



The Determination of Boiling Points and Melting Points of Organic Compounds

During this laboratory session, we will practice determining the boiling point of a liquid organic compound and the melting point (or we could call it the freezing point) of a solid organic compound. The boiling point of a liquid is the temperature at which the pressure of the vapor above a liquid equals the existing pressure. As we heat a liquid, the pressure of the vapor above the liquid slowly increases. When this pressure equals the pressure existing in the container, the liquid begins to boil— the liquid turns to vapor. If not contained, the vapor will “escape” into the atmosphere. In other words, the liquid evaporates. If the vapor is contained, and then passed through an area where the temperature is lower, the vapor will “condense” and enter the liquid state again. This would be a distillation.

Atmospheric pressure is approximately 760 mm Hg; *i.e.*, the weight of a column of mercury measuring 1 mm² and 760 mm tall. This equates to about 29.7 inches of mercury. If we reduce the pressure above the sample that we are heating, we can reduce the boiling point of the liquid. This is referred to as a vacuum distillation or carrying out a distillation *in vacuo*. For example, while water boils at 100° C (or 212° F) at 760 mm Hg, it boils around 22° C at 20 mm Hg.

The boiling point of a liquid is a physical characteristic of a compound. Many factors go into the estimation of the boiling point of a liquid such as the shape (round, oval, elongated), the mass and most importantly, hydrogen bonding (H-bonding). Methane with a mass of 16 does not engage in H-bonding and is a gas at room temperature while water (mass 18) boils at 100° C. While we can often guess the relative boiling points of a series of compounds, it is rather difficult to calculate a boiling point based on first principals.

Similarly, the melting point of a compound is a physical property which we can guess at although we can not predict it on theoretical grounds. The more polar the compound, the higher the melting point; the heavier the molecule, the higher the molecular weight. To determine the melting point of a compound, we simply put a very small amount into a very small “test tube”— actually a melting point capillary— and slowly heat the sample while watching it through a magnifying glass. We can see it begin to melt as liquid is observed and when the melting is completed, and only liquid is visible, we report a melting point range. A pure sample of a melting point generally has a very sharp melting range— no more than 3°— while an impure sample generally has a rather broad melting range, often 6-10° or more. By comparing the melting range of a sample to those in a list presented in a text or reference book, we can often make a case that we know what unknown we have. If possible, we then try a “mixture melting point” to prove our case. Let us assume that we have an unknown which melts at 120-122°. Let us assume that we also know that it is an acid. From a text, we might guess that our sample is benzoic acid which has a reported melting point (or melting range) of 121-122°. To prove the conclusion, we can take a small amount of our unknown and mix it thoroughly with some authentic benzoic acid that we have obtained from a different source. If we have mixed benzoic acid with benzoic acid, the m. pt. of the mixture will be the same as either sample; 120-122°. But if our sample really was not benzoic acid, then we have contaminated the authentic benzoic acid with our sample (or contaminated our sample with benzoic acid), and the melting point will now be lower and broader, perhaps 95-110°.

Today's Experiment

You will set up a distillation apparatus at your workspace as demonstrated during the pre-lab lecture. Two important things to remember: water always goes into the condenser at the lower nozzle and exits from the higher nozzle (it wouldn't fill up if you set it up backwards) and the bulb of the thermometer must be below the exit to the condenser. If it is higher, vapors will simply pass below the thermometer bulb without transferring energy to the bulb. (It wouldn't warm up the thermometer bulb.) If the bulb is too low, then hot liquid splashes on the bulb and your reading will be in error. Have the instructor or the teaching assistant verify that you are correctly set up.

Using the sample assignment at the end of the experiment on the following page, obtain 20-25 mL of the liquid sample and note the volume that you have taken. The sample is introduced into a 50 mL round bottomed flask— the distilling flask— along with 1-2 “boiling chips”. Start the flow of cooling water and then apply heat by turning the knob on the controller for your heating mantle. A setting of 3-4 is likely to be appropriate

for today's experiment. Allow the boiling/distillation to continue until the system comes to equilibrium. At this point, liquid will be dripping from the end of the condenser and the temperature reading on your thermometer will level off and remain constant for a considerable period of time. This is the boiling point or boiling range that you should report. If the boiling point suddenly changes, either upward or downward, turn off the heat and cease the distillation. Determine the volume of product collected. Weigh the isolated product. Report the percent recovery, in terms of volumes, and the b. pt. For example, if you started with 24 mL and collected 18 mL of distilled product, you would have a 75% recovery. From the list below, select the most likely compound for your unknown. Report the experimentally determined density of your compound.

Compound	Methanol	95% Ethanol	1 -Propanol	Methyl <i>t</i> -butyl ether	1-Butanol
B. Pt.	65°	78°	97°	55°	130°
Density (g/mL)	0.791	0.789	0.785	0.741	0.775

Melting Points

Using the unknown assignments below, determine the m. pt. of your sample, and then select the appropriate material for a mixture melting point from the table below and determine the m. pt. of the mixture. Also do a mixture m. pt. with a known which is NOT your unknown. Report the name of the compound that you believe to be your unknown along with the m. pt. of the sample and the mixture.

Compound	Benzoic Acid	Cinnamic Acid	Acetanilide	Methyl <i>m</i> -nitrobenzoate	Naphthalene
Reported m.pt.	121-122°	133-134°	114°	78°	80-82°

Unknown Assignments

Sample	Workstation Number			
A	1	6	11	16
B	2	7	12	17
C	3	8	13	18
D	4	9	14	19
E	5	10	15	20

Report

Your report should include the following:

For the liquid: identifier, name, structure, experimental bp, expected bp, volume, yield based on volume.
 For the solid: identifier, name, structure, experimental mp, expected mp, mp of mixture with correct substance, mp of mixture with incorrect substance.