PROBLEMS

1. Why is solid carbon dioxide called dry ice? How does it differ from solid water in behavior?
2. Under what conditions can you have *liquid* carbon dioxide?
3. A solid substance has a vapor pressure of 800 mmHg at its melting point (80 °C). Describe how the solid behaves as the temperature is raised from room temperature to 80 °C while as the atmospheric pressure is held constant at 760 mmHg.
4. A solid substance has a vapor pressure of 100 mmHg at the melting point (100 °C). Assuming an atmospheric pressure of 760 mmHg, describe the behavior of this solid as the temperature is raised from room temperature to its melting point.
5. A substance has a vapor pressure of 50 mmHg at the melting point (100 °C). Describe how you would experimentally sublime this substance.

18 TECHNIQUE 18

Steam Distillation

Sign in at www.cengage.com/login to access the Pre-Lab Video Exercise for this technique.

The simple, fractional, and vacuum distillations described in Techniques 14, 15, and 16 are applicable to completely soluble (miscible) mixtures only. When liquids are *not* mutually soluble (immiscible), they can also be distilled but with a somewhat different result. A mixture of immiscible liquids will boil at a lower temperature than the boiling points of any of the separate components as pure compounds. When steam is used to provide one of the immiscible phases, the process is called **steam distillation**. The advantage of this technique is that the desired material distills at a temperature below 100°C. Thus, if unstable or very high-boiling substances are to be removed from a mixture, decomposition is avoided. Because all gases mix, the two substances can mix in the vapor and codistill. Once the distillate is cooled, the desired component, which is not miscible, separates from the water. Steam distillation is used widely in isolating liquids from natural sources. It is also used in removing a reaction product from a tarry reaction mixture.

PART A. THEORY

18.1 Differences Between Distillation of Miscible and Immiscible Mixtures

$$\text{Miscible liquids} \qquad P_{\text{total}} = P_{\text{A}}^{0} N_{\text{A}} + P_{\text{B}}^{0} N_{\text{B}} \tag{1}$$

Two liquids A and B that are mutually soluble (miscible) and that do not interact form an ideal solution and follow Raoult's Law, as shown in equation 1. Note that the vapor pressures of pure liquids P_{A}° and P_{B}° are not added directly to give the total pressure P_{total}, but are reduced by the respective mole fractions N_{A} and N_{B}. The total pressure above a miscible or homogeneous solution will depend on P_{A}° and P_{B}° and also on N_{A} and N_{B}. Thus, the composition of the vapor will depend on *both* the vapor pressures and the mole fractions of each component.

$$\text{Immiscible liquids} \qquad P_{\text{total}} = P_{\text{A}}^{0} + P_{\text{B}}^{0} \tag{2}$$

In contrast, when two mutually insoluble (immiscible) liquids are "mixed" to give a heterogeneous mixture, each exerts its own vapor pressure, independently of

the other, as shown in equation 2. The mole fraction term does not appear in this equation, because the compounds are not miscible. You simply add the vapor pressures of the pure liquids P_A^0 and P_B^0 at a given temperature to obtain the total pressure above the mixture. When the total pressure equals 760 mmHg, the mixture boils. The composition of the vapor from an immiscible mixture, in contrast to that of the miscible mixture, is determined only by the vapor pressures of the two substances codistilling. Equation 3 defines the composition of the vapor from an immiscible mixture. Calculations involving this equation are given in Section 18.2.

$$\frac{\text{Moles A}}{\text{Moles B}} = \frac{P_A^0}{P_B^0} \tag{3}$$

A mixture of two immiscible liquids boils at a lower temperature than the boiling points of either component. The explanation for this behavior is similar to that given for minimum-boiling-point azeotropes (see Technique 15, Section 15.7). Immiscible liquids behave as they do because an extreme incompatibility between the two liquids leads to higher combined vapor pressure than Raoult's Law would predict. The higher combined vapor pressures cause a lower boiling point for the mixture than for either single component. Thus, you may think of steam distillation as a special type of azeotropic distillation in which the substance is completely insoluble in water.

