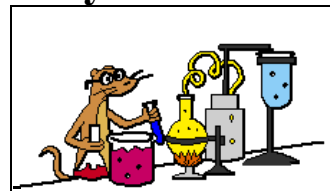


EXPERIMENT 2 (Organic Chemistry I)

Micro Method Determination of Boiling Point of Hydrocarbons



Purpose:

- To become acquainted with procedure in evaluating physical properties such as boiling point and the use of boiling point in identifying liquid.
- To determine the boiling points of various organic compounds and to use these to identify unknowns.

Equipment / Materials:

hot plate	closed end capillary tube	thermometer	beaker tongs
400 mL beaker	small test tube		liquid organic compounds

Discussion

The boiling point of a compound is the temperature at which it changes from a liquid to a gas. This is a physical property often used to identify substances or to check the purity of the compound.

It is difficult, though, to find a **boiling point**. Usually, chemists can only obtain a boiling range of a 2 - 3°C accuracy. This is usually sufficient for most uses of the boiling point.

The Boiling point of a liquid is an important physical property. A liquid boiling point is the temperature when its vapor pressure is equal to the atmospheric pressure. Normally, the boiling point is measured at one atmosphere (101 kPa or 760 mmHg or 760 torr). Like melting points, boiling points are characteristic properties of pure materials. Boiling points are approximately related to their molecular weight, the higher the molecular weight, the higher the boiling point.

Boiling point is the temperature at which the vapor pressure of the liquid exactly equals the pressure exerted on it, causing the liquid to "boil" or change to the gas phase. For purposes of this laboratory experiment, the boiling point of an organic liquid is the **temperature range** over which the state of the organic compound changes from the liquid phase to the gas phase at 760mm of pressure. While the boiling point is a characteristic physical property of a compound, many compounds may have the same boiling point.

The molecules of compounds that exist in the liquid state are relatively close together, compared with molecules of gaseous compounds. The close proximity of molecules in the liquid state allow these molecules to interact via **non-covalent interactions** (dipole-dipole, H-bonding, van der Waals forces). In general, these interactions are favorable and help to hold the molecules together in a defined volume, but still allow free motion or "flow". Conversely, molecules of a gaseous compound are much farther away from each other and are not confined to a specific volume by non-covalent interactions (Fig. 1). If enough energy (often in the form of heat) is provided to the liquid, the molecules begin to move away from each other by "breaking" the non-covalent forces that hold the compound in the liquid state.

Thus, the boiling point is the temperature range over which enough energy is provided to a liquid compound so that its molecules can separate sufficiently to transform to a gaseous state by breaking *non-covalent interactions*. *No covalent bonds are broken during a change from the liquid phase to the gas phase.*

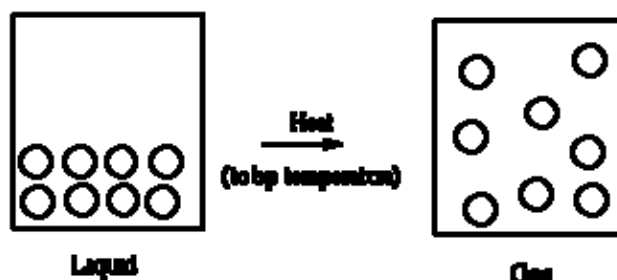


Fig.1: Phase Change from Liquid to Gas at Boiling Point Temperature Range

The vapor pressure, P_{vapor} , exerted by a liquid is directly proportional to the temperature. Thus if the atmospheric pressure, P_{atm} , is lowered, the temperature to which the liquid must be heated in order for P_{vapor} to P_{atm} is lowered. The boiling point will change by approximately 0.5°C for each 10 mm (10 mmHg) change in pressure.

Thus the change in b.p. = $\Delta T_b = [(P_{\text{vapor}} - P_{\text{atm}})](0.5^{\circ}\text{C} / 10 \text{ mm})$

The corrected b.p. = $T_b = \text{normal b.p.} + \Delta T_b$

Example - What will be the boiling point of ethanol at 700 mmHg when its normal point at 760 mmHg is known to be 78.3°C ?

$$\Delta T_b = [(P_{\text{vapor}} - P_{\text{atm}})](0.5^{\circ}\text{C} / 10 \text{ mm}) = (700 - 760)(0.5^{\circ}\text{C} / 10 \text{ mm}) = -3^{\circ}\text{C}$$

$$T_b = \text{normal b.p.} + \Delta T_b = 78.3^{\circ}\text{C} + (-3^{\circ}\text{C}) = 75.3^{\circ}\text{C}$$

In theory when a liquid is at its boiling point one should observe bubbles of vapor forming as the liquid changes to the vapor phase. However in practice this is usually not the case. Typically the liquid becomes superheated as its temperature climbs above the true boiling point commences. Then the solution suddenly “bumps” or boils with tremendous vigor, bumping the hot liquid out of the container. Steps must be taken to guard against this process.

