

Experiment 21

DISTILLATION

Objective

The purpose of this experiment is to introduce distillation, which in organic chemistry is a commonly used method for separation and purification.

Lab techniques

- Simple distillation
- Fractional distillation

Introduction

I. Distillation

Distillation is a method to purify substances. It includes both vaporization and condensation. When a liquid has absorbed enough heat, it will completely vaporize at its boiling point. The vapor will then condense in the condenser for collection. This process is not only capable of purifying a liquid, but also a feasible way to purify a solid if its melting point is low enough.

There are in general four methods of distillation: simple distillation, fractional distillation, vacuum distillation, and steam distillation. Simple distillation is mostly used to separate a volatile liquid from a nonvolatile substance, but it can also be used to separate a mixture of two or more components which have a significant difference in boiling point.

In fact, the boiling point of a liquid will change according to the surrounding pressure. When the pressure is decreased, the boiling point will also be lowered. Therefore, vacuum distillation can be used to separate different compounds from a mixture at a lower temperature to prevent their decomposition at high temperature. In addition, it is safer to carry out separation of compounds under lower temperature by using vacuum distillation.

Under a constant temperature, a number of molecules on the liquid surface should evaporate due to absorption of enough energy. On the other hand, a number of molecules of vapor should also condense due to the loss of energy. When equilibrium is reached under a constant temperature, the pressure resulting from the liquid vapor is called the vapor pressure at this temperature. Vapor pressure increases with temperature, as indicated in Figure 21-1. When the vapor pressure on the liquid surface equals to the surrounding pressure, this temperature is called the boiling point under that particular pressure. The boiling point under one atmospheric pressure (1 atm) is called normal boiling point (nbp).

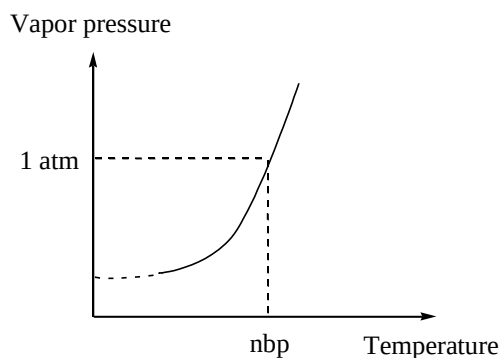


Figure 21-1 Vapor pressure of a liquid

According to Raoult's law, the presence of nonvolatile solute in a solution will lower its vapor pressure. Therefore, the temperature required for distillation is always affected by the composition of the solution, which may cause deviation from that of the pure compound. If a solution mixture is composed of volatile liquids, its vapor pressure can be calculated by the sum of the partial pressures as equation 21-1:

$$P = X_A P_A^\circ + X_B P_B^\circ \quad (21-1)$$

where P is the vapor pressure of the solution

P_A° is the vapor pressure of pure substance A

X_A is the mole fraction of substance A

P_B° is the vapor pressure of pure substance B

X_B is the mole fraction of substance B.

This equation shows that if P_B° is very small, most of the vapor of the solution comes from molecules of substance A. Thus, they can be separated by simple distillation. Otherwise, fractional distillation or other techniques should be used for separation and purification.

II. Fractional distillation

Fractional distillation refers to the addition of a fractionating column, which contains a packing material, on top of the distillation flask. Compounds of different boiling points can be separated through the repeated equilibriums in the column between the liquid and vapor phases. As the vapor ascending the gaseous mixture will condense and vaporize repetitively in the fractionating column. In this process, the concentration of the more volatile component increases during ascending, while that of the less volatile component will decrease at the same time. After a series of condensations and vaporizations (which can be viewed as repeated distillations), all the components can be separated.

