Distillation

Pharmaceutical organic chemistry lab

Dr. Rand Omar Shahin

Purification

- Once the organic compound has been extracted from the reaction mixture it must be purified. There are several methods for purifying compounds but the most common are:
- recrystallization
- distillation/
- fractional distillation
- chromatography.

Fractional distillation & Simple distillation

- Fractional distillation can be used to separate **liquids** that have **quite similar boiling points** –
- whereas **simple distillation** is used to separate liquids with **very different boiling points** or for separating a liquid from a non-volatile residue.

The experimental set-up for fractional distillation is shown in the next Figure

- The column is made of moulded glass or is packed with small beads to give a very large surface area.
- The mixture of liquids is heated and the liquid with the lower boiling point is collected by condensing the vapour.
- **To understand how fractional distillation works you need to understand a bit more about liquid–vapour equilibria**

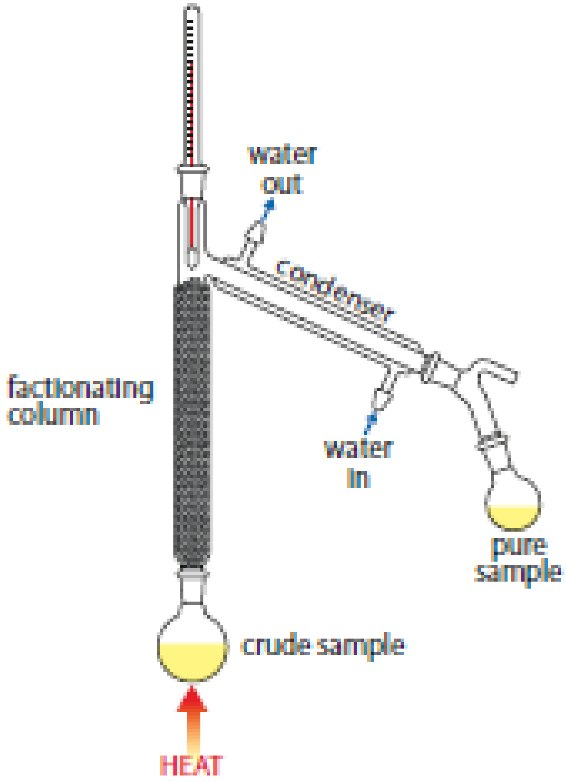


Figure D.44 The experimental set-up for fractional distillation.

Raoult’s law

- The vapour above a liquid in a closed container exerts a pressure on the walls of the container.
- If the vapour is in equilibrium with the liquid, this pressure is called the vapour pressure (or ‘equilibrium vapour pressure’ or ‘saturated vapour pressure’)
- **Vapour pressure** is the pressure exerted by a vapour in equilibrium with a liquid (or a solid).

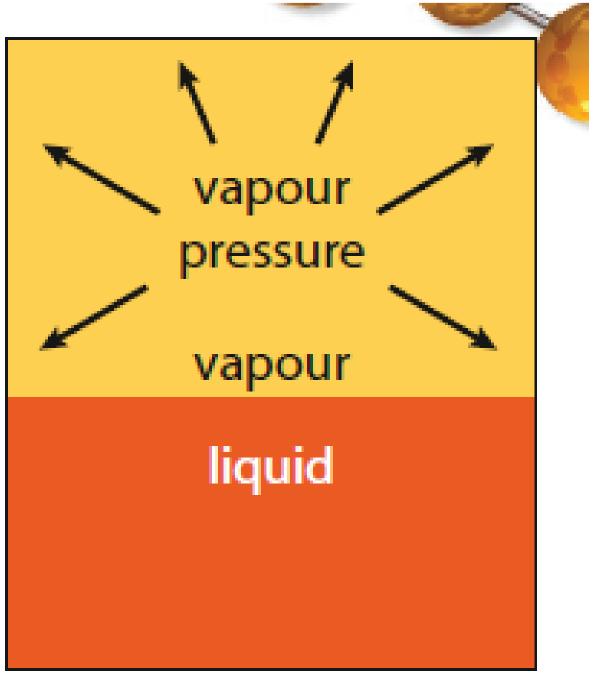
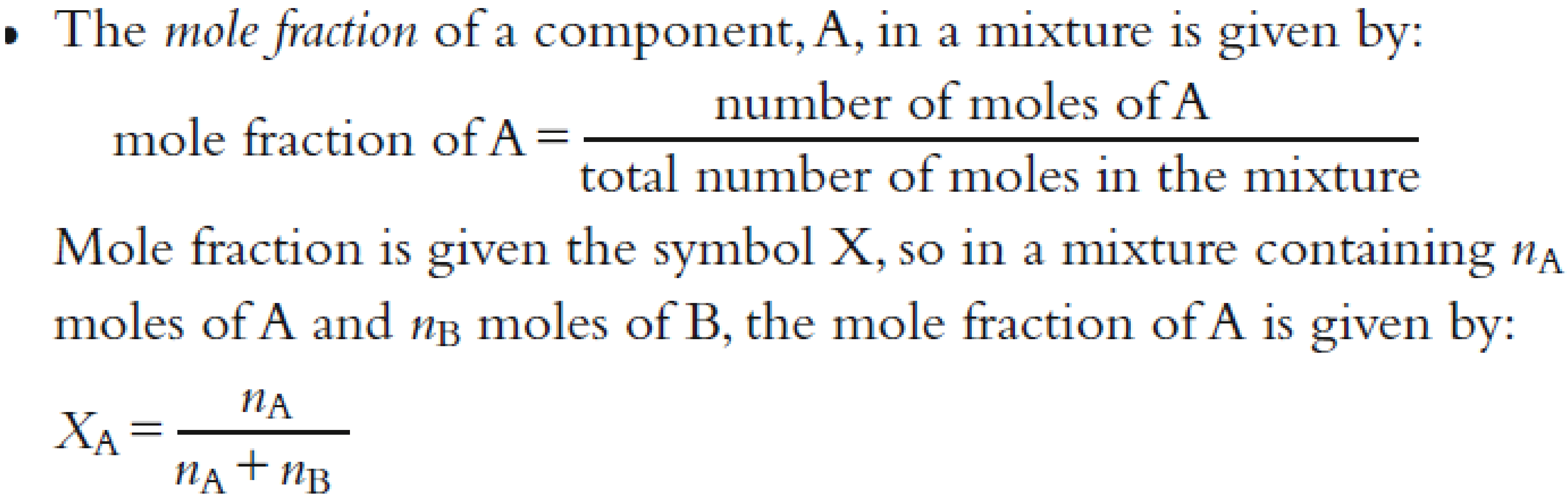


