Chapter 12
Spreading of Substances

So far, the discussion of the chemical potential has concentrated primarily on chemical reactions and phase transitions. But another property of substances is also of great importance: their tendency to spread out or disperse in space. The phenomenon of diffusion will be explained in this context. The subject area of this chapter also includes the discussion of the effect of a small amount of solute on certain properties of a solution. The properties we have in mind are the lowering of vapor pressure of the solvent, the elevation of its boiling point, the lowering of its freezing point, and last but not least the origin of osmotic pressure. These phenomena are found everywhere, in households and in nature but also in engineering. In everyday life, a prime example for freezing-point depression is the melting effect of road salt. Or have you ever asked yourself why juice is drawn out of sugared strawberries but cherries swell up and burst after a long rain? Then have a look at Sect. 12.4 dealing with osmosis. For a quantitative discussion of all these phenomena, we first have to learn about indirect mass action and the corresponding colligative lowering of chemical potential.

12.1 Introduction

Until now, when we have considered the chemical potential we have primarily concentrated upon chemical reactions and phase transitions. However, there is another characteristic of substances that is almost as important. This is the tendency to spread out or disperse in space whether it is "empty" or filled with matter. This phenomenon can easily be illustrated by everyday processes. Mostly, substances migrate extremely slowly and in infinitesimally small amounts so that this migration remains imperceptible. However, there are many examples of spreading that

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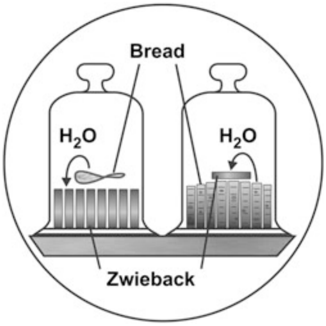
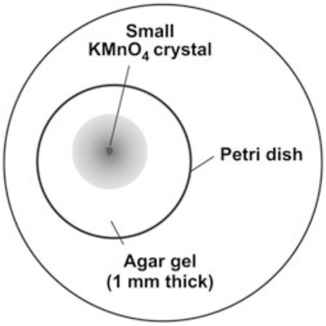


Experiment 12.1 *Redistribution of water between zwieback and bread*: A piece of zwieback stored for 2 or 3 days in a bread box or plastic bag together with fresh bread absorbs moisture and becomes soft and bendable, while a slice of bread in a bag full of zwieback becomes hard and brittle from losing moisture to the dry zwieback.



Experiment 12.2 *Spreading of $KMnO_4$ in agar gel* (view from above on a thin layer of gel in a Petri dish): A few small $KMnO_4$ crystals are cautiously distributed on the agar gel. Immediately, a kind of red violet "halo" is formed around each crystal. Because of its color, the spreading of the "halo" away from the source can be observed easily.

are quite noticeable. When the aroma of freshly ground, unpacked coffee escapes over the course of a few days, when the water in a rain puddle evaporates in a few hours, when glue from a tube congeals in one minute, or when the ink from a felt pen dries within seconds are all examples of how mobile and volatile some substances can be. Experiment 12.1 is an example that shows clearly how substances do not disappear but simply redistribute.

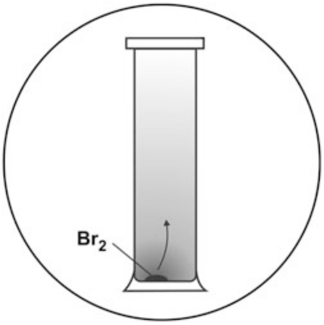
It is easy to follow the spreading of strong smelling or colored substances. The scent of a bouquet of lilacs, a peeled orange, or the pungent odor of potent cheese quickly fills a whole room. The spreading of colored low-molecular chemicals such as potassium permanganate in a liquid, or better, in a gel (to hinder convection) happens so fast that it can readily be observed (Experiment 12.2).

Gases spread out in the atmosphere even faster. This can be observed very easily in the case of reddish-brown bromine vapor (Experiment 12.3).

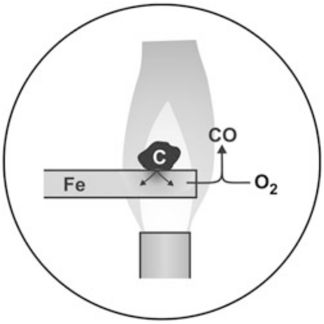
Even crystallized, compact bodies are not impenetrable. This can be illustrated by Experiment 12.4.

These examples may suffice to show that spreading of substances is a very general characteristic of matter.

Experiment 12.3 *Spreading of Br_2 in air*: The reddish-brown vapor from a drop of bromine in a gas jar (filled with air) spreads out quickly and fills the whole space inside it.



Experiment 12.4 *"Carbonizing" and "decarbonizing" of iron* (schematic representation): Iron can be "carbonized" by annealing in charcoal powder at approx. 1,000 °C. This means that the carbon atoms move into it. The changes of the grain structure at the border of the sample are visible to the naked eye as a dark area, but they can be examined in more detail with a microscope. The iron can also be "decarbonized" by heating in an oxidizing flame or in a furnace in air.



The migration of a substance from one place to another can be considered as a transformation

$$\mathrm{B}|\mathrm{Origin} \rightarrow \mathrm{B}|\mathrm{Destination},$$

so it is plausible that the chemical potential also controls this process. The transport of substances always follows the direction of the potential gradient. This means that the substance only moves spontaneously in one direction, the direction where the μ value at the starting point is greater than at the destination (if no other forces play a role like centrifugal forces in a centrifuge or electrical forces in an electrolytic cell). In this case, a characteristic of μ plays a decisive role that we have already been introduced to, namely its concentration dependency (compare Sect. 6.2): *The more diluted a substance is, the lower its chemical potential and the chemical potential can be lowered to any degree if the dilution is strong enough.*

In the following, we will apply this statement to the spreading of substances and other phenomena related to it. Chapter 13 will deal with the special features that result when the rule mentioned above no longer applies which is the case at higher concentrations.

12.2 Diffusion

If the substance is mobile enough, it must distribute in an otherwise homogeneous material or space uniformly over the entire area. This is because at locations of lower concentrations, its chemical potential is lower causing the substance to move from locations of higher concentration into areas of lower concentration (Fig. 12.1). When several substances migrate in an area at the same time, this holds for every one of them. The substances strive intrinsically for homogeneous distribution. This is called *diffusion*.

Although difference of concentration is by far the most important cause for diffusion, it is not the only cause. Other factors influencing the chemical potential can also play a role. It is entirely possible that at certain locations in inhomogeneous areas, a substance is enriched at the cost of neighboring areas. This characteristic is applied in microscopy in order to color areas that would tend to preferentially absorb certain dyes (staining in histology). A dye more or less evenly applied distributes unevenly even without outside influence.

