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Physical Chemistry

UNDERSTANDING OUR CHEMICAL WORLD

 WILEY



5.5 Phase equilibria and colligative properties

Why does a mixed-melting-point determination work?

Effects of impurity on phase equilibria in a two-component system

The best ‘fail-safe’ way of telling whether a freshly prepared compound is identical to a sample prepared previously is to perform a *mixed-melting-point* experiment.

A ‘mixed melting point’ is the *only* absolutely fail-safe way of determining the purity of a sample.

In practice, we take two samples: the first comprises material whose origin and purity we know is good. The second is fresh from the laboratory bench: it may be pure and identical to the first sample, pure but a different compound, or impure, i.e. a mixture. We take the melting point of each separately, and call them respectively $T_{(\text{melt, pure})}$ and $T_{(\text{melt, unknown})}$. We know for sure that the samples are different if these two melting temperatures differ.

Ambiguity remains, though. What if the melting temperatures are the same but, by some strange coincidence, the new sample is different from the pure sample but has the same melting temperature? We therefore determine the melting temperature of a *mixture*. We mix some of the material known to be pure into the sample of unknown compound. If the two melting points are still the same then the two materials are indeed identical. But any decrease in $T_{(\text{melt, impure})}$ means they are not the same. The value of $T_{(\text{melt, mixture})}$ will *always* be lower than $T_{(\text{melt, pure})}$ if the two samples are different, as evidenced by the decrease in $T_{(\text{melt})}$. We call it a *depression of melting point* (or *depression of freezing point*).

Introduction to colligative properties: chemical potential

The depression of a melting point is one of the simplest manifestations of a *colligative* property. Other everyday examples include pressure, osmotic pressure, vapour pressure and elevation of boiling point.

‘Colligative properties’ depend on the *number*, rather than the *nature*, of the chemical particles (atoms or molecules) under study.

For simplicity, we will start by thinking of one compound as the ‘host’ with the other is a ‘contaminant’. We find experimentally that the magnitude of the depression ΔT depends only on the *amount* of contaminant added to the host and not on the *identity* of the compounds involved – this is a general finding when working with colligative properties. A simple example will demonstrate how this finding can occur: consider a gas at room temperature. The ideal-gas equation (Equation (1.13)) says $pV = nRT$, and holds

reasonably well under s.t.p. conditions. The equation makes it clear that the pressure p depends only on n , V and T , where V and T are thermodynamic variables, and n relates to the *number* of the particles but does not depend on the chemical *nature* of the compounds from which the gas is made. Therefore, we see how pressure is a colligative property within the above definition.

Earlier, on p. 181, we looked at the phase changes of a single-component system (our examples included the melting of an ice cube) in terms of changes in the molar Gibbs function ΔG_m . In a similar manner, we now look at changes in the Gibbs function for *each* component within the mixture; and because several components participate, we need to consider more variables, to describe both the host and the contaminant.

We are now in a position to understand why the melting point of a mixture is lower than that of the pure host. Previously, when we considered the melting of a simple single-component system, we framed our thinking in terms of the molar Gibbs function G_m . In a similar way, we now look at the molar Gibbs function of each component i within a mixture. Component i could be a contaminant. But because i is only one part of a system, we call the value of G_m for material i the *partial* molar Gibbs function. The partial molar Gibbs function is also called the *chemical potential*, and is symbolized with the Greek letter mu, μ .

We define the ‘mole fraction’ x_i as the number of moles of component i expressed as a proportion of the total number of moles present:

$$x_i = \frac{\text{number of moles of component } i}{\text{total number of moles}} \quad (5.11)$$

The value of μ_i – the molar Gibbs function of the contaminant – decreases as x_i decreases. In fact, the chemical potential μ_i of the contaminant is a function of its mole fraction within the host, according to Equation (5.11):

$$\mu_i = \mu_i^\ominus + RT \ln x_i \quad (5.12)$$

where x_i is the mole fraction of the species i , and μ_i^\ominus is its *standard chemical potential*. Equation (5.12) should remind us of Equation (4.49), which relates ΔG and ΔG^\ominus .