Figure D.45 A vapour in equilibrium with its liquid exerts a vapour pressure.

Vapour pressure

- For a pure liquid, the vapour pressure depends only on the nature of the liquid and the temperature. For a mixture of liquids, the vapour pressure also depends on how much of each liquid is present.
- Raoult’s law states that the partial vapour pressure of any volatile component of an ideal solution is equal to the vapour pressure of the pure liquid multiplied by the mole fraction of that liquid in the solution.
- To understand what this means we need to introduce a few terms:
- • *Volatile* – something that evaporates readily.
- • *Ideal solution* – a mixture of liquids in which the intermolecular forces are the same as in the pure liquids – i.e. the tendency for a liquid to evaporate is the same in the pure liquid as in the solution.
- An example of a fairly-close-to-ideal solution is a mixture of hexane (C_6H_{14}) and
- heptane (C_7H_{16}).

Raoult’s law cont.



- The *mole fraction* of a component, A, in a mixture is given by:

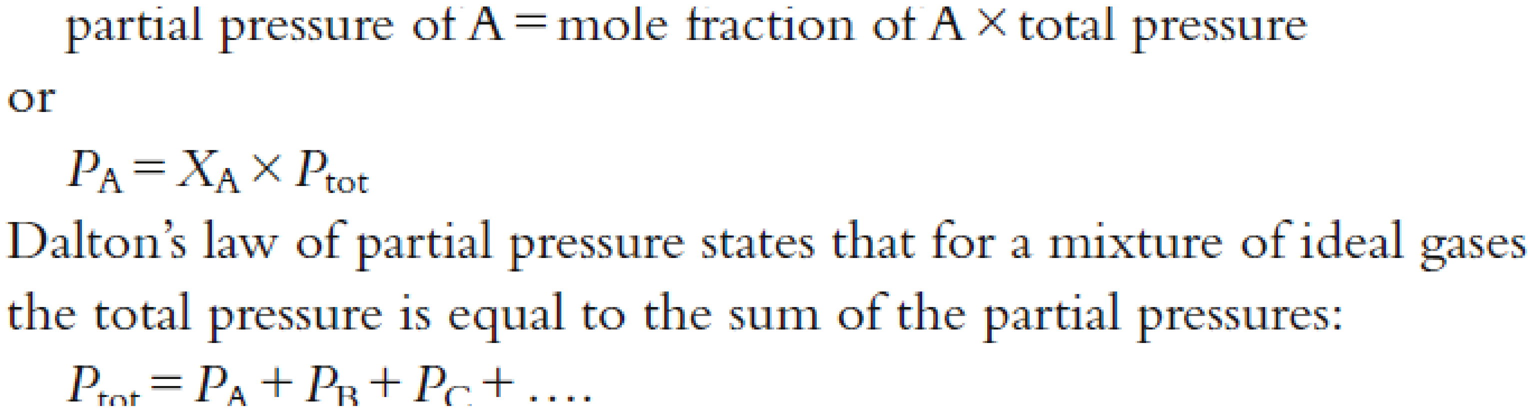
$$\text{mole fraction of A} = \frac{\text{number of moles of A}}{\text{total number of moles in the mixture}}$$

Mole fraction is given the symbol X, so in a mixture containing n_A moles of A and n_B moles of B, the mole fraction of A is given by:

$$X_A = \frac{n_A}{n_A + n_B}$$

Note that mole fraction is a ratio and therefore has no units.

