DISTILLATION

Distillation is the most important method for separation and purification of liquids. This process can be simply described as bringing the liquid to a boil in one vessel, and subsequently condensing the vapors in the other vessel. Thus, a liquid-vapor transition occurs during boiling, and a vapor-liquid transition during cooling, *i.e.,* condensation, will be taking place. If the boiling of the liquid and the condensation of its vapors is done in one vessel, the process will be called reflux.

Upon boiling, the liquid and vapor phases are in equilibrium: the number of molecules that are undergoing a liquid-vapor transition will be equal to the number of molecules that are undergoing a vapor-liquid transition. Therefore, the vapor pressure of a liquid is simply a measure of the ability of the molecules to leave the surface of the liquids. The number of molecules in each phase will depend on the temperature, pressure as well as on the intermolecular interactions in the liquid phase. For example, hydrogen bonding can significantly increase the vapor pressure of the liquid, thus making it less volatile as compared to an analogous compound that cannot engage in intermolecular hydrogen bonding. In order to shift that equilibrium, one of the components, in this case it will be the vapor phase, should be removed from the system.

Quantitatively, for the ideal solutions, which are devoid from any intermolecular interactions, the relationship between the ratio of the liquids **A** and **B** and their respective vapor pressures in the mixture is described by Raoult's law:

$$p_A = x_A \, p_A^{\,o}$$

$$p_B = x_B \, p_B^{\,o}$$

where, p_A and p_B are the partial vapor pressures of **A** and **B** in the mixture; $p_A^{\,o}$ and $p_B^{\,o}$ are the vapor pressures of the pure **A** and **B**; x_A and x_B are the mole fractions of **A** and **B** in the mixture. Obviously, $x_A + x_B = 1$.

Pictorially the above correlations are shown in Figure 1. Most liquids, especially those that are structurally similar, would obey the behavior of the deal solutions. However, when structurally dissimilar liquids are in the mixture, strong deviations from linearity are to be expected. Thus, for the ideal solutions, the partial vapor pressure of a component is a constant, which does not depend on vapor pressures of the other components in the mixture. Fundamentally, this can be rationalized by considering the rates at which the molecules will be undergoing liquid-vapor and vapor-liquid transitions: the rate at which molecules of **A** leave the liquid phase will be affected by the presence of the molecules of **B**, whereas the rate at which **A** will return to the liquid, *i.e.*, undergo vapor-liquid transition, will not be hindered by **B**.
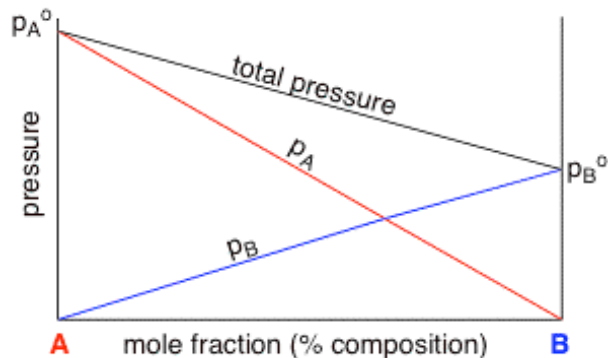

Figure 1.

It should also be noted that the sum of partial pressures of the components in the mixture, *e.g.*, p_A and p_B, will constitute the total vapor pressure: $p_A + p_B = p_{TOTAL}$. This is known as Dalton's law.

The moment the vapor pressure becomes equal to the external pressure will be classified as a boiling point of the liquid. If the external pressure remains the same, a pure liquid will boil at a constant temperature or a narrow temperature range.

It is important to note, that the volatility of the liquid goes up as the total pressure decreases. Qualitatively, this is in accordance with Raoult's law, which relates the vapor pressure of a liquid to the pressure of individual components of the mixture and to the total pressure. To approximately estimate the boiling point at a given pressure, the knowledge of the boiling point at a known pressure is required. In general, reducing the external pressure in half will lead to ~ 15 ^{o}C reduction in the boiling point. For example, a liquid with a boiling point of 200 ^{o}C at the atmospheric pressure (760 mmHg) will boil at about 185 ^{o}C at 380 mmHg); this liquid will boil at ~ 170 ^{o}C at 190 mmHg of pressure. For a precise determination of the effect of pressure on the boiling a pressure-temperature nomograph should be consulted (Figure 2). [For a pressure temperature nomograph, see: http://www.sigmaaldrich.com/Area_of_Interest/Research_Essentials/Solvents/Key_Resources/nomograp h.html]

