1. The Determination of Boiling Point

Objective

In this experiment, you will first check your thermometer for errors by determining the temperature of two stable equilibrium systems. You will then use your calibrated thermometer in determining the boiling point of an unknown substance.

Introduction

The most common laboratory device for the measurement of temperature is, of course, the thermometer. The typical thermometer used in the general chemistry laboratory permits the determination of temperatures from $-20°$ to 120°C. Most laboratory thermometers are constructed of glass, and so they are very fragile. Most general chemistry lab thermometers contain a red-colored organic liquid as the temperature-sensing fluid. This liquid is flammable and may be toxic: If a thermometer is broken, you should shut off any flames in the vicinity and consult with the instructor. Until recently, many lab thermometers contained elemental mercury metal as the temperature-sensing fluid. Mercury, especially its vapor, is very toxic, however, and most labs have replaced mercury thermometers with the red-liquid type.

The typical laboratory thermometer contains a bulb (reservoir) of temperature-sensing liquid at the bottom; it is this portion of the thermometer which actually senses the temperature. The glass barrel of the thermometer above the liquid bulb contains a fine capillary opening in its center, into which the liquid rises as it expands in volume when heated. The capillary tube in the barrel of the thermometer has been manufactured to very strict tolerances, and it is very regular in cross-section along its length. This ensures that the rise in the level of liquid in the capillary tube as the thermometer is heated will be directly related to the temperature of the thermometer's surroundings.

Although the laboratory thermometer may appear similar to the sort of clinical thermometer used for determination of body temperature, the laboratory thermometer does *not* have to be shaken before use. Medical thermometers are manufactured with a constriction in the capillary tube that is intended to prevent the liquid level from changing once it has risen. The liquid level of a laboratory thermometer, however, changes immediately when removed from the substance whose temperature is being measured. For this reason, temperature readings with the laboratory thermometer must be made while the bulb of the thermometer is actually present in the material being determined.

Because the laboratory thermometer is so fragile, it is helpful to check that the thermometer provides reliable readings before any important determinations are made with it. Often, thermometers develop nearly invisible hairline cracks along the barrel, making them unsuitable for further use. This happens especially if you are not careful in opening and closing your laboratory locker.

To check whether or not your thermometer is operating correctly, you will *calibrate* the thermometer. To do this, you will determine the reading given by your thermometer in two systems whose temperature is known with certainty. If the readings given by your thermometer differ by more than one degree from the true temperatures of the systems measured, you should exchange your thermometer, and then calibrate the new thermometer. A mixture of ice and water has an equilibrium temperature of 0°C, and will be used as the first calibration system. A boiling water bath, whose exact temperature can be determined from the day's barometric pressure, will be used as the second calibration system in this experiment.

Once your thermometer has been calibrated, you will use the thermometer to determine the *boiling point* of an unknown liquid as a means of identifying the liquid. The boiling point of a pure substance is important because it is *characteristic* for a given substance (at a particular barometric pressure). That is, under the same laboratory conditions, a given substance will always have the *same* boiling point. Characteristic physical properties (such as the boiling point of a pure substance) are of immense help in the *identification of unknown substances*. Such properties are routinely reported in scientific papers when new substances are isolated or synthesized, and are compiled in tables in the various handbooks of chemical data that are available in science libraries. When an unknown liquid substance is isolated from a chemical system, its boiling point may be measured (along with certain other characteristic properties) and then compared with previously tabulated data. If the experimentally determined physical properties of the unknown match those found in the literature, you can typically assume that you have identified the unknown substance.

The **boiling point** of a liquid is defined as the temperature at which the vapor escaping from the surface of the liquid has a pressure equal to the pressure existing above the liquid. In the most common situation of a liquid boiling in a container open to the atmosphere, the pressure above the liquid will be the day's barometric pressure. In other situations, the pressure above a liquid may be reduced by means of a vacuum pump or aspirator, which enables the liquid to be boiled at a much lower temperature in an open container (this is especially useful in chemistry when a liquid is unstable, possibly decomposing if it were heated to its normal boiling point under atmospheric pressure). When boiling points are tabulated in the chemical literature, the pressure at which the boiling point determinations were made are also listed. The method to be used for the determination of boiling point is a semimicro method that requires only a few drops of liquid.