- *Partial pressure* – refers to the pressure exerted by a particular gas in a mixture of gases. If the gases behave ideally, the partial pressure is the same as the pressure that the same amount of that particular gas would exert if it were in the container by itself.
- If the pressure exerted by a mixture of 80% nitrogen and 20% oxygen is 100 kPa, the partial pressure of nitrogen is 80 kPa and that of oxygen is 20 kPa. Partial pressure is calculated from:



partial pressure of A = mole fraction of A × total pressure

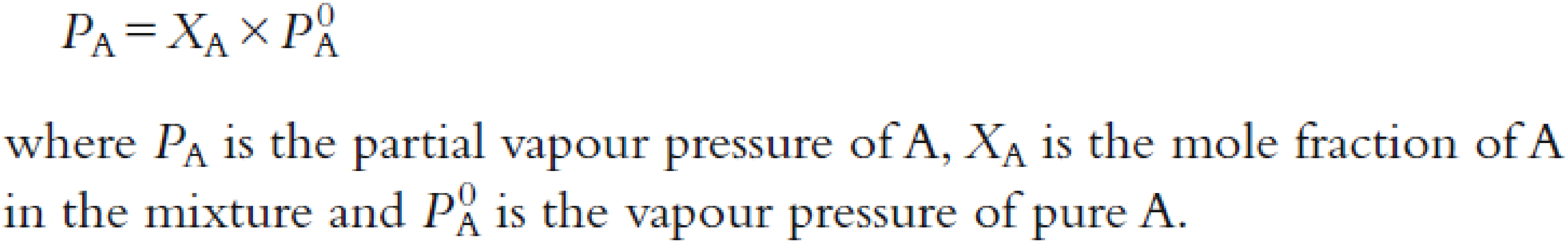
or

$$P_A = X_A \times P_{tot}$$

Dalton's law of partial pressure states that for a mixture of ideal gases the total pressure is equal to the sum of the partial pressures:

$$P_{tot} = P_A + P_B + P_C + \ldots.$$

- Returning to Raoult’s law, it basically says that the contribution of each component of a mixture to the total vapour pressure depends on what the vapour pressure of the pure liquid is and how much is present in the mixture. It can be written:



$$P_A = X_A \times P_A^0$$

where P_A is the partial vapour pressure of A, X_A is the mole fraction of A in the mixture and P_A^0 is the vapour pressure of pure A.

Figure **D.46** shows how the vapour pressure of an ideal mixture varies with the composition of the mixture at constant temperature. At any point, the total vapour pressure is the sum of the partial vapour pressures of the components.

