

• **BOILING POINT DETERMINATION**

The physical properties of a compound, such as melting point and boiling point can provide useful information which can help in the identification of a sample or to establish its purity. Since the boiling point of an unknown sample under the same conditions (*e.g.* same pressure) is a constant, a measured boiling point can be compared to known values (*e.g.* literature value or the measured value of a known sample). Since this used to be a very important method, there are tables and collections of boiling point data available and the boiling point at sea level (as a standard) is one of the physical properties of a compound that is commonly recorded and reported

Background

If a sample of a liquid is placed in an otherwise empty space, some of it will vapourise, and the pressure in the space above the liquid will rise to some constant value. The pressure under these conditions is due entirely to the vapour of the liquid, and is called the equilibrium vapour pressure. The phenomenon of vapour pressure is interpreted in terms of molecules of liquid escaping into the empty space above the liquid. In order for the molecules to escape from the liquid phase into the vapour phase, the intermolecular forces (in order of increasing strength: Van der Waals, dipole-dipole, hydrogen bonding) have to be overcome which requires energy. Since the nature of the intermolecular forces is determined by the molecular structure, then the amount of energy required to vapourise the sample also depends on the molecular structure an example of the relationship between structure and properties. As the number of molecules in the vapour above the liquid becomes larger, the rate of return of the molecules from the vapour to the liquid increases until the rate of return is equal to the rate of escape. This is the equilibrium condition and the corresponding concentration of molecules in the vapour space gives rise to the equilibrium vapour pressure At higher

temperatures, the greater average kinetic energy of the molecules in the liquid results in a greater constant rate of escape. Equilibrium is established at higher temperatures, and so larger numbers of molecules are present in the vapour phase and the pressure is higher

When the vapour pressure of a liquid is equal to the atmospheric (or applied) pressure then boiling occurs. The temperature at which this occurs, for a given pressure, is the boiling point. It should be noted, therefore, that the boiling point of a liquid *decreases* as the atmospheric (or applied) pressure *decreases*. This is illustrated by the Vapour Pressure-Temperature Curve above. For example, at sea level the atmospheric pressure is 760 mm Hg (also expressed as 760 torr, 101325 Pa, 101.3 kPa, 1013.25 mbar or 14.696 psi) and pure water boils at 100°C. However, in Calgary (approx. 1050m above sea level) the atmospheric pressure is approximately 670 mm Hg, and water boils at about 96.6°C.

Boiling point can be determined in a few different ways. If a reasonably large volume of sample is available, then the boiling point of the liquid can be determined using a simple distillation apparatus setup (see simple distillation, technique T.6). However, when large volumes are not available, alternative experimental procedures have to be used. The micro-boiling point method described below can be carried out with just a few mL of a liquid sample and is a reasonably accurate and convenient way to determine the boiling point.

Micro-Boiling Point Determination

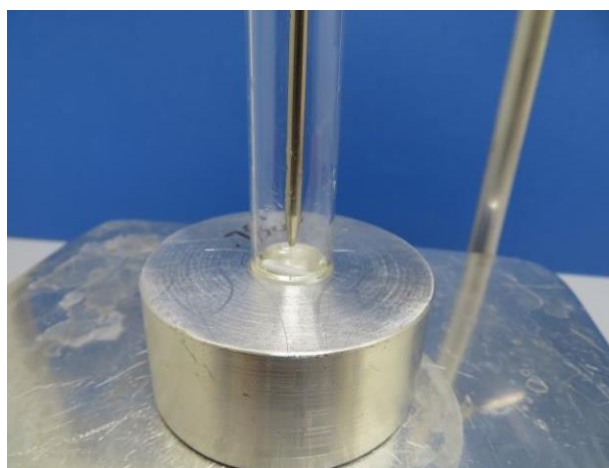
Micro reflux method



Hot apparatus !

The stirrer bar is important to avoid “bumping” of hot liquid Set up and use apparatus in a fumehood

The sample liquid (approx. 0.5 mL) is introduced into a 150mm diameter test tube using a Pasteur pipette and a small magnetic stirring bar is added. The test tube is placed in the metal heating block centered on a hot plate stirrer and carefully clamped in place. The thermometer is clamped in a small piece of rubber tube and lowered in to place such that the bulb or tip of the thermometer is about 1 cm above the surface of the liquid.



Once the set-up is complete, turn on the stirrer to give *gentle* stirring of the liquid and then start to heat. Look for the liquid to be boiling (bubbles) and just above the liquid, the vapour condensing and running back into the boiling liquid (i.e. the liquid is refluxing). This is often visible as a ring of liquid on the walls of the glass. The bulb or tip of the thermometer needs to be at the level of this ring for accurate measurement. Once the liquid is gently refluxing, the thermometer temperature reading should be fairly stable and correspond to the observed boiling point of the liquid sample. Make sure not to boil the sample dry. Once the boiling point has been measured, stop heating the metal block (but leave it stirring).



The equipment will be HOT!

Remove the thermometer assembly and remember to wipe off the thermometer. Remove the test tube and stand in a test tube rack and allow to cool.

The metal block can be cooled in ice by carefully picking it up with metal tongs (as shown to the left) or with a heat resistant glove.

Remember to make sure to remove the magnetic stirrer bar from the boiling point test tube.

The explanation of this method is a very simple one. Once a liquid boils, the temperature of the vapour will not increase until all of the liquid has boiled and converted to the vapour phase. Therefore, provided the liquid sample is being heated at reflux, the temperature of the vapour will match the boiling point of the liquid.

Two problems are common to this method.

