent recovery and, from a melting point measurement, the success of the purification of the vanillin. You will also determine the percent recovery of your unknown compound and, from melting point measurements, identify the unknown.

## Techniques

**PERCENT RECOVERY.** Percent recovery and yield are extremely important from an economic perspective, especially when industrial-sized amounts are used. The percent recovery is calculated by dividing the amount of the recrystallized sample by the mass of the starting solid and multiplying the result by 100%.

**EXPERIMENTAL DETERMINATION OF THE MELTING RANGE.** For most melting point determination devices, a very small amount of sample in a capillary tube is heated and the temperatures recorded for the appearance of the first minute amount of liquid appears and when complete liquefaction has occurred. The temperatures for these two changes are recorded as the melting range (e.g., 91.4 - 93.0°C).

If one had 10 grams of ice at -10°C and wanted to convert it to water at 10°C, using a constant energy input, the following would occur: It would take a short time to heat the ice from -10°C to 0°C. It

takes much more energy to melt the ice than to change its temperature so it would now remain at 0°C for a substantial amount of time. Then it would take a short time to heat the water from 0°C to 10°C. The reverse process would occur if the water were cooled from 10°C to -10°C. Again, the temperature would remain constant for a long time while the water froze. The freezing point of a substance is the same as its melting point.

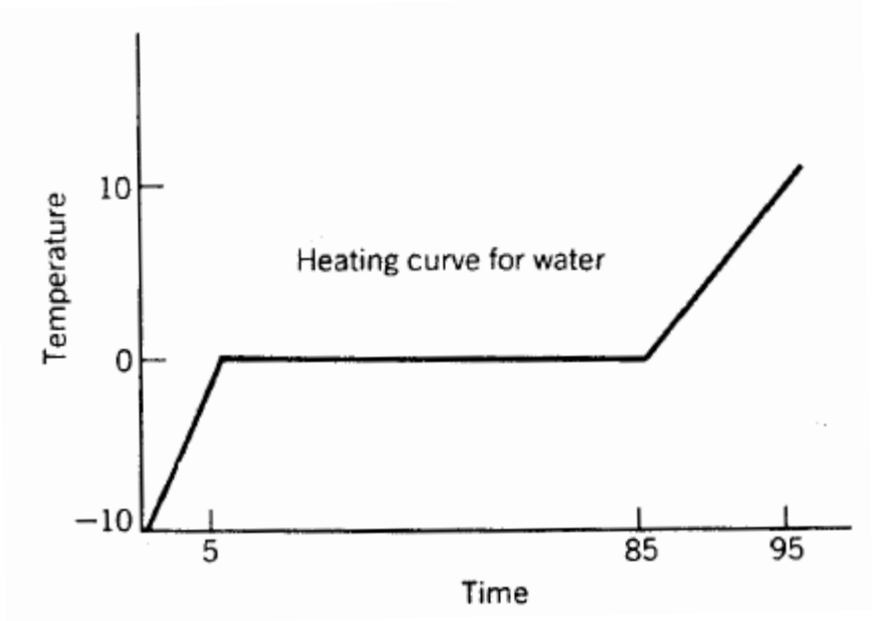
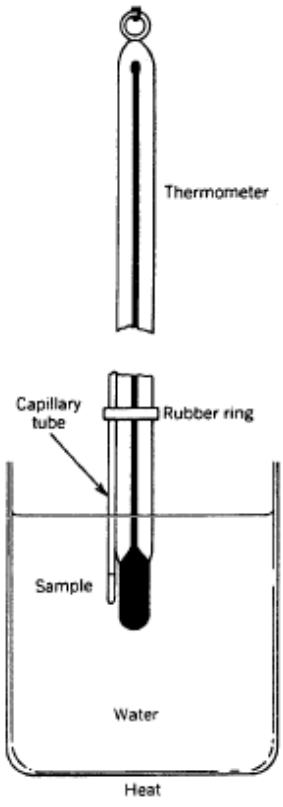



***Figure 2-1***

***Figure 2-2***




Select a thermometer that covers the range -10°C to 110°C. Capillary tubes are very convenient sample holders as they are inexpensive, disposable, and hold very small amounts of sample that can be easily observed during the melting process. Fill the capillary tube by pressing the open end onto the powdered sample until there is about a 0.5 - 1 cm length of sample in the tube. Now drop the capillary tube, sealed end down, through a 1 meter piece of 6 mm glass tubing that is being held on a hard surface. The impact of the capillary with the hard surface seldom results in breaking and causes the sample to drop to the bottom of the tube. Repeat the dropping procedure until the sample is packed in the bottom of the tube.

