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Physical Chemistry

UNDERSTANDING OUR CHEMICAL WORLD

 WILEY



5.6 Phase equilibria involving vapour pressure

Why does petrol sometimes have a strong smell and sometimes not?

Dalton's law

The acrid smell of petrol on a station forecourt is sometimes overpoweringly strong, yet at other times it is so weak as to be almost absent. The smell is usually stronger on a still day with no wind, and inspection shows that someone has spilled some petrol on the ground nearby. At the other extreme, the smell is weaker when there is a breeze, which either blows away the spilt liquid or merely dilutes the petrol in the air.

The subjective experience of how strong a smell is relates to the amount of petrol in the air; and the amount is directly proportional to the pressure of gaseous petrol. We call this pressure of petrol the 'partial pressure' $p_{(\text{petrol})}$.

And if several gases exist together, which is the case for petrol in air, then the total pressure equals the sum of the partial pressures according to *Dalton's law*:

$$p_{(\text{total})} = \sum p_i \quad (5.19)$$

In the case of a petrol smell near a station forecourt, the smell is strong when the partial pressure of the petrol vapour is large, and it is slight when $p_{(\text{petrol})}$ is small.

These differences in $p_{(\text{petrol})}$ need not mean any difference in the overall pressure $p_{(\text{total})}$, merely that the composition of the gaseous mixture we breathe is variable.

SAQ 5.7 What is the total pressure of 10 g of nitrogen gas and 15 g of methane at 298 K, and what is the partial pressure of nitrogen in the mixture? [Hint: you must first calculate the number of moles involved.]

Justification Box 5.4

The total number of moles equals the sum of its constituents, so

$$n_{(\text{total})} = n_A + n_B + \dots$$

The ideal-gas equation (Equation (1.13)) says $pV = nRT$; thus $p_{(\text{petrol})}V = n_{(\text{petrol})}RT$, so $n_{(\text{petrol})} = p_{(\text{petrol})}V \div RT$.

Accordingly, in a mixture of gases such as petrol, oxygen and nitrogen:

$$\frac{p_{(\text{total})}V}{RT} = \frac{p_{(\text{petrol})}V}{RT} + \frac{p_{(\text{oxygen})}V}{RT} + \frac{p_{(\text{nitrogen})}V}{RT}$$

We can cancel the gas constant R , the volume and temperature, which are all constant, to yield

$$P_{(\text{total})} = P_{(\text{petrol})} + P_{(\text{oxygen})} + P_{(\text{nitrogen})}$$

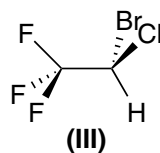
which is *Dalton's law*, Equation (5.19).

How do anaesthetics work?

Gases dissolving in liquids: Henry's law

'Anaesthesia' is the science of making someone unconscious. The word comes from the Greek *aesthēsis*, meaning sensation (from which we get the modern English word 'aesthetic', i.e. to please the sensations). The initial 'ana' makes the word negative, i.e. without sensation.

An anaesthetist administers chemicals such as halothane (**III**) to a patient before and during an operation to promote unconsciousness. Medical procedures such as operations would be impossible for the surgeon if the patient were awake and could move; and they would also be traumatic for a patient who was aware of what the surgery entailed.



A really deep, chemically induced sleep is termed 'narcosis', from the Greek *narke*, meaning 'numbness'. Similarly, we similarly call a class-A drug a 'narcotic'.

Although the topic of anaesthesia is hugely complicated, it is clear that the physiological effect of the compounds depends on their entrapment in the blood. Once dissolved, the compounds pass to the brain where they promote their narcotic effects. It is now clear that the best anaesthetics dissolve in the lipids from which cell membranes are generally made. The anaesthetic probably alters the properties of the cell membranes, altering the rates at which neurotransmitters enter and leave the cell.

A really deep 'sleep' requires a large amount of anaesthetic and a shallower sleep requires less material. A trained anaesthetist knows just how much anaesthetic to administer to induce the correct depth of sleep, and achieves this by varying the relative pressures of the gases breathed by the patient.

Henry's law is named after William Henry (1775–1836), and says that the amount of gas dissolved in a liquid or solid is in direct proportion to the partial pressure of the gas.

