Experiment 1

Melting Points

Melting Points:

Physical properties are often utilized by chemists in identifying an organic compound. These physical properties include :
color, odor, physical state, melting point (M.P.), boiling point (B.P.), density (d), infrared (IR) spectrum, nuclear magnetic (NMR) spectrum and ultraviolet (UV) spectrum.

As long as the physical constants are determined under standard conditions (temperature, pressure, etc.), they are invariant and, therefore, useful in helping to determine the identity of unknown substances.

There are a number of reference books that contain tables of physical properties and physical constants of compounds.

One of the most common is the *Handbook of Chemistry and Physics*. If the physical properties of an unknown compound are identical to the physical properties of a compound listed in the tables, the two compounds are probably the same.

Definitions:

*The **melting point of a solid** is defined as the **temperature** at which the liquid and solid phases are in equilibrium.*

The **freezing point of a liquid** is the same temperature as the melting point of its solid. However, freezing points are *rarely* measured in practice because they are more difficult to determine. One reason for this is that solidification may not occur at the correct temperature due to the phenomenon of **supercooling.**

Supercooling occurs when a liquid is cooled below its freezing point does not solidify.

Thus, in practice, most **melting points** are determined as capillary melting points, which can be done quickly with a small amount of sample in a capillary tube. A **capillary melting point** is defined as the temperature range over which a small amount of solid in a thin walled capillary tube first visibly softens (first drop of liquid) and then completely liquefies.

Melting Points and Mixed Melting points:

Melting points are determined for three reasons.

1-If the compound is a **known one**: the melting point will help to **characterize** the sample in hand.
2-If the compound is **new** then the melting point is recorded in order to allow **future characterization** by others.
3- The **range** of the melting point is indicative of the **purity of the compound**; an impure compound will melt over a wide range of temperatures.

*Pure organic compounds generally have sharp melting points. An **impurity** lowers the melting point and widens the range. Impurities in a solid cause a melting point depression because the impurity disrupts the crystal lattice energies*

A technique for proving the identity of an unknown compound is the **mixed melting point**. Advantage is taken of the depression of melting points of mixtures to prove whether two compounds having the same melting points are identical.
If X and Y are identical, then a mixture of the two will have the same melting point; but if X and Y are not identical, then a small amount of X in Y or of Y in X will cause the melting point to be lowered.

Eutectic Mixtures:

Eutectic mixture is defined as a **mixture** of two or more components which usually **do not interact** to form a new chemical compound but, which at certain ratios, inhibit the crystallization process of one another resulting in a system having a **lower melting point** than either of the components

Eutectic Mixtures:

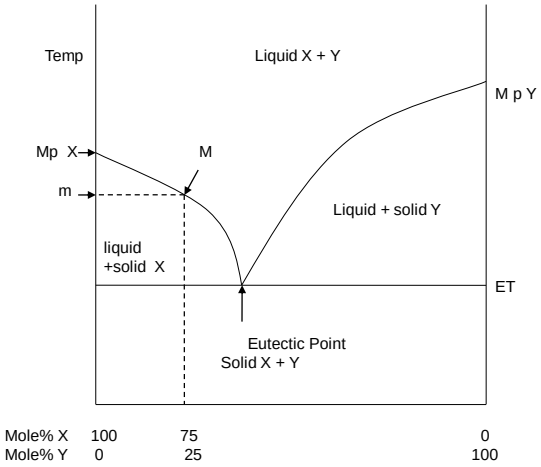
The melting point behavior of impure compounds is best understood by consideration of a simple binary mixture of compounds X and Y (Fig. 1).

This melting point-composition diagram shows the melting point behavior as a function of composition. The **melting point of a pure** compound is the temperature at which the **vapor pressures** of the solid and liquid are equal.

But in dealing with a mixture the situation is different. Consider the case of a mixture of 75% X and 25% Y.
At a temperature below ET, the eutectic temperature, the mixture is solid Y and solid X.
At the eutectic temperature the solid begins to melt. The melt is a solution of Y dissolved in liquid X. The vapor pressure of the solution of X and Y together is less than that of pure X at the melting point; therefore, the temperature at which X will melt is lower when mixed with Y.

As the temperature is raised, more and more of solid X melts until it is all gone at point M (temperature m). The melting point range is thus from ET to m.

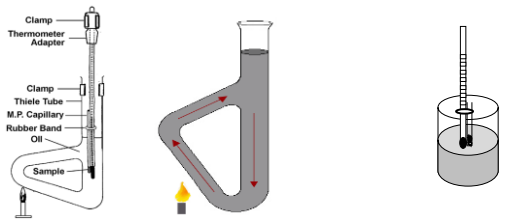
Eutectic Mixtures



The Thiele apparatus

This apparatus achieves stirring and **uniform heat distribution** by convection. It is filled to the base of the neck with silicone oil (the oil expands on heating). and equipped with a thermometer clamp to hold the thermometer.

The tube is heated at the base of the bend.
The bulb of the thermometer should be halfway down the tube to assure uniform heating.
Melting points are also easily determined in a beaker.
The beaker can be heated on a hot plate or a Bunsen burner.
Do not discard the oil used in the apparatus because it will be necessary to determine a number of melting points in future experiments.



Filling Melting Point Capillaries

1-The dry sample is ground to a **fine powder** on a watch glass or a piece of paper on a hard surface using the flat portion of a spatula.

2-It is formed into a small pile and the melting point **capillary forced down** into the **pile**.

3-The sample is **shaken into** the closed end of the capillary by rapping sharply on a hard surface or by dropping it down a 50 cm length of glass tubing onto a hard surface.

Note: The height of the sample should be no more **than 2-3 mm**.

Determining the Melting Point

The accuracy of the melting point depends on the accuracy of the thermometer, so the first exercise in this experiment will be to calibrate the thermometer.

1- **Melting points of pure**, known compounds will be determined and deviations recorded so that a correction can be applied to future melting points.

2- The most critical factor in determining an accurate melting point is the **rate of heating**. At the melting point the temperature rise should not be greater than 1°C per minute. This may seem extraordinarily slow, but it is necessary in order that heat from the bath be transferred **equally** to the **sample** and to the **glass and mercury of the thermometer**.

Part 1: Calibration of the Thermometer

Determine the melting point of standard substances (Table 1) over the temperature range of interest.

Include both temperatures making up the **melting point range**. Use your data to graph a correction curve for your thermometer.

Compound	Observed m.p. Range (Ti-Tf)	Average	Literature m.p.
1,4-Dichlorobenzene			
Acetanilide			
Salicylic Acid			
4-Nitrobenzoic acid			

Part 2: Melting Points of Unknown

To determine the melting point of an unknown provided by your instructor:

Prepare **two capillaries of each unknown**. Run a very **fast** determination on the first sample to ascertain the approximate melting point and then cool the melting point bath to just below the melting point and make a **slow**, careful determination using the other capillary.

You may wish to run a **mixed melting** point as well.