We shall now take a closer look at transport of matter. As we have already seen, the determining quantity is the chemical potential. The substance moves spontaneously only in the direction in which the potential falls. If the transfer of a substance B from position x_1 to position x_2 (Fig. 12.2) is formulated as a reaction, then

$$\mathrm{B}|x_1 \rightarrow \mathrm{B}|x_2 \text{ occurs spontaneously if } \mu_\mathrm{B}(x_1) > \mu_\mathrm{B}(x_2).$$

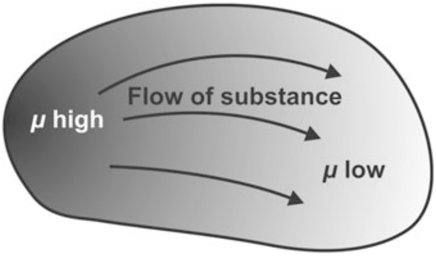


Fig. 12.1 Flow of substance caused by an inhomogeneous distribution of the substance in an otherwise homogeneous area.

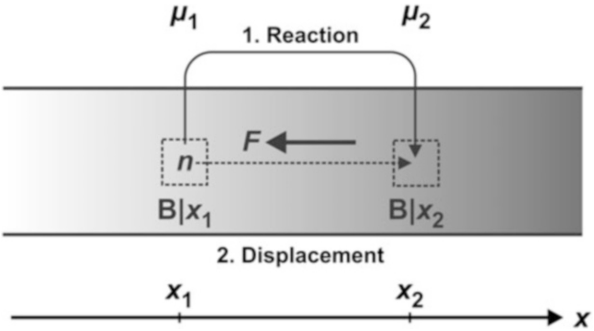


Fig. 12.2 Determination of force F upon a small sample of amount n of a substance B in a gradient of chemical potential.

The chemical drive $\mathcal{A}$ of this process is the corresponding potential difference,

$$\mathcal{A} = \mu_B(x_1) - \mu_B(x_2) = -\Delta\mu_B,$$

and the conversion $\Delta\xi$ is the amount of substance n_B transferred from position x_1 to position x_2. The potential gradient causes a force F that pushes the substance in the direction of the falling potential. F is easy to calculate if the energy W for transporting a small amount n_B from position x_1 to position x_2 (against the potential gradient) is expressed first as expenditure for the reaction and then as that required for the displacement against the force F. For this, let us consider that the potential μ_B increases in the x direction and that the substance is transported "uphill" opposite to the potential gradient. The energy W is then > 0, while the chemical drive $\mathcal{A}$ is negative. F also counts as negative because it is oriented opposite to the positive x-axis. In general, F depends upon the position x. If the segment $\Delta x = x_2 - x_1$ is made small enough, F can be considered constant. As a consequence, we obtain:

$$W = -\mathcal{A} \cdot \Delta\xi = \Delta\mu_B \cdot n_B \quad \text{and} \quad W = -F \cdot \Delta x \quad \text{for small } \Delta x.$$

When both equations are combined, we find

$$F_B = -n_B \cdot \frac{\Delta\mu_B}{\Delta x} \quad \text{or more precisely} \quad F_B = -n_B \cdot \frac{d\mu_B}{dx}. \tag{12.1}$$

It is fitting to call F *diffusion force* because F is the driving force behind the kind of transport called diffusion. In Chap. 20, which deals with transport phenomena, we will discuss the velocity of substance transport and the laws pertaining to it (Sect. 20.2).

When we apply molecular kinetic considerations, diffusion tends to be conceptualized as a result of random motion of molecules and not as an effect of a directed force. When the boundaries of two areas of different concentrations of a substance B touch each other, a totally random movement of molecules occurs where, on average, more particles move from the concentrated area into the diluted area than vice versa. Random chance suffices to explain that B gradually moves from areas of higher concentration into ones of lower concentration until it is evenly distributed. No special driving force is necessary for this. Actually, there is no discrepancy between the two models. The greater number of molecular collisions occurring at higher concentrations of the diffusing substance B must lead to a directed force at the transition to the area of lower concentration. This is the diffusion force F calculated above.

Other phenomena already familiar to us also belong to the category of spreading. Water (Sect. 6.1) but also alcohol, ether, etc., evaporate into the air. They convert to a gaseous state although the chemical potential of liquid A is smaller below its boiling point than that of *pure* vapor. What makes this possible is the fact that the vapor is not pure but so diluted by air that $\mu(A|g) < \mu(A|l)$.

Any substance B dissolves in finite amounts in any other substance A (even if these amounts are immeasurably small) because when it is diluted enough, the chemical potential of the dissolved substance B falls below the fixed μ value of the non-dissolved solute of B, so that B begins to migrate away from it (Sect. 6.6).

Finally, the mass action law that is so important in chemistry can also be mentioned in this context as long as it deals with an exchange of substances taking place between spatially separate areas. Nernst's law of distribution, Henry's law of gas solubility, and even the vapor pressure formula of pure substances are all examples of this.

12.3 Indirect Mass Action

When a *small* amount n_B of a foreign substance is dissolved in a liquid A, the chemical potential μ of this liquid will decrease at constant p and T. In fact, it decreases in proportion to the mole fraction $x_B = n_B/(n_A + n_B)$ of the foreign substance, *independent of the kind of solute in question*:

$$\mu_A = \overset{\bullet}{\mu}_A - RT \cdot x_B \quad \text{for } x_B \ll 1 \quad \text{“colligative lowering of potential.”} \tag{12.2}$$

(The term "colligative" is explained at the end of this section). $\overset{\bullet}{\mu}_A$ (pronounced "mu-A-pure") designates the potential of A in its pure state ($x_A = 1$). Until now, we have ignored the "moderating influence" that the addition of a small amount of foreign substance can have upon another substance's tendency to transform. An example would be the application of the mass action law when the solvent takes part in the reaction in question. The reason for this is that for dilute solutions, the contribution $-RTx_B$ is small compared to the concentration-dependent contributions $\overset{\times}{\mu} = RT\ln c_r$ of the dissolved substances. The latter tend to $-\infty$ for decreasing concentration. In the mass action law which applies in the limit of strong dilution, the contribution $-RTx_B$ disappears, but the mass action terms $\overset{\times}{\mu}$ do not; they actually increase without limit.

In order to describe the dependency of the chemical potential μ of any substance upon composition (concentration c, partial pressure p, mole fraction x, etc.), chemists generally separate the potential μ into two parts: a basic component $\overset{\circ}{\mu}$ independent of the composition and a residual that is dependent upon it (compare Sect. 6.2). In the sense explained here, $\overset{\bullet}{\mu}$ represents a particular basic value. Only when this needs to be emphasized will we use the notation $\overset{\bullet}{\mu}$; otherwise we will stay with $\overset{\circ}{\mu}$.

Equation (12.2) for the lowering of potential is valid as long as the foreign substance B or foreign substances F (there can be several different ones, B, C, D, …, since their kind does not matter) dissolve molecularly but do not associate or dissociate, meaning they may not decompose into smaller components or form aggregates of several molecules. This remarkable relation, which is valid for all substances, is the indirect result of the mass action of the dissolved substances. Remember that mass action is independent of what kind of substances make up solvent A and solute B (see the mass action equations in Chap. 6).

