

Fig. 3-1



Antoine Lavoisier (1743 - 1794)

One of first scientists to make chemistry quantitative.

<http://www.homepages.hetnet.nl/~b1beukema/wohler.html>

## Experiment 3

# MELTING POINTS AND RANGES

### New Technique

Melting points and ranges.

### Discussion

The second experiment delved into the separation and purification technique called recrystallization. Following separation and purification, it is usually necessary to verify or determine the identity and purity of the recovered substance. This experiment will focus on one very important identification technique, the determination of the melting point of a solid. Since the melting point does not depend on the amount of the material being tested, it is an intensive physical property (as contrasted to extensive physical properties such as volume and mass which do depend on the amount of the substance and are not, by themselves, useful for identification purposes). Intensive physical properties such as melting point, boiling point, density and refractive index are extremely useful for verification purposes because they are quickly measured and involve relatively inexpensive instrumentation and accurate procedures.

Melting points also provide a simple method of obtaining an 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°C but experimentally it is found that heating causes it to begin softening at 58°C and totally liquify at 62°C, we report that the sample has a melting range of 58 - 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 range observed will be lower (and broader) than the melting point of the major compound. Since all samples contain at least a tiny amount of impurity, all melting observations should be recorded as ranges as a melting point would only be observed for a 100% pure substance. It is good technique to experimentally determine the melting ranges 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 and broaden melting ranges enables us to distinguish between two compounds with similar 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 range (e.g., 64 - 65°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?

## Techniques

**MELTING RANGE MEASUREMENTS.** 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 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). Refer to the figures for this discussion. 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.

Place the capillary tube in your melting point apparatus and gently turn on the heating until you get a feel for the heating rate. 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. Remember that except for digital outputs, you should record one more digit than indicated by the finest set of graduations on the measuring device. 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 high point of the melting range.



Figure 3-2

The figures show a “homemade” melting apparatus consisting of a heater-stirrer and a beaker containing water (only useful if the melting range is below 90°C) or mineral oil and a magnetic stirring bar. A thermometer with the capillary strapped to it (use a small piece of rubber tubing) is suspended near the front of the beaker. The other two figures show common commercial apparatus. The apparatus on the right above uses capillary tubes much like the homemade apparatus. In the apparatus on the lower left, the sample is squeezed between microscope slides. If your lab has the commercial types, you will probably use them for most experiments. Today, however, students will be doing many melting points simultaneously and it should save time if the vanillin melting ranges are determined using a “homemade” apparatus.

**MIXED MELTING POINTS.** Prepare a mixture for a mixed melting point determination by adding a small amount of each compound to a **mortar and pestle** using a spatula. **Thoroughly grind the two together to make an intimate mixture** and then pack a capillary and proceed as above.

**Procedure** [For this section of your report, it is not necessary to repeat the procedure given but the source of the procedure should be cited. The report should contain explanations of the italicized questions.]

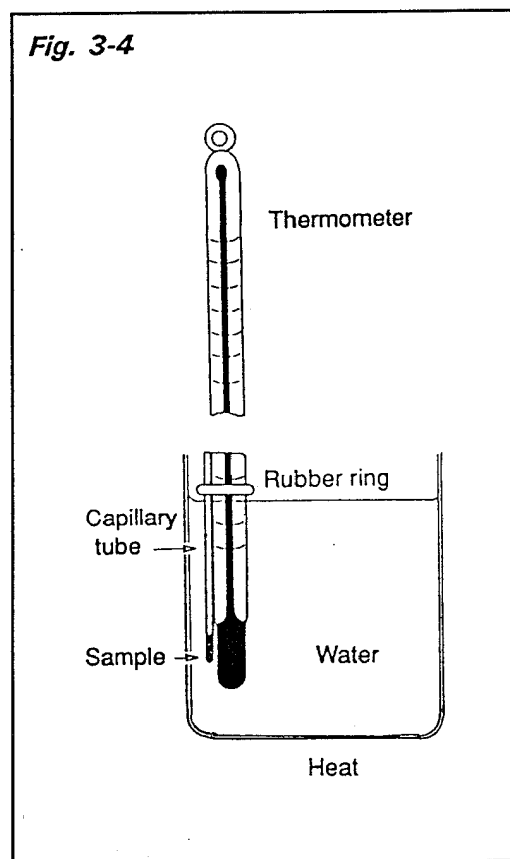
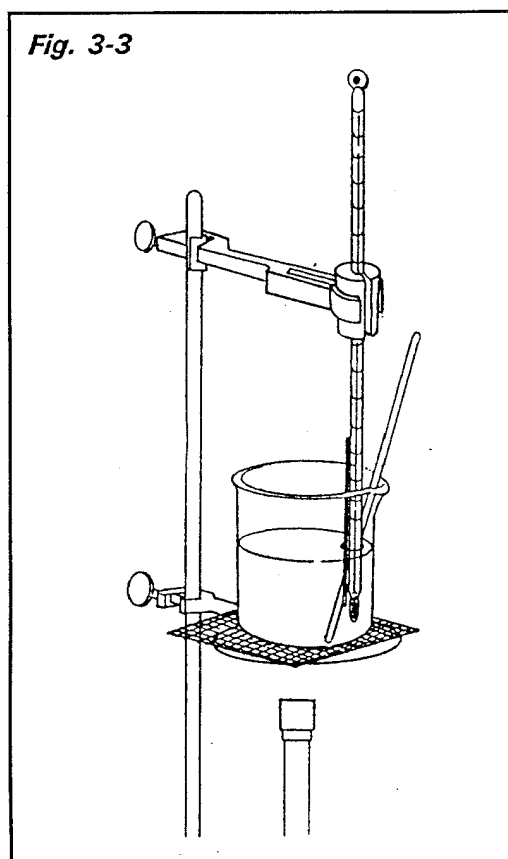
**A. PERCENT RECOVERY.** Percent recovery and yield are extremely important from an economic perspective, especially when industrial-sized amounts are used. The percent recovery is calculated by dividing the amount of the recrystallized sample by the mass of the starting solid and multiplying the result by 100%. Weigh the recrystallized vanillin and unknown samples from last week's experiment and determine the percent recoveries.