The apparatus used for heating samples in this experiment is called a **Thiele tube**. The Thiele tube contains oil (typically mineral oil) as a fluid, which permits the determination of temperatures up to about 200°C. The Thiele tube is constructed in such a way that when the side arm is heated, the warm oil will rise and enter the main chamber of the tube, which provides for circulation of the oil and for a more uniform temperature. Samples to be placed in the Thiele tube are ordinarily positioned so that the sample is aligned with the top branch of the side arm. When using a Thiele tube, ***remember that it contains hot oil,*** which can be dangerous if caution is not exercised.

SAFETY PRECAUTIONS

- **Wear safety glasses at all times while in the laboratory.**
- **Thermometers are often fitted with rubber stoppers as an aid in supporting the thermometer with a clamp. Inserting a thermometer through a stopper must be done carefully to prevent breaking of the thermometer, which would release mercury and possibly cut you. Your instructor will demonstrate the proper technique for inserting your thermometer through the hole of a rubber stopper. Glycerine is used to lubricate the thermometer and stopper. Protect your hands with a towel during this procedure.**
- **The red liquid used as the temperature-sensing liquid in lab thermometers is flammable. If a red-liquid thermometer breaks, extinguish all flames in the vicinity. Mercury is poisonous and is absorbed through the skin. Its vapor is toxic. If mercury is spilled from a broken thermometer, inform the instructor immediately so that the mercury can be removed. Do not attempt to handle spilled mercury.**
- **The liquids used in this experiment are flammable. Although only small samples of the liquids are used, the danger of fire is not completely eliminated. Keep all liquids away from open flames.**
- **The liquids used in this experiment are toxic if inhaled or absorbed through the skin. The liquids should be disposed of in the manner indicated by the instructor.**
- ***Caution*: Oil is used as the heating fluid in the Thiele tube used for the boiling/melting point determinations that follow. Hot oil may spatter if it is heated too strongly, especially if any moisture is introduced into the oil from glassware that is not completely dry. The oil may smoke or ignite if heated above 200°C.**

Apparatus/Reagents Required

Thermometer and clamp, several beakers, Thiele tube, melting point capillaries, glass tubing (5–6-mm-diameter), burner and rubber tubing, file, scissors, medicine dropper, unknown sample for boiling point determination, ice

Procedure

Record all data and observations directly in your notebook in ink.

A. Calibration of the Thermometer

Fill a 400-mL beaker with ice, and add tap water to the beaker until the ice is covered with water. Stir the mixture with a stirring rod for 30 seconds.

Clamp the thermometer to a ringstand so that the bottom 2–3 inches of the thermometer is dipping into the ice bath. Make certain that the thermometer is suspended freely in the ice bath and is not touching either the walls or the bottom of the beaker.

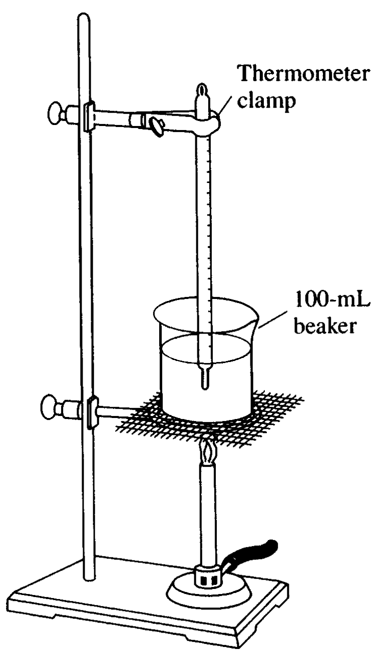
Allow the thermometer to stand in the ice bath for 2 minutes, and then read the temperature indicated by the thermometer to the nearest 0.2 degree. Remember that the thermometer must be read while still in the ice bath. If the reading indicated by the thermometer differs from 0°C by more than one degree, replace the thermometer and repeat the ice bath calibration.

