Purpose

The goal is to measure the boiling points of known and unknown compounds applying Siwoloboff's method and using microscale equipment.

Learning Objectives

Explain basic principles of evaporation, boiling, and distillation

Set up apparatus for microscale boiling points and record boiling point

Review Material –

Vollhardt, P.; Schore, N. E.; Organic Chemistry: Structure and Function, Chapter 2.4

Reference –

Pavia, D. L.; Lampman, G. M.; Kriz, G. S.; Engel, R. G.; Introduction to Laboratory Techniques: A Microscale Approach, 4th Ed., Brooks-Cole, 2007 pg 674–699

Equipment

- Hotplate
- Silicone oil bath
- Thermometer
- Culture tubes, 6 × 50 mm
- Melting point capillary tube
- Rubber bands
- Teflon stir bar

Chemicals

- Cyclohexane
- Acetone
- Unknown organic liquid

Theory and Background

Introduction

Evaporation or vaporization is the process of converting a liquid to a gas. The escaping vapor produces a vapor pressure of the gaseous form of the substance over the liquid form of the substance. In a liquid the particles of a substance are in contact and the potential energy of the intermolecular forces holds them in a condensed phase. Different molecules will move at different speeds with the overall average speed being dependent on the identity of the substance and the temperature. When a molecule that is moving faster (greater kinetic energy) reaches the surface of the liquid it has a chance to escape if it's kinetic energy (speed) is greater than it's potential energy of attraction (intermolecular forces) the molecule can leave the condensed phase and escape as vapor.

As temperature increases the average speed of the particles increases and a greater percentage of particles will tend to convert to vapor at the surface of the liquid. The vapor pressure over the liquid will increase and the rate of evaporation will increase. When the temperature increases sufficiently that the average molecule has enough kinetic energy to escape, the whole sample will begin to evaporate from any available surface, the vapor pressure of the liquid will be equal to outside pressure, and we say the substance ***boils***. All further increases in energy will go to converting liquid to gas rather than warming (increasing average kinetic energy) until the entire sample has evaporated.

When intentionally boiling substances in laboratory settings, we often add boiling chips or stir the liquid. Both of these provide small microscopic air bubbles, which increase the overall 'surface' of the liquid in contact with gas and aid in the smooth evaporation. If a substance does not have sufficient surface for vapor to escape from, it is possible to increase the temperature of the liquid past its normal boiling point and super-heat the solution. This can cause an unstable system, which will at some point rapidly and violently release the stored energy by explosive boiling (bumping), which can break glass or send boiling liquid splattering. Always heat systems carefully and use stirring, or boiling chips when instructed, to prevent bumping. Bumping is a particular issue in lab as the glassware does not tend to have microscratches that hold microscopic bubbles of gas the way normal pots and pans will in our homes.

Measuring Boiling Point

The temperature at which a substance boils at atmospheric pressure, the boiling point, is a physical constant, and is typically a 1–2 °C window that is dependent on the intermolecular forces in a substance (its identity) and the outside pressure. So chemists use the boiling point as a means of identification of a substance.

If the sample is large (several milliliters) boiling points can be measured by distillation. The sample is heated and the vapor collected in a secondary flask (see lab C). As the vapor is distilled, the temperature of the vapor (or more accurately the temperature at which the vapor condenses to a liquid on the surface of the thermometer) is measured. The constant flow of vapor from the initial sample to the distillate gives an accurate measure of the boiling point at that pressure. Note that even with stirring it is possible that the liquid may get hotter than the boiling point, especially on a strong heat source, so it is preferable to measure the temperature of the vapor condensation rather than that of the liquid itself. Additionally, many thermometers are immersion thermometers that require a certain amount of the thermometer to be in contact with the measured substance to read accurately. So when setting up a distillation it best to set up the thermometer so the maximum amount of the thermometer is in contact with the distilling vapor without touching the boiling liquid.

