Chapter 14
Binary Systems

The average chemical potential of a mixture depends not only upon the composition but also upon the temperature (and pressure). These dependencies and the fact that the phase with the lowest chemical potential at a given temperature (or pressure) will be stable can be used to construct the phase diagrams of different mixtures. First, we will discuss the temperature–composition diagrams of two liquid phases. With the help of these diagrams, we can judge under which conditions the two liquids are mutually miscible and under which they are not; the diagrams are therefore also called miscibility diagrams. Liquid–solid phase diagrams are used to identify the regions of temperature and composition at which solids and liquids exist in a two-component system. Such diagrams are of great commercial and industrial relevance; they play an important role in metallurgy but also in the manufacture of ceramics and semiconductors. In the last section, the phase diagrams of binary mixtures of two volatile components are discussed. This kind of diagram is important for understanding distillation, one of the most significant processes used in chemical laboratories and industry for separating liquid mixtures. It has been in use since ancient times to extract essential oils such as attar of roses. An important industrial application is distilling of petroleum in oil refineries that produce the heavy and light gasoline used to fuel engines.

14.1 Binary Phase Diagrams

In Chap. 11, we were introduced to the phase diagrams of pure substances. They can be used to find which phase is the most stable under given conditions (such as temperature or pressure). Analogous to these, phase diagrams for mixtures can be constructed. In the following, we will confine ourselves to two-component systems, meaning so-called *binary* mixtures of two components. In this case, the composition x of the mixture appears as third variable along with temperature T and pressure p. Hence, a complete description of the system is only possible using

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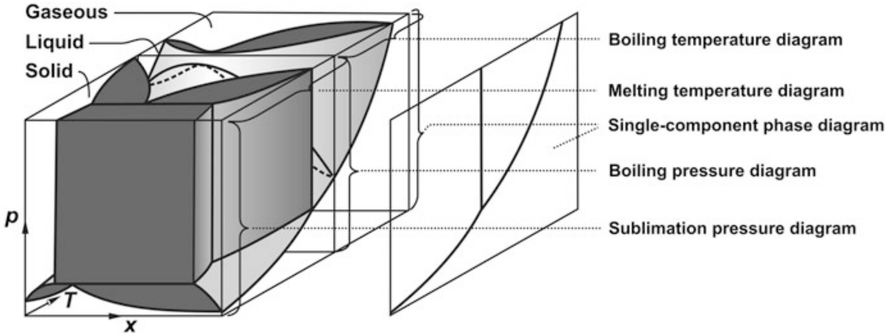


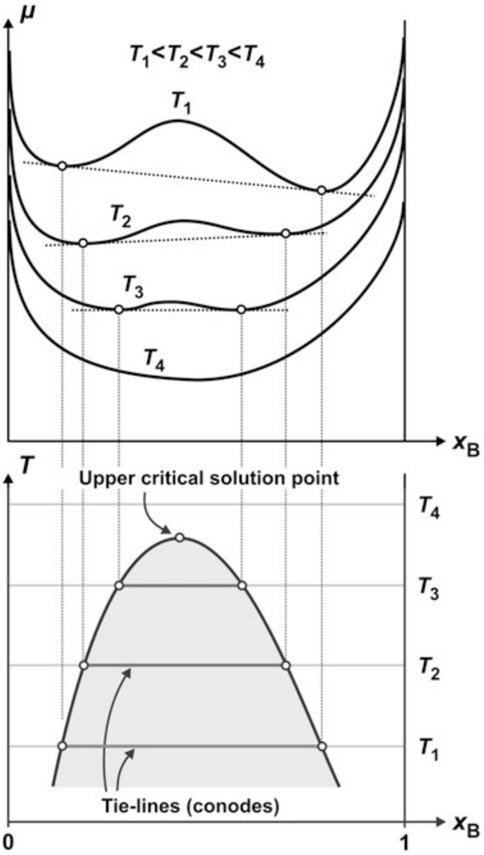
Fig. 14.1 Three-dimensional phase diagram.

three-dimensional phase diagrams. Figure 14.1 shows an example. The curved surfaces divide the diagram into single-phase and two-phase (dark colored) spatial regions. It is limited on the left ($x = 0$) and on the right ($x = 1$) by the already familiar plane phase diagrams of pure components (compare the diagram on the right with Fig. 11.10). The whole thing looks rather complicated at first, but don't worry, one variable is usually left out and either the temperature or pressure is kept constant, resulting in a phase diagram that is just two-dimensional. It gives us, for example, the most stable phase as a function of temperature and composition of the mixture. To this end, the temperature is plotted on one of the axes and the mole fraction of one of the components on the other. (Because it is a binary system, the mole fraction of the second component is then known as well.) Such a $T(x)$ diagram is equivalent to an isobaric cut through the three-dimensional diagram. Examples would be miscibility diagrams, and melting and boiling temperature diagrams which we will go into in more detail in the next sections. A $p(x)$ diagram is analogous to an isothermal cut. Examples of this would be boiling pressure and sublimation pressure diagrams.