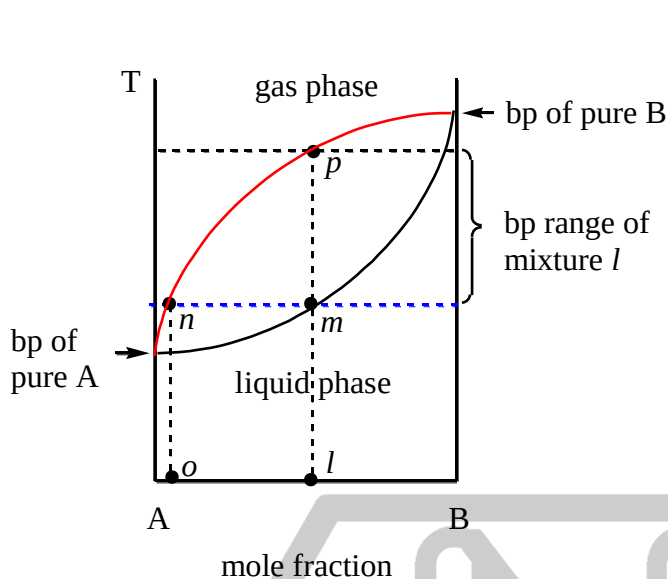


Figure 21-2 Phase diagram of temperature and mole fraction

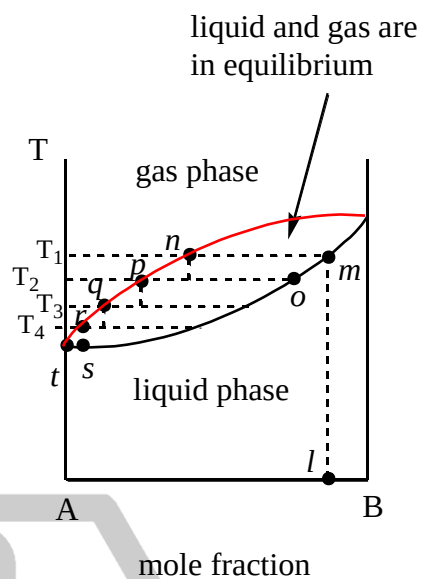


Figure 21-3 Diagram showing the principle of fractional distillation

Consider the liquid mixture of A and B in Figure 21-2. The lower curve shows the corresponding boiling points of different compositions of the mixture. For example, the vertical line drawn from point *l* intercepts the lower curve at point *m*. The temperature at *m* is then the boiling point of the mixture with a composition of *l*. On the other hand, the upper curve indicates the relationship between the compositions of the vapor at equilibrium with the boiling liquid under the boiling point temperature. For example, the horizontal line drawn from point *m* intercepts the upper curve at point *n*, which corresponds to a composition of *o*. This shows that the amount of A, which is more volatile, is larger at point *n* than that at point *m*. In conclusion, this figure reveals that for the vapor and liquid phases at equilibrium, the more volatile substance will be enriched in the vapor phase.

As shown in Figure 21-3, a mixture with a composition enriched in B at point *l* boils at temperature T_1 at point *m*, and the vapor in equilibrium with liquid *m* is *n*. As the vapor rises along the fractionating column, the temperature decreases to T_2 . Hence, a new equilibrium is attained, with the liquid phase at point *o* and the vapor phase at point *p*. The vapor at point *p* moves up farther, the temperature becomes T_3 , and a new equilibrium is attained. The vapor phase at point *q* then reaches a temperature of T_4 . Finally, the vapor at point *r* reaches point *t*, at which pure substance A is obtained. In summary, the temperature of the lower compartment of the fractionating column is higher than that of the upper. When vapor rises from the bottom to the top of the fractionating column, it will condense when it reaches a cooler surface and will then vaporize again. Thus, a series of vaporizations and condensations occurs in the

fractionating column. Due to the enrichment of the more volatile component in the gas phase as the vapor rises, separation is realized. In an ideal case, the vapor at the top of the column is the more volatile component, while that remaining in the flask is the less volatile component.

III. Azeotrope

The boiling point of a pure substance should be a constant. At the boiling point, the liquid phase is at equilibrium with the vapor phase. Once the temperature exceeds the boiling point, all the liquid will vaporize. In contrast, there is a range of temperature for a liquid mixture to change from the liquid-gas equilibrium state to the gas phase. For instance, as shown in Figure 21-2, the mixture with a composition l starts to boil at point m . However, it only completely changes to gas phase at point p , with the liquid-gas equilibrium state existing between point p and point m . In comparison, a pure compound has a constant boiling point under constant pressure. In general, a very narrow boiling point range is a good indication that the substance is very pure. Note that a substance with a constant boiling point is not necessarily a pure compound, as it may be an azeotrope.