Note that this new equation holds only in the *limit* of a small amount of a foreign substance being added to the solvent. Admittedly, this change of potential is small. However, because substance A is highly concentrated, it can have significant effects, which we will look into in the next sections.

For the mathematically interested: In order to derive Eq. (12.2), we will refer back to the cross relation discussed in Sect. 9.3 known as *n*–*n* coupling. When one substance tries to displace (or favor) another one, this happens reciprocally and with equal strength. The corresponding displacement coefficients are equal as can easily be shown by applying the flip rule (main equation $\mathrm{d}W = -p\mathrm{d}V + T\mathrm{d}S + \mu_{\mathrm{A}}\mathrm{d}n_{\mathrm{A}} + \mu_{\mathrm{B}}\mathrm{d}n_{\mathrm{B}}$):

$$\left(\frac{\partial \mu_{\mathrm{A}}}{\partial n_{\mathrm{B}}}\right)_{p,T,n_{\mathrm{A}}} = \left(\frac{\partial \mu_{\mathrm{B}}}{\partial n_{\mathrm{A}}}\right)_{p,T,n_{\mathrm{B}}}.$$

Taking into account that μ_{B} is dependent upon c_{B} and c_{B} is dependent upon n_{A}, $\mu_{\mathrm{B}}(c_{\mathrm{B}}(n_{\mathrm{A}}))$, which means that we have to apply the chain rule [see Eq. (A.1.13 in the Appendix)] in order to calculate the derivative on the right, the result is:

$$\left(\frac{\partial \mu_{\mathrm{B}}}{\partial n_{\mathrm{A}}}\right)_{p,T,n_{\mathrm{B}}} = \left(\frac{\partial \mu_{\mathrm{B}}}{\partial c_{\mathrm{B}}}\right)_{p,T} \left(\frac{\partial c_{\mathrm{B}}}{\partial n_{\mathrm{A}}}\right)_{p,T,n_{\mathrm{B}}}.$$

When we started examining the phenomenon called mass action, we chose the situation where the concentration coefficient $\overset{\times}{\gamma}$ of the chemical potential at low concentrations c is a universal quantity (Sect. 6.2). When applied to substance B, this means:

$$\left(\frac{\partial \mu_{\mathrm{B}}}{\partial c_{\mathrm{B}}}\right)_{p,T} = \overset{\times}{\gamma} = \frac{RT}{c_{\mathrm{B}}}.$$

Now, $c_{\mathrm{B}} = n_{\mathrm{B}}/V$ is indirectly dependent upon n_{A} even at a constant n_{B}, because $V = n_{\mathrm{A}}V_{\mathrm{A}} + n_{\mathrm{B}}V_{\mathrm{B}} \approx n_{\mathrm{A}}V_{\mathrm{A}}$. Since $n_{\mathrm{B}} \ll n_{\mathrm{A}}$, the contribution $n_{\mathrm{B}}V_{\mathrm{B}}$ to the volume V can be ignored and V_{A} can be considered equal to the volume demand of the pure substance A and therefore independent of n_{A}. When we take the derivative of $c_{\mathrm{B}} = n_{\mathrm{B}}/(n_{\mathrm{A}}V_{\mathrm{A}})$ with respect to n_{A} [by using rule (A.1.6) for calculating derivatives in the Appendix],

$$\left(\frac{\partial c_{\mathrm{B}}}{\partial n_{\mathrm{A}}}\right)_{p,T,n_{\mathrm{B}}} = -\frac{n_{\mathrm{B}}}{n_{\mathrm{A}}{}^2 V_{\mathrm{A}}} = -\frac{n_{\mathrm{B}}}{n_{\mathrm{A}}V} = -\frac{c_{\mathrm{B}}}{n_{\mathrm{A}}},$$

and insert the result further above, we obtain:

$$\left(\frac{\partial \mu_{\mathrm{A}}}{\partial n_{\mathrm{B}}}\right)_{p,T,n_{\mathrm{A}}} = \frac{RT}{c_{\mathrm{B}}} \cdot \frac{-c_{\mathrm{B}}}{n_{\mathrm{A}}} = -\frac{RT}{n_{\mathrm{A}}}.$$

The derivative is not dependent upon n_{B}, meaning that, with increasing amounts n_{B}, μ_{A} decreases linearly with constant slope from the initial value $\overset{\bullet}{\mu}_{\mathrm{A}}$:

$$\mu_{\mathrm{A}} = \overset{\bullet}{\mu}_{\mathrm{A}} - \frac{RT}{n_{\mathrm{A}}} \cdot n_{\mathrm{B}} \approx \overset{\bullet}{\mu}_{\mathrm{A}} - RT \cdot x_{\mathrm{B}}.$$

Figure 12.3 shows the chemical potential μ as a function of x within the entire range from $x = 0$ to 1. The solid curve illustrates the logarithmic relation considered the ideal case. If the mole fraction is reduced by a power of ten each time, the chemical potential always decreases by the same value, the decapotential μ_d of 5.7 kG at room temperature. As already stated (and derived above), all $\mu(x)$ curves must show the same slope RT for $x \approx 1$ (that is $x \approx 0$ for the second component of the mixture). We will go more deeply into this subject in Sect. 13.2.

"Colligative lowering of potential" leads to several effects: development of osmotic pressure, lowering of vapor pressure of a solution (compared with the pure solvent), raising of its boiling point, and lowering of its freezing point. These effects are determined solely by the mole fraction of the foreign substances, i.e., the *number* of dissolved particles ("assemblies of atoms") and not their chemical nature, size, and form. For this reason, the term *colligative properties* is used (from the Latin colligare "to assemble"). An aqueous solution with a mole fraction of glucose of 0.001 corresponds quite well to a urea solution with the same mole fraction for all the properties just mentioned (osmotic pressure, vapor pressure, freezing point, and boiling point). However, each type of particle in the solution must be treated as an individual substance. For example, the cations and anions in an electrolyte solution need to be counted separately. For a solution of table salt with $x_{NaCl} = 0.001, x_F = x_{Na^+} + x_{Cl^-} = 2 \cdot x_{NaCl} = 0.002$; this is so because NaCl is fully dissociated into the Na^+ and Cl^- ions. In a calcium chloride solution, we even have $x_F = x_{Ca^{2+}} + x_{Cl^-} = 3 \cdot x_{CaCl_2} = 0.003$.

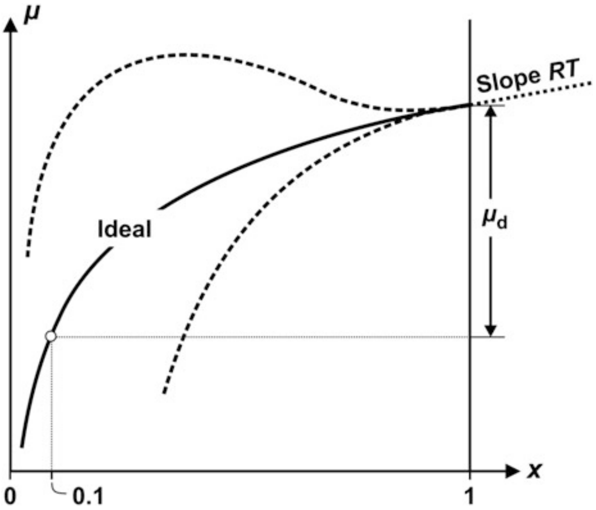


Fig. 12.3 Dependency of chemical potential upon mole fraction x.