The value of distillation comes in separating the mixtures of liquids. Depending on the nature of the mixture that needs to be separated, different distillation techniques can be used.
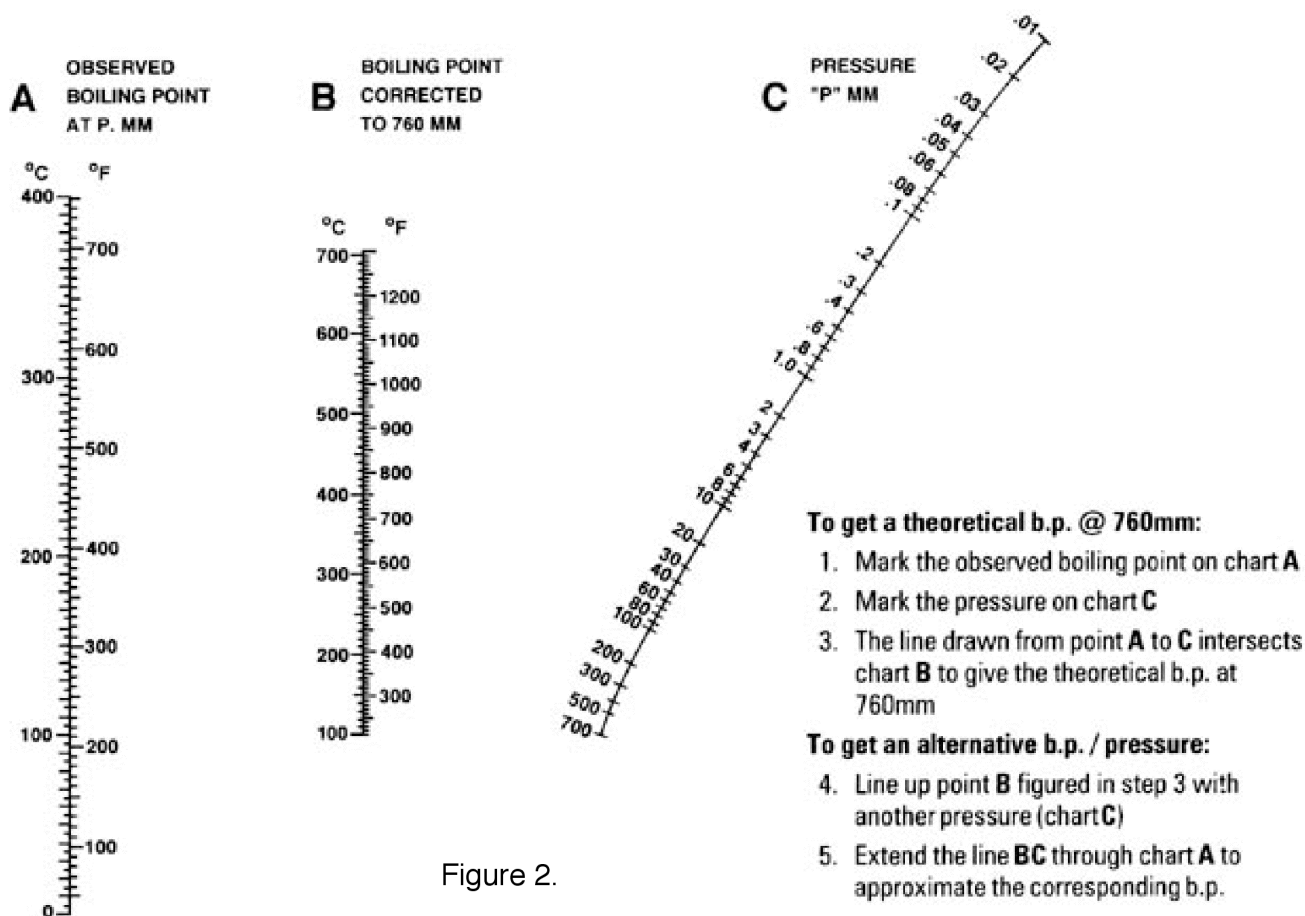

PRESSURE-TEMPERATURE NOMOGRAPH

To get a theoretical b.p. @ 760mm:
1. Mark the observed boiling point on chart **A**
2. Mark the pressure on chart **C**
3. The line drawn from point **A** to **C** intersects chart **B** to give the theoretical b.p. at 760mm

To get an alternative b.p. / pressure:
4. Line up point **B** figured in step 3 with another pressure (chart **C**)
5. Extend the line **BC** through chart **A** to approximate the corresponding b.p.

Figure 2.

Simple distillation

Simple distillation is best used for liquids with 40 – 150 ^{o}C boiling point range. Above 150 ^{o}C many liquids will tend to decompose (in this case a vacuum distillation should be used, below), liquids with boiling point below 40 ^{o}C are difficult to distill without significant losses. Simple distillation is applicable for separation of liquids with boiling points differing by more than 80 ^{o}C.

