CHEM 344 Distillation of liquid mixtures

1. Distillation basics

The vaporization of a liquid and condensation of the resulting vapor is the basis of distillation. Organic liquids containing small amounts (<15%) of impurities or non-volatile substances are easily purified by **simple distillation**, as are liquid mixtures where the difference in boiling point of the components is >70 °C. **Fractional distillation** is more useful for separating mixtures of liquids where the boiling points of the components differ by <70 °C (see later).

A typical simple distillation setup is shown in Figure 1. It consists of a flask containing the liquid to be distilled, an adapter to hold a thermometer and to connect the flask to a water-cooled condenser, and a flask to hold the condensed liquid (the distillate).

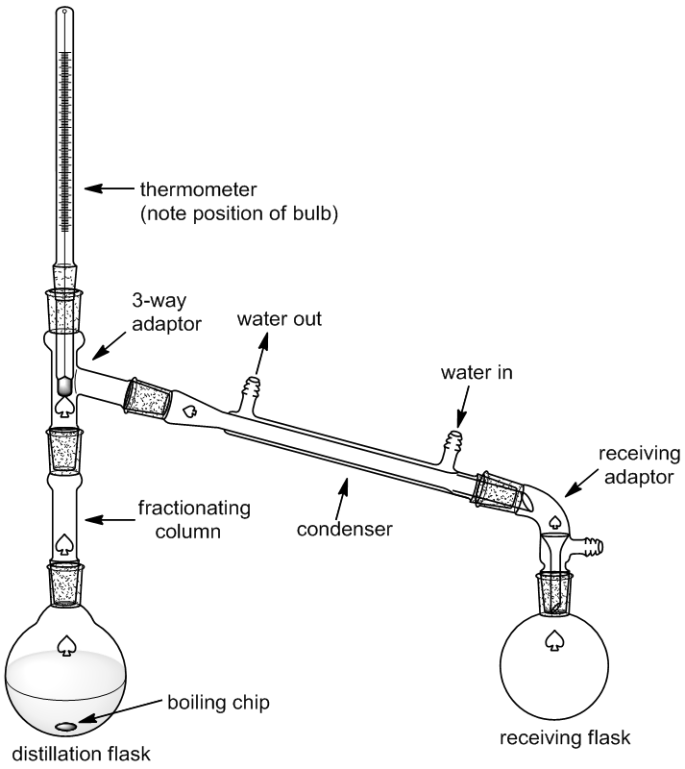

Figure 1: Apparatus for a simple distillation.

1.1 The distillation flask

The distillation flask is a round-bottom flask. The liquid to be distilled should fill the distillation flask to ~50-60% of its capacity. To promote even heating of the liquid, a boiling chip or a magnetic stir bar is added **before** heat is applied to the distillation flask. The irregular chips provide sites for bubbles of vapor to form, or alternatively the liquid is agitated with the magnetic stirrer as it is being heated. **Never add a boiling chip or a stir bar to a hot liquid**! Doing so can cause a seemingly calm liquid to boil suddenly and violently.

1.2 The distilling adapter

The adapter connects the distillation flask, the condenser, and the thermometer. This type of adapter is often referred to as a distillation head. The ground glass joints must be lined up and connected tightly to avoid leakage of the vaporized liquid. Leakage will result in loss of some of the liquid and will pollute the laboratory environment. The position of the thermometer is adjusted so the bulb is approximately level with the adapter sidearm connected to the condenser. The vapors of the heated liquid must totally surround and contact the thermometer bulb in order to obtain reliable temperature data from the thermometer during the distillation.

1.3 The condenser

The condenser cools the vapor causing it to liquify (condense) and directs this condensate into the receiving flask. The most common type of condenser is the water-jacketed type shown in Figure 1. The water supply is connected to the condenser with rubber hoses. The water flows into the lower hose connection (most remote from the distillation flask) and out of the upper hose connection (i.e. "**in at the bottom, out at the top**"). Before turning on the water flow, check the hose connections carefully to ensure that they are secure and will not become loose. An extra margin of security can be gained by twisting wire around the hose connections. The water flow is adjusted so there is a **constant flow of cold water** into the condenser.