In effect, the anaesthetist relies on *Henry's law*, which states that the equilibrium amount of gas that dissolves in a liquid is proportional to the mole fraction of the gas above the liquid. Henry published his studies in 1803, and showed how the amount of gas dissolved in a liquid is directly proportional to the pressure (or

Table 5.4 Henry's law constants
 k_H for gases in water at 25 °C

Gas	$k_H/\text{mol dm}^{-3} \text{ bar}^{-1}$
CO ₂	3.38×10^{-2}
O ₂	1.28×10^{-3}
CH ₄	1.34×10^{-3}
N ₂	6.48×10^{-4}

partial pressure) of the gas above it. Stated in another form, Henry's law says:

$$[i_{(\text{soln})}] = k_H p_i \quad (5.20)$$

where p_i is the partial pressure of the gas i , and $[i_{(\text{soln})}]$ is the concentration of the material i in solution. The constant of proportionality k_H is the respective value of Henry's constant for the gas, which relates to the solubility of the gas in the medium of choice. Table 5.4 lists a few Henry's law constants, which relate to the solubility of gases in water.

Worked Example 5.7 What is the concentration of molecular oxygen in water at 25 °C? The atmosphere above the water has a pressure of 10^5 Pa and contains 21 per cent of oxygen.

Strategy. (1) We calculate the partial pressure of oxygen $p_{(\text{O}_2)}$. (2) We calculate the concentration $[\text{O}_{2(\text{aq})}]$ using Henry's law, Equation (5.20), $[\text{O}_{2(\text{aq})}] = p_{(\text{O}_2)} \times k_{H(\text{O}_2)}$.

- (1) From the partial of oxygen $p_{(\text{O}_2)} = x_{(\text{O}_2)} \times$ the total pressure $p_{(\text{total})}$, where x is the mole fraction:

$$p_{(\text{O}_2)} = 0.21 \times 10^5 \text{ Pa}$$

$$p_{(\text{O}_2)} = 2.1 \times 10^4 \text{ Pa or } 0.21 \text{ bar}$$

- (2) To obtain the concentration of oxygen, we insert values into Henry's law, Equation (5.20):

$$[\text{O}_{2(\text{aq})}] = 0.21 \times p^\ominus \times 1.28 \times 10^{-3} \text{ mol dm}^{-3} \text{ bar}^{-1}$$

$$[\text{O}_{2(\text{aq})}] = 2.69 \times 10^{-4} \text{ mol dm}^{-3}$$

We need to be aware that k_H is an equilibrium constant, so its value depends strongly on temperature. For example, at 35 °C, water only accommodates 7.03 mg of oxygen per litre, which explains why fish in warm water sometimes die from oxygen starvation.

One of the simplest ways of removing gaseous oxygen from water is to bubble nitrogen gas through it (a process called 'sparging').

Strictly, Henry's law only holds for *dilute* systems, typically in the mole-fraction range 0–2 per cent. The law tends to break down as the mole fraction x increases.

This relatively high concentration of oxygen helps explain why fish can survive in water.

How do carbon monoxide sensors work?

Henry's law and solid-state systems

Small, portable sensors are now available to monitor the air we breathe for such toxins as carbon monoxide, CO. As soon as the air contains more than a critical concentration of CO, the sensor alerts the householder, who then opens a window or identifies the source of the gas.

At the 'heart' of the sensor is a slab of doped transition-metal oxide. Its mode of operation is to detect the concentration of CO *within* the oxide slab, which is in direct proportion to the concentration of CO gas in the air surrounding it, according to Henry's law.

A small voltage is applied across the metal oxide. When it contains no CO, the electrical conductivity of the oxide is quite poor, so the current through the sensor is minute (we argue this corollary from Ohm's law). But increasing the concentration of CO in the air causes a proportionate increase in the amount of CO incorporating into the solid oxide, which has a profound influence on electrical conductivity through the slab, causing the current through the slab to increase dramatically. A microchip within

the sensor continually monitors the current. As soon as the current increases above its minimum permissible level, the alarm sounds.

So, in summary, CO gas partitions between the air and carefully formulated solid oxides. Henry's law dictates the amount of CO in the oxide.

In general, Henry's law only applies over relatively small ranges of gas pressure.

Why does green petrol smell different from leaded petrol?

Effects of amount of material on vapour pressure

A car engine requires petrol as its source of fuel. Such petrol has a low boiling temperature of about 60°C. Being so volatile, the liquid petrol is always surrounded with petrol vapour. We say it has a high *vapour pressure* (also called 'saturated vapour pressure'), which explains why we smell it so readily.