12.4 Osmosis

When two solutions with different concentrations of a dissolved substance B are separated by a thin wall that only allows solvent A to pass through (a so-called *semipermeable* membrane, Fig. 12.4), solvent A will migrate through this membrane from the more diluted solution (with respect to B) to the one of higher concentration. In this case, one of the solutions can be composed of the pure solvent for which $c_B = 0$. In the solution having a higher concentration of B, substance A appears more strongly diluted due to its solution partner B. This means that the concentration of solvent is smaller, and because of this, its chemical potential μ_A is also smaller. Thus, the chemical drive for this process called *osmosis* is the difference of potential generated by different concentrations of foreign substances.

In the simple membrane model shown in Fig. 12.4, selective permeability results from the maximum pore size: Only the smaller solvent molecules manage to move through the membrane. But semipermeability can also occur through other mechanisms. The biological membranes surrounding living cells are also semipermeable. They allow water and molecules of comparable size through while holding back enzymes and proteins inside cells. In biology, osmotic exchange of water represents a ubiquitous phenomenon. It is responsible for the effect that juice is "drawn out" from strawberries that are sugared (Experiment 12.5) or that cherries swell up and burst after a long rain. In the first case, water migrates out through the peel into the concentrated, therefore water-poor, sugar solution. In the second case, water flows inward, because the water is more diluted there.

Another good example of the first effect would be salted slices of white radish (Experiment 12.6).

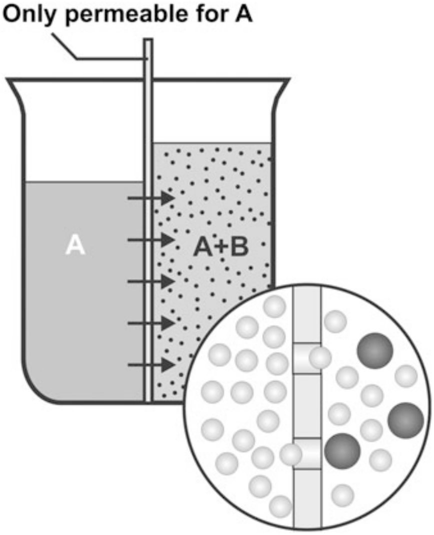
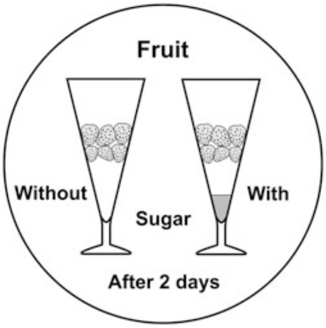
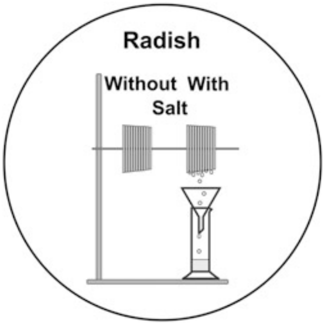


Fig. 12.4 Migration of solvent A in the direction opposite to a pressure gradient into a solution. The molecules of the dissolved substance B are shown as *dots*; for clarity, solvent A is shown as a continuum, where the slightly different *gray tones* indicate the differences of concentrations. The detail shows spheres symbolizing the molecules of the dissolved substance (*dark*) as well as the solvent (*light*).

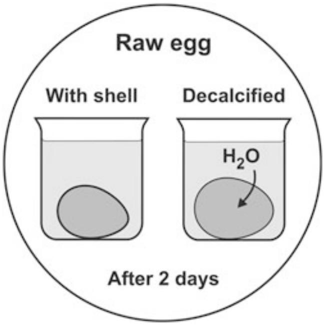
Experiment 12.5 *Juice "extraction" from sugared fruit*: Two handfuls of strawberries (or slices of mandarins) are carefully dabbed dry with a paper towel. One half of the strawberries is filled in a goblet so that there is some space left at the bottom. A lot of dry sugar is sprinkled on the other part of the strawberries, and subsequently, they are cautiously filled in the same way in the second goblet. After some hours, a watery syrup begins to gather on the bottom of the glass beneath the sugared fruit; after 2 days, a volume of 30–40 mL can be obtained. However, there is no formation of a liquid in the case of the unsugared fruit.



Experiment 12.6 *Juice "extraction" from slices of salted white radish*: The radish is cut into thin slices and these slices are piled in two stacks. The slices of one of the stacks are picked up in turn, salted very well, and piled up again. Subsequently, both stacks are speared on the wire. Immediately, juice begins to drip out of the stack with the salted slices. The measuring cylinder contains approx. 30 mL juice after 15 min.



Experiment 12.7 *Swelling of a decalcified egg in water*: One of two raw eggs (as equal as possible in size) is placed in a beaker with hydrochloric acid (or vinegar) to dissolve the calcareous egg shell—without breaking the membrane surrounding the egg. Subsequently, each of the eggs is put in a separate beaker filled with water. After 2 days, the shell-less egg has grown visibly in size.



The second effect can also be demonstrated on a raw decalcified egg which is cautiously placed in water (Experiment 12.7).

A gradual excess pressure results from the flow of solvent A into the concentrated solution. The chemical potential μ_A also gradually increases so that the potential gradient decreases. The process stops when μ_A on the right and on the left of the wall becomes equal (or when the substance A completely disappears from one side). The resulting excess pressure is called *osmotic pressure*.

We will now take a closer look at osmosis. We consider a vessel containing an amount n_A of a liquid A. When a small amount n_B of a foreign substance is dissolved in it, the chemical potential μ_A of the solvent decreases [“colligative lowering of potential,” Eq. (12.2)]:

$$\mu_A = \overset{\bullet}{\mu}_A - RT \cdot x_B \quad \text{for } x_B \ll 1. \tag{12.3}$$

Let us imagine the container connected to another one by a wall that is permeable only for the solvent (Fig. 12.5). The liquid in the second container is in its pure state. The potential gradient causes this liquid to flow through the wall into the solution. This flow can be suppressed by compensating for the loss of potential by raising the pressure on the solution. The chemical potential grows with increasing pressure (compare Sect. 5.3):

$$\mu_A = \overset{\bullet}{\mu}_A - RT \cdot x_B + \beta_A \cdot \Delta p, \tag{12.4}$$

where the pressure coefficient β_A corresponds to the molar volume V_A of the pure solvent (compare Sect. 9.3). The following is then valid for the osmotic equilibrium:

$$\overset{\bullet}{\mu}_A - RT \cdot x_B + V_A \cdot \Delta p = \overset{\bullet}{\mu}_A \text{ and respectively, } -RT \cdot x_B + V_A \cdot \Delta p = 0. \tag{12.5}$$