14.2 Liquid–Liquid Phase Diagrams (Miscibility Diagrams)

Using what we learned from the section on mixing processes in the last chapter, we will now deal with mixtures of two liquid phases A and B. We saw that (at particular values of temperature and pressure) the substances can be indifferent, highly compatible, lowly compatible, or even incompatible with each other. However, this behavior can change with temperature (at constant pressure). For example, there are substances such as phenol and water or hexane and nitrobenzene that are quite compatible at high temperatures and incompatible at lower temperatures.

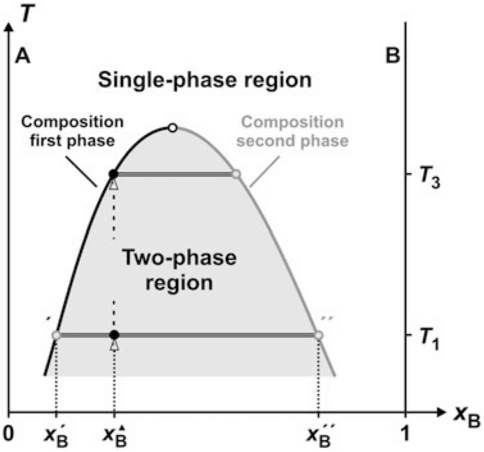
Fig. 14.2 Behavior of (average) chemical potential $\mu(x_B)$ in a mixture of two liquid components depending upon temperature (*top*) and the corresponding phase diagram at constant pressure with an upper critical solution point (*bottom*).



We can now determine $\mu(x)$ for every temperature (at a constant pressure, such as standard pressure of 100 kPa) as we learned to do in the last chapter (Fig. 14.2, above).

We see that the miscibility gap is greatest at the lowest temperature (T_1). Both the chemical potential and the contribution from the extra potential decrease as the temperature increases (T_2, T_3). The miscibility gap becomes increasingly smaller as the temperature goes up. The difference of the composition x_B in the two separate mixed phases becomes increasingly smaller as well. Finally, at the temperature T_4, there is only one phase left. It is possible to construct a $T(x)$ diagram (Fig. 14.2, below, a so-called *miscibility diagram*) from the $\mu(x)$ isotherms by plotting the double tangent's points of contact for every temperature and connecting them to form a curve. The horizontal line, which relates a pair of coexisting phases to each other, is called a *tie-line* or *conode* and their end points are called *nodes*. During heating, the tie-lines become continuously shorter until the end points finally coincide at the *upper critical solution point*. The corresponding temperature is the

Fig. 14.3 Applying the "lever rule" using the example of a phase diagram with an upper critical solution point.



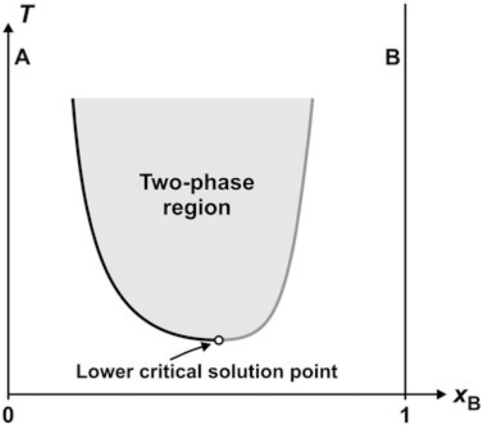
highest temperature at which a phase separation can take place. Above this *upper critical solution temperature,* both substances are completely miscible. The system phenol/water, for example, shows an upper critical solution temperature of 339 K.