Refer to the *Figure 2-2* for this discussion. If you are using a water bath to heat your melting point capillary, fill a 250 mL beaker half full with water and add a stir bar. Attach the capillary tube with a rubber ring (cut off of a piece of rubber tubing) to a thermometer with the sample even with the bulb of the thermometer. Place the thermometer in the 250 mL beaker on a hot plate. Support the thermometer with a 3-finger clamp on a support stand, making sure that the stir bar will not hit the thermometer as you start stirring the water slowly. Gently heat the water with *continual stirring* and observe the sample. As you approach the melting range, the heating rate should be **very slow** (no more than 2°C/min.) or large errors will be incurred. At the first indication of sample melting, record the temperature to the nearest 0.1°C. The last digit is an estimate but has meaning and is therefore a significant figure. Be sure to record a zero if the estimated digit is zero. Continue to slowly heat until the sample has totally liquified and record the end of the melting range.

If you are using a commercial apparatus, make sure that the apparatus has sufficiently cooled before placing the capillary tube in it. Gently turn on the heating until you get a feel for the heating rate. Heat as above and record the melting range. Turn down the heat and shut off the apparatus as soon as you are done so that it will begin cooling for the next person.

**MIXED MELTING POINTS**. Prepare a mixture for a mixed melting point determination by adding a small amount of each compound to a piece of weighing paper using a spatula. **Thoroughly mix the two together with a spatula** and then pack a capillary and proceed as above.

## Procedure

**Chemical Hazard Summary:** All chemicals may cause irritation of eyes, skin, and respiratory tract. Wear proper goggles and gloves. Avoid inhaling vapors/dust. The following notes are summaries and do not supplant reading the entire MSDS.

**Vanillin** is light and moisture sensitive.

**Acenaphthene** is harmful if inhaled and causes eye, skin, and respiratory tract irritation.

**Phenanthrene** is a suspected carcinogen that may form explosive dust-air mixtures. Avoid creating dust.

**Acetone** is extremely flammable and causes eye, skin, and respiratory tract irritation. Inhalation can cause drowsiness and dizziness. Keep away from open flame and sources of ignition.

**RECOVERED VANILLIN.** Weigh the recrystallized vanillin from last week's experiment and determine its percent recovery.

**CAPILLARY TUBE METHOD OF MELTING RANGE DETERMINATION.** Using the technique described above for a water bath, determine the melting ranges of samples 1 and 2 below. [Hint: The melting ranges should occur between 60°C and 85°C.]

1. Crude vanillin from *Experiment 1* (in jars at balances).
2. Recrystallized vanillin from *Experiment 1*.

When done, place remaining vanillin in the "Recrystallized Vanillin" bottle. Wash out the plastic beaker and place it back in the section bin. Toss all used melting point capillaries in the "Chemical Contaminated Items" container. Return the stir bar, washed and dried, to the jar.

**IDENTIFICATION OF AN UNKNOWN**. Weigh the dried, recrystallized unknown and determine its percent recovery. Using a commercial apparatus, determine the melting range of your unknown. Look up the structures and melting points of the possible unknowns (triphenylmethane, acenaphthene, or phenanthrene) and try to identify your unknown. It will be necessary to use the mixed melting point technique to confirm the identity your unknown. The laboratory will have the possible

unknowns available in labeled jars. When done, place remaining unknown in the "Recrystallized Unknown" bottle. Wash out the plastic beaker and place it back in the section bin. Toss all used melting point capillaries in the "Chemical Contaminated Items" container.

**CLEANING UP**. Pour your remaining vanillin in the "Recrystallized Vanillin" bottle. Pour your remaining unknown in the "Recrystallized Unknown" bottle. Toss all used melting point capillaries in the "Chemical Contaminated Items" container. Clean out the plastic beakers with soap and water and a final rinse with distilled water before drying it and putting it back in your section's bin. Wipe down your table top with a paper towel dampened with water.

# Prelaboratory Preparation - *Experiment 2*

First, be sure to list all the goals of the experiment. You should prepare a table that includes the literature melting range of vanillin and the 3 possible compounds for your unknown. Also, you should prepare a table that will contain all the pertinent observations and percent recoveries. Be sure to include references for all sources of information.

# Observations

Report all relevant observations including masses, percent recoveries, and melting points.

**Percent Recovery**

1. Mass of plastic beaker (from *Experiment 1)* _____
2. Mass of plastic beaker + recrystallized vanillin _____
3. Mass of recrystallized vanillin _____
4. Mass of crude vanillin (from *Experiment 1*) _____
5. Percent recovery _____

# Conclusions

This section should include the following:

1. Were the goals of the experiment achieved? Explain your answer.
2. Why were the percent recoveries less than 100% and how could they be improved?
3. Were the recrystallizations effective (did purification result)?
4. What was the identity of your unknown, how did you come to this conclusion, and how confident are you in your conclusion?