Once started, the engine carburettor squirts a mixture of air and volatile petrol into a hot engine cylinder, where the mixture is ignited with a spark. The resultant explosion (we call it 'firing') provides the ultimate source of kinetic energy to propel the car.

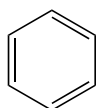
A car engine typically requires four cylinders, which fire in a carefully synchronized manner. Unfortunately, these explosions sometimes occur prematurely, before

Petrol is only useful in a car engine because it is *volatile*.

the spark has been applied, so the explosions cease to be synchronized. It is clearly undesirable for a cylinder to fire out of sequence, since the kinetic energy is supplied in a jerky, irreproducible manner. The engine sounds dreadful, hence the word 'knock'.

Modern petrol contains small amounts of additives to inhibit this knocking. 'Leaded' petrol, for example, contains the organometallic compound lead tetraethyl, PbEt_4 . Although PbEt_4 is excellent at stopping knocking, the lead by-products are toxic. In fact, most EU countries now ban PbEt_4 .

So-called 'green' petrol is a preferred alternative to leaded petrol: it contains about 3 per cent of the aromatic hydrocarbon benzene (C_6H_6 , **IV**) as an additive, the benzene acting as a lead-free alternative to PbEt_4 as an 'anti-knocking' compound.



(IV)

The PbEt_4 in petrol does not smell much because it is not volatile. By contrast, benzene is much more volatile – almost as volatile as petrol. The vapour above 'green' petrol, therefore, contains quite a high proportion of benzene (as detected by its cloying, sweet smell) as well as gaseous petrol. That is why green petrol has a sweeter smell than petrol on its own.

We experience *knocking* (which we colloquially call 'pinking') when explosions within a car engine are not synchronized.

Lead tetraethyl is the most widely made *organometallic* compound in the world. It is toxic, and killed over 40 chemical workers during its early development.

Why do some brands of 'green' petrol smell different from others?

Raoult's law

The 'petrol' we buy comprises a mixture of naturally occurring hydrocarbons, a principal component of which is octane; but the mixture also contains a small amount of benzene. Some brands of petrol contain more benzene than others, both because of variations in the conditions with which the crude oil is distilled into fractions, and also variations in the reservoir from which the crude oil is obtained. The proportion varies quite widely: the average is presently about 3 per cent.

Petrol containing a lot of benzene smells more strongly of benzene than petrol containing less of it. In fact, the intensity of the smell is in direct proportion to the amount of benzene in the petrol: at equilibrium, the pressure of vapour above a liquid mixture

In the countries of North America, petrol is often called 'gas', which is short for gasoline'.

Raoult's law is merely a special form of Henry's law.

depends on the liquid's composition, according to *Raoult's law*:

$$p_{(\text{benzene})} = p_{(\text{benzene})}^{\ominus} x_{(\text{benzene})} \quad (5.21)$$

Raoult's law states that (at constant temperature) the partial pressure of component i in the vapour residing at equilibrium above a liquid is proportional to the mole fraction x_i of component in the liquid.

where $x_{(\text{benzene})}$ is the mole fraction of the benzene in the liquid. If we assume that liquid benzene and petrol have the same densities (which is entirely reasonable), then petrol containing 3 per cent of benzene represents a mole fraction $x_{(\text{benzene})} = 0.03$; the mole fraction of the petrol in the liquid mixture is therefore 0.97 (or 97 per cent). The vapour above the petrol mixture will also be a mixture, containing some of each hydrocarbon in the petrol. We call the pressure due to the benzene component its partial pressure $p_{(\text{benzene})}$. The constant of proportionality in Equation (5.21) is $p_{(\text{benzene})}^{\ominus}$, which represents the pressure of gaseous benzene above *pure* (i.e. unmixed) liquid benzene.

Calculations with Raoult's law

If a two-component system of A and B forms an ideal mixture, then we can calculate x_A if we know x_B because $x_A + x_B = 1$, so $x_B = (1 - x_A)$.

If we know the mole fraction of a liquid i (via Equation (5.11)) and the vapour pressures of the pure liquids p_i^{\ominus} , then we can ascertain the total vapour pressure of the gaseous mixture hovering at equilibrium above the liquid.

The intensity of the benzene smell is proportional to the amount of benzene in the vapour, $p_{(\text{benzene})}$. According to Equation (5.21), $p_{(\text{benzene})}$ is a simple function of how much benzene resides within the liquid petrol mixture. Figure 5.21 shows a graph of the partial pressures of benzene and octane above a mixture of the two liquids.