The differences in behavior of miscible and immiscible liquids, where it is assumed that P_A^0 equals P_B^0, are shown in Figure 18.1. Note that with miscible liquids, the composition of the vapor depends on the relative amounts of A and B present (see Figure 18.1A). Thus, the composition of the vapor must change during a distillation. In contrast, the composition of the vapor with immiscible liquids is independent of the amounts of A and B present (see Figure 18.1B). Hence, the vapor composition must remain *constant* during the distillation of such liquids, as predicted by equation 3. Immiscible liquids act as if they were being distilled simultaneously from separate

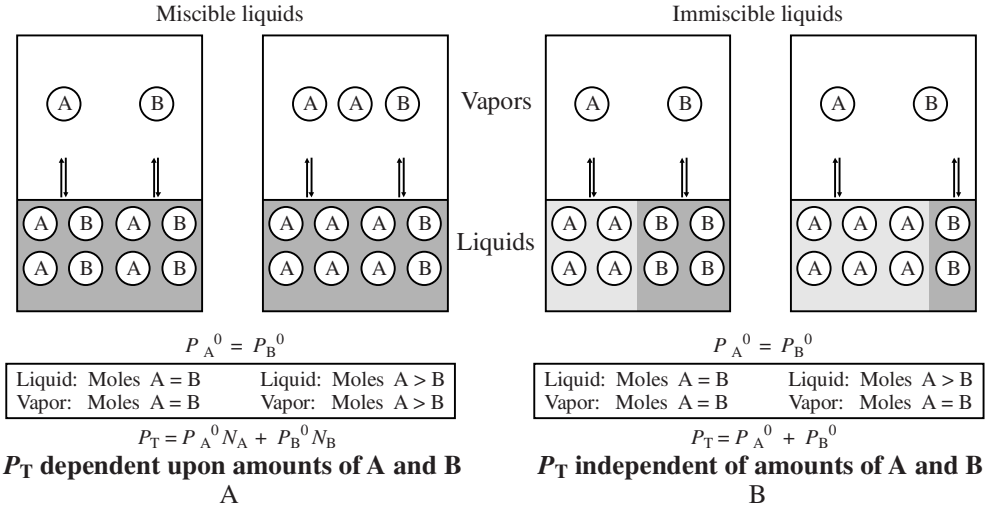

Figure 18.1 Total pressure behavior for miscible and immiscible liquids. (A) Ideal miscible liquids follow Raoult's Law: P_T depends on the mole fractions and vapor pressures of A and B. (B) Immiscible liquids do not follow Raoult's Law: P_T depends only on the vapor pressures of A and B.

compartments, as shown in Figure 18.1B, even though in practice they are "mixed" during a steam distillation. Because all gases mix, they do give rise to a homogeneous vapor and codistill.

18.2 Immiscible Mixtures: Calculations

The composition of the distillate is constant during a steam distillation, as is the boiling point of the mixture. The boiling points of steam-distilled mixtures will always be below the boiling point of water (bp 100°C), as well as the boiling point of any of the other substances distilled. Some representative boiling points and compositions of steam distillates are given in Table 18.1. Note that the higher the boiling point of a pure substance, the more closely the temperature of the steam distillate approaches, but does not exceed, 100°C. This is a reasonably low temperature, and it avoids the decomposition that might result at high temperatures with a simple distillation.

For immiscible liquids, the molar proportions of two components in a distillate equal the ratio of their vapor pressures in the boiling mixture, as given in equation 3. When equation 3 is rewritten for an immiscible mixture involving water, equation 4 results. Equation 4 can be modified by substituting the relationship moles = (weight/molecular weight) to give equation 5.

$$\frac{\text{Moles substance}}{\text{Moles water}} = \frac{P^0_{\text{substance}}}{P^0_{\text{water}}} \tag{4}$$

$$\frac{\text{Wt substance}}{\text{Wt water}} = \frac{(P^0_{\text{substance}})(\text{Molecular weight}_{\text{substance}})}{(P^0_{\text{water}})(\text{Molecular weight}_{\text{water}})} \tag{5}$$

A sample calculation using this equation is given in Table 18.2. Notice that the result of this calculation is very close to the experimental value given in Table 18.1.