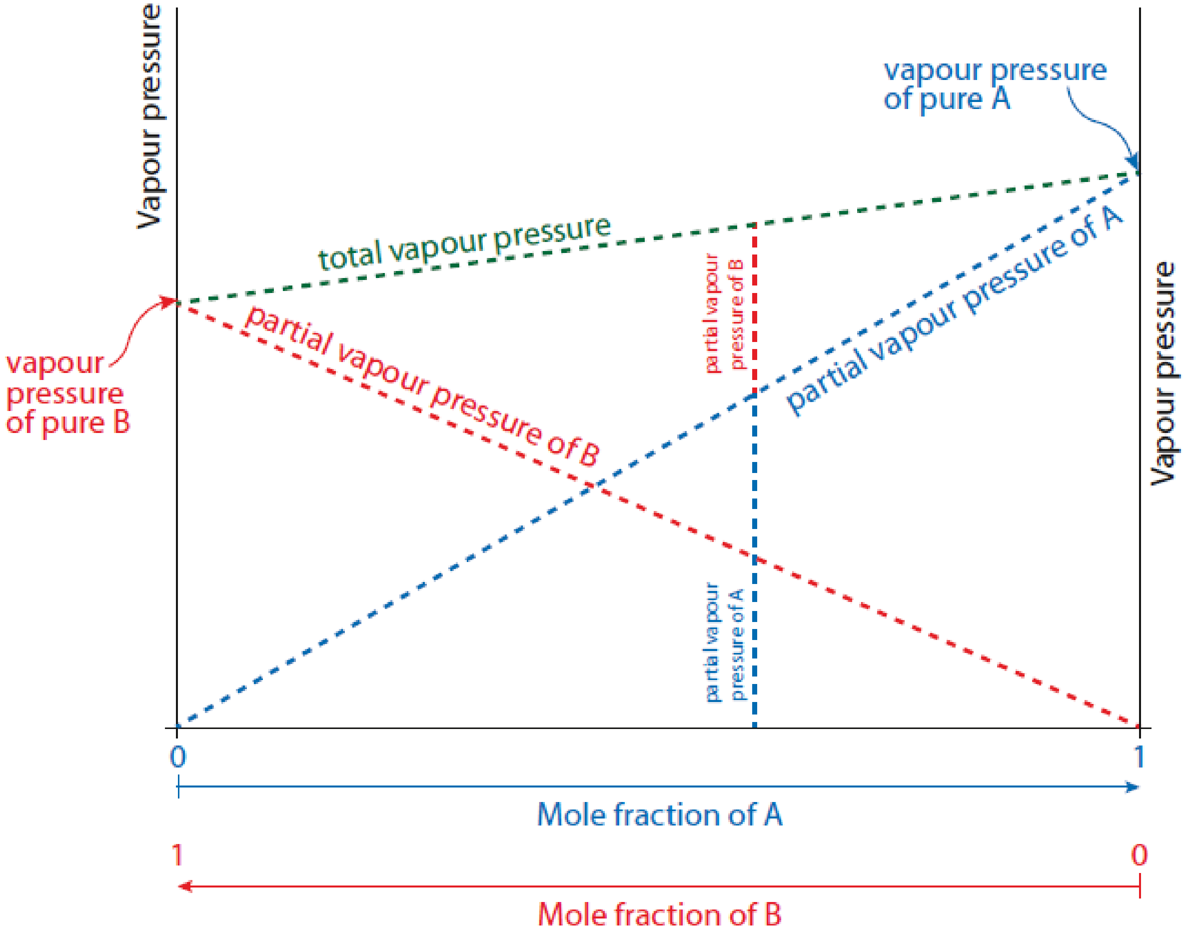


Figure D.46 The variation of vapour pressure with composition for an ideal solution.

Worked example

D.18 Given that the vapour pressures of pure hexane and heptane at 25 °C are 20.5 kPa and 6.10 kPa respectively, calculate the vapour pressure of an ideal solution containing 4.00 mol hexane and 4.00 mol heptane at 25 °C. Then calculate the mole fraction of each in the vapour.

Using Raoult's Law:

$$P_A = X_A \times P_A^0$$

$$X_A = \frac{n_A}{n_A + n_B}$$

$$X_{\text{hexane}} = \frac{4.00}{4.00 + 4.00} = 0.500$$

$$X_{\text{heptane}} = \frac{4.00}{4.00 + 4.00} = 0.500$$

$$P_{\text{hexane}} = 0.500 \times 20.5 = 10.25\ \text{kPa}$$

$$P_{\text{heptane}} = 0.500 \times 6.10 = 3.05\ \text{kPa}$$

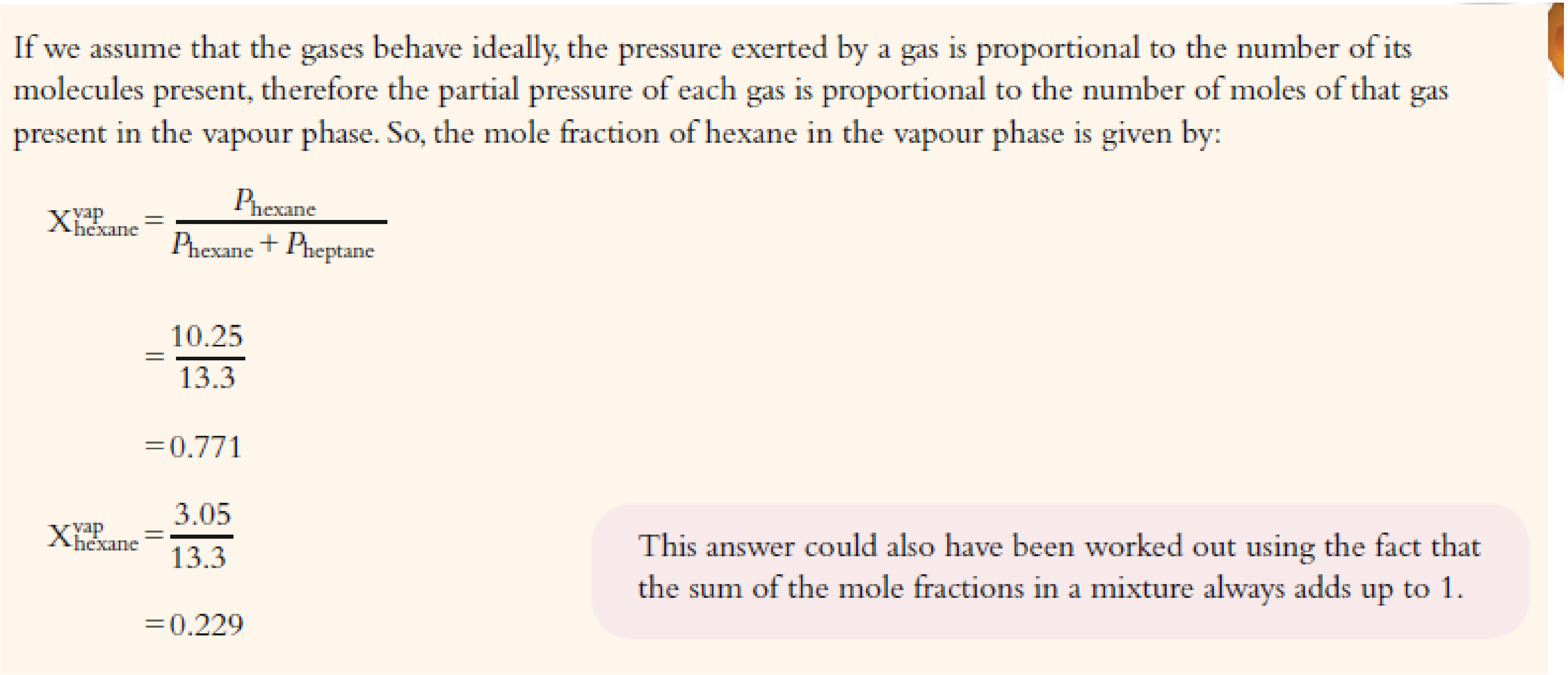
Using Dalton's Law of partial pressures:

$$P_{\text{tot}} = P_{\text{hexane}} + P_{\text{heptane}}$$

$$= 10.25 + 3.05$$

$$= 13.3\ \text{kPa}$$

So the total vapour pressure of the solution is 13.3 kPa.



If we assume that the gases behave ideally, the pressure exerted by a gas is proportional to the number of its molecules present, therefore the partial pressure of each gas is proportional to the number of moles of that gas present in the vapour phase. So, the mole fraction of hexane in the vapour phase is given by:

$$X^{\mathrm{vap}}_{\mathrm{hexane}} = \frac{P_{\mathrm{hexane}}}{P_{\mathrm{hexane}} + P_{\mathrm{heptane}}}$$

$$= \frac{10.25}{13.3}$$

$$= 0.771$$

$$X^{\mathrm{vap}}_{\mathrm{hexane}} = \frac{3.05}{13.3}$$

$$= 0.229$$

This answer could also have been worked out using the fact that the sum of the mole fractions in a mixture always adds up to 1.

The boiling point of a liquid

- Boiling occurs when bubbles of vapour form in a liquid and escape.
- Bubbles of vapour cannot be formed until the vapour pressure equals the external pressure.
- A liquid boils when its vapour pressure equals the external pressure. So the normal boiling point of a liquid is the temperature at which the vapour pressure of the liquid is one atmosphere.

The boiling point of a liquid

- The more volatile a liquid is, the higher its vapour pressure will be at a certain temperature – and therefore the lower its boiling point will be.
- Dissolving a non-volatile solute in a solvent will increase the boiling point of the solvent (boiling point ‘elevation’) because the vapour pressure is lowered and therefore the liquid must be heated more so that its vapour pressure is equal to atmospheric pressure (see the calculation above).
- Because the vapour pressure of a mixture of two liquids varies with the composition, the boiling point also varies with the composition of the mixture. The richer a mixture is in the more volatile component, the lower the boiling point.

Boiling point–composition diagram for an ideal solution with two components – liquid A and liquid B.

- The red line shows how the boiling point changes with composition and
- the blue line shows the vapour with which a particular mixture is in equilibrium.
- A is the more volatile component (higher vapour pressure in Figure **D.46**) and has the lower boiling point.