What is an azeotrope? As we all know, the magnitude of intermolecular forces between solvent and solute molecules in a solution will cause deviation from an ideal solution. When the intermolecular forces between solvent and solute molecules in a mixture are smaller than those in the pure solvent or solute, such as that between water (bp 100°C) and ethanol (bp 78.5°C), the liquid mixture becomes more volatile. Hence, a positive deviation from Raoult's law can be observed (Figure 21-4), in which a constant-boiling mixture with a lower boiling point is formed, as is the case of a mixture of water and ethanol (78.2°C).

On the contrary, when the intermolecular forces between solvent and solute molecules are larger, such as those between acetone (bp 56.5°C) and chloroform (bp 61.2°C), the liquid solution becomes less volatile. In this case, a negative deviation from Raoult's law can be observed, in which a constant-boiling mixture with a higher boiling point is formed (Figure 21-4), as is the case of a mixture of acetone and chloroform (64.7°C).

Although an azeotrope is a mixture, its property in phase change is the same as a pure substance – exhibiting a constant boiling point. A mixture with the property of an azeotrope cannot be separated by fractional distillation. At the boiling point of the azeotrope, both liquid and vapor phases in equilibrium have the same composition; therefore, fractional distillation cannot be used for further separation. For example, ethanol and water will form an azeotrope with a lower boiling point. This mixture is composed of 95.6% ethanol and 4.4% water (by weight); hence, the maximum purity of ethanol after fractional distillation is only 95.6%.

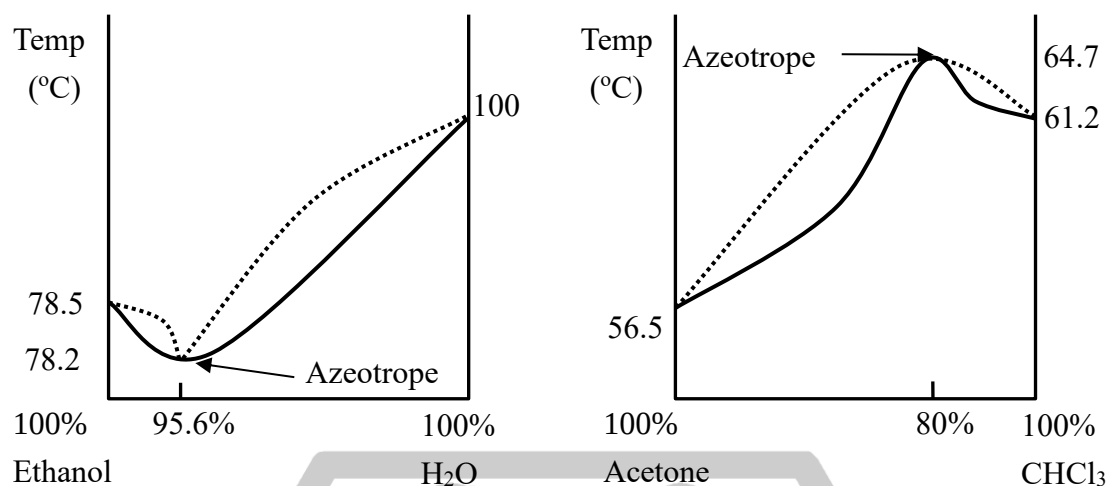


Figure 21-4 Diagram showing boiling point deviation. The left figure shows a positive deviation. In contrast, the right figure shows a negative deviation. (Solid line: composition of liquid. Dashed line: composition of vapor.)

IV. Apparatus for distillation

The set-up for distillation is composed of 6 parts: distillation flask, distillation head (or still-head), thermometer, condenser, vacuum adaptor, and receiving flask. The size of the distillation flask should be chosen carefully, and the volume of the sample put into the flask should range from 1/3 to 2/3 of its volume. When the distillation flask is over-filled, the sample might bump over to the receiving flask. In contrast, a distillation flask filled with only a small amount of sample will certainly result in a large portion of sample hold-up on the glassware surface.