The required set-up for the simple distillation is shown in Figure 3. A round bottom flask (referred to as a distillation flask since it contains a liquid that needs to be distilled) is placed into the heating mantle, which usually is filled with sand to provide good thermoisolation. The distillation flask is equipped with a boiling chip, followed by a stillhead. The top joint 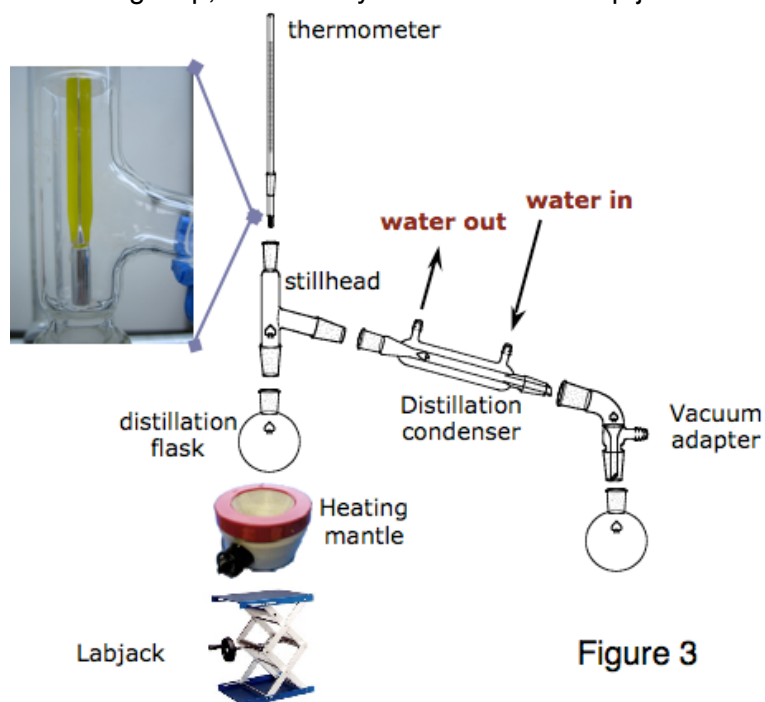of the stillhead (also known as distillation head) is connected to a thermometer adapter with the neoprene fitting, and then the thermometer. The position of the thermometer's bulb is crucial for the correct determination of the temperature (Figure 3). The top of the thermometer bulb should be aligned with the bottom of the side-arm of the stillhead, *i.e.*, the point where the vapor will start to condense; placing the bulb above or below the arm will lead to lower or higher boiling point reading, respectively. Remember: **"top of the mercury bulb aligned with bottom of the side-arm"**. All the female-to-male connections must be clean and dry to fit tightly; this is done to avoid possible release of distillate vapors and the loss of the distillate as well as to prevent the joints from being stuck together. Teflon tape should be used to insure a proper seal between the joints. The condenser is attached to still head on one end, and to the vacuum adapter on the other end using keck-clips. The water hoses are attached as shown in the Figure 3: **water should come in at the bottom of the condenser and leave from the top outlet**. For safety reasons, the condenser is usually clamped in the middle. A receiving flask is then connected to the vacuum adapter using a keck-clip. The use of keck-clips and clamps assures that the distillation set-up is stable throughout the distillation. The receiving flask should be lower than the distillation flask to allow a free flow of the condensed liquid into the receiving flask. Importantly, always place the heating mantle on a labjack. This allows for quick and convenient removal of heat, if necessary to prevent the distilling mixture from overheating.

Figure 3

It is important to keep in mind that the systems should always be open to the atmosphere. Closed systems should never be heated; the pressure build-up of the heated vapor will lead to an explosion. In case of a simple distillation, the vacuum adapter serves as an opening to the atmosphere.

For the distillation of moisture sensitive liquids, the vacuum adapter is fitted with a drying tube, which is packed with $CaCl_2$ or any other appropriate drying agent. The drying tube should be assembled fresh for each distillation since the absorbed moisture leads to "melting" of the drying agent and creates plugs, which are not air-permeable; thus leading to a closed system. Also, in cases when the liquid is either volatile or temperature sensitive, the receiving flask is submersed into an ice bath.

A boiling chip should always be used when a distillation is carried out. The boiling chip (a.k.a. boiling stone) is usually a piece of glass, ceramic, etc. The purpose for the boiling chip is to remove temperature gradient and to assure a smooth boil. A more sophisticated set-up involves the use of the stirring/heating plate and a stirring bar.

