Appendix 4: Melting Points

Melting points of Pure Substances

The melting point of a substance is the temperature at which the solid phase of the substance is at equilibrium with the liquid phase. Consider a substance with which you are very familiar, water. The melting point (or its freezing point – they are the same) is 0.0ºC. At this temperature, a mixture of liquid water and solid water can exist at equilibrium indefinitely. Molecules of liquid water become part of the solid mass of water at the same rate as molecules of water in that solid mass enter the liquid phase. If we take solid water, ice, at -10ºC and begin to heat it, the vibrational energy of the water molecules in the ice crystal will increase. Eventually, at 0ºC, the vibrational energy will be great enough that the intermolecular forces binding water molecules to each other in the solid phase will begin to break, and water molecules will begin to enter the liquid phase. In other words, they will melt. As heat continues to be applied to the melting solid sample, all of the energy goes into breaking these intermolecular forces, and the temperature remains at 0ºC as more and more molecules enter the liquid state. When the last of the molecules of ice have melted, the temperature of the now-liquid water begins to rise. This melting of pure solid is represented in the diagram below.

From -10º to 0º, the solid is getting warmer as the vibrational energy of the molecules increases. At 0º, melting begins and the temperature remains constant until melting is complete. Once this occurs, then the temperature of the liquid begins to rise, because the
heat energy is now causing the molecules of the liquid to move about faster in its container.

In theory, the melting point *range* of a pure solid, the difference in temperature between the time when the sample begins to melt and the temperature where it has melted completely, should be zero. But in practice, achieving a zero degree melting point range is nearly impossible. The thermometer or thermocouple used to measure temperature in most melting point devices does not sit in the sample. It sits in the medium in which the sample is being melted. In most devices this medium is a metal block. Once the melting point of the sample has been reached, the temperature of the sample does indeed remain constant. But the temperature of the metal block is still rising during the heating process. Since the thermometer or thermocouple is measuring the block temperature, not the sample temperature, there is always a non-zero melting point range reported. If a melting point is measured correctly, for a pure substance, this melting point range should be no greater than 1.0ºC. To achieve this 1.0ºC melting point range, it is important to heat the sample to be melted very slowly near its melting point. An example should illustrate why.

Let’s assume that a pure solid sample in a capillary tube is placed in a melting point apparatus. And, let’s assume that this sample takes thirty seconds to melt from beginning to end. If the temperature of the metal block is being heated at a rate of 10ºC/minute, during the 30 seconds it takes for the sample to melt, the temperature of the metal block will increase by 5ºC during the melting process. Even though the sample is pure, this melting point range is not indicative of a pure solid. On the other hand, if the metal block is heated at a rate of 2ºC/minute, then the temperature of the metal block will increase only 1ºC during the process, a melting point range indicative of the sample’s purity.

To achieve an accurate melting point range, the sample should be heated no faster than 2ºC/minute. Fortunately, it is possible to control this heating rate fairly accurately with the new generation of melting point devices.

Melting points are to solids what boiling points are to liquids, a good means of identifying an unknown solid. Most pure organic compounds have a definite melting point, and solids in the CRC Handbook of Tables for Organic Compound Identification and other reference books are listed in order of increasing melting point the way that liquids are listed by boiling point. Thus, we are aided in the identification of an unknown solid by its melting point, and we are given some indication of a solid’s purity by its melting point range. Melting point ranges of 1.0ºC or less are indicative of a pure substance. Ranges of more than 1.0ºC suggest that the solid is not pure.

**Melting Points of Mixtures**

When a solid, let’s call it X, is contaminated with an impurity that is soluble in molten X, the melting point of the impure sample is lowered and the melting point range is
broadened. For example, when a sample of pure X (mp 125°C) is contaminated with a small amount of Y (mp 175°C), a substance soluble in molten X, the melting point will drop below the melting point of pure X, even though Y has a higher melting point than X, and the melting point range will broaden. The more impurity is present, the lower and broader the melting point and range will be. Similarly, when a sample of Y is contaminated with some X, the melting point will drop below the melting point of pure Y.

For mixtures containing two components, melting point diagrams like the one shown below can be drawn. Consider compounds X and Y again. If a series of mixtures of X and Y of known composition are made, and the melting points of the mixtures are determined, a plot of melting temperature vs. composition might look like this.

As you can see from this melting point diagram, as more and more Y is added to X and the percentage of X decreases, the melting point of the mixture decreases. Similarly, as more and more X is added to Y, and the percentage of Y decreases, the melting point of the mixture decreases. The point where the two melting point lines meet is called the eutectic point. (Eutectic means “easy melting” in Greek). The mixture of X and Y that has the composition shown at this point is called a eutectic mixture. The eutectic mixture has the lowest melting point that a mixture of two substances, in this case X and Y, can have. Unlike all other mixtures of X and Y, the eutectic mixture has a constant melting
point, much like that of a pure substance. It begins and finishes melting at the same temperature.

Overall, we can use melting point not only to identify a substance, but also to obtain an indication of the sample's purity. Any lowering or broadening of the melting point is indicative of impurities, such as residual solvent or other by-products, in the sample.

**Determination of Melting Points**

Melting points of organic solids are generally taken by putting the sample in a capillary tube sealed at one end. The sample must be thoroughly crushed to get the solid crystals as small as possible so that they will pack together tightly and conduct heat well during the heating process. This is generally done by taking the flat end of a spatula and crushing the crystals with a pulling motion on a piece of dry filter paper. After doing this repeatedly, the solid should be very finely ground and ready to be put in a capillary tube. Take the capillary tube and push it into a small pile of the ground up solid until there are 2-3 mm of solid in the open end of the tube. Then invert the tube and tap it firmly on the desk top to pack the crystals tightly in the bottom of the tube. Do this repeatedly. There should be 2-3 mm of well-packed solid in the tube when you are ready. Then place the tube in the melting point apparatus (photos below) and follow the instrument instructions to determine the melting point. Be sure to maintain a heating rate of no more than 2°C/minute when you are near the melting point of the sample.

**MEL-TEMP 3.0**