The distillation-head is mainly used for connecting the distillation flask, thermometer, and condenser. The bulb of the thermometer should be placed at the opening of the condenser in order to measure the correct temperature. The upper level of the thermometer bulb should be at the same level as the lower rim of the side arm opening. A higher level will cause a lower reading of the boiling point, while a lower level will give a higher reading.

The condenser is an apparatus with cold water flowing on the outer surface of the central condensation tube. It should be noted that water should flow from the lower inlet to the upper outlet. This can help increase the efficiency of the vapor condensation. If the distillate is a solid, it may block the lumen of the condenser. In this situation, air-cooling can be used. Air-cooling can also be used if the boiling point of the distillate is over 100°C.

The purpose of the side arm on the vacuum adaptor (so named because this opening can be connected to a vacuum pump) is to balance the pressure inside the system with that of the outside. **It should not be blocked, as a closed system may**

cause an explosion. All the connections in this set-up should consist of ground glass joints for tight fit. When carrying out distillation under normal pressure, the ground glass joints need not to be greased. However, in vacuum distillation, it is necessary to grease the ground glass joints with Vaseline or vacuum grease (which has higher viscosity at higher temperature) to ensure the seal in order to maintain a good vacuum within the system. Grease only the top-half portion of the joint of the receiving flask to avoid contamination.

V. Precautions when carrying out distillation

The temperature should be recorded when the first drop of distillate is collected. This temperature is the starting point of the boiling point range. If the distillate is pure, the boiling point range should be very narrow. However, if the distillate contains some impurities, the boiling point range will be larger. For a known compound, the distillate with a maximum of 2°C difference from its true value of boiling point is generally collected to ensure its purity. As boiling point is affected by the atmospheric pressure, it is necessary to record the atmospheric pressure along with the boiling point. All in all, boiling point is a very important physical property to register, as it is an important indicator of the purity of a compound.

During the process of distillation, if the temperature of heating is set too high, often occurs when trying to speed up the process, it is easy for the vapor temperature to become too high. This phenomenon is called **overheating**. Bumping may result, and the temperature of the vapor may become so high that inaccurate measurement of the boiling point is observed. In contrast, if the rate of heating is too low, it will not only prolong the distillation process, but also a temporary shortage of vapor may cause the boiling point measured to be lower than the true value.

As overheating may result at the point of contact with the heat source, it is vital to stir during heating to avoid bumping. This can be done easily by using a magnetic stirrer or by adding one or two boiling chips. As boiling chips will lead to the formation of gas bubbles due to their porous structure, convection will result. This convection can prevent bumping. It should be noted that boiling chips should not be added during the heating process; otherwise, strong bumping may result due to sudden boiling if the solution has already reached the boiling point. Thus, heating should be stopped and the solution allowed to cool below its boiling point before any boiling chips are added. Moreover, boiling chips are not reusable, and fresh boiling chips should be added whenever distillation is restarted.

VI. The apparatus for fractional distillation

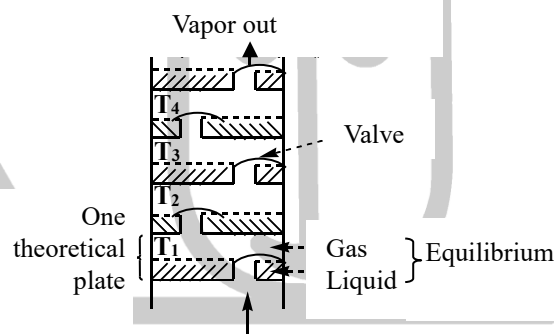
The fractionating column is the most important part in fractional distillation. There are several factors which may affect the distillation efficiency: (1) the type of packing materials inside the fractionating column; (2) temperature control of the

fractionating column; (3) the length of the fractionating column; and (4) the difference between the boiling points of the components of the mixture.

Numerous liquid-vapor equilibrium zones are present in the fractionating column. All these zones are on the surface of the packing inside the column. Therefore, a larger surface area of the packing will allow more equilibrium zones to be present, and hence the efficiency of the separation will be better. Note that packing materials should not react with the distillates. Glass beads, glass helices, and steel wool are some commonly used packing materials.