(For convenience, we assume here that the mixture comprises only these two components.)

The extreme mole fractions, 0 and 1, at either end of the graph relate to pure petrol ($x = 0$) and pure benzene ($x = 1$) respectively. The mole fractions between these values represent mixtures of the two. The solid, bold line represents the total mole fraction while the dashed lines represent the vapour pressures of the two constituent vapours. It is clear that the sum of the two dashed lines equals the bold line, and represents another way of saying Dalton's law: the total vapour pressure above a mixture of liquids is the sum of the individual vapour pressures.

Benzene is more volatile than bromobenzene because its vapour pressure is higher.

Worked Example 5.8 The two liquids benzene and bromobenzene are mixed intimately at 298 K. At equilibrium, the pressures of the gases above beakers of the *pure* liquids are 100.1 kPa and 60.4 kPa respectively. What is the vapour pressure above the mixture if 3 mol of benzene are mixed with 4 mol of bromobenzene?

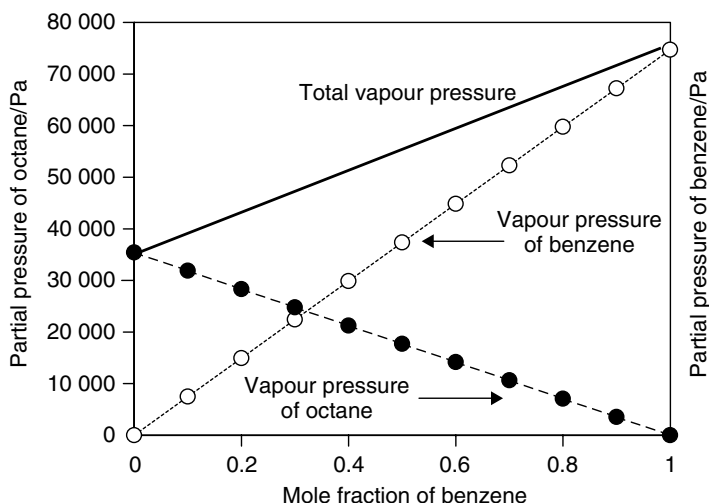


Figure 5.21 Petrol ('gasoline') is a mixture of liquid hydrocarbons. The partial pressure of benzene is nearly twice that of octane, making it much more volatile. The bold line represents the *total* pressure of vapour above a basin of petrol, and comprises the sum of two *partial* pressures: benzene (open circles) and octane (filled circles). Each partial pressure is proportional to the mole fraction of the respective liquid in the petrol mixture

From Dalton's law, the total vapour pressure is simply the sum of the individual vapour pressures:

$$p_{(\text{total})} = p_{(\text{benzene})} + p_{(\text{bromobenzene})}$$

so, from Raoult's law, these partial pressures may be obtained by substituting each p term with $p_i^\ominus \times x_i$:

$$p_{(\text{total})} = (p_{(\text{benzene})}^\ominus \times x_{(\text{benzene})}) + (p_{(\text{bromobenzene})}^\ominus \times x_{(\text{bromobenzene})}) \quad (5.22)$$

Care: do not confuse p^\ominus (the standard pressure of 10^5 Pa) with p_i^\ominus , the vapour pressure of pure i .

We know from the question that there are 7 mol of liquid. We obtain the respective mole fractions x from Equation (5.11): the mole fraction of benzene is $\frac{3}{7}$ and the mole fraction of bromobenzene is $\frac{4}{7}$.

Substituting values of x_i and p_i^\ominus into Equation (5.22) yields the total pressure $p_{(\text{total})}$ as

$$p_{(\text{total})} = (100.1 \text{ kPa} \times \frac{3}{7}) + (60.4 \text{ kPa} \times \frac{4}{7})$$

$$p_{(\text{total})} = (42.9 \text{ kPa}) + (34.5 \text{ kPa})$$

so

$$p_{(\text{total})} = 77.4 \text{ kPa}$$

An *ideal mixture* comprises a pair (or more) of liquids that obey Raoult's law.

Because these two liquids, when mixed, obey Raoult's law, we say they form an *ideal mixture*. In fact, relatively few pairs of liquids form ideal mixtures: a few examples include benzene and bromobenzene, benzene and toluene, bromobenzene and chlorobenzene, *n*-pentane and *i*-pentane. Note how each set represents a pair of liquids showing a significant extent of similarity.