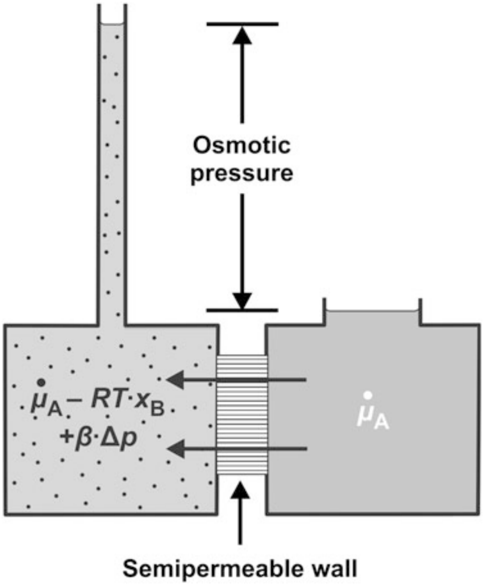


Fig. 12.5 Experiment illustrating osmotic pressure. The riser pipe on the *left* serves as manometer.

This means that the chemical potential of the solution again corresponds to that of the pure solvent. The excess pressure Δp necessary for establishing equilibrium serves as measure for the *osmotic pressure* p_{osm} in the solution.

The simple arrangement in Fig. 12.5 shows the pressure working against the flow of solvent into the solution as a result of the gravitational pressure of the column of solution in the riser pipe on the left. This pressure is produced by the osmosis itself as the pure solvent moves through the semipermeable wall into the solution. In the process, the difference of level between the two riser pipes gradually becomes greater until, eventually, the gravitational pressure compensates for the effect of osmotic pressure. This means that osmotic equilibrium has been established. The osmotic pressure $p_{\mathrm{osm}} = \rho g h$ can be easily calculated from the resulting rise h of the column of liquid, the density ρ of the solution, and the gravitational acceleration g.

With the help of a carrot and a riser pipe with a funnel-shaped end, it is easy to construct an experiment to prove the existence of osmotic pressure (Experiment 12.8).

We have $x_{\mathrm{B}} = n_{\mathrm{B}}/(n_{\mathrm{A}} + n_{\mathrm{B}}) \approx n_{\mathrm{B}}/n_{\mathrm{A}}$ for a diluted solution because the amount n_{B} of solute is so small compared to the amount n_{A} of the solvent that it can be ignored. Multiplying Eq. (12.5) by n_{A} yields:

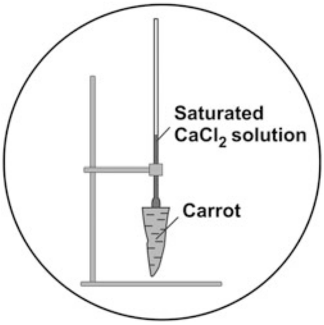
$$-RT \cdot n_{\mathrm{B}} + n_{\mathrm{A}} V_{\mathrm{A}} \cdot p_{\mathrm{osm}} = 0. \qquad (12.6)$$

If $V \approx n_{\mathrm{A}} \cdot V_{\mathrm{A}}$ indicates the volume of liquid (ignoring the small amount $n_{\mathrm{B}} \cdot V_{\mathrm{B}}$ of foreign substance), then the osmotic pressure p_{osm} results in:

$$p_{\mathrm{osm}} = n_{\mathrm{B}} \frac{RT}{V} \quad \text{Van't Hoff's equation.} \qquad (12.7)$$

At room temperature ($T = 298$ K), a solution of an arbitrary non-electrolyte with a concentration of 0.1 kmol m^{-3} results in an osmotic pressure of 250 kPa (2.5 bar). This would be enough to raise the column of liquid more than 25 m. Even at very small concentrations, osmotic pressure is of such a magnitude that it is easy to measure with sufficient precision.

Experiment 12.8 *Experimental demonstration of osmotic pressure*: The inside of the carrot is hollowed out in a cylindrical form and filled with a colored saturated calcium chloride solution. Then the riser pipe is attached. After a short time, one observes a continuous rise of the solution in the riser pipe. In this case, the cell membranes in the carrot act as the semipermeable wall.



Van't Hoff's equation is very similar to the general gas law. In fact, both equations can be interpreted in the same way. Here we need to keep in mind that the forces of attraction between the A particles keep the liquid together (compare Sect. 11.1, keyword "cohesion pressure"). The contribution of the external pressure p is comparatively small. The B particles that drift far away from each other and scarcely influence each other cause a pressure like that of a dilute gas. However, in this case the pressure is not compensated by the container walls but by the cohesion of the A particles. When the osmotic pressure p_{osm} is higher than the external pressure—a condition that is often attained—the liquid A behaves as if it were under negative pressure. If we calculate the potential μ_{A} of the liquid for a pressure reduced by p_{osm} and keep in mind that for dilute solutions $V \approx n_{\text{A}} \cdot V_{\text{A}}$ and $n_{\text{B}}/n_{\text{A}} \approx x_{\text{B}}$, we again end up with Eq. (12.3). This demonstrates that both descriptions are equivalent:

$$\overset{\bullet}{\mu}_{\text{A}} - \beta_{\text{A}} \cdot p_{\text{osm}} = \overset{\bullet}{\mu}_{\text{A}} - V_{\text{A}} \frac{n_{\text{B}} RT}{V} = \overset{\bullet}{\mu}_{\text{A}} - x_{\text{B}} RT.$$

If the dilute solution contains several types of particles which cannot penetrate the membrane, we have

$$p_{\text{osm}} = n_{\text{F}} \frac{RT}{V} = c_{\text{F}} RT, \tag{12.8}$$

where n_{F} as well as c_{F} are the sum of the amounts of substance and the sum of concentrations of all types of particles, respectively. c_{F} is called the *osmotic concentration* (formerly known as *osmolarity*) of the solution. Since the total number of dissolved particles must be taken into account when calculating the osmotic concentration, the number of ions that form an ionic substance must also be considered. For example, the osmotic concentration of an aqueous solution of the salt CaCl_2 with a concentration c is three times as great as this concentration. Correspondingly, the osmotic pressure of the solution of this salt is three times that of a solution of a non-electrolyte with concentration c.