Sometimes it is beneficial to know how the temperature will influence the volume of the distilled liquid. A graduated cylinder is used as a receiving flask. The vacuum adapter should be placed right at the top of the cylinder to minimize the potential loss of the liquid to spillage. About 10-15 data points are required to obtain. In general, the distillation curve has a few distinct phases (Figure 4). Distillation

between points *1* and *2* corresponds to some lower boiling impurities, and the corresponding amount of liquid should be discarded. Once the impurities are removed the temperature starts to stabilize, from *2* to *3*. A pure liquid will be distilling at a very narrow temperature range; this corresponds to the region between *3* and *4*. At the end of distillation the temperature tends to rise, simply because the vapors are much easier overheating than the liquid.
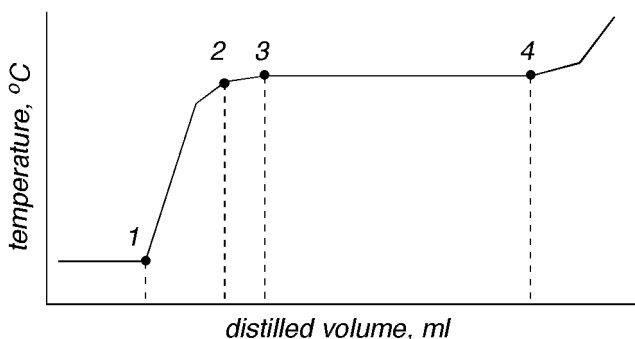

Figure 4

Importantly, following the above description, the first fractions of the distillate should always be discarded, and a new receiving flask should be connected to the vacuum adapter. It should be kept in mind that the liquid should never be distilled to dryness! A small amount of liquid, usually a dime size, should always be left in the distillation flask. Since vapors can be heated to much higher temperatures than liquids, overheating and potential explosion might occur when the distillation flask is heated after the solvent is removed.

Fractional distillation

Liquids of comparable volatility cannot be sufficiently separated by simple distillation, i.e., by a single vaporization – condensation sequence. In principle, multiple simple distillations should yield a single compound from the mixture. However, this is a tedious and non-economical process. A better way is to use fractional distillation, which provides a possibility for separating liquids that have a boiling point difference of less than 80 ^{o}C. The set-up for the fractional distillation is quite similar to the simple distillation, with the only important exception – the distillation flask is connected to the stillhead with an additional column (Figure 5). This column, known as a fractional column, is packed with an inert material to increase the surface area, such as glass beads, metal turnings, etc. In the fractional column the vapor and the condensate are constantly moving in the opposite directions. The vapor is condensing on the packing material and returning to the distillation flask. The composition of the vapor and liquid will be changing in favor of more volatile component as one moves up the fractional column from the distillation flask to the stillhead. Multiple single vaporization-condensation cycles are taking place in the packed column.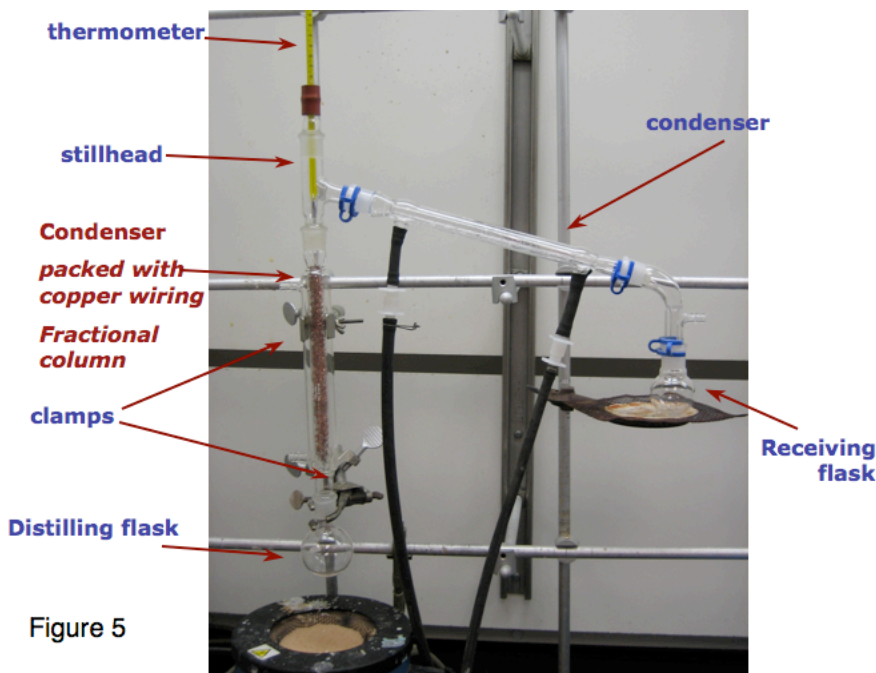 The single cycle is usually referred to as a theoretical plate. In general, the longer the column and the larger the surface area of the packing material, the more efficient the separation between the mixture components. In other words, the more theoretical plates, the better the column.