Distillation is good for larger samples, however if a sample is small (< 1 mL) there may not be enough vapor to fully equilibrate a thermometer. It is still possible to measure the boiling point, but a different method must be used. Siwoloboff's method uses a small inverted capillary tube inside test tube to measure the boiling point. The sample is heated to boiling and any vapor formed inside the capillary tube is trapped in the tube. If sufficient vapor is trapped to fill the capillary tube, additional vapor will 'bubble' out and be visible to the observer. The same problem exists as with a distillation, in that the liquid may get to be superheated several degrees warmer than the actual boiling point when the visible bubbling starts, so it is more accurate to measure the temperature of the vapor when it condenses. In Siwoloboff's method, the temperature of condensation is measured by cooling the sample after boiling begins. When the sample is cooled below the boiling point all the vapor form of the substance condenses. Liquid is ~1000× denser than gas and the area that was filled with gaseous substance visibly contracts. The temperature of the sample at the point of that contraction is the condensation point/boiling point.

Practical Uses for Boiling

Beyond just being a physical constant for identification of a substance, the process of boiling a liquid has many practical laboratory uses.

1. **Distillation –** Substances that easily convert to gases (volatile or low-boiling compounds) can be purified by distillation and separated from materials that do not easily convert to gas (non-volatile compounds) or from substance that require a greater amount of heating to convert to gas (high-boiling compounds). A mixture can be heated and the volatile compounds will evaporate and can be recollected (distillate) while the non-volatile materials remain behind (distiland). Simple distillation (Figure B.1), is a single heating and cooling cycle that can remove a liquid from a solid or non-volatile substance. Fractional distillation involves a series of heating and cooling cycles and can separate volatile substances whose boiling points vary only by a few degrees.

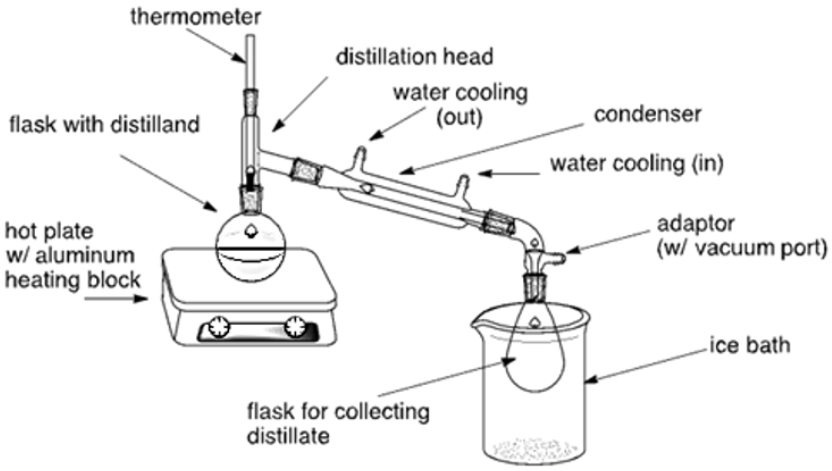

Figure B.1: A macroscale (5 mL–1000 mL) simple distillation setup

2. **Solvents –** Relatively volatile liquids can be used as solvents to aid substances mixing together in the same phase and speeding up reactions. These solvents can be easily removed by evaporation/distillation to leave behind the desired non-volatile products.

3. **Reflux –** If a reaction needs to take place at a particular temperature, it may be done 'at reflux'. Refluxing takes advantage of the constant temperature at boiling so a solution is heated to it's boiling point, but as any additional heat goes into evaporating the solvent it does not heat past that point. The solvent evaporates as in a distillation, but rather than collecting the solvent/distilland in a separate flask the condensed vapor is allowed to flow back into the reaction flask (Figure B.2). The visible condensing and dripping downward of the liquid solvent is described as 'reflux'. This permits a reaction to run at a specific temperature (the boiling point of the chosen solvent) without constant need to add more solvent as it evaporates or careful watching of the heat source to avoid variations. If a different temperature is needed the solvent is changed to one that boils at the desired temperature.