TABLE 18.1 Boiling Points and Compositions of Steam Distillates

Mixture	Boiling Point of Pure Substance (°C)	Boiling Point of Mixture (°C)	Composition (% water)
Benzene–water	80.1	69.4	8.9%
Toluene–water	110.6	85.0	20.2%
Hexane–water	69.0	61.6	5.6%
Heptane–water	98.4	79.2	12.9%
Octane–water	125.7	89.6	25.5%
Nonane–water	150.8	95.0	39.8%
1-Octanol–water	195.0	99.4	90.0%

TABLE 18.2 Sample Calculations for a Steam Distillation

Problem How many grams of water must be distilled to steam distill 1.55 g of 1-octanol from an aqueous solution? What will be the composition (wt%) of the distillate? The mixture distills at 99.4°C.

Answer The vapor pressure of water at 99.4°C must be obtained from the CRC Handbook (= 744 mmHg).

a. Obtain the partial pressure of 1-octanol.

$$P^{\circ}_{\text{1-octanol}} = P_{\text{total}} - P^{\circ}_{\text{water}}$$

$$P^{\circ}_{\text{1-octanol}} = (760 - 744) = 16 \text{ mmHg}$$

b. Obtain the composition of the distillate.

$$\frac{\text{wt 1-octanol}}{\text{wt water}} = \frac{(16)(130)}{(744)(18)} = 0.155 \text{ g/g-water}$$

c. Clearly, 10 g of water must be distilled.

$$(0.155 \text{ g/g-water})(10 \text{ g-water}) = 1.55 \text{ g 1-octanol}$$

d. Calculate the weight percentages.

$$\text{1-octanol} = 1.55 \text{ g}/(10 \text{ g} + 1.55 \text{ g}) = 13.4\cdots$$

$$\text{water} = 10 \text{ g}/(10 \text{ g} + 1.55 \text{ g}) = 86.6\cdots$$

PART B. MACROSCALE DISTILLATION

18.3 Steam Distillation—Macroscale Methods

Two methods for steam distillation are generally used in the laboratory: the **direct method** and the **live steam method**. In the first method, steam is generated *in situ* (in place) by heating a distillation flask containing the compound and water. In the second method, steam is generated outside and is passed into the distillation flask using an inlet tube.

A. Direct Method

A macroscale direct method steam distillation is illustrated in Figure 18.2. Although a heating mantle may be used, it is probably best to use a flame with this method, because a large volume of water must be heated rapidly. A boiling stone must be used to prevent bumping. The separatory funnel allows more water to be added during the course of the distillation.

Distillate is collected as long as it is either cloudy or milky white in appearance. Cloudiness indicates that an immiscible liquid is separating. When the distillate runs clear in the distillation, it is usually a sign that only water is distilling. However, there are some steam distillations where the distillate is never cloudy, even though material has codistilled. You must observe carefully, and be sure to collect enough distillate so that all of the organic material codistills.

