Melting Point: Identification of an Unknown Solid

Introduction * ***Procedure***

(Adapted from Mount Holyoke College's Organic Experiments: Profs. Hamilton & Li, 2007)

Introduction:

(Read Lab Text/Guide pp.47-51)

The melting point of an organic solid is a unique physical property that can be easily and accurately determined with very small amounts of material. Historically, in combination with other physical and chemical data such as that from combustion analysis, it has been an important piece of information in determining an organic compound's identity. A physical chemist uses a very accurate method of determination, which is to record a cooling curve of temperature versus time for the pure compound. However, this approach requires relatively large amounts of material and is not necessary for a qualitative identification. A *"capillary method"* that is relatively quick, easy and accurate is used in its stead..

Capillary Melting Point Determination

The method involves placing a very small amount of sample in the bottom of a narrow capillary tube that has been sealed at one end, which are relatively inexpensive and available commercially. The determination is made using a Melting Point Apparatus that simultaneously heats both the sample tube and a thermometer or thermocouple sensor. The temperature range over which the sample is observed to melt is recorded. Some pure materials posses a very narrow melting range, perhaps as little as 0.5–1.0°C, while more typically a 2–3°C range is observed. A compound almost always melts within a temperature range. The "melting point" is not a single temperature, but actually a range and is recorded as such, for example, mp 232–234°C. Though it is a melting range, the data is referred to as the melting point (mp).

The rate of heating, controlled by a dial, should be kept relatively low, especially for low melting samples, to ensure that the thermometer reading represents as accurately as possible the true temperature experienced by the sample tube (since the transfer of heat within the apparatus is relatively slow). With this fact in mind, it is sensible when recording a melting point of an unknown material to perform a trial run where the temperature is increased relatively rapidly in order to ascertain a rough melting range. The determination is then repeated by heating rapidly to within around ten to twenty degrees of the expected melting point and then very carefully increasing the temperature the remaining few degrees until the melting point is reached. If the melting point of the material is known with some confidence, for instance if the determination is being made to confirm identity, then the trial run is unnecessary.

The observation of a melting range may be a result of the heating process involved in capillary measurements (mentioned above), reveal the presence of inhomogeneities in the macroscopic nature of the solid sample, or may indicate the presence of other substances in the sample (contaminants or by–products of the method used to prepare the materials). Remember from general chemistry the effects of freezing depression of mixtures which relates to the melting point.

Melting Points as Criteria of Purity

Thermodynamics tells us that the freezing point of a pure material falls as the amount of an impurity is increased. The presence of an impurity in a sample will both lower the observed melting point and cause melting to occur over a broader range of temperatures. Generally, a melting temperature range of 0.5–1.0°C is indicative of a relatively high level of purity. It follows that for a material whose identity is known an estimate of the degree of purity can be made by comparing melting characteristics with those of a pure sample.

Melting Points as a Means of Identification and Characterization

For pure samples a clear difference of melting point between two materials reveals that they must possess different arrangements of atoms, or configurations. If two materials are found to have the same melting point then they may, but not necessarily, have the same structure. Clearly, the recording of a melting point is a

desirable check of purity and identity but must be combined with measurements from other analytical techniques in order to unambiguously identify a material and assess its purity. Part of the need for additional verification derives from the subjective nature of capillary melting point determination. Even when heating is very finely controlled, to ensure consistency of sample and thermometer temperature, then the human element of visual inspection of the melting point introduces significant variation.

Mixed Melting Points
Mixtures of different substances generally melt over a range of temperatures that concludes at a point below the melting point of either of the pure components—each component acts as an impurity in the other. Two pure substances, with sharp melting points, can be shown to be different by mixing them and recording the lowered melting point range. This type of experiment provides a means by which to confirm a proposed identity for an unknown sample: if a sharp melting point is observed for a mixture of the unknown with a genuine sample then it is highly likely that the samples are identical.

Melting Points and Molecular Structure
Melting points are notoriously difficult to predict with any accuracy or confidence. Systematic variations of melting point with variation in structure are not as obvious or predictable as with boiling points. However, the sometimes surprising variations are often only highlighted in very closely related molecules and the obvious general rule can be applied: melting points do generally increase with increasing molecular weight.

The difficulties involved in predicting melting points are a result of the problems associated with predicting molecular packing in crystals. Many, potentially conflicting, factors play a role in determining melting points including molecular shape, interactions between groups within the molecule, and the degrees of freedom the molecule possesses within the crystal.

Procedure: ***(Follow on from Recrystallization: Budget 0.5 lab periods)***

Refer to the experiment:
Recrystallization: **Purification of Solids**

Determine the unknown's melting point. Confirm the unknown's identity by doing a mixed melting point with an authentic sample which is available for each of the unknowns.