**B. MELTING RANGE DETERMINATION OF VANILLIN SAMPLES.** For the melting ranges of the vanillin samples, most students will be doing this experiment at the same time. Since your laboratory is probably equipped with only a few commercial melting point instruments, it will be more convenient to make your own melting point apparatus for this measurement. As the melting ranges of the vanillin samples are all under 90°C, a water bath works fine for this measurement and involves quick and simple construction of an apparatus. For the melting ranges of the unknown samples, the commercial instruments should be used. If some students start with the unknowns (Part C), backup on the commercial instruments should be minimized.

Refer to *Figures 3-4 and 3-5* for this discussion. Select a thermometer that covers the range -10°C to 110°C. Fill the capillary tube as described in the *Technique* section above. Attach the capillary tube with a rubber ring (cut off a piece of rubber hose) to a thermometer with the sample even with the mercury bulb of the thermometer. Place the thermometer in a 250 mL beaker half full of water mounted above a Bunsen burner. Support the thermometer with a *split* rubber stopper and a clamp on a stand. Gently heat the water with *continual stirring* and observe the sample. As you approach the melting range, the heating rate should be very slow (around 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. Continue to **slowly** heat until the sample has totally liquified and record the high point of the melting range.

Using the technique described above, determine the melting ranges of samples *1, 2 and 3* below. [Hint: The melting ranges should occur between 60°C and 85°C.] For the mixed sample, add approximately equal amounts of each compound to a mortar and grind them together with the pestle before inserting them into a capillary tube.

1. Crude vanillin from *Experiment 2*.
2. Recrystallized vanillin from *Experiment 2*.
3. ~50% recrystallized + ~50% phenyl carbonate (melting point ~ 80°C)



**C. DETERMINATION OF THE MELTING RANGE OF UNKNOWN SAMPLES.** Using a commercial apparatus, determine the melting range of impure and recrystallized unknown samples. Based on a comparison of your melting range with the literature value for the melting ranges of triphenylmethane, acenaphthene and phenanthrene, choose one of the three and determine a mixed melting range with the suspected substance. If you choose correctly (how will you know?), you can stop. However, if you decide your selection was incorrect, you should run mixed melting points with the other possibilities until you have strong support for your conclusion.

## Reference

Murov, S.: Stedjee, B., *Experiments and Exercises in Basic Chemistry*, 7<sup>th</sup> ed., Wiley, **2009**, 67.  
Murov, S. *Experiments in General Chemistry*, 5<sup>th</sup> ed., Brooks/Cole, **2007**, 33.

## Prelaboratory Preparation - Experiment 3

At the beginning of your report in your notebook, you should list the goals of this experiment. You should prepare a table that contains the literature melting ranges of vanillin, triphenylmethane, acenaphthene and phenanthrene. Refer to the *Chemistry Resources* section of this text for possible sources of melting range information. The best hard copy sources are probably the *Aldrich Catalog* and the *Handbook of Chemistry and Physics*. The best online sources are listed on pages 8 and include *Aldrich* and *ChemIDplus*. Be sure to include references for all sources of information. Also be sure to prepare a table with the masses of the impure vanillin and unknown samples and space for the mass and percent recovery of the purified samples.

Generally, it is not necessary to repeat the procedure given but the source of the procedure should be cited. However, if the procedure is modified in any way, complete documentation of the nature of the changes and the reasons for the changes is required.

## Observations

Before determining melting ranges, weigh all recovered and dry samples so that percent recoveries can be calculated. Be sure to carefully observe and record melting ranges for all samples to the nearest 0.1 degree. The tenth of a degree reading will be an estimate but recognize that it still is a significant figure and needs to be recorded. Remember that slow heating is the key to reliable measurements and continuous stirring is important for the vanillin measurements in the water bath.

## Conclusions

This section should include the following:

1. In the **Prelaboratory Preparation** section, you were asked to list the goals of this experiment. Were the goals achieved? Explain your answer.
2. Explain any losses of materials. In other words, why weren't the % recoveries 100%?
3. How could the percent recovery have been improved?
4. Did the recrystallizations successfully purify the vanillin and unknown samples? Explain your answer.
5. What was the identity of your unknown. Present all the evidence for your conclusion.