As we have mentioned at the beginning, osmotic phenomena play an essential role in biological processes. They have great importance for the balance of water in living organisms and influence the shape of their cells. The osmotic concentration c_{F} of cell liquid in human red blood cells, for example, is approximately 300 mol m^{-3}. In this case, we can apply Van't Hoff's law only with reservations due to this relatively high concentration. However, for body temperature, an osmotic pressure of $p_{\text{osm}} = 300 \text{ mol m}^{-3} \times 8.3 \text{ J mol}^{-1} \text{ K}^{-1} \times 310 \text{ K} = 770 \text{ kPa}$ can be at least estimated. If red blood cells were to be suspended in pure water, they would have to withstand about 8 times normal atmospheric pressure. In fact, they swell up and burst long before this point (Fig. 12.6, left). On the other hand, if red blood cells are put into contact with an aqueous saline solution that has a much higher osmotic pressure than 770 kPa, the water in the cells will flow out and they will shrink (the membranes of red blood cells are almost impenetrable for Na^+, Fig. 12.6, right). Only if the osmotic pressure is the same inside the red blood cells

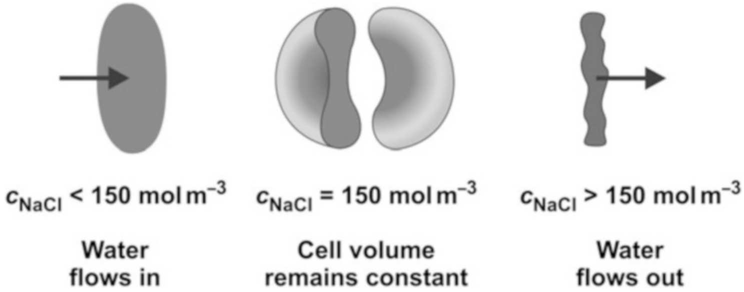


Fig. 12.6 Osmotic behavior of red blood cells in aqueous NaCl solutions at concentration c.

and the surrounding solution (which is the case for blood plasma) do the cells keep their normal shape (Fig. 12.6, middle).

Solutions where the water content of the cells remains constant [$\mu(H_2O)$ is the same inside and outside the cells] are described as *isotonic*. When giving intravenous infusions, it is important to be aware that in order not to damage the blood cells, only an isotonic solution matching the blood may be used. A physiological saline solution has a concentration of 150 mol m^{-3} and therefore an osmotic concentration of 300 mol m^{-3}. On the other hand, the cell damaging effects of concentrated saline solutions can be put to good use in order to preserve foods. One example is salting of meat (pickling) where the water is removed from possibly unhealthy microorganisms through osmosis. This hinders their cell functions and strongly reduces their reproduction.

In *reverse osmosis*, an external excess pressure is exerted upon the side of the concentrated solution that is higher than the osmotic pressure p_{osm} of this solution. This causes the solvent's molecules to be "forced" in the direction opposite to the osmotic effect. They are forced through the semipermeable membrane and into the more diluted solution where they are enriched. This procedure is used in desalinization of water as well as wine processing.

12.5 Lowering of Vapor Pressure

A pure liquid A is assumed to be in equilibrium with its vapor at a pressure of p_{lg} (initial situation: $\overset{\bullet}{\mu}_{A|l} = \overset{\bullet}{\mu}_{A|g}$). The *vapor pressure* of A is lowered if a low-volatile foreign substance B is dissolved in it (Fig. 12.7).

Qualitatively, this can be understood immediately. Adding B dilutes liquid A|l, thereby lowering its chemical potential $\mu_{A|l}$. The dissolved substance B should have low volatility so it contributes nothing to the vapor A|g and the potential $\mu_{A|g}$ remains unchanged. Because $\mu_{A|l}$ is now lower than $\mu_{A|g}$, the vapor has to condense on the surface of the solution, thereby causing the pressure to fall.

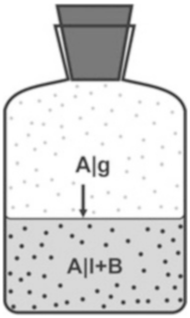


Fig. 12.7 Establishment of equilibrium between a solution of a foreign substance B in a liquid A and the pure vapor phase of A.

The quantitative discussion is also not difficult. The process continues until equality of potentials is regained, $\mu_{\mathrm{A|g}} = \mu_{\mathrm{A|l}}$. For this purpose, reducing the pressure by a small amount Δp is sufficient. The chemical potential $\mu_{\mathrm{A|g}}$ of the vapor falls steeply with decreasing pressure because of its high pressure coefficient, $\beta_{\mathrm{A|g}} >>> \beta_{\mathrm{A|l}}$, whereas the change of the potential $\mu_{\mathrm{A|l}}$ is so small that it can be neglected. If we consider the "colligative potential lowering" $-RTx_{\mathrm{B}}$ caused by B we obtain for the equilibrium condition:

$$\mu_{\mathrm{A|g}} = \overset{\bullet}{\mu}_{\mathrm{A|g}} + \beta_{\mathrm{A|g}} \cdot \Delta p = \overset{\bullet}{\mu}_{\mathrm{A|l}} - RT \cdot x_{\mathrm{B}} = \mu_{\mathrm{A|l}}. \tag{12.9}$$

We act on the assumption that $\overset{\bullet}{\mu}_{\mathrm{A|l}} = \overset{\bullet}{\mu}_{\mathrm{A|g}}$; therefore these contributions cancel each other out. Because we also have $\beta_{\mathrm{A|g}} = V_{\mathrm{A|g}} = RT/p$ (see Sect. 9.3), the equation can be simplified according to:

$$RT\frac{\Delta p}{p} = -RT \cdot x_{\mathrm{B}}. \tag{12.10}$$

In this context, p corresponds to the vapor pressure p_{lg} of the *pure* solvent. If it is important to emphasize this fact, we add the symbol • and write $\overset{\bullet}{p}_{\mathrm{lg}}$ instead of p_{lg}. For the "lowering of vapor pressure" Δp_{lg}, we obtain a relation that was discovered empirically in 1890 by the French Chemist François Marie Raoult:

$$\Delta p_{\mathrm{lg}} = -x_{\mathrm{B}} \cdot \overset{\bullet}{p}_{\mathrm{lg}} \quad \text{Raoult's law.} \tag{12.11}$$

Let us have a look at Fig. 12.8 for illustration: At the intersection of the potentials for pure solvent and pure vapor, there is equilibrium between the liquid and its vapor phase at the vapor pressure p_{lg}. A dissolved substance of low volatility lowers the chemical potential of the solvent by $-RTx_{\mathrm{B}}$ ("colligative potential lowering" corresponding to the distance between the almost horizontal straight lines), but

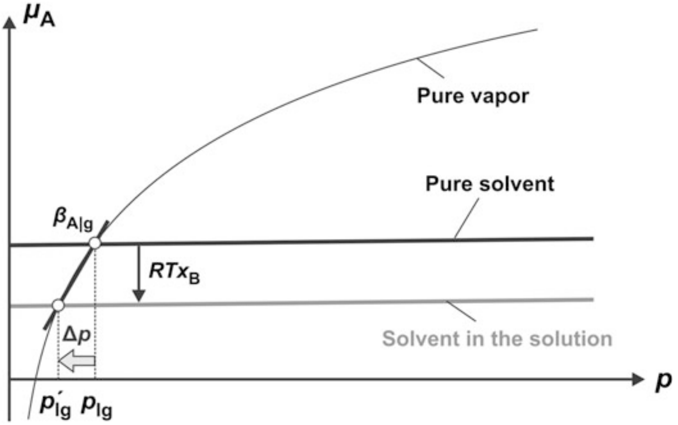
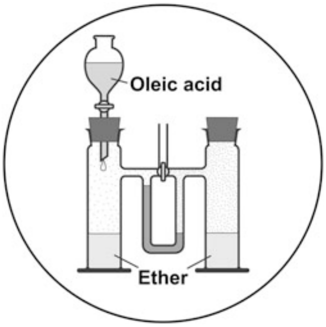


Fig. 12.8 Dependence of the chemical potential upon pressure, and lowering of vapor pressure.

