Experimental Organic Chemistry

A Miniscale and Microscale Approach

FIFTH EDITION

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27. In the process of a recrystallization, if crystals do not form upon cooling the solution, it is often recommended that the inside of the flask be scratched at the air–liquid interface with a glass stirring rod. What purpose does this serve, and how does it work? What else might be done to induce crystallization?

28. Should some loss of sample mass be expected even after the most carefully executed recrystallization? Explain.

29. In general, what solvent should be used to rinse the filter cake during the vacuum filtration step of a recrystallization? Should this solvent be cooled prior to use?

30. Why do you seldom see high-boiling solvents used as recrystallization solvents?

31. At the end of a recrystallization, where should the *impurities* be located?

32. A student has been asked to recrystallize 1.0 g of impure stilbene from ethanol. Provide a set of standard step-by-step instructions for recrystallization of this sample so as to maximize the purity and yield obtained.

33. An important product from a multistep synthesis must be recrystallized to remove a small amount of an impurity. However, all the available solvents each individually fail to be suitable recrystallization solvents. Offer a solution to this problem using only the available solvents. (*Hint:* Consider binary solvents.)

34. A suspension of decolorizing carbon (charcoal) is often administered to poison victims.

    a. Speculate on the purpose decolorizing carbon serves in this particular application. (*Hint:* It is similar to the way in which decolorizing carbon is used in a recrystallization.)

    b. How is the charcoal ultimately removed from the victim?

3.3 PHYSICAL CONSTANTS: MELTING POINTS

Physical Constants

See more on *Melting Point*

Physical constants of compounds are numerical values associated with measurable properties of these substances. These properties are *invariant* and are useful in the identification and characterization of substances encountered in the laboratory so long as accurate measurements are made under specified conditions such as temperature and pressure. Physical constants are useful only in the identification of *previously known* compounds, however, because it is not possible to predict the values of such properties accurately. Among the more frequently measured physical properties of organic compounds are **melting point (mp), boiling point (bp), index of refraction (n), density (d), specific rotation ([α]), and solubility.** Melting points, discussed below, boiling points, described in Section 4.2, and solubilities, outlined in Section 3.2, are the properties most commonly encountered. Index of refraction and density are mentioned in Chapter 25. Specific rotation is discussed in Chapters 7 and 23 but applies only to molecules that are **optically active.** Whether the substance is known or unknown, such values, along with other properties like color, odor, and crystal form, should be recorded in the laboratory notebook.

The values of one or two of the common physical properties *may* be identical for more than one compound, but it is most unlikely that values of several such

properties will be the same for two different compounds. Consequently, a list of physical constants is a highly useful way to characterize a substance. Extensive compilations of the physical constants are available (Chap. 26). One of the most convenient is the *CRC Handbook of Chemistry and Physics*, which contains a tabulation of the physical constants and properties of a large number of inorganic and organic compounds. *The Handbook of Tables for Organic Compounds* is especially useful for organic compounds. Neither of these books is comprehensive; rather, they contain entries for only the more common organic and inorganic substances. So many compounds are known that multi-volume sets of books are required to list their physical properties (Chap. 26).

Melting Point of a Pure Substance

The melting point of a substance is defined as the temperature at which the liquid and solid phases exist in equilibrium with one another without change of temperature. Ideally, addition of heat to a mixture of the solid and liquid phases of a pure substance at the melting point will cause no rise in temperature until all the solid has melted. Conversely, removal of heat from the equilibrium mixture will produce no decrease in temperature until all the liquid solidifies. This means that the melting and freezing points of a pure substance are identical.

The melting point is expressed as the temperature *range* over which the solid starts to melt and then is completely converted to liquid. Consequently, rather than a melting *point*, what is actually measured is a **melting range,** although the two terms are used interchangeably. If a crystalline substance is pure, it should melt over a narrow or sharp range, which will normally be no more than 1 °C if the melting point is determined carefully. The melting ranges reported for many "pure" compounds may be greater than 1 °C because the particular compound was not quite pure or the melting point was not measured properly. The process of melting may actually begin by "softening," as evidenced by an apparent shrinking of the solid, but such softening is difficult to observe. Thus, for our purposes, the start of melting is defined as the temperature at which the first tiny droplet of liquid can be detected. Note that it is improper and inexact to report a single temperature, such as 118 °C, for a melting point; rather, a range of 117–119 °C or 117.5–118.0 °C, for example, should be recorded.