Theoretically, there are a number of “chambers of liquid-vapor equilibrium” within the column, and the vapor gradually rises from one chamber to another. These chambers are called **theoretical plates** (Figure 21-5). A higher number of these chambers increases the separating power. This relationship can be further expressed with a parameter called “height equivalent to a theoretical plate” (HETP). For a fractionating column of fixed length, the smaller the value of HETP is, the greater the number of theoretical plates and hence the better the efficiency of separation.

The value of HETP is based on the type of packing materials used. The properties of some commonly used packing materials are listed in Table 21-1 for reference. In this table, it can be seen that a larger surface area corresponds to a smaller value of HETP. However, the loss of components due to hold-up on the surface of the packing will also increase.



Vapor goes up through valve. Temperature: $T_1 > T_2 > T_3 > T_4$

Figure 21-5 Diagram of theoretical plates

Table 21-1 Properties of some commonly used packing materials

Packing materials	HETP (cm)	Column length: 20 cm width: 2 cm		Separable boiling point difference (°C)
		Number of plates	Hold-up (mL)	
Vigreux column	8	2.5	1	60
Glass beads	7	3	3	54
Glass helices	4	5	5	36

During the process of fractional distillation, the over-condensation of liquid inside the fractionating column should be avoided to prevent flooding. In the worst case, the whole column is filled with liquid. If flooding occurs, the liquid-vapor equilibrium zones will be destroyed and the rising vapor will push the liquid above into the condenser. Obviously, this will affect the quality of the separation. Several factors can cause flooding. The main reason of flooding is a large temperature difference between the interior and the exterior of the column. If the difference is too great, the vapor will condense inside the column to a large extent. Since a higher temperature within the column will lead to a greater difference, and thus a greater condensation effect, insulation should be wrapped around the fractionating column to minimize heat loss. Other factors that can increase the chance of flooding are an excessively high heating rate causing a high vapor generation rate, and a larger surface area to volume ratio of the packing. In the latter respect, it is suggested that the hold-up should not exceed about 10 percent of the amount of sample to be distilled.

In an ideal fractional distillation, the temperature of the vapor at the bottom of the fractionating column would be very close to that of the liquid in the distillation flask. The temperature of the vapor will gradually decrease as it rises up the column. The temperature at the top of the column will therefore be very close to the boiling point of the component with the lower boiling point. If the solution is heated too rapidly or the vapor generation rate is too high, the vapor will rise very quickly, leading to a very small temperature difference between the top and the bottom of the column. Hence, full liquid-vapor equilibrium cannot be attained, and the result of the fractional distillation will be affected. Thus, an ideal temperature gradient should be created by both adjusting the distillation rate carefully and minimizing heat loss inside the fractionating column at the same time.

For a fixed amount of mixture, using a greater amount of packing in the fractional distillation increases the total surface area, which in turn increases the number of liquid-vapor equilibria attained. Thus, the efficiency of separation will be better. It follows that increasing the length of a fractionating column will allow better results. Note that the result of fractional distillation will not be affected by increasing the diameter of the column, as the temperature at the same level should be the same. However, the diameter of the column does affect the time of distillation. Generally speaking, a wider column is required for distillation of a large amount of a mixture. Although it is better to use a long fractionating column, the resulting increase in the surface area of the packing will result in more distillate being lost as hold-up, and the amount of distillate collected will decrease. Thus, a fractionating column of suitable length should be chosen after weighing up both the purity and the amount of

the product collected carefully.

The boiling point range of the distillate, the length of the fractionating column, and the type of packing used should be recorded, as these are important parameters for fractional distillation.

More sophisticated fractionation devices can control the rate of reflux and the rate of collection. The ratio between the two is called the reflux ratio. When the collection rate is high, the reflux ratio is low, the gas-liquid balance is less likely to be complete, and the separation is poor. However, when a very high reflux ratio is used, the whole process becomes too long due to the slow collection rate. Therefore, the reflux ratio needs to be properly controlled to achieve the most efficient results. When using a more common device for fractionation, since the reflux rate cannot be controlled, the heating temperature must be appropriately controlled to avoid overheating, which may cause the collection rate to be too fast.