Notice that the mole fraction x has a maximum value of unity. The value of x decreases as the proportion of contaminant increases. Since the logarithm of a number less than one is always negative, we see how the $RT \ln x_i$ term on the right-hand side of Equation (5.12) is zero for a pure material (implying $\mu_i = \mu_i^\ominus$). At all other times, $x_i < 1$, causing the term $RT \ln x_i$ to be negative. In other words, the value of μ will always *decrease* from a maximum value of μ_i^\ominus as the amount of contaminant increases.

Figure 5.18 depicts graphically the relationship in Equation (5.12), and shows the partial molar Gibbs function of the host material as a function of temperature. We first consider the heavy bold lines, which relate to a pure host material, i.e. before contamination. The figure clearly shows two bold lines, one each for the material when solid and another at higher temperatures for the

For a *pure* substance, the chemical potential μ is merely another name for the molar Gibbs function.

The mole fraction x of the host DEcreases as the amount of contaminant INcreases. The sum of all the mole fractions must always equal one; and the mole fraction of a pure material is also one.

Strictly, Equation (5.12) relates to an ideal mixture at constant p and T .

Remember: in this type of graph, the lines for solid and liquid intersect at the *melting temperature*.

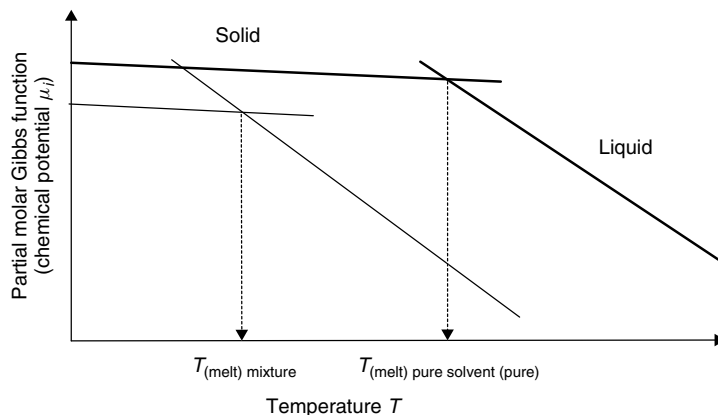


Figure 5.18 Adding a chemical to a host (mixing) causes its chemical potential μ to decrease, thereby explaining why a melting-point temperature is a good test of purity. The heavy solid lines represent the chemical potential of the pure material and the thin lines are those of the host containing impurities

respective liquid. In fact, when we remember that the chemical potential for a pure material is the same as the molar Gibbs function, we see how this graph (the bold line for the pure host material) is identical to Figure 5.2. And we recall from the start of this chapter how the lines representing G_m for solid and G_m for liquid intersect at the melting temperature, because liquid and solid are in equilibrium at $T_{(\text{melt})}$, i.e. $G_{m(\text{liquid})} = G_{m(\text{solid})}$ at $T_{(\text{melt})}$.

We look once more at Figure 5.18, but this time we concentrate on the thinner lines. These lines are seen to be parallel to the bold lines, but have been displaced down the page. These thin lines represent the values of G_m of the host within the mixture (i.e. the once pure material following contamination). The line for the solid

mixture has been displaced to a lesser extent than the line for the liquid, simply because the Gibbs function for liquid phases is more sensitive to contamination.

The vertical difference between the upper bold line (representing μ^\ominus) and the lower thin line (which is μ) arises from Eq. (5.12): it is a direct consequence of mixing. In fact, the mathematical composition of Eq. (5.12) dictates that we draw the line for an impure material (when $x_i < 1$) lower on the page than the line for the pure material.

It is now time to draw all the threads together, and look at the temperature at which the thin lines intersect. It is clear from Figure 5.18 that the intersection temperature for the mixture occurs at a cooler temperature than that for the pure material, showing why the melting point temperature for a mixture is depressed relative to a pure compound. The depression of freezing point is a direct consequence of chemical potentials as defined in Equation (5.12).

As the mole fraction of contaminant increases (as x_i gets larger), so we are forced to draw the line progressively lower down the figure.

A mixed-melting-point experiment is an ideal test of a material's purity since $T_{(\text{melt})}$ never drops unless the compound is impure.

We now see why the melting-point temperature decreases following contamination, when its mole fraction deviates from unity. Conversely, the mole fraction does not change at all if the two components within the mixed-melting-point experiment are the same, in which $T_{(\text{melt})}$ remains the same.