SAQ 5.8 Benzene and toluene form an ideal mixture, i.e. they obey Raoult's law. At 20 °C, the pressure p^\ominus of benzene and toluene are $0.747 \times p^\ominus$ and $0.223 \times p^\ominus$ respectively. What is the pressure above a mixture of these two liquids that contains 12 mol% of benzene?

Worked Example 5.9 (Continuing from Worked Example 5.8.) What are the mole fractions of benzene and bromobenzene in the *vapour*?

From the definition of mole fraction x in Equation (5.11) above, we say

$$x_{(\text{benzene, vapour})} = \frac{\text{moles of benzene in the vapour}}{\text{total number of moles in the vapour phase}}$$

The numbers of moles n_i are directly proportional to the partial pressures p_i if we assume that each vapour behaves as an ideal gas (we assume here that T , R and V are constant). Accordingly, we can say

$$x_{(\text{benzene})} = \frac{\text{pressure of benzene}}{\text{total pressure}}$$

Substituting numbers from Worked Example 5.8:

Note how the units cancel to yield a *dimensionless* mole fraction.

$$x_{(\text{benzene})} = \frac{42.9 \text{ kPa}}{77.4 \text{ kPa}}$$

$$x_{(\text{benzene})} = 0.554$$

We need *four* mole fractions to define this two-component system – two for the liquid phases and two for the vapour phases.

The mole fraction of benzene in the vapour is 0.554, so it contains 55.4 per cent benzene. The remainder of the vapour comprises the second component bromobenzene, so the vapour contains $(100 - 55.4)\% = 44.6\%$ of bromobenzene.

Note how the liquid comprises 43 per cent benzene and 57 per cent bromobenzene, but the vapour contains proportionately more of the volatile benzene. We should expect the vapour to be richer in the more volatile component.

SAQ 5.9 Continuing with the system in SAQ 5.8, what is the mole fraction of toluene in the vapour above the mixture?

In fact, most liquid mixtures do not obey Raoult's law particularly well, owing to molecular interactions.

Why does a cup of hot coffee yield more steam than above a cup of boiling water at the same temperature?

The effects of poor mixing (immiscibility)

Prepare two cups: put boiling water into one and boiling coffee in the other. The temperature of each is the same because the water comes from the same kettle, yet the amount of steam coming from the coffee is seen to be greater. (We obtain a better view of the steam by placing both cups on a sunny window sill, and looking at the shadows cast on the opposing wall as the light passes through the vapour as it rises from the cups.)

When performing this little experiment, we will probably notice how the steam above the coffee has an extremely strong smell of coffee, although the smell dissipates rapidly as the rate of steam production decreases.

This experiment is a simple example of *steam distillation*. Adding steam promotes the volatilization of otherwise non-volatile components, simplifying their extraction. For simplicity, we will say that the smell derives from a single sweet-smelling chemical ‘coffee’. Coffee and water are not wholly miscible, with some of the essential oils from the coffee existing as tiny globules – we call the mixture a *colloid* (see Chapter 10). We have generated a two-phase system. Both phases, the water and the coffee, are saturated with each other. In fact, these globules would cause strong coffee to appear slightly misty, but for its strong colour blocking all light. We never see *phase separation* in the coffee cup, with a layer of oil floating above a layer of water, because the coffee’s concentration is never high enough.

We say a pure liquid boils when its vapour pressure equals the external, atmospheric pressure (see p. 188). Similarly, when boiling a mixture, boiling occurs when the sum of the partial pressures ($p_{\text{(water)}} + p_{\text{(coffee)}}$) equals p^\ominus . It is for this reason that the steam above the coffee cup smells strongly of coffee, because the vapour contains the essential oils (e.g. esters) that impart the smell. But the water generates steam at a pressure of p^\ominus when the water added to the cup is boiling, so the partial pressure of the coffee $p_{\text{(coffee)}}$ is additional. For this reason, we produce more steam than above the cup containing only water.

The rate of steam production decreases with time as the water cools down because energy is lost from the cup as water molecules enter the gas phase.

The boiling of such a mixture requires the *sum* of the pressures, not just the pressure of one component, to equal p^\ominus .