1.4 The receiving flask

The container to collect the liquefied vapor is named the receiving flask. It may be a round-bottom flask, an Erlenmeyer flask, a bottle or a graduated cylinder. In Figure 1, the receiver is connected to the condenser *via* an adapter. A key feature is that **the system is open to the atmosphere – NEVER HEAT AN ENTIRELY CLOSED SYSTEM!**

1.5 How it happens

Heat is slowly applied to the distillation flask. The amount of heat to apply is determined by the rate of distillation. The liquid should gently bubble and vaporize. As vapor rises from the liquid, it raises the temperature of the apparatus. The vapor will fill the distillation flask and most of the distillation head. The thermometer bulb should be completely surrounded by the vapor. **If vapor creeps past the thermometer bulb without contacting it, the measured boiling point will be low.** The vapor condenses and drips into the receiving flask via the condenser tube. Typically, the liquid should drip into the receiving flask at a rate of about 15-20 drops per minute. If the rate of distillation is too rapid, the distillation flask must be removed from the sand bath. **With too rapid a rate, the measured boiling point is likely to be inaccurate and the purity of the distilled liquid will be decreased.** If the liquid being collected has a low boiling point (<40 ^{o}C), the receiving flask should be cooled in an ice-water bath (think about why this might be necessary).

The behavior of the measured boiling point during the course of a simple distillation is plotted in Figure 2. As the liquid evaporates and the vapor comes into contact with the thermometer bulb, the temperature rises. The temperature stabilizes at the boiling point and most of the liquid distills over into the receiving flask. The temperature drops when almost all of the liquid has been distilled (but **never boil a liquid to dryness**!).

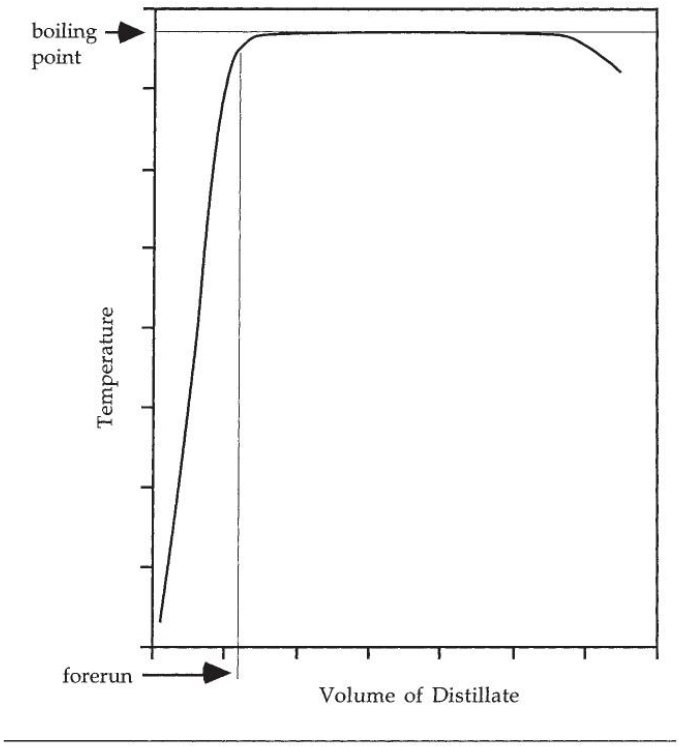

Figure 2: Boiling point of a pure substance as a function of amount of liquid distilled.

When the temperature begins to drop, the distillation is halted by removing the distillation flask from the sand bath. Note that the boiling point of the collected material is actually a range rather than a single point.

2. Distillation of Mixtures

Purifying mixtures of liquids

The graph produced by plotting the boiling points of a series of ethanol-butanol mixtures *vs*. their compositions (mole fractions) is shown in Figure 3. **Notice that the boiling point for any mixture is between the boiling points of the pure components**. The curve connecting the points can be used to determine the boiling point of any mixture of these two components. For example, an ethanol-butanol mixture that is 0.50 mole fraction in ethanol (i.e. 50% ethanol 50% butanol) will boil at 91.3 °C.