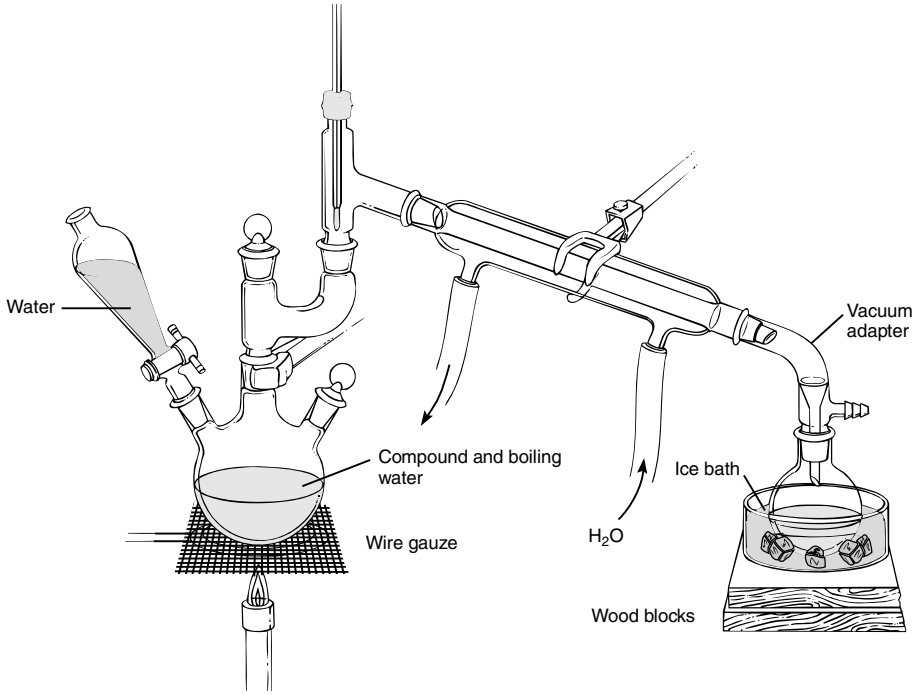

Figure 18.2 A macroscale direct method steam distillation.

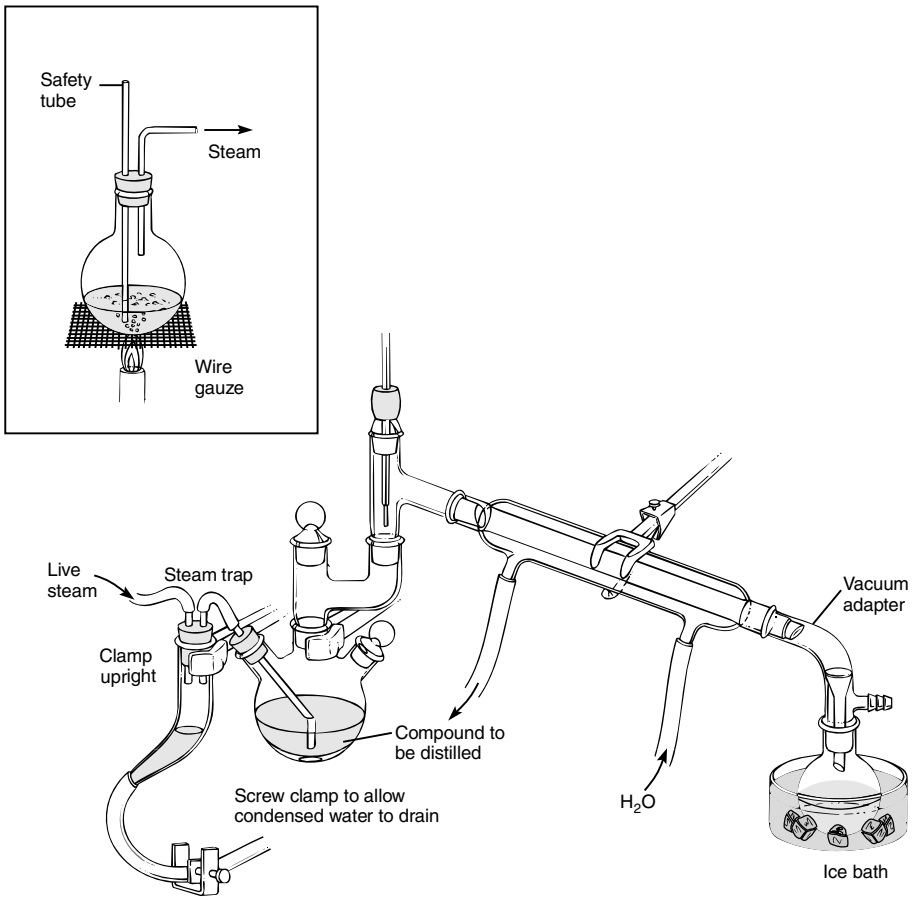

Figure 18.3 A macroscale steam distillation using live steam.