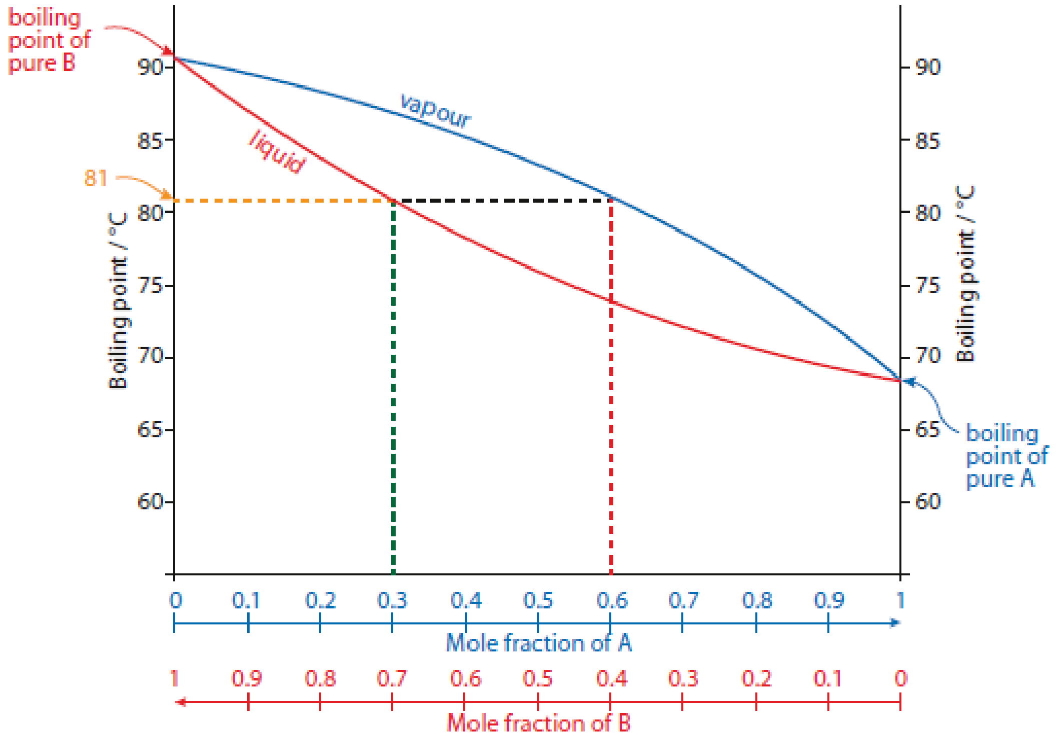


Figure D.47 A boiling point–composition diagram for an ideal solution.

Boiling point–composition diagram for an ideal solution with two components – liquid A and liquid B.

- Consider a mixture in which the mole fraction of A is 0.3 (and that of B is 0.7) – the green dashed line (in Figure **D.47**) is drawn up from this composition to the liquid line and it can be seen that the boiling point of this mixture is 81 °C.
- The horizontal line across to the vapour curve (black dashed line) indicates the composition of the vapour with which this liquid is in equilibrium.
- It can be seen that the mole fraction of A in the vapour is 0.6, compared to 0.3 in the liquid – the vapour is richer in the more volatile component.

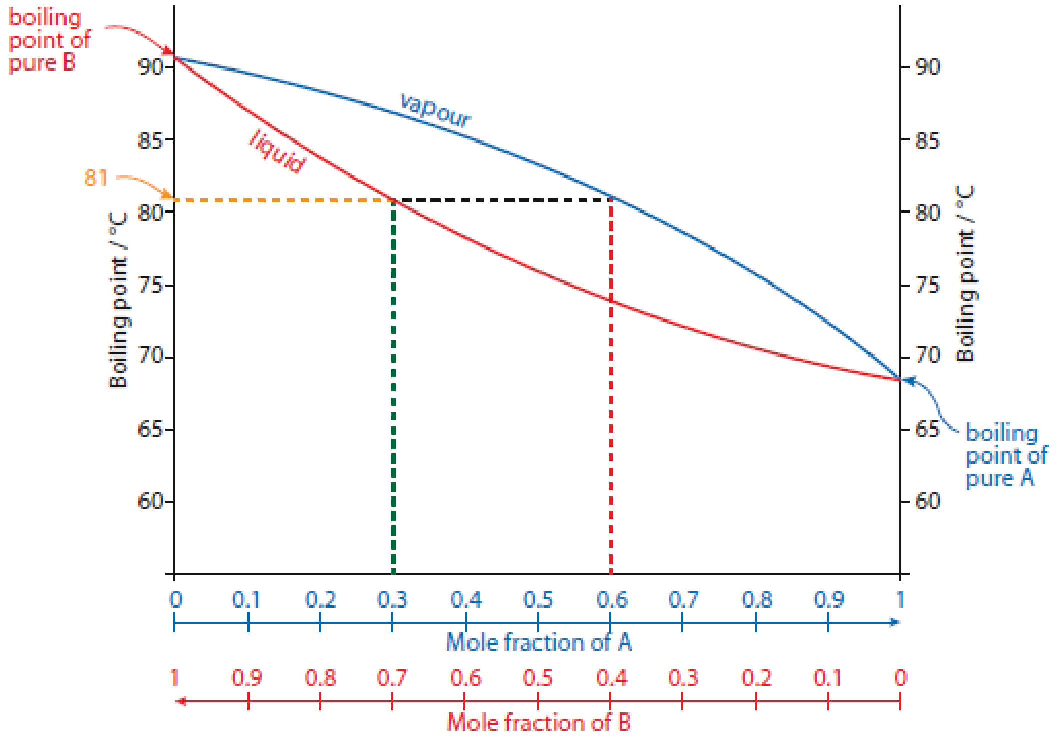


Figure D.47 A boiling point–composition diagram for an ideal solution.

Fractional distillation cont.

- The previous discussion can be used to explain how fractional distillation separates a mixture of liquids.
- If a mixture containing 0.1 mol A and 0.9 mol B is heated in the ask, **it will boil at 87 °C (Figure D.48).**
- The mole fractions in the vapour will be XA = 0.3 and XB = 0.7 – so the vapour is richer in the more volatile component.
- The fractionating column is hot at the bottom and cooler at the top so, as the vapour rises up the column to the cooler parts, it condenses on the beads in the column to form a liquid with composition XA = 0.3 and XB = 0.7.
- This liquid will then trickle down the column, where it is heated by hotter vapour coming up from below and will boil again, but this timeat a lower temperature (81 °C) because it is richer in the more volatile component.