Let us clarify these relations by using Fig. 14.3: For example, if we have a pure substance A, and small amounts of B are successively added to it at a temperature T_1, the two liquids will completely mix at first. This will be the case until the miscibility limit is reached at point ′. However, a homogeneous mixture with a higher B content (e.g., $x_{\mathrm{B}}^{\blacktriangle}$) is impossible to produce. Instead, two separate liquid mixed phases occur. One of these is a B-poor phase with the composition x'_{B} and the other a B-rich phase with the composition x''_{B}. The ratio of amounts of the two coexisting mixed phases results from the lever rule [analogous to the procedure in the case of $\mu(x)$ curves (Chap. 13)] from which the $T(x)$ diagram was constructed. If B continues to be added to the mixture, we still have two mixed phases ′ and ″. However, the amount of B-rich phase increases at the expense of the B-poor one because the corresponding lever arm shortens. When the phase boundary is crossed at point ″, the two mixed phases finally merge into one.

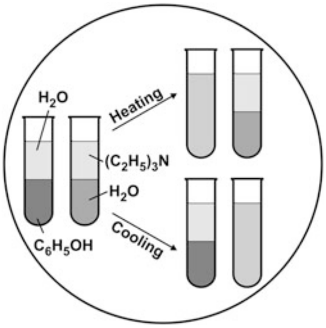
On the other hand, if a sample with the mole fraction $x_{\mathrm{B}}^{\blacktriangle}$ at temperature T_1 is continuously heated (vertical dotted line), the compositions of the liquid mixed phases that are in equilibrium with each other change. The B-poor phase becomes gradually richer in B (while the composition remains below $x_{\mathrm{B}}^{\blacktriangle}$), whereas the B-rich phase loses some B. The ratio of the amounts of the two mixed phases changes according to the lever rule. The phase richer in B gradually disappears because as the temperature rises, the ratio of lever arms shifts in its favor and therefore the ratio of amounts in its disfavor. When the phase boundary line is finally crossed at temperature T_3, only one mixed phase with the composition $x_{\mathrm{B}}^{\blacktriangle}$ is present.

Some systems exhibit a lower critical solution point (Fig. 14.4). At higher temperatures (and depending upon the composition), two phases can be present. At lower temperatures, the two substances are totally miscible. An example of this

Fig. 14.4 Phase diagram of a system with a lower critical solution point.



Experiment 14.1 *Demonstration of the presence of a miscibility gap with the help of the systems phenol/water and triethylamine/water*: When heated, a heterogeneous mixture of phenol and water will become a homogeneous solution when the upper critical solution temperature (approx. 339 K) is exceeded. However, even at higher temperatures, a heterogeneous mixture of triethylamine and water remains separated, but when cooled with ice to below the lower critical solution temperature (approx. 292 K), it will become a homogeneous solution. The phenol–water mixture, however, continues to consist of two phases after cooling.

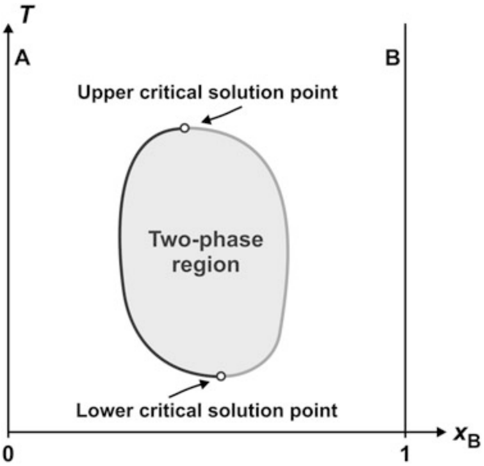


would be a system of triethylamine and water which has a lower critical solution temperature of 292 K.

Let us illustrate these relationships by a demonstration experiment using on the one hand a mixture of phenol (C_6H_5OH) (the phenol is colored with methyl red for visibility) and water and on the other hand a mixture of triethylamine ($(C_2H_5)_3N$) and water colored with orange G (Experiment 14.1).

Some systems have both an upper and a lower critical solution point (Fig. 14.5). These kinds of systems are mostly found at higher pressures. It is therefore plausible to assume that all systems having a lower critical solution point will also exhibit an upper critical solution point if the temperature and pressure are high

Fig. 14.5 Phase diagram of a system with an upper and a lower critical solution point.