The first arises when the liquid sample in the test tube is heated too strongly such that it evaporates or is boiled away. This is more likely to be a problem for liquids with low boiling points. Once the test tube and block have cooled, add more liquid sample to the test tube and resume heating but more gently.

Second, for liquids with high boiling points it might be difficult to reach reflux and it might be necessary to move the tip or bulb of the thermometer closer to the liquid surface.

Don't forget to apply a correction due to the reduced atmospheric pressure in Calgary (altitude). To ensure accuracy, you should carry out at least two separate boiling point determinations on your unknown sample.

Thiele tube method (quick link to videos : [version 1](#), [version 2](#))



Before using a Bunsen burner make sure all flammable materials (e.g. solvents) are removed from the area around the Bunsen burner.

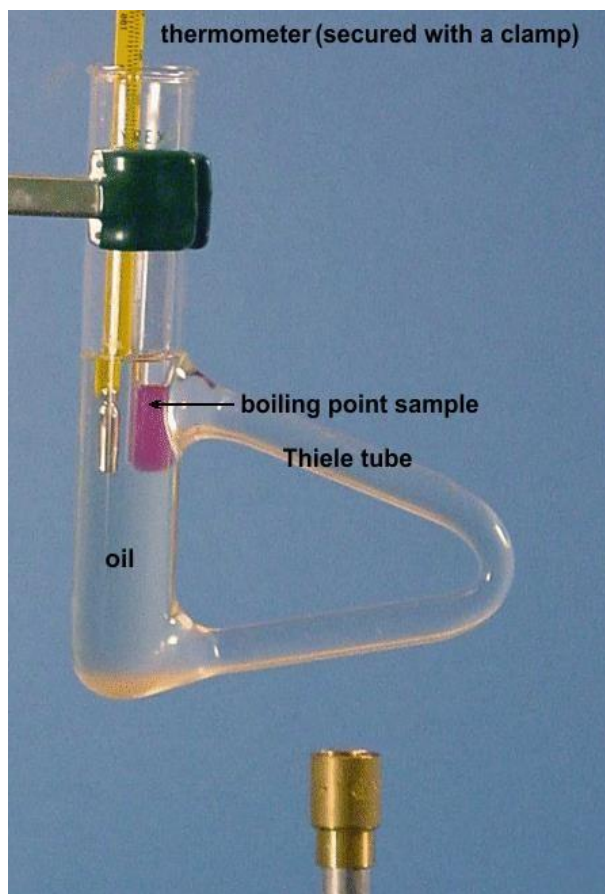
This means not only your

workspace but also all the students near to you.

When using the Bunsen burner, make sure that you adjust it to a small flame.

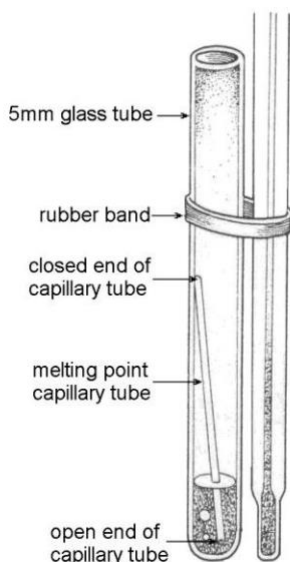
If you are unsure of how to set up and use a Bunsen burner, see the “[heat sources](#)” techniques document and the video on the [Bunsen burner](#).

If only small amounts of liquid material are available for boiling point determination, then a micro boiling point apparatus based on a Thiele tube can be used. The Thiele tube is a glass tube designed to contain heating oil and a thermometer to which a micro test tube containing the boiling point sample is attached. The shape of the Thiele tube allows for formation of convection currents in the oil when it is heated. These currents maintain a fairly uniform temperature



distribution throughout the oil in the tube. The side arm of the tube is designed to generate these convection currents and thus transfer the heat from the flame evenly and rapidly throughout the heating oil. Don't clamp the Thiele tube too tightly otherwise it might crack as it expands as it is heated, yet of course it needs to be secure.

The sample liquid is introduced by Pasteur pipette into a micro test tube (no more than 0.5ml, which is about 10mm depth in the small test tube), and a piece of melting point capillary tubing (sealed at one end) is dropped in with the open end down. The micro test tube assembly is then attached to a thermometer with a rubber band or a thin slice of rubber tubing. The whole unit is then placed in a Thiele tube.



The placement of the test tube / thermometer unit in the Thiele tube is important:

- i. the micro test tube should be on the same side of the Thiele tube as the elbow
- ii. neither the test tube nor the thermometer bulb should be touching the glass walls of the Thiele tube
- iii. the base of the micro test tube should be just below the joint to the upper part of the elbow (see photograph above)
- iv. the rubber band should be placed well above the level of the oil in the Thiele tube, and,
- v. the oil level should be just above the top elbow joint. If the rubber band enters the oil, the band may soften and break in the hot oil allowing the micro test tube to fall into the oil.

When positioning the band, one should bear in mind that the oil will expand when it is heated.

Once the set up has been complete, the lower part of the side arm of the Thiele tube is **carefully** heated with a **small flame** from the Bunsen burner moving the flame back and forth along the arm. During the heating, there is an initial stream of bubbles as air is expelled and then, a little later, a rapid and continuous stream of bubbles emerges from the inverted capillary tube. At this point stop heating. Soon the stream of bubbles will slow down and stop. When they stop, the liquid sample will be drawn up in to the capillary tube. The moment when the liquid enters the capillary corresponds to the boiling point of the liquid, and the temperature should be recorded.