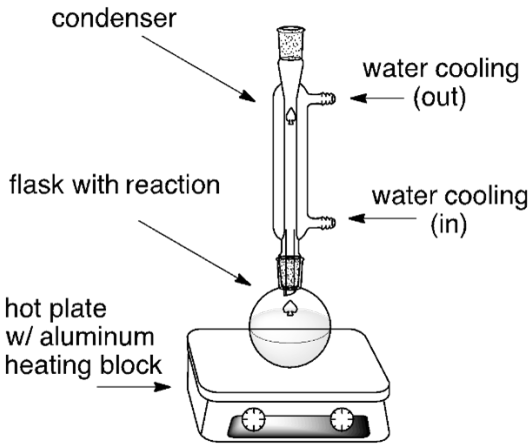

Figure B.2: A macroscale (5 mL–1000 mL) reflux setup (normal atmosphere)

4. **Pharmaceuticals –** Most pharmaceuticals are solids, but several key materials are actually low boiling liquids. Inhaled pharmaceuticals may be aerosolized solids or solutions (e.g. fluticasone propionate—a steroid anti-inflammatory used for asthma) but some are low boiling liquids that produce high vapor pressures. Ether (a.k.a diethyl ether or ethoxyethane, $CH_3CH_2OCH_2CH_3$) was used in surgeries as inhaled anesthetic in the 1840s and into the early 20th century. Ether boils at 34.6 °C and a cloth soaked in it produced enough vapor to knock someone unconscious. Chloroform ($CHCl_3$, bp = 61.2 °C) was also widely used in the 1850s to early 20th century, but was eventually shown to have far greater toxic properties than ether. To this day, inhaled anesthetics are used during surgery, including halothane ($CF_3CHBrCl$, bp = 50.2 °C), isoflurane ($CF_3CHClOCHF_2$, bp = 48.5 °C) and sevoflurane ($CH_2FOCH(CF_3)_2$, bp = 58.6 °C.)

Procedure

Safety Precautions

1. We will be using a silicone oil heating bath for this lab. The liquid inside this flask is silicone oil, which is unreactive, has a very high boiling point, and is immiscible with water.
2. DO NOT pour silicone oil in the sink.
3. DO NOT add water to the oil bath if the liquid is low.
4. If you see two layers inside the flask DO NOT heat it or use it for the experiment. Bring it to the dispensary to be replaced (Room 3314 or 2350).
5. When transporting the oil bath, take care not to tip it or the oil will drip from the side arm.
6. If a culture tube, capillary tube, or rubber band falls into the oil bring it to the dispensary for removal. DO NOT try to remove it yourself.
7. If silicone oil is spilled on the counter, it can be cleaned up with a paper towel.
8. **This experiment will be done in PAIRS.**

1. First, Siwoloboff's method will be tested by using a known compound: cyclohexane has a boiling point of 81 °C.

2. Fill a 6 × 50 mm culture tube approximately 1/3 to 1/2 full with sample. Attach this to a thermometer with a thin band of rubber tubing as shown in Figure B.3. Position the bottom of the test tube about mid-way along the bottom bulb of the thermometer and position the rubber band near the top of the tube.

3. Obtain a short piece of melting point capillary tubing (about 30 mm long), which is sealed at one end. Invert the capillary tube and place it inside the 6 × 50 mm test tube so the open end is down and the capillary is partially submerged in the liquid sample (Figure B.3).