Justification Box 5.3

When we formulated the *total differential* of G (Equation (4.30)) in Chapter 4, we only considered the case of a pure substance, saying

$$dG = \left(\frac{\partial G}{\partial p} \right) dp + \left(\frac{\partial G}{\partial T} \right) dT$$

We assumed then the only variables were temperature and pressure. We must now rewrite Equation (4.30), but we add another variable, the amount of substance n_i in a mixture:

$$dG = \left(\frac{\partial G_i}{\partial p} \right) dp + \left(\frac{\partial G_i}{\partial T} \right) dT + \left(\frac{\partial G_i}{\partial n_i} \right) dn_i \quad (5.13)$$

We append an additional subscript to this expression for dG to emphasize that we refer to the material i within a mixture. As written, Equation (5.13) could refer to either the host or the contaminant – so long as we define which is i .

The term $\partial G_i / \partial n_i$ occurs so often in second law of thermodynamics that it has its own name: the ‘chemical potential’ μ , which is defined more formally as

$$\mu_i = \left(\frac{\partial G_i}{\partial n_i} \right)_{p, T, n_j} \quad (5.14)$$

where the subscripts to the bracket indicate that the variables p , T , and the amounts of all other components n_j in the mixture, each remain constant. The chemical potential is therefore seen to be the slope on a graph of Gibbs function G (as ‘ y ’) against the amount of substance n_i (as ‘ x ’); see Figure 5.19. In general, the chemical potential varies with composition, according to Equation (5.12).

The chemical potential μ can be thought of as the constant of proportionality between a change in the amount of a species and the resultant change in the Gibbs function of a system.

The way we wrote ∂G in Equation (5.13) suggests the chemical potential μ is the Gibbs function of 1 mol of species i mixed into an infinite amount of host material. For example, if we dissolve 1 mol of sugar in a roomful of tea then the increase in Gibbs function is $\mu_{(\text{sugar})}$. An alternative way to think of the chemical potential μ is to consider dissolving an infinitesimal amount of chemical i in 1 mol of host.

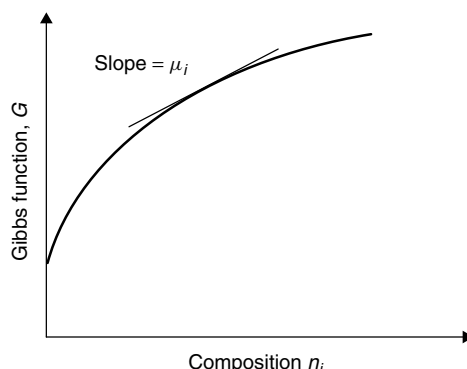


Figure 5.19 The chemical potential μ_i (the partial molar Gibbs function) of a species in a mixture is obtained as the slope of a graph of Gibbs function G as a function of composition

We need to employ ‘mental acrobatics’ of this type merely to ensure that our definition of μ is watertight – the overall composition of the mixture cannot be allowed to change significantly.

How did the Victorians make ice cream?

Cryoscopy and the depression of freezing point

The people of London and Paris in Victorian times (the second half of the nineteenth century) were always keen to experience the latest fad or novelty, just like many rich and prosperous people today. And one of their favourite ‘new inventions’ was ice cream and sorbets made of frozen fruit.

The ice cream was made this way: the fruit and/or cream to be frozen is packed into a small tub and suspended in an ice bath. Rock salt is then added to the ice, which depresses its freezing temperature (in effect causing the ice to melt). Energy is needed to melt the ice. $\Delta H_{\text{(melt)}} = 6.0 \text{ kJ mol}^{-1}$ for pure water. This energy comes from the fruit and cream in the tub. As energy from the cream and fruit passes through the tub wall to the ice, it freezes. Again, we see how a body’s temperature is a good gauge of its internal energy (see p. 34).