B. Live Steam Method

A macroscale steam distillation using the live steam method is shown in Figure 18.3. If steam lines are available in the laboratory, they may be attached directly to the steam trap (purge them first to drain water). If steam lines are not available, an external steam generator (see inset) must be prepared. The external generator usually will require a flame to produce steam at a rate fast enough for the distillation. When the distillation is first started, the clamp at the bottom of the steam trap is left open. The steam lines will have a large quantity of condensed water in them until they are well heated. When the lines become hot and condensation of steam ceases, the clamp may be closed. Occasionally, the clamp will have to be reopened to remove condensate. In this method, the steam agitates the mixture as it enters the bottom of the flask, and a stirrer or boiling stone is not required.

CAUTION

Hot steam can produce very severe burns.

Sometimes it is helpful to heat the three-necked distilling flask with a heating mantle (or flame) to prevent excessive condensation at that point. Steam must be admitted at a fast enough rate for you to see the distillate condensing as a milky white fluid in the condenser. The vapors that codistill will separate on cooling to give this cloudiness. When the condensate becomes clear, the distillation is near the end. The flow of water through the condenser should be faster than in other types of distillation to help cool the vapors. Make sure the vacuum adapter remains cool to the touch. An ice bath may be used to cool the receiving flask if desired. When the distillation is to be stopped, the screw clamp on the steam trap should be opened, and the steam inlet tube must be removed from the three-necked flask. If this is not done, liquid will back up into the tube and steam trap.

PART C. MICROSCALE DISTILLATION

18.4 Steam Distillation—Microscale Methods

The direct method of steam distillation is the only one suitable for microscale experiments. Steam is produced in the conical vial or distillation flask (*in situ*) by heating water to its boiling point in the presence of the compound to be distilled. This method works well for small amounts of materials. A microscale steam distillation apparatus is shown in Figure 18.4. Water and the compound to be distilled are placed in the flask and heated. A stirring bar or a boiling stone should be used to prevent bumping. The vapors of the water and the desired compound codistill when they are heated. They are condensed and collect in the Hickman head. When the Hickman head fills, the distillate is removed with a Pasteur pipet and placed in another vial for storage. For the typical microscale experiment, it will be necessary to fill the well and remove the distillate three or four times. All of these distillate fractions are placed in the same storage container. The efficiency in collecting the distillate can sometimes be improved if the inside walls of the Hickman head are rinsed several times into the well. A Pasteur pipet is used to perform the rinsing. Distillate is withdrawn from the well, and then it is used to wash the walls of the Hickman head all the way around the head. After the walls have been washed and