Experiment 12.9 *Comparison of the vapor pressures of ether and an ether–oleic acid mixture*: Both gas-washing bottles are filled about one-fifth of their volumes with ether. After removal of most of the air with the help of a pump, the stop cock is closed. Subsequently, the oleic acid is added drop by drop. The vapor pressure of ether in the gas-washing bottle with added oleic acid decreases in comparison to that of pure ether. This is shown by the level of liquid in the manometer.



leaves that of the vapor unchanged. Thus, the intersection of the curves (axis of abscissas p'_{lg}) shifts to the left. This means that the vapor pressure is lowered by Δp ($\Delta p < 0!$).

With the aid of the “slope triangle” drawn in the figure, the slope $\beta_{A|g}$ of the potential curve for pure vapor results in

$$\beta_{A|g} = \frac{-RTx_B}{\Delta p}.$$

Considering that $\beta_{A|g} = V_{A|g} = RT/p$ and solving the equation for Δp results in Raoult’s law. Whether one prefers the first pure mathematical or the second more geometrical derivation is a question of personal preference.

The simple setup shown in Experiment 12.9 illustrates the discussed effect.

12.6 Lowering of Freezing Point and Raising of Boiling Point

A frozen liquid A melts more easily when a substance B that is soluble in the liquid but not in the solid is added (Fig. 12.9). At the normal freezing point T_{sl} of the liquid A, the chemical potentials for the solid and the liquid state are equal ($\overset{\bullet}{\mu}_{\mathrm{A|s}} = \overset{\bullet}{\mu}_{\mathrm{A|l}}$). If a foreign substance is dissolved in the liquid phase, the chemical potential of this phase decreases so that it falls below that of the solid phase which then begins to melt. The entropy required for the phase transition solid → liquid is not added from outside but has to be brought up by the system itself. Therefore, the entire mixture cools down and the chemical potentials rise due to their negative temperature coefficients. However, because the temperature coefficient for a liquid is smaller than for a solid ($\alpha_{\mathrm{A|l}} < \alpha_{\mathrm{A|s}} < 0$), $\mu_{\mathrm{A|l}}$ grows faster with decreasing temperature than does $\mu_{\mathrm{A|s}}$. This causes the potential gradient to disappear again at a certain lower temperature and the melting process stops.

An illustration (Fig. 12.10) explains this phenomenon: When the chemical potentials for the pure solvent as well as for the pure solid are drawn as functions of temperature, the intersection of the two curves yields the freezing point T_{sl}. The dissolved substance lowers the chemical potential of the liquid but does not influence the solid phase. The intersection of the curves ($T_{\mathrm{sl}'}$) is therefore shifted to the left. This means that the freezing point is lowered by ΔT_{sl} ($\Delta T_{\mathrm{sl}} < 0$).

In the corresponding calculation, we again assume a reestablished equilibrium. This time it is between the liquid and solid phase, $\mu_{\mathrm{A|l}} = \mu_{\mathrm{A|s}}$. Because the changes in temperature T we are interested in are mostly small, we can assume a linear dependency of the chemical potential upon T. At constant pressure, we obtain the following result (keep in mind that in this case the freezing point T_{sl} is the reference point for the temperature coefficient):

$$\mu_{\mathrm{A|l}} = \overset{\bullet}{\mu}_{\mathrm{A|l}} - RT_{\mathrm{sl}} \cdot x_{\mathrm{B}} + \alpha_{\mathrm{A|l}} \cdot \Delta T = \overset{\bullet}{\mu}_{\mathrm{A|s}} + \alpha_{\mathrm{A|s}} \cdot \Delta T = \mu_{\mathrm{A|s}}. \qquad (12.12)$$

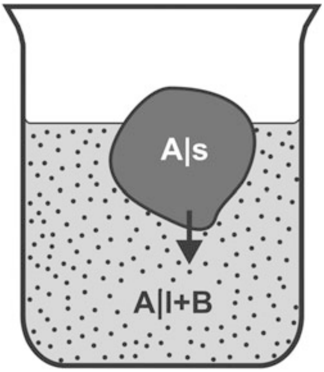


Fig. 12.9 Melting of a frozen liquid in a solution.

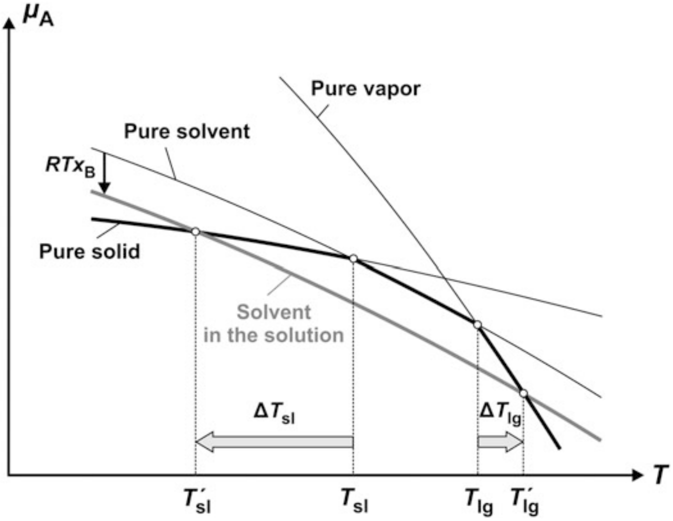


Fig. 12.10 Temperature dependence of chemical potentials, lowering of freezing point, as well as raising of boiling point. The lowering of potential of solvent A by $-RTx_B$ caused by the foreign substance B is compensated at the freezing point T_{sl} by a lowering and at the boiling point T_{lg} by a raising of temperature.

Again the basic values cancel each other out, $\overset{\bullet}{\mu}_{A|l} = \overset{\bullet}{\mu}_{A|s}$. When the equation is solved for ΔT (or rather ΔT_{sl}), the freezing-point depression results in:

$$\Delta T_{sl} = \frac{RT_{sl} \cdot x_B}{\alpha_{A|l} - \alpha_{A|s}}. \tag{12.13}$$

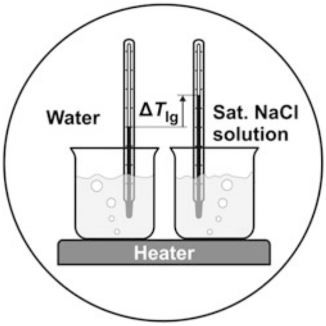
Here, the temperature coefficient corresponds to the negative molar entropy of the substance (compare Sect. 9.3). Subsequently, the difference $S_{A|l} - S_{A|s}$ can be summarized as the molar entropy of fusion $\Delta_{fus}S_A$ of the pure solvent (at the freezing point) (compare Sect. 11.5):

$$\Delta T_{sl} = -\frac{RT^{\bullet}_{sl} \cdot x_B}{\Delta_{fus}S_A}. \tag{12.14}$$

Like the vapor pressure lowering, the freezing-point depression is directly proportional to the mole fraction x_B of dissolved substance. The additional character •, indicating that the labeled quantity applies to the pure substance, can be omitted if misunderstandings are not possible.