VII. Set-up and operation of distillation

Refer to Figure 21-6, place a heating device or heating mantle on the lab jack and fix the distillation flask with a clamp. A lab jack under the heating mantle will be helpful in adjusting the level of the mantle. Then install the still-head and thermometer accordingly. If necessary, fill the gap between the flask and the mantle with sea sand for better heat transfer. If the sample has a low boiling point, a hot water bath can be used for heating. Next, connect the condenser to the side arm of the still-head and fix the condenser with a clamp. Care should be taken to avoid building up any mechanical torque, as it may cause the still-head to crack. Afterwards, connect the vacuum adaptor to the condenser and then place the receiving flask below the adaptor, fixed with a clamp. Do not use a beaker with a large opening for collection as the distillate will evaporate into the surrounding atmosphere. In addition, the receiving flask should be cleaned thoroughly, dried, and then weighed before use. Furthermore, the lumen of the condenser should not contain any foreign substances.

Heating will cause the sample to boil; the vapor will then be condensed in the condenser and collected in the receiving flask. It is crucial to adjust the heat source when the sample starts to boil. The rate of heating at this stage should be adjusted to maintain a rate of about 1 drop of distillate per second, and the boiling point range should be recorded. Finally, the receiving flask with the collected sample should be weighed to obtain the amount of distillate collected. However, for the special purpose of this experiment we use a graduated cylinder fitted with a funnel as the receiver instead.

Apparatus

Lab jack, heating mantle, temperature controller, round bottom flask (25 mL), condenser, rubber tube (2), distillation head, vacuum adaptor, fractionating column,

thermometer, septum stopper, graduated cylinder (10 mL, 2), three prong clamp (4), funnel, Keck clip (2), boiling chips.

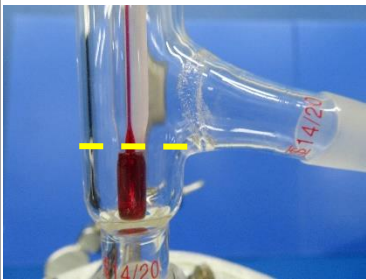
Shared: Air compressor, sea sand.

Chemicals

Toluene ($\text{C}_6\text{H}_5\text{CH}_3$), ethyl acetate ($\text{CH}_3\text{COOC}_2\text{H}_5$).

Procedures

Procedure	Illustration
I. Simple distillation of a liquid mixture	
1. Record the atmospheric pressure (posted on the blackboard by the student on duty) on that day.	
2. Add 8 mL of toluene, 6 mL of ethyl acetate, and one or two boiling chips into a 25 mL round bottom flask.	
3. Assemble and setup the distillation apparatus as illustrated in Figure 21-6; replace the receiving flask with a 10-mL graduated cylinder held in place with a clamp. In this way the volume of the distillate can be measured in milliliters. Ensure that all joints are tight. Connect the heating mantle to the temperature controller. Note 1: The solvents and compounds used in organic chemistry are mostly flammable. Therefore, direct heating should be avoided. Note 2: The apparatus should be set vertically, without tilting to one side. Care should be taken in using the clamp so as to avoid cracking the glassware. Note 3: The upper level of the thermometer bulb of the thermometer should be at the same level as the lower rim of the opening in order to measure the accurate temperature.	  

	Note 4: Turn on the tap before heating to allow water flow through the condenser from the bottom inlet to the top outlet. Only a small stream of water is needed to avoid excessive water pressure.	
4.	Turn the power on and start heating the solution slowly to a boil. Observe the temperature of the vapor when the first drop of distillate is collected. Adjust the heating rate to obtain a collection rate of about 1 drop of distillate per second.	
5.	Record the temperature once for every 0.5 mL of distillate collected until 10 mL of distillate has been collected. Turn off the heating. Lower the heating mantle to detach the distillation flask from the mantle quickly. Note: Never distill to dryness. A dry residue containing peroxides may explode on overheating, or the flask may crack.	
6.	Remove the heating mantle carefully and do not spill any chemicals on it. Carefully pour the hot sea sand into a 150 mL beaker to cool down. Caution: Wear linen cotton gloves while removing the heating mantle.	
II. Fractional distillation of a liquid mixture		
7.	Take the distillation apparatus apart, rinse the condenser and adaptor with small portions of acetone, then blow to dry.	