The first satisfactory theory to explain how this cooling process works was that of François-Marie Raoult, in 1878. Though forgotten now, Raoult already knew ‘Blag-

Dissolving a solute in a solvent causes a depression of freezing point, in the same way as mixing solids.

den’s law’: a dissolved substance lowers the freezing point of a solvent in direct proportion to the concentration of the solute. In practice, this law was interpreted by saying that an ice–brine mixture (made with five cups of ice to one of rock salt) had a freezing point at about -2.7°C . Adding too much salt caused the temperature to fall too far and too fast, causing the outside of the ice

cream to freeze prematurely while the core remained liquid. Adding too little salt meant that the ice did not melt, or remained at a temperature close to 0°C , so the cream and fruit juices remained liquid.

This depression of the freezing point occurs in just the same way as the lower melting point of an impure sample, as discussed previously. This determination of the depression of the freezing point is termed *cryoscopy*.

The word 'cryoscopy' comes from the Greek *kryos*, which literally means 'frost'.

Why boil vegetables in salted water?

Ebullioscopy and the elevation of boiling point

We often boil vegetables in salted water (the concentration of table salt is usually in the range $0.01\text{--}0.05\text{ mol dm}^{-3}$). The salt makes the food taste nicer, although we should wash off any excess salt water if we wish to maintain a healthy blood pressure.

But salted water boils at a higher temperature than does pure water, so the food cooks more quickly. (We saw on p. 203 how a hotter temperature promotes faster cooking.) The salt causes an *elevation of boiling point*, which is another colligative property. We call the determination of such an elevation *ebullioscopy*.

Look at Figure 5.20, the left-hand side of which should remind us of Figure 5.18; it has *two* intersection points. At the low-temperature end of the graph, we see again why the French ice-cream makers added salt to the ice, to depress its freezing point. But, when we look at the right-hand side of the figure, we see a second intersection, this time between the lines for liquid and gas: the temperature at which the lines intersect gives us the boiling point $T_{(\text{boil})}$.

The word 'ebullioscopy' comes from the Latin (*e*)*bulirre*, meaning 'bubbles' or 'bubbly'. In a related way, we say that someone is 'ebullient' if they have a 'bubbly' personality.

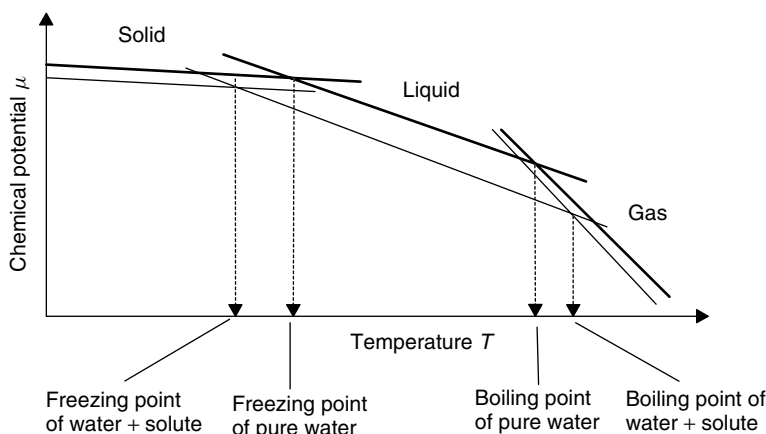


Figure 5.20 Salt in water causes the water to boil at a higher temperature and freeze at a lower temperature; adding a solute to a solvent decreases the chemical potential μ of the solvent. The bold lines represent pure water and the thinner lines represent water-containing solute

The figure shows how adding salt to the water has caused both the lines for liquid and for gas to drop down the page, thus causing the intersection temperature to change. Therefore, a second consequence of adding salt to water, in addition to changing its chemical potential, is to change the temperature at which boiling occurs. Note that the boiling temperature is raised, relative to that of pure water.

Why does the ice on a path melt when sprinkled with salt?

Quantitative cryoscopy

The ice on a path or road is slippery and dangerous, as we saw when considering black ice and ice skaters. One of the simplest ways to make a road or path safer is to sprinkle salt on it, which causes the ice to melt. In practice, rock salt is preferred to table salt, because it is cheap (it does not need to be purified) and because its coarse grains lend additional grip underfoot, even before the salt has dissolved fully.

The depression of freezing temperature occurs because ions from the salt enter the lattice of the solid ice. The contaminated ice melts at a lower temperature than does pure ice, and so the freezing point decreases. Even at temperatures below the normal melting temperatures of pure ice, salted water remains a liquid – which explains why the path or road is safer.