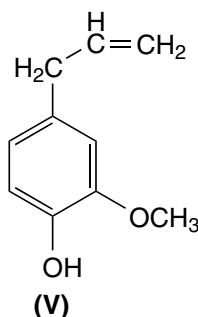
How are essential oils for aromatherapy extracted from plants?

Steam distillation

The ‘essential oils’ of a plant or crop usually comprise a mixture of esters. At its simplest, the oils are extracted from a plant by distillation, as employed in a standard

undergraduate laboratory. Since plants contain such a small amount of this precious oil, a ton of plant may be needed to produce a single fluid ounce. Some flowers, such as jasmine or tuberose, contain very small amounts of essential oil, and the petals are very temperature sensitive, so heating them would destroy the blossoms before releasing the essential oils.

To add to the cost further, many of these compounds are rather sensitive to temperature and would decompose before vaporizing. For example, oil of cloves (from *Eugenia caryophyllata*) is rich in the phenol eugenol (V), which has a boiling point of 250 °C). We cannot extract the oils via a conventional distillation apparatus.



Heat-sensitive or water-immiscible compounds are purified by *steam distillation* at temperatures considerably lower than their usual boiling temperatures.

Solvent extraction of essential oils tends to generate material that is contaminated with solvent (and cannot be sold); and *mechanical pressing* of a plant usually generates too poor a yield to be economically viable.

The most common method of extracting essential oils is *steam distillation*. The plant is first crushed mechanically, to ensure a high surface area, and placed in a closed still. High-pressure steam is forced through the still, with the plant pulp becoming hot as the steam yields its heat of vaporization (see p. 79). The steam forces the microscopic pockets holding the essential oils to open and to release their contents. Tiny droplets of essential oil evaporate and mix in the gas-phase mixture with the steam. The mixture is then swept through the still before condensing in a similar manner to a conventional distillation.

Such 'steam heating' is even, and avoids the risk of overheating and decomposition that can occur in hot spots when external heating is used. The steam condenses back into water and the droplets coagulate to form liquid oil. Esters and essential oils do not mix with water, so phase separation occurs on cooling, and we see a layer of oil forming above a layer of condensed water. The oil is decanted or skimmed off the surface of the water, dried, and packaged.

The only practical problem encountered when collecting organic compounds by steam distillation is that liquids of low volatility will usually distil slowly, since the proportion of compound in the vapour is proportional to the vapour pressure, according to

$$\frac{P_{(\text{oil})}}{P_{(\text{water})}} = \frac{n_{(\text{oil})}}{n_{(\text{water})}} \quad (5.23)$$

In practice, we force water vapour (steam) at high pressure through the clove pulp to obtain a significant partial pressure of eugenol (V).

Justification Box 5.5

When considering the theory behind steam distillation, we start with the ideal-gas equation (Equation (1.13)), $pV = nRT$. We will consider two components: oil and water. For the oil, we say $p_{(\text{oil})}V = n_{(\text{oil})}RT$, and for the water $p_{(\text{water})}V = n_{(\text{water})}RT$. Dividing the two equations by R and V (which are both constant) yields

$$\begin{aligned} p_{(\text{oil})} &= n_{(\text{oil})} \times T && \text{for the oil} \\ p_{(\text{water})} &= n_{(\text{water})} \times T && \text{for the water} \end{aligned}$$

We then divide each pressure by the respective number of moles n_i , to obtain

$$\begin{aligned} p_{(\text{oil})} \div n_{(\text{oil})} &= T && \text{for the oil} \\ p_{(\text{water})} \div n_{(\text{water})} &= T && \text{for the water} \end{aligned}$$

The temperature of the two materials will be T , which is the same for each as they are in thermal equilibrium. We therefore equate the two expressions, saying

$$p_{(\text{oil})} \div n_{(\text{oil})} = p_{(\text{water})} \div n_{(\text{water})}$$

Dividing both sides by $p_{(\text{water})}$ and multiplying both sides by $n_{(\text{oil})}$ yields Equation (5.23):

$$\frac{p_{(\text{oil})}}{p_{(\text{water})}} = \frac{n_{(\text{oil})}}{n_{(\text{water})}}$$

so we see how the percentage of each constituent in the vapour depends only on its vapour pressure at the distillation temperature.

To extract a relatively involatile oil such as eugenol (V) without charring requires a high pressure of steam, although the steam will not be hotter than 100°C , so we generate a mixture of vapours at a temperature lower than that of the less volatile component.