Think Melting Points

Sample Preparation

Preparing the Sample

Careless sample preparation is the leading cause of inaccurate and irreproducible results. **Substances must be fully dry, homogeneous and in fine powdered form.** Moist samples must be dried first. Coarse crystalline and non-homogeneous samples must be crushed into a fine powder in a mortar.

Filling the Capillary

Press the open end of the capillary into the substance several times until the capillary holds 2-3 mm of sample. For consistent results, it is very important that the capillary is not over or under filled.

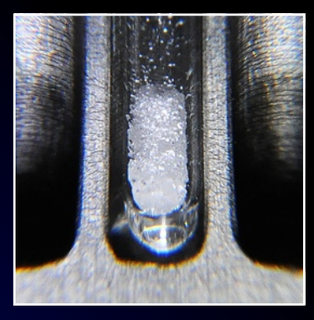
Packing the Sample

Push the powder to the closed bottom of the tube by repeatedly tapping the bottom of the tube against a hard surface. More sample can be added if the level is too low. Tight packing and a fixed level of sample are very important for optimum results.

Visual Observations

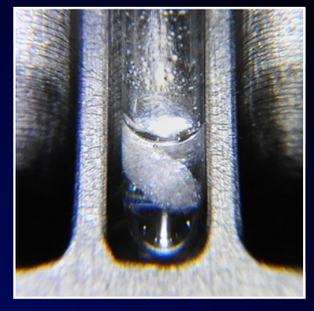
Onset Point

The onset point, also called the collapse point, is considered the start of the melt. Liquid clearly appears for the first time as a separate phase in coexistence with the crystals. The sample has changed appearance and collapsed away from the walls. It must not be confused with the "sintering point" which corresponds to just isolated drops due to a few surface crystals melted (often on the capillary walls).



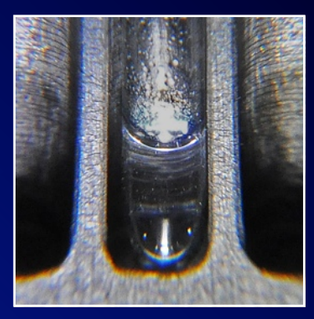
Meniscus Point

The meniscus point is when a liquid meniscus becomes clearly visible. There is solid phase at the bottom and a clear liquid phase on top with a complete and well defined meniscus. The meniscus point is often listed in European melting point tables and is the preferred value of British Pharmacopeia.



Clear Point

The clear point is when the substance becomes completely liquid and there is no solid remaining. The clear point is more dependent on the ramp rate than the onset point. The clear point is the temperature most often listed in U.S. based melting point tables. When a single temperature is listed, it is usually the clear point.



Ramp Rate

Thermodynamic Melting Point

The temperature obtained for the clear point is dependent on the ramp rate. This is because the transition from solid to liquid does not take place instantaneously, it requires a finite amount of time. This time depends on the (1) heat of fusion of the sample, (2) the thermal conductivity of the sample, (3) the thermal conductivity of the glass capillary, (4) the sample preparation/packing method, (5) sample size and (6) the geometry and construction of the oven.

The temperature being measured is not the temperature of the sample itself, but rather that of the heating block which holds the sample capillary. The melting process begins at the temperature where liquid first appears – the onset point. At this point the block and the sample are at the same temperature. As soon as the melt starts the sample temperature stabilizes. As the melt progresses, the sample remains at constant temperature (the thermodynamic melting point) while the block continues to heat up. Heat is constantly transferred from the block to the sample at a rate that is proportional to the temperature difference between the sample and the block. Thus, the temperature of the block continues to rise while the sample finishes melting. When all of the sample has become liquid, the temperature of the block is recorded as the clear point. The rise in the block temperature during melting is larger for higher ramp rates. As a result, **the higher the ramp rate, the higher the clear point**.

Measurements of melting points are comparable with one another only if they were taken with the same ramp rates. It is good laboratory practice to use the lowest ramp rate that time allows.

Mixtures

Melting Point Depression

Mixtures of substances, whose components are insoluble in each other in the liquid phase, display a melting point depression and, instead of a sharp melting point, a melting range. The size of the melting point depression depends on the composition of the mixture.

Generally, a 1% impurity results in a 0.5 °C depression.

Purity Tracking

In preparative organic chemistry the purity of a substance often has to be evaluated without a pure reference sample being available. This is the case, for example, when a new chemical compound is synthesized. The raw product is generally subjected to a few purification steps (i.e. recrystallization or resublimation) and the melting point is determined at each stage. The onset point continues to increase, and the melting range continues to decrease, until the substance is either pure, or as pure as it is going to get through the purification method being applied. Careful and consistent sample preparation, particularly drying and grinding, is essential for purity tracking.

Mixed Melting Point

If two compounds melt at the same temperature, a mixed melting point determination can reveal if they are one and the same substance. For example, if an unknown sample has the same melting point as a known reference compound, prepare 3 capillaries: (1) unknown sample, (2) reference and (3) 1:1 mixture of unknown and reference. Put all three capillaries in the apparatus simultaneously and perform a melting point determination. If the melting point of the mixture remains the same as the other two, then the two substances are the same. If the mixture melts at a lower temperature, then they are two different substances.

SRS

DigiMelt is the new, low cost, digital melting point apparatus designed specifically for the teaching lab. DigiMelt rapidly heats the oven to the programmed start temperature, then ramps at the specified rate. The student carefully observes the samples and records the melting points with a touch of a button.

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