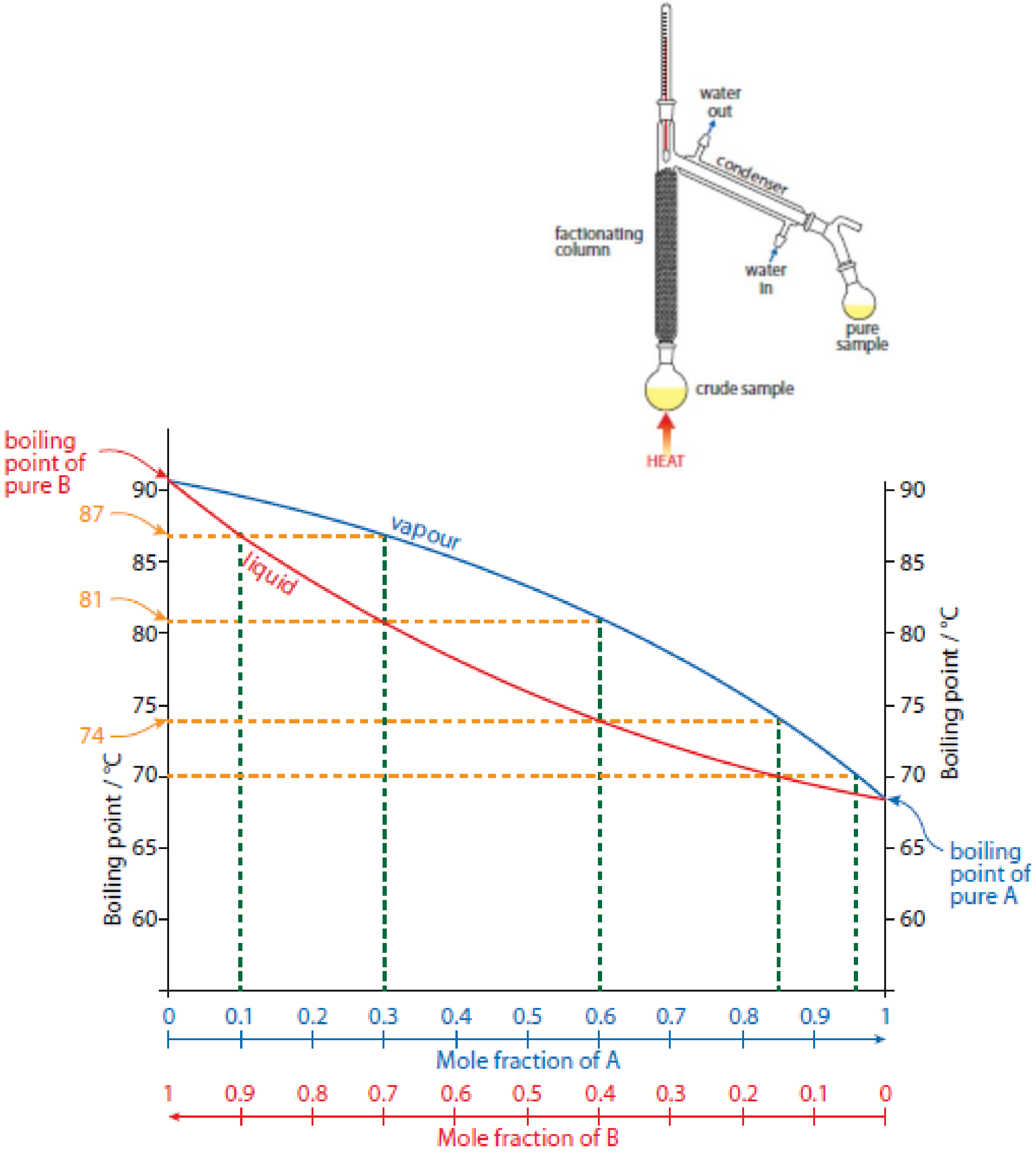


Figure D.48 Fractional distillation allows separation of a mixture of liquids.

Fractional distillation

- This liquid will boil to form a vapour with composition XA = 0.6 and XB = 0.4. This vapour is richer in the more volatile component and rises higher up the column before it condenses to form a liquid of the same composition.
- The liquid trickles down the column where it is heated again and boils at 74 °C to form a vapour of composition XA = 0.84 and XB = 0.16.
- Each time the liquid boils and condenses it becomes richer in the more volatile component and rises higher up the column until, if the column is long enough, essentially pure A will be obtained from the top of the column.
- The closer the boiling points of the liquids, the more series of boiling and condensing processes are required and therefore the longer the column required for good separation of the liquids.
- Not all liquids can be completely separated by fractional distillation and, for instance, ethanol and water form a constant-boiling-point mixture (95.6% ethanol).

