Experiment 1:
Melting-point Determinations

Objectives

1. This experiment is designed to introduce you to the use of a typical "melting-point apparatus". Which of the numerous types of "melting-point apparatus" you will use may depend on the location at which you carry out the laboratory component of this course. You will use the "melting-point apparatus" repeatedly throughout this course.

2. To demonstrate that pure compounds have "sharp" melting points; that is that pure compounds melt over a small temperature range.

3. To demonstrate how an impurity lowers the melting point of a substance and broadens its melting range.

4. To illustrate the use of the "mixed melting-point" procedure.

Introduction to Melting Points

Despite the increased use of spectrophotometers, the determination of a compound's melting point is still one of the most common techniques used to assist in the identification of unknown compounds and assessing the purity of a given sample. The melting point of a compound is a unique property of that compound. Most organic compounds melt below 300° C. Contrast this with the very high melting points of inorganic compounds (e.g., the melting point of sodium chloride is 801° C).

The melting point occurs when a compound is at the temperature at which the solid and liquid phases are in equilibrium at a pressure of 1 atmosphere. Most pure organic compounds melt over a 'sharp and narrow' range of one or two degrees Celsius, hence, the term **"melting range"** is more appropriate than "melting point". Some handbooks and reference tables only list one number, the upper limit. **Note**: The small temperature difference observed between the temperature at which a compound starts to melt and that at which the compound is liquid is caused by 'heat transfer'. It takes a little time for the heat to transfer from the heating block, through the glass of the tube, and into the organic sample.

When an organic compound is impure, its melting point is lowered and broadened (>3 °C range). Determining the melting point of a product at the end of an experiment gives us an approximate idea of its purity, because the melting point decreases "almost' linearly as the amount of impurity increases (see Figure 1.1 below). **Note**: in Figure 1.1, the distance between the dashed and solid lines indicates the melting range.

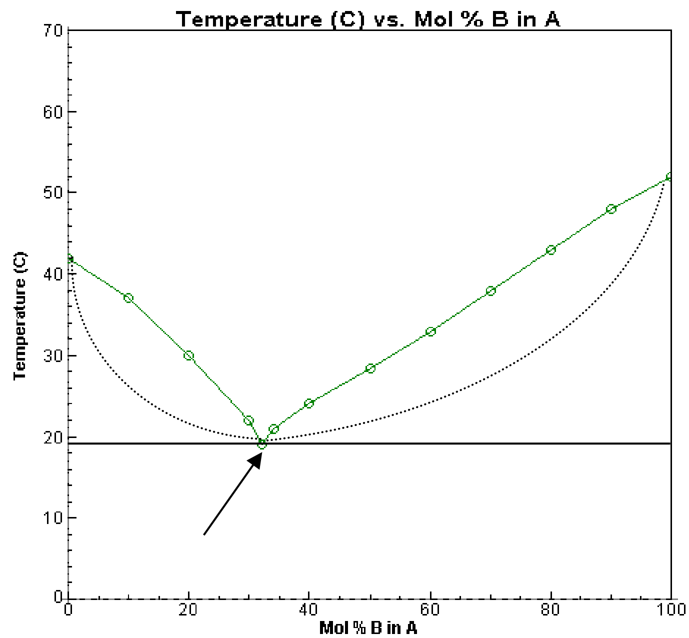

Figure 1.1: Melting Point Phase Diagram

Eutectic Points and Mixtures

Note the low point in the melting point phase diagram (Fig. 1.1). It shows that there is a minimum melting point for a mixture of these two compounds, and it occurs at a very specific ratio of mixtures of compound A and B. This point is called the **eutectic point** or eutectic temperature. The **eutectic mixture** is the composition of the mixture of A and B at the eutectic point (in this case, 68% A, 32% B). At the eutectic point, both compounds are melting simultaneously, resulting in a sharp melting point rather than the broad melting point typically seen for impure compounds. **Note:** Expect all mixtures of two different compounds in this lab course to exhibit a broad melting range. We have not given you any eutectic mixtures, only impure compounds!

Mixed Melting Points

We can use a procedure known as a "**mixed melting-point**" to help find the identity of an unknown compound. Suppose we suspect that a given "unknown" compound is benzoic acid (m.p. 120−121 °C). First, we determine the compound's melting point, and let us suppose that we find it to be 118–119 °C. This is quite close to the expected value, so the compound could well be benzoic acid. However, there are probably hundreds of organic compounds that melt in the range 118–121 °C. (See “Melting Point Index of Organic Compounds” in *The Handbook of Physics and Chemistry* to verify this fact.)

How can we determine whether or not our compound is benzoic acid? What we do is to obtain a genuine sample of benzoic acid from the stockroom and mix a small amount of this pure substance with our “unknown” compound. If the melting point of the mixture so formed is still 118-119 °C, we know that the unknown compound was benzoic acid—all we have done is to mix benzoic acid with benzoic acid, so that the melting point remains unchanged. If the “unknown” was not benzoic acid, then the benzoic acid that we have added acts as an impurity, and the melting point of our unknown will be lowered. It should also melt over a much broader range.

Melting Point Hints

- Use a small amount of sample in the melting point tube. Over-filling the tube will cause it to heat unevenly and result in broader ranges (and a false indication of impurity).

- Pack your sample well. Loose sample will heat unevenly with the results described above.

- Be prepared to make multiple melting point determination of a sample.

- Once a sample has been melted, discard it. The sample may have decomposed, oxidized or rearranged (‘polymorphed’) during heating and cooling.

- Use a small Ramp Rate (not more than 1 °C/min) near the melting point for more precise measurements.