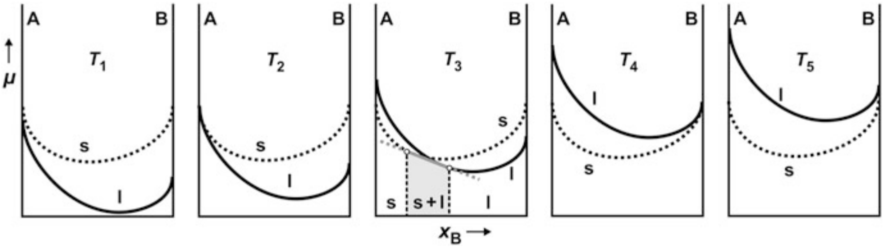


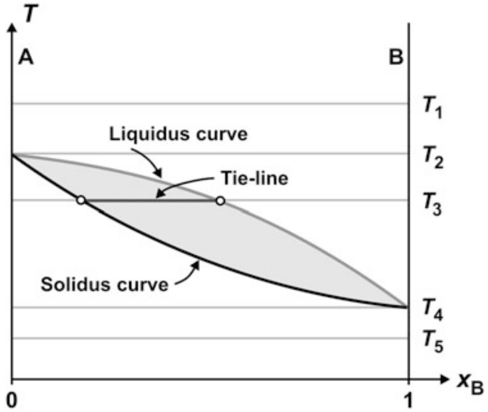
Fig. 14.6 Behavior of (average) chemical potential $\mu(x_B)$ for mixtures of two components that are indifferent both in their solid and liquid states for various temperatures ($T_1 > T_2 > T_3 > T_4 > T_5$).

enough. A well-known example is the system nicotine/water which exhibits a closed miscibility gap with the critical temperatures 334 and 483 K.

14.3 Solid–Liquid Phase Diagrams (Melting Point Diagrams)

Solid Solution Systems We will now take a look at phase diagrams containing both solid and liquid phases. They are also called *melting temperature diagrams* or *melting point diagrams* that, for example, play a big role in metallurgy. Especially simple melting point diagrams represent systems whose components A and B are infinitely soluble with each other both in the melted (l) as well as the solid states (s), meaning that they form *mixed crystals*. For constructing these diagrams, the $\mu(x)$ curves of the liquid and solid mixed phases must be considered as functions of temperature (Fig. 14.6).

Fig. 14.7 Melting point diagram of a system of two substances showing indifferent behavior in both the liquid and solid states (constructed using Fig. 14.6).



At very high temperatures (T_1), μ_l has for any arbitrary composition a smaller value than μ_s, which means the melting process mixed phase|s $\longrightarrow$ mixed phase|l always proceeds spontaneously. For this reason, the system is liquid independent of the composition. When the system is cooled, it will eventually reach the point (T_2) where the two $\mu(x)$ curves touch for the first time. This means that they exhibit the same value ($\mu_l = \mu_s$). In our example, this is at $x_B = 0$ and therefore at the melting point of the pure substance A. At the melting temperature of A, a solid phase (in equilibrium with a liquid phase) is present only at a mole fraction of $x_B = 0$, while the phases with all other compositions are still completely liquid. When the temperature is further reduced (e.g., to T_3), separate regions of composition appear in which either the solid phase s or the melted phase l exhibits the smaller chemical potential. Between these regions, the smallest chemical potential is obtained through a heterogeneous mixture of melt and solid phases (l + s) as we have seen in the last section of the previous chapter. The compositions that are determined by the double tangent on the μ_l and μ_s curves define the solidus and liquidus points at a given temperature. Further cooling causes the tangent's points of contact to move. This means that the range of the two-phase region shifts. When the melting temperature of substance B (which melts at a lower temperature) is finally reached, the chemical potential of the solid phase is smaller than that of the liquid phase for all compositions except for $x_B = 1$. On the other hand, at $x_B = 1$ the chemical potentials are equal so that melt is still present. The solid state is present at any and all compositions below this temperature (e.g., at T_5).

It is possible to construct a phase diagram by applying these considerations consistently for as many temperatures as possible (Fig. 14.7). The result is a spindle-shaped two-phase region. The upper curve shows the composition of melt (*liquidus curve* or freezing curve, at which freezing begins as the mixture is cooled down) and the lower one shows that of the solid phase (*solidus curve* or melting curve, at which melting begins as the mixture is heated). Above the liquidus curve is only melt and beneath the solidus curve is only the solid phase. Between the two

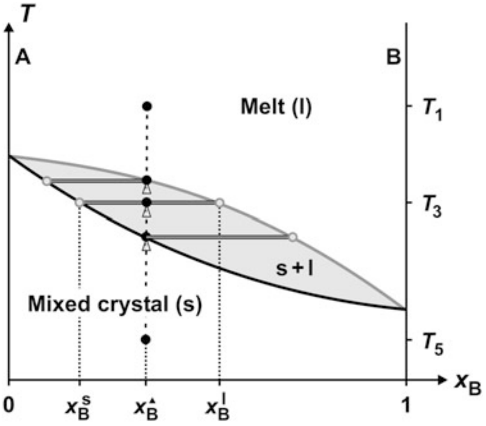


Fig. 14.8 Applying the "lever rule" in a melting point diagram for a system containing two substances that are indifferent in liquid and solid states.

curves a separation into melt and mixed crystals of the compositions given by the intersection points of the tie-line with the liquidus and the solidus curve takes place.