The 'molaLity' m is the number of moles of solute dissolved per unit *mass* of solvent; 'molaRity' (note the different spelling) is the number of moles of solute dissolved per unit *volume*.

We must appreciate, however, that no *chemical* reaction occurs between the salt and the water; more or less, any ionic salt, when put on ice, will therefore cause it to melt. The chemical identity of the salt is irrelevant – it need not be sodium chloride at all. What matters is the *amount* of the salt added to the ice, which relates eventually to the mole fraction of salt. So, what is the magnitude of the freezing-point depression?

Let the depression of the freezing point be ΔT , the magnitude of which depends entirely on the amount of solute in the solvent. Re-interpreting Blagden's law gives

$$\Delta T \propto \text{molality} \quad (5.15)$$

The amount is measured in terms of the *molality* of the solute. Molality (note the spelling) is defined as the amount of solute dissolved per unit *mass* of solvent:

$$\text{molality, } m = \frac{\text{moles of solute}}{\text{mass of solvent}} \quad (5.16)$$

where the number of moles of solute is equal to 'mass of solute \div molar mass of solute'. The proportionality constant in Equation (5.15) is the *cryoscopic constant* $K_{(\text{cryoscopic})}$. Table 5.3 contains a few typical values of $K_{(\text{cryoscopic})}$, from which it can be seen that

We prefer 'molaL-ity' m to 'molaRity' (i.e. concentration c) because the volume of a liquid or solution changes with temperature, whereas that of a mass does not. Accordingly, molality is temperature independent whereas concentration is not.

Table 5.3 Sample values of boiling and freezing points, and cryoscopic and ebullioscopic constants

Substance	Boiling point/°C	Freezing point/°C	$K_{\text{(ebullioscopic)}}$ /K kg mol ⁻¹	$K_{\text{(cryoscopic)}}$ /K kg mol ⁻¹
Acetic acid	118.5	16.60	3.08	3.59
Acetone	56.1	-94.7	1.71	—
Benzene	80.2	5.455	2.61	5.065
Camphor	208.0	179.5	5.95	40
Carbon disulphide	46.3	-111.5	2.40	3.83
Carbon tetrachloride	76.5	-22.99	5.03	29.8
Chloroform	61.2	-65.5	3.63	4.70
Cyclohexane	80.74	6.55	2.79	20.0
Ethanol	78.3	-114.6	1.07	1.99
Ethyl acetate	77.1	-83.6	2.77	—
Ethyl ether	34.5	-116.2	2.02	1.79
Methanol	64.7	-97.7	0.83	—
Methyl acetate	57	-98.1	2.15	—
<i>n</i> -Hexane	68.7	-95.3	2.75	—
<i>n</i> -Octane	125.7	-56.8	4.02	—
Naphthalene	217.9	80.3	6.94	5.80
Nitrobenzene	210.8	5.7	5.24	8.1
Phenol	181.8	40.9	3.56	7.27
Toluene	110.6	-95.0	3.33	—
Water	100	0	0.512	1.858

camphor as a solvent causes the largest depression. Note that K has the units of K kg mol⁻¹, whereas mass and molar mass are both expressed with the units in units of grammes, so any combination of Equations (5.15) and (5.16) requires a correction term of 1000 g kg⁻¹. Accordingly, Equation (5.15) becomes

$$\Delta T = K_{\text{(cryoscopic)}} \times 1000 \times \left(\frac{\text{mass of solute}}{\text{molar mass of solute}} \right) \times \frac{1}{\text{mass of solvent}} \quad (5.17)$$

where the term in parentheses is n , the number of moles of solute.

Worked Example 5.6 10 g of pure sodium chloride is dissolved in 1000 g of water. By how much is the freezing temperature depressed from its normal melting temperature of $T = 273.15$ K? Take $K_{\text{(cryoscopic)}}$ from Table 5.3 as 1.86 K kg mol⁻¹.

Inserting values into Equation (5.17) yields

$$\Delta T = 1.86 \text{ K kg mol}^{-1} \times 1000 \text{ g kg}^{-1} \times \frac{10 \text{ g}}{58.5 \text{ g mol}^{-1}} \times \frac{1}{1000 \text{ g}}$$

so $\Delta T = 0.32$ K

This value of ΔT represents the depression of the freezing temperature, so it is negative

showing that the water will freeze at the lower temperature of $(273.16 - 0.32)$ K.