Allow the thermometer to warm to room temperature by resting it in a safe place on the laboratory bench.

Set up an apparatus for boiling as indicated in Figure 1-1, using a 100-mL beaker containing approximately 75 mL of water. Add 2–3 boiling chips to the water, and heat the water to boiling.

FIGURE 1-1

Apparatus for boiling. Make certain that the thermometer is freely suspended in the water and is not touching the walls of the beaker.



Using a clamp, suspend the thermometer so that it is dipping halfway into the boiling water bath. Make certain that the thermometer is not touching the walls or bottom of the beaker. Allow the thermometer to stand in the boiling water for 2 minutes; then record the thermometer reading to the nearest 0.2°C.

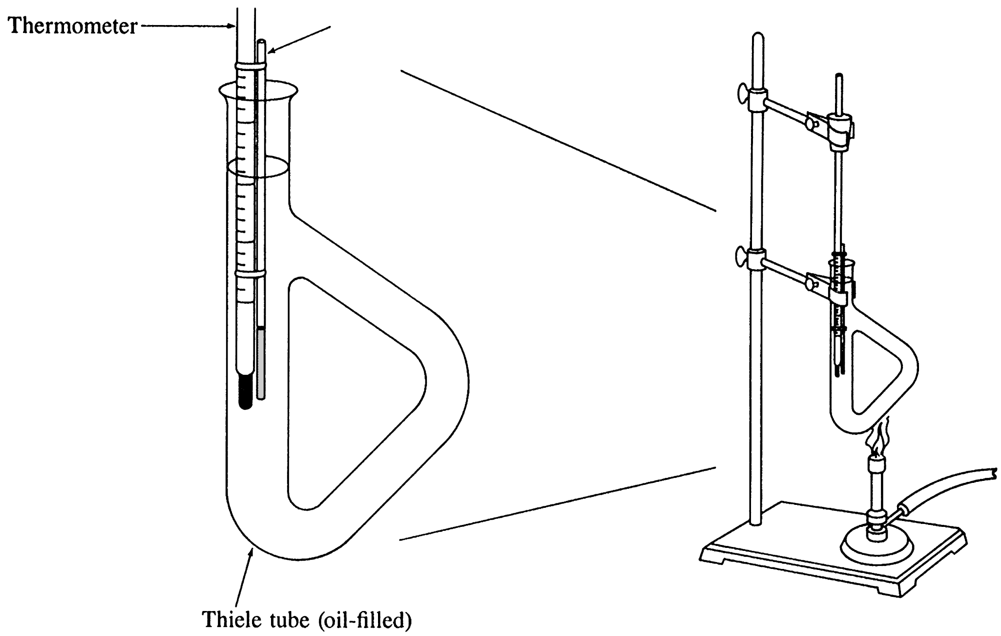
A boiling water bath has a temperature near 100°C, but the actual temperature of boiling water is dependent on the barometric pressure and changes with the weather from day to day. Your instructor will list the current barometric pressure on the chalkboard. Using a handbook of chemical data, look up the actual boiling point of water for this barometric pressure and record.

If your measured boiling point differs from the handbook value for the provided barometric pressure by more than one degree, exchange your thermometer at the stockroom, and repeat the calibration of the thermometer in both the ice bath and the boiling water bath.

B. Determination of Boiling Point

Set up a Thiele tube filled with oil as indicated in Figure 1-2. Examine the oil to make certain that it is not cloudy or contaminated with any substance. If the oil appears cloudy or contaminated, consult with the instructor about replacing the oil. The oil bath will be used to heat the boiling point sample evenly. Remember that hot oil can spatter or ignite if heated too quickly or too strongly.

FIGURE 1-2 Thiele tube oil bath for boiling/melting determinations. Exercise caution when dealing with heated oil.