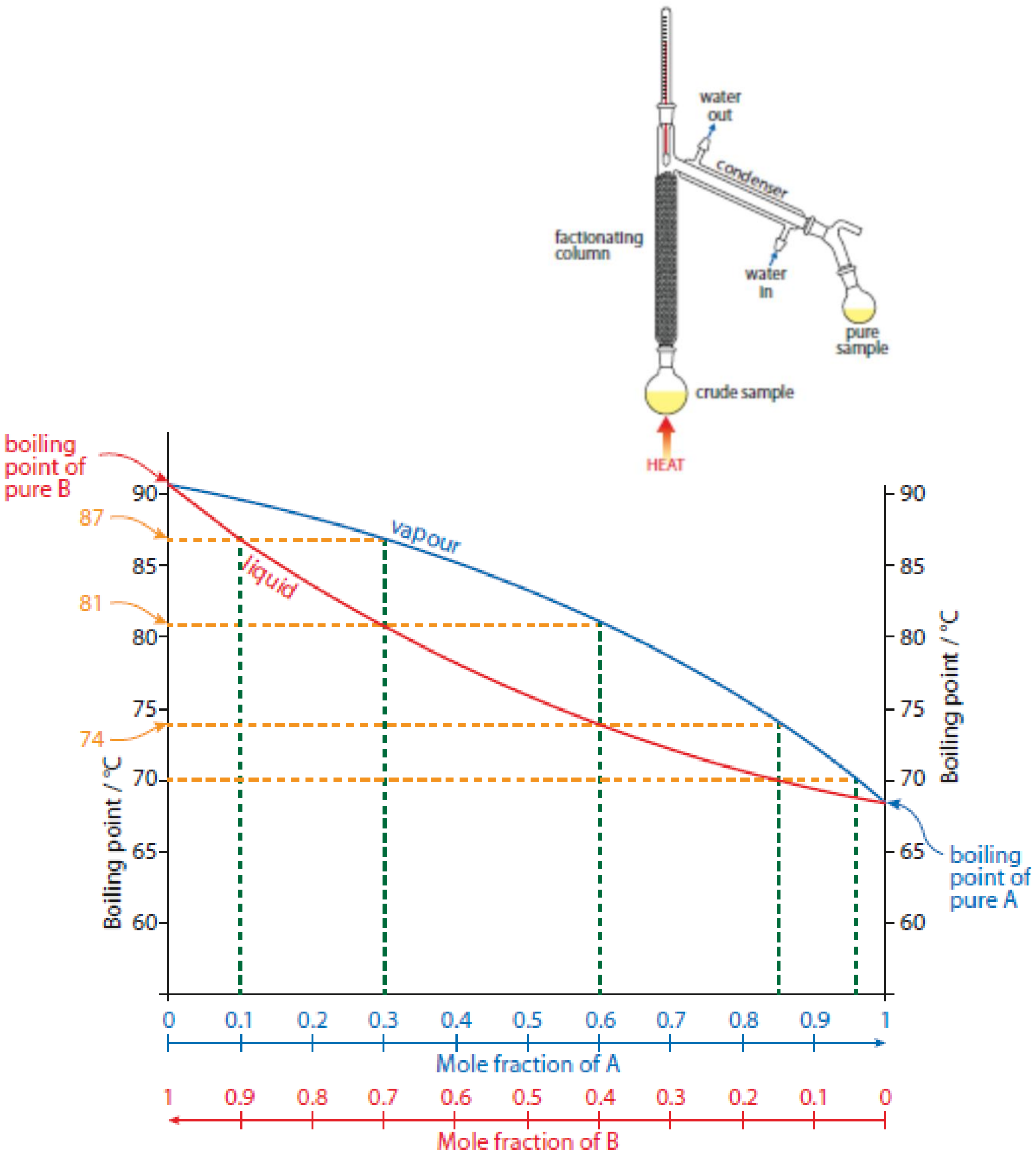


Figure D.48 Fractional distillation allows separation of a mixture of liquids.

When carrying out a distillation, the following practical points should be observed:

a. The boiling flask should not be more than half full.

b. Boiling stones are added to the liquid to prevent bumping.

c. Each ground joint should be greased to ensure a completely sealed system.

d. Cooling water in the condenser should enter at the lower end and exit at the upper end. This ensures that the condenser jacket is always full of water.

e. The bulb of the thermometer should be below the opening of the side arm so as to measure the temperature at which liquid and vapor are in equilibrium.

f. Heat sources used depend on the nature of the liquid. A water bath is used to distil low-boiling and flammable liquids, while a burner with a wire gauze is used for higher boiling and less flammable liquids

OBJECTIVES

- 1. Distilling a pure liquid (acetone) and determining its boiling point.
- 2. Separating a mixture of acetone and water by simple distillation.