SAQ 5.6 Pure water has a normal freezing point of 273.15 K. What will be the new normal freezing point of water if 11 g of KCl is dissolved in 0.9 dm^3 of water?

The cryoscopic constant of water is $1.86 \text{ K kg}^{-1} \text{ mol}^{-1}$; assume the density of water is 1 g cm^{-3} , i.e. molality and molarity are the same.

An almost identical equation relates the *elevation of boiling point* to the molality:

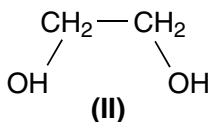
$$\Delta T_{(\text{elevation})} = K_{(\text{ebullioscopic})} \times 1000 \times \text{molality of the salt} \quad (5.18)$$

where $K_{(\text{ebullioscopic})}$ relates to the elevation of boiling temperature. Table 5.3 contains a few sample values of $K_{(\text{ebullioscopic})}$. It can be seen from the relative values of $K_{(\text{ebullioscopic})}$ and $K_{(\text{cryoscopic})}$ in Table 5.3 that dissolving a solute in a solvent has a more pronounced effect on the freezing temperature than on the boiling temperature.

Aside

The ice on a car windscreen will also melt when squirted with *de-icer*. Similarly, we add *anti-freeze* to the water circulating in a car radiator to prevent it freezing; the radiator would probably crack on freezing without it; see the note on p. 194.

Windscreen de-icer and engine anti-freeze both depress the freezing point of water via the same principle as rock salt depressing the temperature at which ice freezes on a road. The active ingredient in these cryoscopic products is ethylene glycol (**II**), which is more environmentally friendly than rock salt. It has two physicochemical advantages over rock salt: (1) being liquid, it can more readily enter between the microscopic crystals of solid ice, thereby speeding up the process of cryoscopic melting; (2) rock salt is impure, whereas **II** is pure, so we need less **II** to effect the same depression of freezing point.



Ethylene glycol is also less destructive to the paintwork of a car than rock salt is, but it is toxic to humans.

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

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

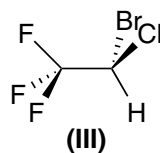
which is *Dalton's law*, Equation (5.19).

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.

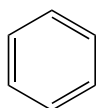
A car engine typically requires four cylinders, which fire in a carefully synchronized manner. Unfortunately, these explosions sometimes occur prematurely, before

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 i 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?

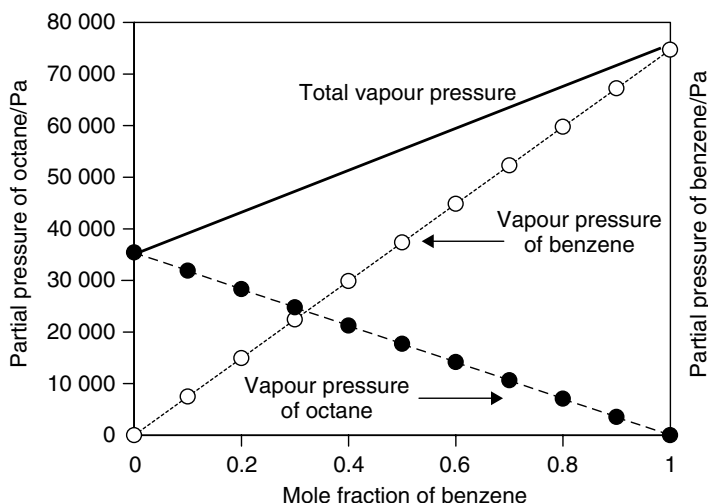


Figure 5.21 Petrol ('gasoline') is a mixture of liquid hydrocarbons. The partial pressure of benzene is nearly twice that of octane, making it much more volatile. The bold line represents the *total* pressure of vapour above a basin of petrol, and comprises the sum of two *partial* pressures: benzene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

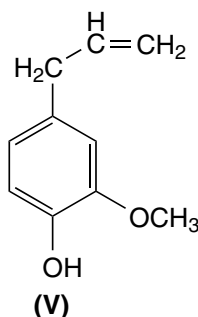
How are essential oils for aromatherapy extracted from plants?

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.