Effect of Impurities on Melting Points

Many solid substances prepared in the organic laboratory are initially impure, so the effect of impurities on melting-point ranges deserves further discussion. Although this topic is discussed in freshman chemistry textbooks, a brief review of its basic principles is given here.

The presence of an impurity generally *decreases* the melting point of a pure solid. This is shown graphically by the melting-point–composition diagram of Figure 3.1, in which points *a* and *b* represent the melting points of pure *A* and *B*, respectively. Point *E* is called the **eutectic point** and is determined by the equilibrium composition at which *A* and *B* melt in constant ratio. In Figure 3.1, this ratio is 60 mol % *A* and 40 mol % *B*; an impure solid composed of *A* and *B* in this ratio would be called a **eutectic mixture.** The temperature at the eutectic point is designated by *e.*

Now consider the result of heating a solid mixture composed of 80 mol % *A* and 20 mol % *B*, a sample that might be considered as "impure *A*." As heat is applied to the solid, its temperature will rise. When the temperature reaches *e*, *A* and *B* will both begin to melt in the constant ratio defined by the composition at the eutectic point. Once all of the "impurity" *B* has melted, only solid *A* will be left in equilibrium with the melt. The remaining solid *A* will continue to melt as additional heat is supplied, and the percentage of *A* in the melt will increase, changing the composition of the
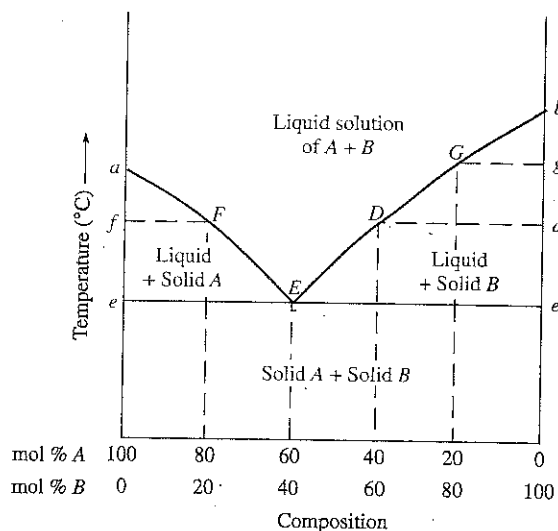
Figure 3.1
Melting-point–composition diagram for two hypothetical solids, A and B.

melt from that of the eutectic mixture. This increases the vapor pressure of A in the solution according to Raoult's law (Eq. 4.2) and raises the temperature at which solid A is in equilibrium with the molten solution. The relationship between the equilibrium temperature and the composition of the molten solution is then represented by curve EF in Figure 3.1. When the temperature reaches f, no solid A will remain and melting of the sample will be complete. The impure sample A exhibits a melting "point" that extends over the relatively broad temperature range e–f. Because melting both begins and ends below the melting point of pure A, the melting point of A is said to be *depressed*.

The foregoing analysis is easily extended to the case in which substance B contains A as an impurity. In Figure 3.1, this simply means that the composition of the solid mixture is to the right of point E. The temperature during the melting process would follow curve ED or EG, and the melting range would now be e–d or e–g.

A sample whose composition is exactly that of the eutectic mixture (point E, Fig. 3.1) will exhibit a sharp melting point at the eutectic temperature. This means a eutectic mixture can be mistaken for a pure compound, because both have a sharp melting point.

From a practical standpoint, it may be very difficult to observe the initial melting point of solid mixtures, particularly with the capillary-tube melting-point technique used in the Experimental Procedure that follows. This is because the presence of only a minor amount of impurity means that only a tiny amount of liquid is formed in the stage of melting that occurs at the eutectic temperature. In contrast, the temperature at which the last of the solid melts (points d and g, Fig. 3.1) can be determined accurately. Consequently, a mixture containing smaller amounts of impurities will generally have both a higher final melting point and a narrower observed melting-point range than one that is less pure.

The broadening of the melting-point range that results from introducing an impurity into a pure compound may be used to advantage for identifying a pure substance. The technique is commonly known as a **mixed melting-point** and is illustrated by the following example. Assume that an unknown compound X melts at 134–135 °C, and you suspect it is either urea, H_2NCONH_2, or *trans*-cinnamic acid, $C_6H_5CH{=}CHCO_2H$, both of which melt in this range. If X is mixed intimately with urea and the melting point of this mixture is found to be lower than that of the pure

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