Figure 5

Theoretical rationale for the fractional distillation is shown in Figure 6. The region between the lines is a two-phase region; the upper curve (vapor composition) is derived from Raoult's law; the lower

curve defines the boiling point of liquid at a given ratio of the components. When a given mixture of **A** and **B**, *i.e.*, *1*, is heated to the temperature *T1*, it will start to boil. At this temperature, the vapor composition will have a composition of **A** and **B** that is reflected by *2* (note that *1* and *2* have different mole fractions of **A** and **B**). If that vapor pressure is condensed to a liquid phase, the resulting mixture *2* will have a different boiling point, *T2*. The vapor composition at *T2* is *3* contains a distinctly different mole fractions of **A** and **B** than at *T1*. Notably, the mole fraction of **B** in the mixture is progressively increased as two boiling-condensation cycles were carried out, since the fraction of **B**, which is the more volatile component, is constantly increasing in the vapor phase. Thus, Figure 6 describes a two-theoretical plates separation process.
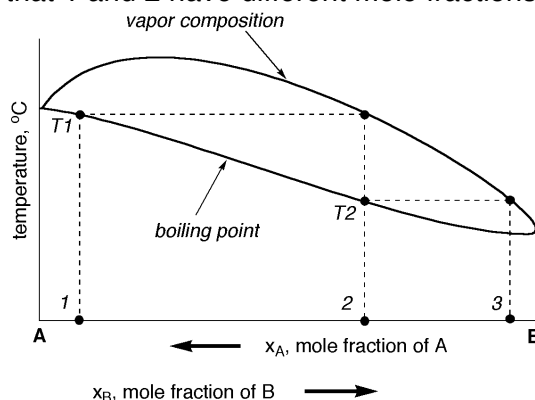

Figure 6.

Vacuum distillation

Only those compounds that are stable at their boiling point can be distilled at atmospheric pressure. If the compound decomposes at elevated temperatures, vacuum distillation has to be used. Also, if the boiling point of the compound is higher than 150 ^{o}C, vacuum distillation should be used. The set-up for the vacuum distillation is virtually identical to either simple or fractional distillations, with the only difference that the vacuum adapter is connected to a vacuum pump. Reduced pressures are obtained either by water aspirator pump or by a mechanical vacuum pump. Most modern laboratories are equipped with central, so called in-house vacuum.

Importantly, the distillation system should be placed under vacuum before the heating is initiated. Vacuum should never be applied to hot or refluxing solutions! The boiling temperature is strongly dependent on pressure: once the pressure drops, the boiling point decreases, and the liquid is quickly sucked from the distillation flask through the condenser into the receiving flask, and subsequently into the pump.

Sometimes, liquids contain small amounts of low boiling impurities, which will cause some foaming/bubbling once the vacuum is applied. In this instance, the vacuum should be adjusted. This operation might be repeated several times, until the surface of the liquid is quiet. Once the distillation is complete, the heating mantle is removed, and the whole set up is allowed to cool. After that, the vacuum should be slowly released.

Another distinction of the vacuum distillation is that the receiving flask should always be a round bottom flask, and never a flat bottom flask, such as an Erlenmeyer flask. Glassware should always be examined for cracks, since the weak glass will shatter under pressure.

AZEOTROPES

Most homogeneous solutions follow the behavior of ideal solutions, and thus they follow Raoult's law. However, there are certain combinations of particular liquids that exhibit deviations from the ideal solution: the vapor pressure of these liquids is either higher or lower than that predicted by Raoult's law. This phenomenon implies that the interactions between the components are causing the deviation from ideal solution behavior.

These non-ideal mixtures are commonly called azeotropes. Azeotropes cannot be separated by any types of distillation, because the liquid and the vapor phases have identical compositions. The boiling point of such mixtures will not change, until one of the components of the azeotrope has been completely removed.
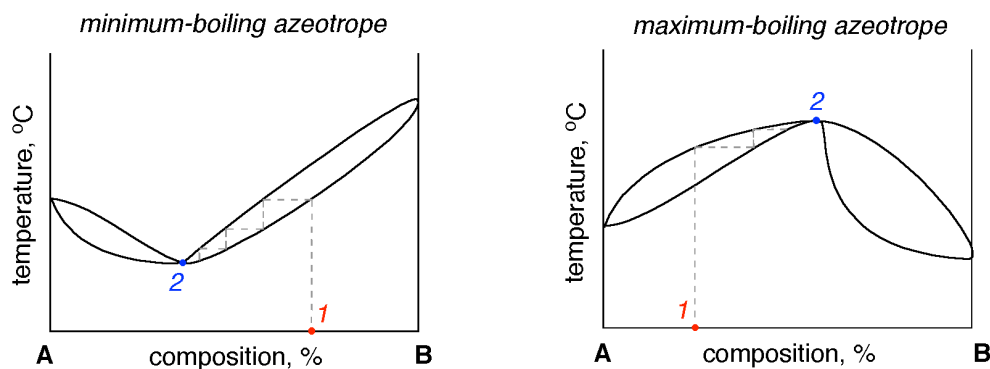
minimum-boiling azeotrope