In order to promote smooth boiling the solution can be stirred, or boiling stones (boiling chips) can be added to the liquid. These glassy type devices work by providing a sharp surface upon which bubbles naturally forms which promote smooth generation of bubbles (prevent bumping and formation of large bubbles).

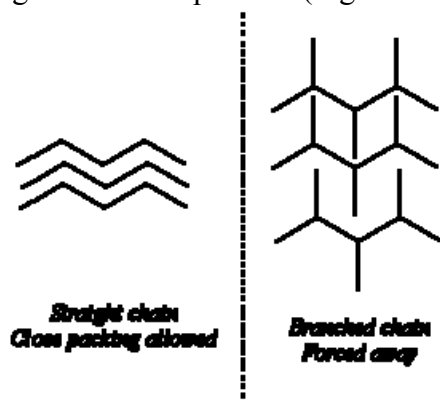
If the volume of the liquid is small, it is more advantageous to use the micro method, as in this experiment. However, if the volume of the liquid is large, its boiling point can be determined by distillation, as in later experiment.

Factors Influencing Boiling Point

Structural features of a compound influence the boiling point by increasing or decreasing the molecules' ability to establish and maintain non-covalent interactions that hold the molecules close together in the liquid state.

The structural features of a compound that influence boiling point are:

- a) **Polarity** - Increased H-bonds, polar covalent bonds or formal charges in a molecule tend to increase the boiling point. More polar elements in a molecule increase the total number of dipole-dipole, ion-dipole and/or H-bonding interactions. More energy (higher boiling point temperature) is necessary to break these interactions and allow the molecules to move away from each other into a gaseous state.
- b) **Molecular Weight**: Increased molecular weight increases boiling point. A higher molecular weight compound has more atoms that can be involved in non-covalent interactions. The greater the number of non-covalent interactions, the more energy (higher boiling point temperature) that is necessary to break the non-covalent interactions to transform the compound from the liquid phase to the gas phase.
- c) **Branching**: Branching decreases boiling point. Branching blocks molecules from packing together too closely. The closer molecules are, the stronger the non-covalent interactions. Thus, molecules that are forced to be farther away from each other due to branching have weaker non-covalent interactions. Less energy (lower temperatures) is needed to induce a phase change from the liquid phase to the gas for branched compounds relative to straight chain compounds. (Fig. below)



Experimental Procedure

A small volume (≈ 5 ml) of the liquid is placed in a small test tube. A capillary, sealed at one end, is placed open-end down into the liquid (Fig. 1). The test tube is firmly attached to a thermometer with a rubber band, and this entire assembly, and clamps the apparatus to a ring stand (Fig. 2). Immerse the assembly in a water bath (or and oil bath for samples with boiling point higher than 100°C) (Fig. 3). As the temperature is slowly increased, a rapid evolution of bubbles from the end of the tube begins. Continue heating for about 5-10 seconds to be sure that all of the air has been expelled from the capillary, and the vapors of the liquid remains in the capillary. Remove the heat, but do not take the assembly out of water bath (or oil bath), and carefully watch the capillary. Bubbles continue to be seen until the pressure exerted by the vapor of the liquid becomes equal to the atmospheric pressure. As the temperature decreases, the bubbles will slow down and at some point, the liquid will rise into the capillary. The boiling point of the sample is reached when the bubbles stops. Read the thermometer and record the temperature. The temperature observed when this happens should be the observed boiling point of the liquid. Compare your experimental result to the literature value (Table below) of the boiling point for the liquid used. If your technique is good, your experimental value should not differ from the known value (literature value) by more than $2\text{-}3^\circ\text{C}$. Repeat the procedure with the known liquids. Each time you perform the procedure, you must use a new capillary. It will also be necessary to allow the hot bath to cool at least $15\text{ - }20^\circ\text{C}$ below the suspected boiling point before repeating your experiment.