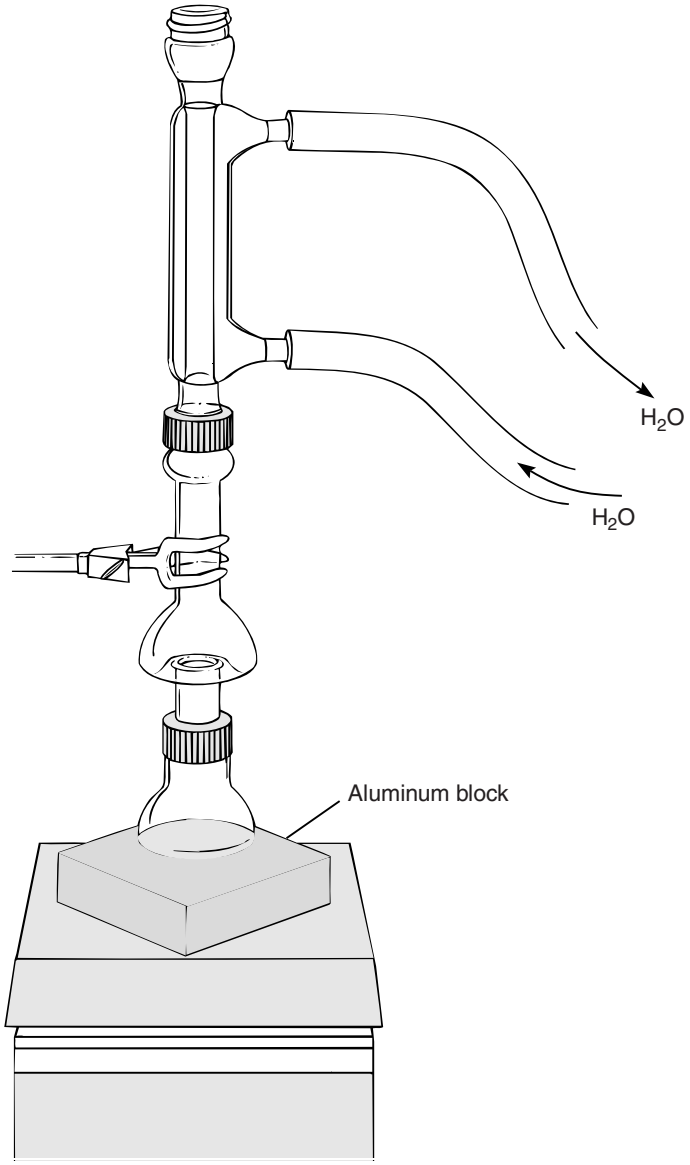

Figure 18.4 Microscale steam distillation.

when the well is full, the distillate can be withdrawn and transferred to the storage container. It may be necessary to add more water during the course of the distillation. More water is added (remove the condenser if used) through the center of the Hickman head by using a Pasteur pipet.

PART D. SEMI-MICROSCALE DISTILLATION

18.5 Steam Distillation—Semi-Microscale Methods

The apparatus shown in Technique 14, Figure 14.5, may also be used to perform a steam distillation at the microscale level or slightly above. This apparatus avoids the need to empty the collected distillate during the course of the distillation, as is required when a Hickman head is used.

PROBLEMS

1. Calculate the weight of benzene codistilled with each gram of water and the percentage composition of the vapor produced during a steam distillation. The boiling point of the mixture is 69.4°C. The vapor pressure of water at 69.4°C is 227.7 mmHg. Compare the result with the data in Table 18.1.
2. Calculate the approximate boiling point of a mixture of bromobenzene and water at atmospheric pressure. A table of vapor pressure of water and bromobenzene at various temperatures is given.

	Vapor Pressures (mmHg)	
Temperature (°C)	**Water**	**Bromobenzene**
93	588	110
94	611	114
95	634	118
96	657	122
97	682	127
98	707	131
99	733	136

3. Calculate the weight of nitrobenzene that codistills (bp 99°C of mixture) with each gram of water during a steam distillation. You may need the data given in problem 2.
4. A mixture of *p*-nitrophenol and *o*-nitrophenol can be separated by steam distillation. The *o*-nitrophenol is steam volatile, and the *para* isomer is not volatile. Explain. Base your answer on the ability of the isomers to form hydrogen bonds internally.

19 TECHNIQUE 19

Column Chromatography

Sign in at www.cengage.com/login to access the Pre-Lab Video Exercise for this technique.

The most modern and sophisticated methods of separating mixtures available to the organic chemist all involve **chromatography**. Chromatography is defined as the separation of a mixture of two or more different compounds or ions by distribution between two phases, one of which is stationary and the other is moving. Various types of chromatography are possible, depending on the nature of the two phases involved: **solid–liquid** (column, thin-layer, and paper), **liquid–liquid** (high-performance liquid), and **gas–liquid** (vapor-phase) chromatographic methods are common.

All chromatography works on much the same principle as solvent extraction (see Technique 12). Basically, the methods depend on the differential solubilities or adsorptivities of the substances to be separated relative to the two phases between which they are to be partitioned. Here, column chromatography, a solid–liquid method, is considered. Thin-layer chromatography is examined in Technique 20;