maximum-boiling azeotrope

Figure 7

Depending on the nature of the interaction between the liquid components of the mixture. In those instances, when the mixture is destabilized relative to the ideal solution, the interaction is lower and leads to a minimum-boiling azeotrope (and vice versa). Examples of a low-boiling and a high-boiling azeotropes are shown in Figure 7. In both cases, when the mixture of two liquids, *e.g.*, **A** and **B**, with a given composition *1* is distilled, the change will only occur up to *2*. Therefore, the separation of **A** and **B** can only be achieved before their ratio has reached *2*. As long as both components are present in the mixture, the boiling will be taking place at a constant temperature. However, as soon as one of the components is removed, the distillation will follow the profile for an ideal liquid.

Azeotropes are of great practical significance, since they are used for the separation of one compound from a mixture as well as for the removal of water from organic solvents, *i.e.*, drying. Table 1 contains physical characteristics of several of the binary (most commonly used) and ternary azeotrope mixtures. Noteworthy, the nature of the components of the azeotropes varies greatly. For example, both ethanol and toluene form an azeotrope with water, despite the fact the former resembles water, and the latter is completely different from water, in terms of structural and physical characteristics.

Table 1.

Azeotrope (b. p., ^{o}C)	composition of the azeotrope mixture, %			b. p. of the azeotrope, ^{o}C
water(100) – ethanol(78)	4	96		78
water(100) – toluene(110)	20	80		84
chloroform(61) – acetone (56)	80	20		65
ethanol(78) – ethyl acetate (78)	30	70		72
ethanol(78) – benzene(81) – water(100)	19	74	7	65

From the practical point of view, azeotropes mixtures can be removed by the use of a special apparatus, such as a Dean-Stark trap, shown in Figure 8. For example, ethanol water mixture boils at a constant temperature (78 ^{o}C) when the water content is 4 % by mass. In order to remove water from ethanol and thus obtain anhydrous ethanol, the azeotropic distillation with toluene is applied. Ethanol, containing water is placed into the distillation flask equipped with a magnetic stirrer or a boiling chip. Upon heating, azeotrope will be removing into the graduated side arm of the Dean-Stark appartus. The composition of the mixture in the receiving side arm will not be the same at different time points. Once the ratio between toluene and water changes from 80 – 20, a phase separation will take place, and the formation of two layers in the side arm receiver will be observed. Based on the densities of the two components, toluene will be the top layer, and the water will be the bottom layer. Water can be periodically drained from the receiving arm. It is possible to
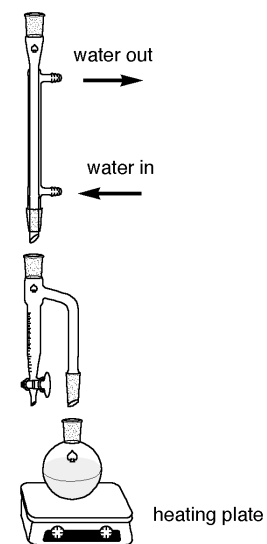

water out

water in

heating plate

Figure 8

5

measure the amount of the water that has been present on the original liquid. Notably, due to the toxic, cancerogenic nature of toluene, anhydrous should never be used for any types of human consumption!