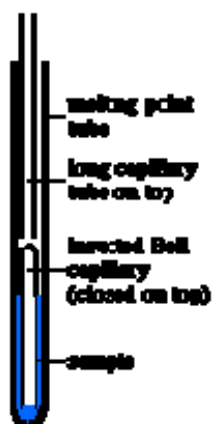


Fig. 2 - Small test tube and capillary, sealed at one end

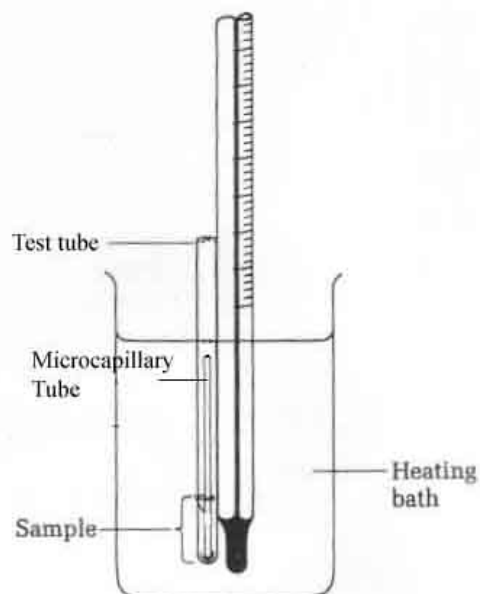


Fig. 3- Small Scale Boiling Point Apparatus

Substance	Boiling Point (°C)
Pentane	36.1
Hexane	69
Heptane	98.4
Octane	125.7
2-Methylheptane	117.7
3-Methylheptane	119
2,2-Dimethylhexane	106.8
3-Ethylpentane	93.5
2,2,4-Trimethylpentane	99.2
Acetone	56- 57
Methanol	65
Ethanol	78-79
Propanol	97-98
2-Propanol(isopropanol)	82-83
Water	100
t-Butyl alcohol	83
Cyclohexane	80.7
Methylene chloride	39.8
Bromoform	146-150

Table - 1

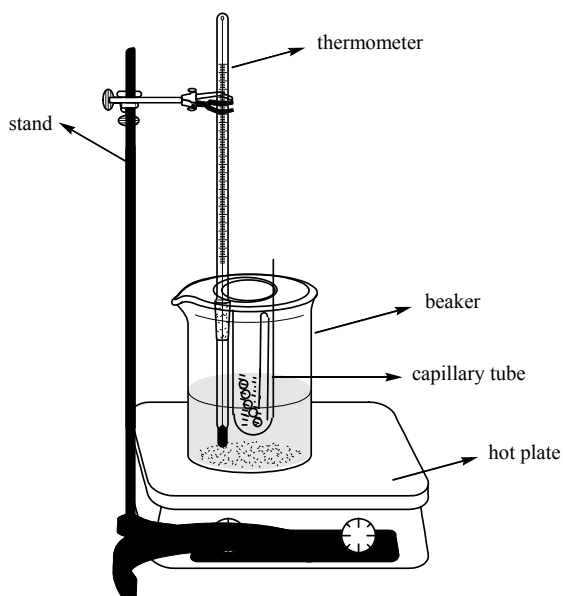


Fig. 4 - Boiling Point Apparatus Set Up

EXPERIMENT 2 – Boiling Point Determination

Data and Results (Boiling Point)

REPORT FORM

Name _____

Instructor _____

Date _____

Part I. Boiling Points of known compounds

(Practice compounds)

<u>Name of compound</u>	<u>B.P., °C (range)</u> <u>(Experimental)</u>	<u>B.P., °C</u> <u>(Literature)</u>
(a) _____	(_____ - _____)	_____
(b) _____	(_____ - _____)	_____
(c) _____	(_____ - _____)	_____

Part II. Boiling Point of an unknown Sample

(Unknown)

Unknown Sample Number = _____

Boiling Point of unknown sample

Trial 1: _____ - _____ °C (range)

Trial 2: _____ - _____ °C (range)

Trial 3: _____ - _____ °C (range)

My unknown compound is _____
(name of compound)

Pre-Laboratory Questions–EXP 2 Name:

Due before lab begins. Answer in space provided.

1. Which of the compounds, ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, or methanol, CH_3OH , should have the higher boiling point? Why?
2. How would the boiling point change if the atmospheric pressure increased or decreased?
3. What is the effect of a small amount of impurity on the boiling point of an organic compound?
4. List five physical properties of organic compounds that are often measured by organic chemists.
5. The boiling point of acetic acid is usually stated to be 118°C . Is it possible to have acetic acid boil at 90°C ? Explain.

Post-Laboratory Questions–EXP 2 Name:

Due after completing the lab.

1. What is the difference between evaporation and condensation? Define each.
2. Boiling point determination can be used for several purposes. What are those purposes?
3. What effect on the boiling point is produced by:
 - (a) a soluble non-volatile impurity, such as table salt
 - (b) an insoluble foreign substance, such as sand
4. A liquid “X” has a normal boiling point of 75 °C. What will be the approximate boiling point of the liquid at 800 mmHg pressure?
5. The density of a liquid whose boiling point is 63-65 °C was determined to be 0.74 ± 0.05 g/ml. What is the liquid?