For example, in an aqueous non-electrolyte solution with a mole fraction of $x_B = 0.01$, ΔT_{sl} is about –1 K. An example from everyday life is shown in Experiment 12.10. A prime example of an application of freezing-point depression is, however, the melting effect of road salt.

Experiment 12.10 *Whisky "on the rocks"*: When rum, schnaps, whisky, or, alternatively, ethanol is poured over ice, it will become considerably colder than 0 °C.



Experiment 12.11 *Raising of boiling point of a saturated solution of table salt*: A saturated solution of table salt begins to boil at a noticeable higher temperature than tap water.

In contrast to the freezing point, the boiling point of a solution is raised as demonstrated in Experiment 12.11. Correspondingly, the position of the equilibrium between liquid and vapor is shifted to a higher temperature in Fig. 12.10. However, this raising of boiling point is much smaller than the lowering of freezing point which can be attributed to the different slopes of the curves representing the potentials. These, in turn, are determined by the molar entropies, which naturally leads to the steepest drop for the gaseous state of the solvent.

A consideration similar to that for lowering the freezing point leads to the equation for raising the boiling point:

$$\Delta T_{\mathrm{lg}} = -\frac{RT_{\mathrm{lg}} \cdot x_{\mathrm{B}}}{\alpha_{\mathrm{A|g}} - \alpha_{\mathrm{A|l}}} \quad \text{and correspondingly,} \quad \Delta T_{\mathrm{lg}} = \frac{RT^{\bullet}_{\mathrm{lg}} \cdot x_{\mathrm{B}}}{\Delta_{\mathrm{vap}} S_{\mathrm{A}}}, \qquad (12.15)$$

where $\Delta_{\mathrm{vap}} S_{\mathrm{A}}$ now represents the molar entropy of vaporization $(S_{\mathrm{A|g}} - S_{\mathrm{A|l}})$ at the boiling point T_{lg}. In an aqueous solution of a non-electrolyte with a mole fraction of $x_{\mathrm{B}} = 0.01$, ΔT_{lg} is only about 0.3 K.

In summary, when a low-volatile foreign substance is dissolved in a liquid, the potential of the pure vapor, which is then higher than that of the solution, can be lowered in two ways. First, by lowering the pressure (Sect. 12.5), and second, by raising the temperature.

12.7 Colligative Properties and Determining Molar Mass

The four phenomena just described (osmosis, lowering of vapor pressure, lowering of freezing point, and raising of boiling point) have a common feature: they are all dependent upon the indirect mass action of dissolved substances, i.e., the lowering of the chemical potential by mixing in small amounts of foreign substances. These so-called colligative phenomena depend solely upon the mole fraction of these foreign substances and therefore the number of dissolved particles. However, what type of substances they are is unimportant.

Because of this peculiarity, the colligative properties can be used to determine the amount of substance n_B of a sample of an unknown substance B and, therefore, if the mass m_B of the sample is known, also the molar mass $M_B = m_B/n_B$. Let us take a quick look at this by considering the example of lowering of freezing point. $x_B \approx n_B/n_A$ is valid at high dilution, and because of $n_A = m_A/M_A$, we have $x_B \approx n_B \cdot M_A/m_A$. The quotient n_B/m_A corresponds to the molality b_B (compare Sect. 1.5). Inserting these expressions in Eq. (12.14) for the freezing-point depression results in

$$\Delta T_{sl} = -k_f \cdot \frac{n_B}{m_A} = -k_f \cdot b_B \quad \text{with} \quad k_f = -\frac{RT_{sl}M_A}{\Delta_{sl}S_A}, \tag{12.16}$$

a coefficient called "*cryoscopic constant*" which is only dependent upon pressure and type of solvent. k_f corresponds to the lowering of freezing point which is obtained from 1 mol of dissolved substance in 1 kg of solvent. At such high concentrations, the equation above can only be an approximation. For measuring the temperature changes at low concentrations with sufficient precision, it is advisable to use solvents with k_f values as high as possible. Table 12.1 shows the "cryoscopic constants" of some solvents.

There are analogous relations and applications for the raising of boiling point:

$$\Delta T_{lg} = +k_b \cdot \frac{n_B}{m_A} = +k_b \cdot b_B \quad \text{with} \quad k_b = \frac{RT_{lg}M_A}{\Delta_{lg}S_A}. \tag{12.17}$$

The "ebullioscopic constant" k_b that corresponds to k_f is positive, and because of its higher denominator ($\Delta_{vap}S_A > \Delta_{fus}S_A$), it is (in absolute terms) smaller than k_f

Table 12.1 Cryoscopic and ebullioscopic constants of some solvents (from: Lide D R (ed) (2008) CRC Handbook of Chemistry and Physics, 89th edn. CRC Press, Boca Raton).

Solvent	T_{sl} (K)	k_f (K kg mol^{-1})	T_{lg} (K)	k_b (K kg mol^{-1})
Water	273.2	1.86	373.2	0.51
Benzene	278.6	5.07	353.2	2.64
Cyclohexane	279.7	20.8	353.9	2.92
Cyclohexanol	299.1	42.2	434.0	3.5
Campfor	452.0	37.8	–	–

(compare Table 12.1). For this reason, the change of temperature here is smaller than for lowering of the freezing temperature and therefore more difficult to measure. Finally, the desired molar mass M_B results from the equations above by solving for n_B and calculating according to $M_\mathrm{B} = m_\mathrm{B}/n_\mathrm{B}$.

Development of osmotic pressure can also be used in determining amounts of substances and thereby molar masses. The principle of this method, which is also known as *osmometry*, is to measure the osmotic pressure of a solution of known molality. The advantage of this method compared to the other methods using colligative properties is that it is much more sensitive. For instance, an aqueous solution of cane sugar with a concentration of 0.01 mol kg^{-1} exhibits a raising of boiling point of 0.005 K and a lowering of freezing point of 0.02 K. However, the osmotic pressure is 25 kPa (0.25 bar), which can be measured both easily and precisely. Because of its sensitivity, osmometry is useful particularly for the investigation of macromolecular substances such as synthetic polymers, proteins, or enzymes having molar mass between 10^4 and 10^6 g mol^{-1}. The lowering of the freezing point is commonly used in medicine for determining the total osmolality of aqueous solutions such as blood plasma or urine.

The gas law also belongs to the colligative properties, but often it is not mentioned in this context. It can be used for the same purposes. The vacuum appears here in the role of the solvent, whereas the gas pressure corresponds to the osmotic pressure.