BOILING POINT DETERMINATION

Boiling point of a liquid is usually determined during its distillation. However, this requires substantial amounts of liquid. In those cases, when only small amount of liquids are available, the set-up shown in Figure 9 is used. About 1 mL of the liquid is placed into a small test tube, containing a boiling chip. The test tube is clamped onto a support stand, at a distance that 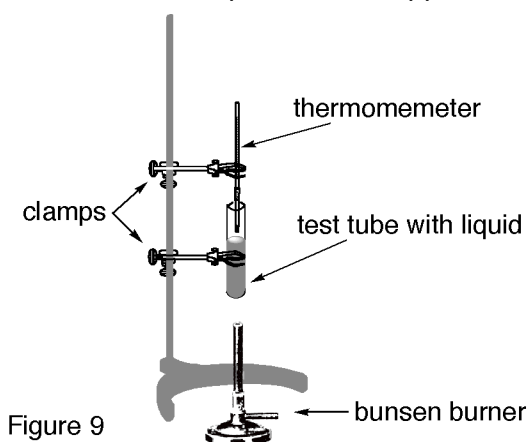allows for a rapid application and removal of heat, usually with a Bunsen burner. Then the thermometer is clamped in such a way that the bulb of the thermometer is about 2 cm above the liquid level. Heating of the bottom of the test tube will lead to a reflux of the liquid, and its vapors will be washing the bulb of the thermometer. Once the temperature rise stops, the reading of the boiling point can be made. This procedure should be repeated several times, and average should be taken. Care should be exercised while heating the test tube; rapid heating can cause the liquid to overheat and splash out of the test tube, also the test tube might crack and the liquid will leak out. Due to the open flame heating, the liquid can catch fire, which will present a serious hazard, which can also lead to a potential injury. Therefore, the area around the boiling point set-up should be clean and free from any potential hazards.

thermomemeter

clamps

test tube with liquid

Figure 9

bunsen burner

REFRACTIVE INDEX

In addition to boiling point and density, the refractive index (n) is considered as one of the main physical properties of the liquids. It is constant at a given temperature, pressure and the wavelength of the applied irradiation. Usually measurements of the refractive index are done at 20 $^{\circ}$C and the D line of the sodium spectrum is used for irradiation. Therefore, the refractive indexes are denoted as n^{20}_D.

The refractive index measures the ratio of the velocity of liquid through vacuum to the velocity of light through a give liquid. Refraction is a process in which light changes directions when it crosses the interface of two media, *i.e.*, when it leaves one isotropic medium and enters a different isotropic medium. Light traveling through the liquid will interact with the molecules, *i.e.*, with the electrons of the bonding and non-bonding orbitals that composed the liquid, and therefore, its speed should be distinct from that in vacuum, where light travel is not obscured. Since various compound posses various structural and functional features, the interaction of light with distinct compounds will be unique.

Refractive indexes of most organic compounds fall in the range between 1.3 and 1.7 Water and alcohols are at the lower and, whereas highly light absorbing compounds, such as chloroform, aniline, toluene, etc at the higher end of the range. The precision of refractive index determination is within 0.0002 units. Refractive index is very sensitive to the small amounts of impurities, therefore, all the reading should be taken with caution, when comparing to the tabulated values.

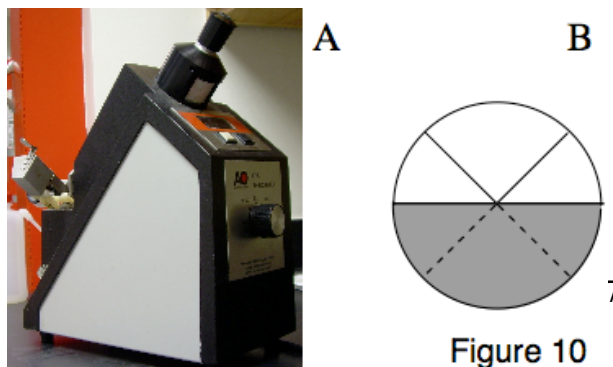Abbe refractometer (Figure 10A) is the most common apparatus that is used for the determination of

A   B

7

Figure 10

the refractive index. The procedure to measure n is fairly straightforward: the refractometer prisms (both upper and lower prisms) are cleaned (95% ethanol is usually used) and allowed to dry thoroughly. A small amount of sample is applied with an eyedropper onto the lower prism (contact of the pipette with the prism should be avoided, since the prism can get scratched). The upper part of the prism is brought into contact with the lower part of the prism, thus the liquid forms a uniform layer between the prisms. Next, the controls wheels are manipulated to bring the light and dark fields into focus (Figure 10B), with the dark-light interface being position at the crossing of the lines in the eyepiece. At this point, the reading of the refractive index is made. The temperature at which the reading was made should be recorded, and the necessary correction for the refractive index, using the equation given below, should be made:

$$n^{20}{}_D = n_{obs} + [(T_{obs} - 20)(0.000450]$$

where, n_{obs} and T_{obs} are the observed refractive index and temperature, respectively.

Distillation profiles (volume collected versus temperature).
Here is additional information for the distillation of two components (A and B).
The fractions collected for the "pure" compounds should be within a narrow range of temperature (ie. the temperature stays relatively constant within a few degrees, while a relatively large volume is being collected). In other words, it is the 'flat portions" which should be collected. When the temperature changes quickly, a flask should be placed to collect the liquid, and when the temperature is stable, a different flask should be used. So in principle, 4 different fractions should be obtained (corresponding to a, b, c, and d in the graph below).
The bottom line is that a pure compound can only be obtained within a narrow (a few degrees) range of temperatures (the boiling range). The known boiling point of the compounds should be within that range.