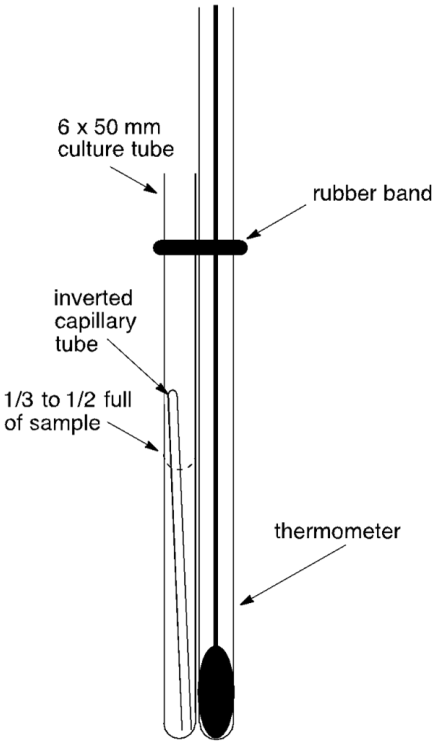

Figure B.3: Boiling point setup

4. Then, mount the thermometer with the test tube attached in the silicone oil bath, making certain that the rubber band is above the level of the oil (Figure B.4).

5. Make sure a white Teflon stir bar is present in the oil bath.

Safety Precautions

Check the oil bath for immiscible liquid. ***If any immiscible liquid is present DO NOT use the oil bath***, the other liquid is likely water, which will boil suddenly and splatter hot oil everywhere. Take it to the dispensary for replacement.

6. Set up a ring stand, with a lab jack on top of the foot plate as shown in Figure B.4. Elevate the lab jack approximately one 1/2 turn. Place a hot-plate on the lab jack and use a **two-prong clamp** to attach the neck of the oil bath (near the side-arm) and sample apparatus to the ring stand. The oil bath should be centered on the hot plate to keep the stir bar in the center of the flask.

Figure B.4: Setup for bp measurement.

7. Adjust the stirring so the oil is mixing thoroughly and adjust the thermometer so it is just high enough to let the stir bar spin freely.

8. Heat the oil bath carefully on a hot plate until a **steady** stream of bubbles is coming out of the open end of the small, inverted capillary. A setting of 5–6 on the hot plate will heat the sample efficiently and cool rapidly enough to not boil away all the sample. Lowering the hood sash will also minimize the flow of air past the sample and increase the rate of heating. You may see occasional bubbles as the sample expands on heating; the sample is not boiling until the bubble stream is steady and continuous.

9. When you see **steady and continuous** stream of bubbles coming from the capillary tube, remove the heat by lowering the lab jack and turning off the heat, and allow the oil bath to cool. Maintain the stirring by leaving the stirring knob on. Raising the fume hood sash will also allow more air flow past and speed the cooling of the sample. Note that the temperature at the instant bubbles cease to come out of the capillary and liquid is sucked up into the capillary. This temperature is the boiling point. If the sample has all boiled away before the boiling point is read, the test must be repeated with fresh sample.

10. Provided that the sample has not all boiled away, as a check on the result repeat the heating and cooling of the sample an additional time. If the sample is pure, the two boiling points measured will agree within a few degrees.

11. Rinse any remaining sample into the waste bottle with acetone. DO NOT DISCARD THE OIL BATH.

12. Repeat the above process with your unknown.

13. Replace the oil bath where directed by the TA and don't forget to take back your thermometer.

Data Collection

Known Substance: _____

Boiling point 1st attempt: _____°C

Boiling point 2nd attempt: _____°C

Unknown: _____

Boiling point 1st attempt: _____°C

Boiling point 2nd attempt: _____°C

Comments

Describe any special conditions, errors or deviations from the stated procedure below:

Questions

1. Why does the liquid rise in the capillary tube when the boiling substance cools below the boiling point?

2. If we start with a pure substance (2-bromo-2-methylpropane bp = 72 °C) what will happen to the boiling point if we repeat several trials with the same sample? Will it go up, down or stay the same? Why?

3. If we started with a mixed substance (1:1, 2-bromo-2-methylpropane (bp = 72 °C) and 1-bromo-2-methylpropane (bp = 91 °C)) what would happen to the boiling point if we repeat several trials with the same sample? Will it go up, down or stay the same? Why?

4. How does purifying a compound by distillation work with the principles of green chemistry? (In particular comment on principles 6 and 7.)