

Reporting Melting Points and Describing Solids in the Gladysz Group

1. Melting or decomposition points should be determined for all solid compounds. The first step is to purify the sample. In principle, the melting point should be determined on the same sample that passes microanalysis. If you are unable to obtain analytically pure material, then use the "purest material available." However, melting points for mixtures of isomers (cis/trans mixtures, diastereomers, etc.) are not physically meaningful and should not be recorded. With air sensitive compounds, use flame- or wax-sealed capillaries.

The melting point range is defined as follows. The lower temperature is that at which some liquefaction is first noted. A common approach here is to record the temperature at which the sample column collapses against the side of the capillary (the theory is that the onset of liquefaction is structurally similar to cutting a v-notch in a tree that causes it to lean). The higher temperature corresponds to the temperature at which liquefaction is complete.

Limiting examples:

- 1.1 "mp 150-151 °C (open capillary)" This indicates that the compound melts but does not decompose at 150-151 °C. In order to establish that decomposition does not occur, you must resolidify and remelt the sample. A depression of a few °C is allowable on the second melt. Slight discoloration is also ok.
- 1.2 More reliable data will be obtained if the capillary is sealed under an inert atmosphere or vacuum, reported as "mp 150-151 °C (sealed capillary)". Then melt/O₂ reactions will be avoided, and depression of the second melt will be minimized.
- 1.3 "mp 150-151 °C dec (open OR sealed capillary)" This indicates that the compound melts (becomes a liquid) and decomposes at the same time. The decomposition can be verified as in example a (allow the sample to solidify and observe a different melting or decomposition point the second time), or better by crushing the capillary and recording an IR spectrum (or something similar). Alternatively, a DSC trace will show an endotherm for a true melting point, but usually an exotherm for melting with decomposition.
- 1.4 "dec pt 150-151 °C (capillary, no melting)" This indicates that the compound decomposes to another solid without melting. This is a very common situation, especially with metal-containing compounds. If the statement "no melting" is eliminated, than example 1.3 is not excluded. The decomposition can be verified as in 1.3, but often there is a distinct color change.
- 1.5 "when in doubt, write it out" Sometimes it is impossible to classify a sample into one of the above categories. Then write something like "the sample showed slight discolorization at 145 °C, turned black at 180 °C, liquefied at 190 °C, and erupted like a volcanic lava flow at 200 °C."

Be careful with respect to heating rates. Starting ca. 5 °C below the melting point, the temperature increase should not exceed 1 °C/minute. For compounds that do not decompose, it is permissible to record the melting points to a tenth of a degree in your lab notebooks. Depending upon the type of paper written, these may later be rounded to the nearest half degree or whole degree (or not rounded at all).

2. Another point concerns the thermometer. Most commercial thermometers in chemistry

laboratories are calibrated to give accurate readings when immersed in a fluid to the "immersion line". This is usually 76 mm, and is always given in the technical specifications when ordering a thermometer. If you just want a thermometer for determining the temperature of the air, a "total immersion" thermometer is appropriate.

The terms "corrected" or "uncorrected" melting points refer to a determination where the wrong type of thermometer was used, and a fudge factor is employed to compensate. This is nicely treated in an article by G. V. D. Tiers, *J. Chem. Educ.* **1990**, *67*, 258. This distinction is seldom or never necessary in Gladysz group research.

You have the option of reporting your melting points vs. a calibrated thermometer (more elegant), or vs. an uncalibrated thermometer. Clearly specify the case. A PDF version of a data sheet for a melting point standard is attached. This British vendor sells standards with particularly narrow melting point ranges.

3.

3.1 Be as precise as possible in the way you describe solids. "Crystals" are always sought (by definition, a crystal diffracts), but sometimes you are stuck with a "powder", "foam", or "gum". Use precise, unambiguous color designations. A box of crayons is always a good guide. "Tan" or "beige" might be more accurate in some cases than "brown".

3.2 With crystals, always note the morphology. For example
... yellow prisms, mp yellow needles, mp yellow platelets,
mp yellow irregularly-shaped crystals, mpyellow irregularly-
shaped needles, mp... ... yellow clusters of rods, mp yellow
crystals of varying morphology, mp ...