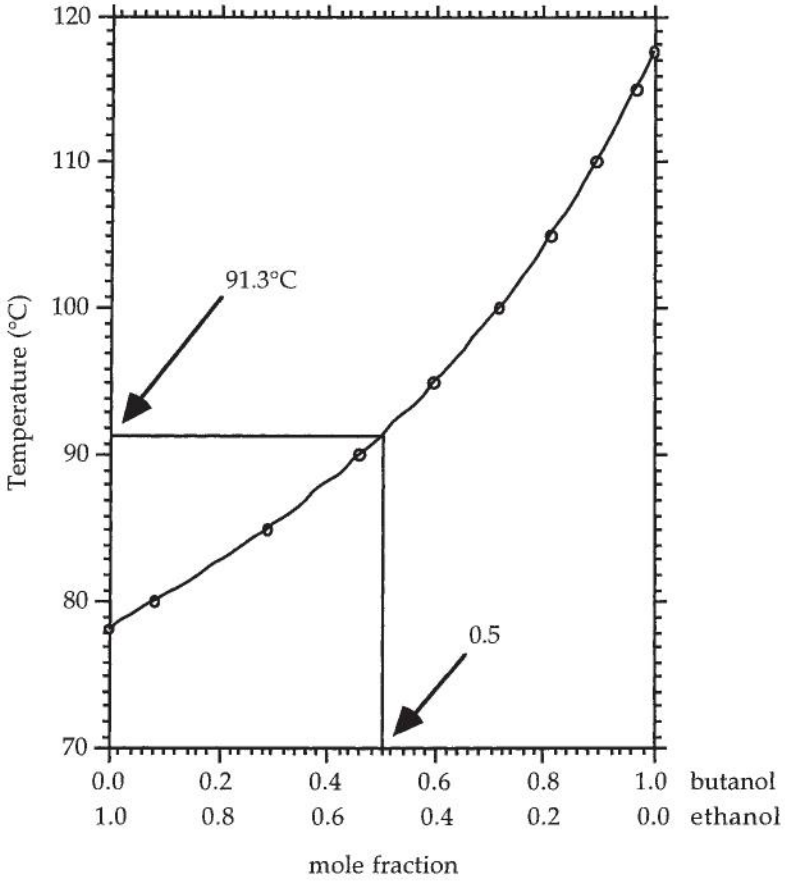

Figure 3: Boiling point as a function of composition for mixtures of ethanol and butanol.

A simple distillation is limited in its utility. It can be used if the boiling point difference between the two components is large (generally >70^{o}C) but even then separation is not complete. It can also be used to purify a liquid that is contaminated with a small amount (<15%) of a compound with a lower boiling point. In this case, the condensate which distills first contains the lower boiling substance. The purified higher boiling substance that remains in the flask is collected when the temperature of the vapor stabilizes at its boiling point.

By carrying out successive simple distillations on the initial distillate of each distillation, it is possible to obtain the lower boiling substance with very little contamination. However it is a tedious and length process to purify substances by multiple cycles of simple distillations. Instead, **fractional distillation** is used. Figure 4 shows a fractional distillation set up.

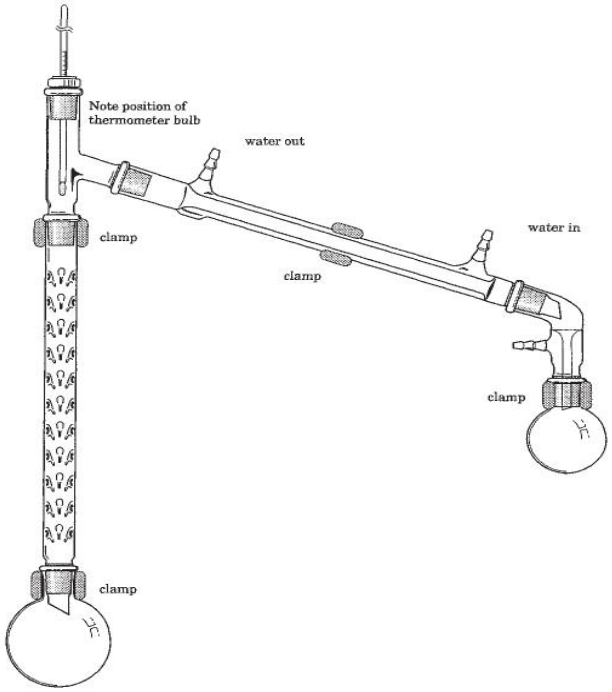

Figure 4: Apparatus for a fractional distillation.

Separations are achieved in fractional distillations by setting up multiple equilibria between the liquid and its vapor before condensing and collecting it. In effect, multiple successive simple distillations are carried out inside the apparatus before the liquid is collected.

The apparatus for a fractional distillation is similar to that for a simple distillation except that an extension is added to the flask in order to increase the distance travelled by the vapor and the surface area available for condensation. The extension is named a **fractionating column** and may be open (such as the columns used in this lab) or loosely packed with an inert substance such as glass beads. The purpose of the packing, if present, is to further increase the surface area with which the vapor contacts. The length of the column and the type of packing are a large factor in determining the degree of separation that can be achieved with a fractional distillation.

Another factor in determining the degree of separation that can be achieved with a fractional distillation is the rate at which the distillation is carried out. The best separations are achieved using a slow, steady distillation rate. A slow distillation rate maximizes the number of vaporizations and condensations in the fractionating column.