8.	Transfer the distillate collected in part I to the distillation flask and add fresh boiling chips. Note: If the volume of collected liquid is less than 10 mL, an appropriate amount of toluene and ethyl acetate mixture (4:3, v/v) can be added.	
9.	Setup the fractional distillation apparatus as illustrated, secure the fractionating column with a clamp, and collect the distillate in a graduated cylinder directly.	
10.	Heat gently. Register the temperature when the first drop of distillate is collected. Keep track of the temperature once for every 0.5 mL collected. When the collection of the first component is completed, record the total volume and the corresponding temperature range of the distillate. Note: You may insulate the fractionating column with aluminum foil loosely to maintain the vapor-liquid equilibrium if the material to be distilled has a high boiling point.	
11.	After the entire lower boiling component has been distilled, use another graduated cylinder to collect the higher boiling component. Raise the voltage in order to provide enough energy to distill the higher boiling material. Keep recording the temperature until small portions of residue remains. Turn off the heating, lower the heating mantle to quickly disengage from the distillation flask to avoid heating to dryness.	
12.	Discard the liquid waste in the organic waste container. Recycle the sea sand and collect the used boiling chips in designated containers; then wash the apparatus and clean up the bench.	

References

1. National Taiwan University, Department of Chemistry; *Experiments of Organic Chemistry*, 8th ed.; NTU Press: Taipei, 2006.
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3. Pavia, D. L. *Introduction to Organic Laboratory Techniques: A Microscale Approach*, 1st ed.; Saunders College Pub.: Philadelphia, 1990.
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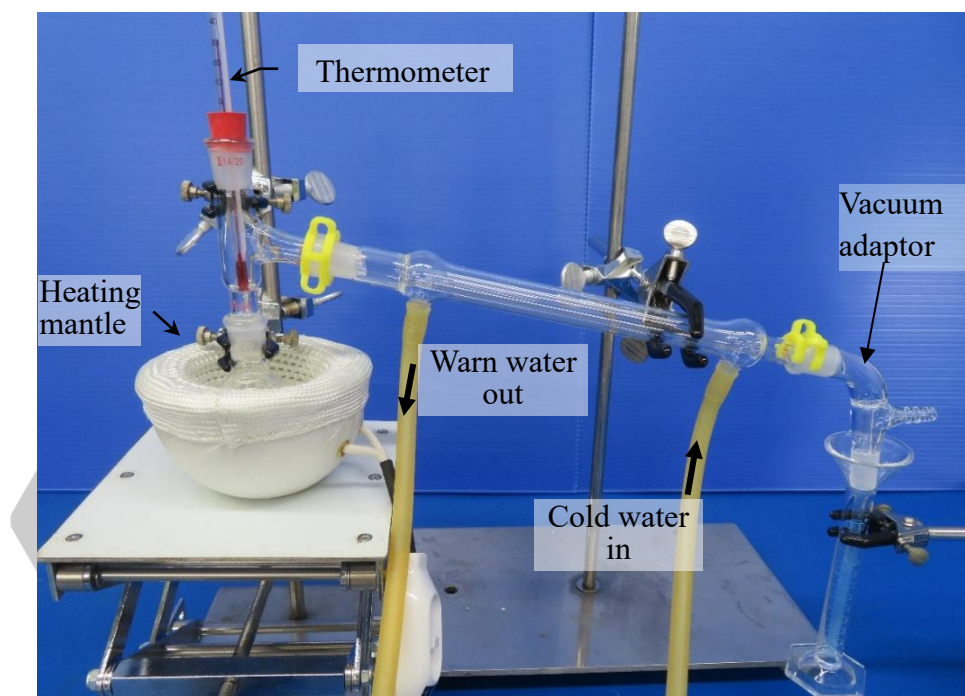


Figure 21-6 The set-up of simple distillation
(In this experiment graduated cylinder is used as receiver)