Obtain a clean 10×75-mm semimicro test tube, which will contain the boiling point sample. Attach the test tube to the lower end of your thermometer with two small rubber bands.

Obtain an unknown liquid for boiling point determination from your instructor, and record the identification code number of the unknown in your notebook and on the lab report page. Transfer part of the unknown sample to the small test tube, until the test tube is approximately half full.

Obtain a melting point capillary. If the capillary tube is open at both ends, heat one end briefly in a flame to seal it off. Using a glass file, carefully cut the capillary about 1 inch from the sealed end. Do *not* fire-polish the cut end of the capillary. Place the small portion of capillary *sealed end up* into the boiling point sample in the test tube.

The capillary has a rough edge at the cut end, which serves as a surface at which bubbles can form during boiling. The capillary is filled with air when inserted sealed end up into the liquid, and the presence of this air can be used to judge when the vapor pressure of the unknown liquid reaches atmospheric pressure.

Lower the thermometer/sample into the oil bath, so that the bulb of the thermometer and the sample are level with the upper branch of the Thiele tube's side arm. The Thiele tube is constructed in such a manner that when the side arm is heated, oil will circulate from the side arm into the main chamber. This makes it unnecessary to stir the oil bath.

Begin heating the side arm of the Thiele tube with a low flame, so that the temperature rises by one or two degrees per minute. Watch the small capillary tube in the unknown sample while heating. As the sample is heated, air in the capillary tube will begin to bubble from the capillary. As the air bubbles from the capillary, it is gradually replaced by vapor of the unknown. As the liquid begins to boil, the bubbles coming from the capillary will form a continuous, rapid stream. When the capillary begins to bubble continuously, remove the heat from the Thiele tube. The liquid will continue to boil.

Watch the capillary in the unknown sample carefully after removing the heat. The bubbling will slow down and stop after a few minutes, and the capillary will begin to fill with the unknown liquid. Record the temperature at which the bubbling stops. At this point (where bubbling stops), the vapor pressure of the liquid is just equal to the barometric pressure.

Allow the oil bath to cool by at least 20°C. Add additional unknown liquid to the small test tube, as well as a fresh length of capillary tube (it is not necessary to remove the previous capillary). Repeat the determination of the boiling point of the unknown. If the repeat determination of boiling point differs from the first determination by more than one degree, do a third determination.

Your instructor may provide you with the identity of your boiling point sample. If so, look up the true boiling point of your sample in a handbook of chemical data. Calculate the percent difference between your measured boiling point and the literature value.

The Determination of Boiling Point

Date:	....	Student name:	....
Course:	....	Team members:	....
Section:	....		....
Instructor:	....		....

Prelaboratory Questions

1. Why is a *mixture* of ice and water, rather than ice alone, used in calibrating a thermometer?

2. Why does the boiling point of a liquid vary with the *barometric pressure*?

3. Using a handbook of chemical data, find the boiling points of water at the pressures indicated below. Give the reference for the data you list.

   75 mm Hg ....

   375 mm Hg ....

   760 mm Hg ....

   799 mm Hg ....

   Reference ....

The Determination of Boiling Point

Date: ....
Course: ....
Section: ....
Instructor: ....

Student name: ....
Team members: ....
....
....

Results/Observations

A. Calibration of the Thermometer

Temperature in ice/water bath ....

Thermometer error at ice/water temperature ....

Temperature in boiling water ....

Barometric pressure ....

True boiling point of water at this pressure ....

Thermometer error in boiling point of water ....

B. Determination of Boiling Point

Identification number of unknown liquid sample ....

First determination of boiling point ....

Second determination of boiling point ....

Mean value for unknown boiling point ....

Questions

1. What is meant by the *normal* boiling point of a substance?

2. Food products such as cake mixes often list special directions for cooking the products in high-altitude areas. Why are special directions needed for such situations? Would a food take a longer or shorter time period to cook under such conditions? Why?