Ideal
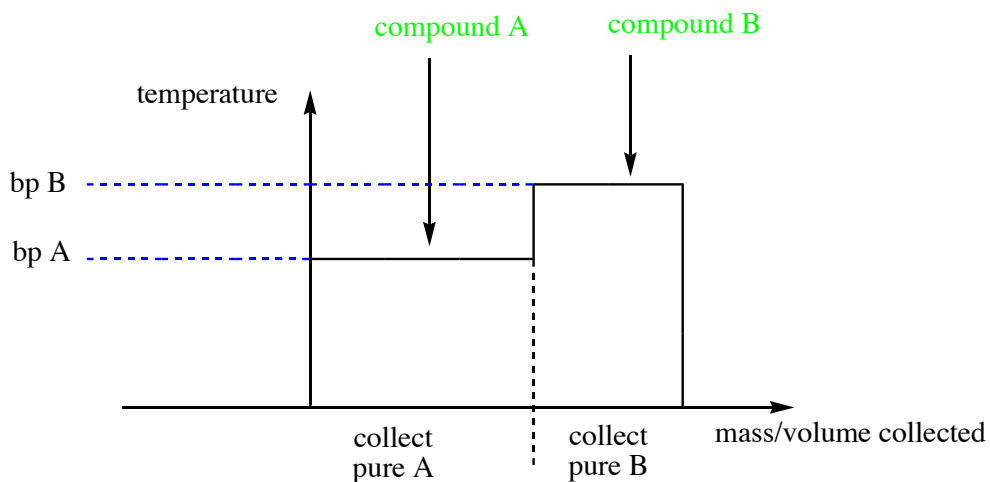
Ideal behavior during the distillation of a mixture A + B
(Note: in this example, the mixture would be 60% A + 40% B by mass or by volume)

The vertical parts mean that the temperature changes with no change in mass/volume. The horizontal parts mean the collection of pure compounds.

In reality, some liquid is collected before the flat (horizontal or plateau) portions, and instead of a single temperature boiling point, a small boiling range (a few degrees) is collected.

Real

compound A   compound B

temperature

boiling range
B

boiling range
A

a   b   c   d

mass/volume collected
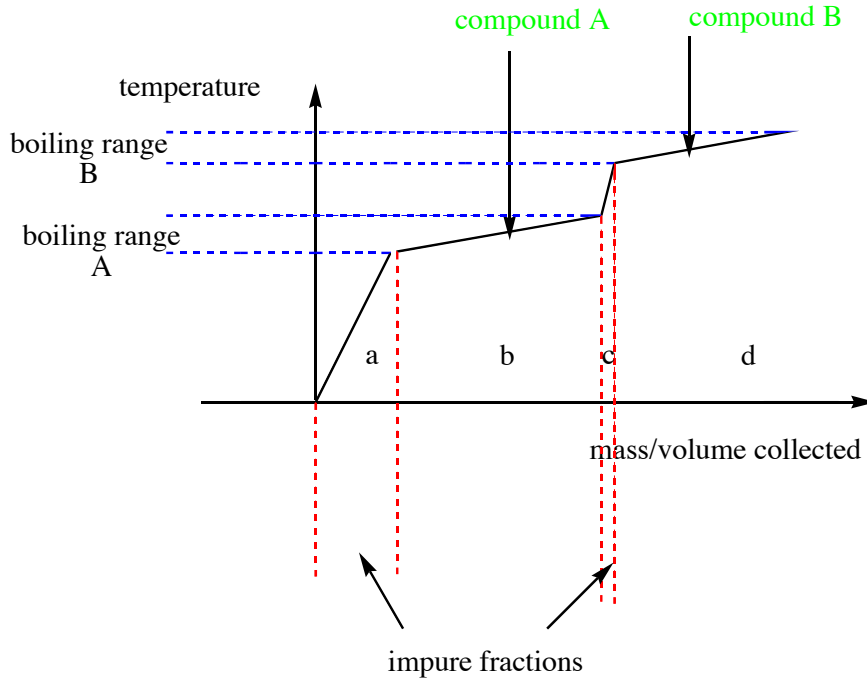
impure fractions

The boiling range should be only a few degrees wide
In principle, 4 fractions should be collected. The two fractions (b & d) which are within a few degrees ("pure" compounds) and the two fractions (a and c) where the temperature changes rapidly (impure fractions)