To illustrate this we will take a look at the solidification process of a homogeneous melt with the composition $x_B^\blacktriangle$, starting at a temperature T_1 (Fig. 14.8, vertical dotted line). When the liquidus curve is reached, a rather B-poor mixed crystal begins to separate in miniscule amounts. Its composition results from the intersection point of the tie-line with the solidus curve. However, the melt exhibits a composition that is (almost) the same as the initial one. With a lowering of temperature, the melt becomes gradually richer in the component B (which melts at a lower temperature) because we are moving downward on the liquidus curve. If the melt remains in equilibrium with the mixed crystals, their B content increases again along with progressive crystallization. For example, a melt at temperature T_3 with the composition x_B^l can coexist with a mixed crystal having the composition x_B^s. The ratio of the amounts of the two phases can be found with the help of the now familiar lever rule. As mentioned before, the downward movement on the solidus curve means that the composition of the already crystallized fraction must change continuously during cooling (which is conceptualized as an equilibrium process). In reality, such changes of composition are not that simple since the diffusion of atoms in solids takes a very long time (see Sect. 20.2). If we cool the substance further very slowly, we finally reach the solidus curve. The intersection point of the tie-line with the liquidus curve shows the composition of the last tiny drop of melt. Below the solidus curve, the entire melt has solidified. All that is left is a mixed crystal having the same composition $x_B^\blacktriangle$ as the original melt.

Melting point diagrams with complete miscibility only appear when the form and size of the particles allow them to be inserted into a common lattice. Examples of this are copper/nickel as well as the minerals fayalite (Fe_2SiO_4)/forsterite (Mg_2SiO_4).

More Complicated Melting Point Diagrams More complicated phase diagrams can be developed by considering the $\mu(x)$ curves of the participating components.

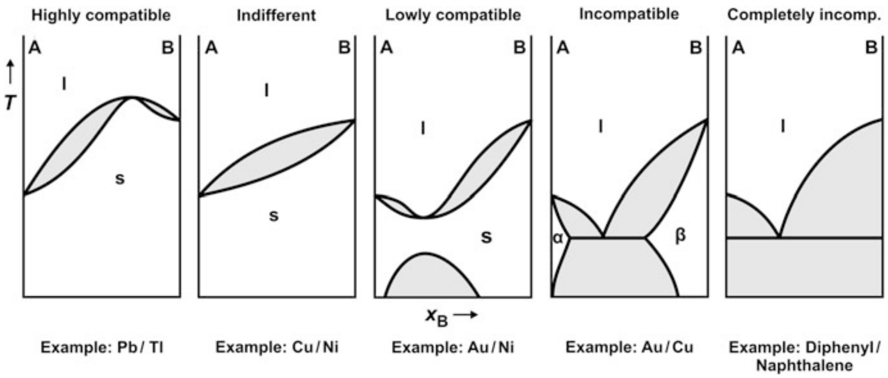


Fig. 14.9 Melting point diagrams for systems containing components having indifferent behavior in the liquid state and varying behaviors in the solid state.

While components A and B in their liquid states are mostly infinitely soluble with each other, they may be indifferent in their solid states, as just discussed, but also highly compatible, lowly compatible, or even incompatible or completely incompatible. We will take a short look at the corresponding melting point diagrams (Fig. 14.9).

α and β mean different mixed crystals. For example, in the case of Au/Cu, this would be a gold-rich and a copper-rich mixed crystal.

Although this may look somewhat complicated at first, a phase diagram can be compared to a map. It is difficult and time-consuming to create a map by topographical survey, but it is easy to use it when that has already been done and when some rules and conventions are known. It is just as difficult to calculate a phase diagram and very time-consuming to measure it. However, once it is known it can be used like a map assuming one observes also in this case some rules and conventions which we have already learned about to some extent. We will illustrate this using the melting point diagram for two components that are incompatible in their solid states (Fig. 14.10).

There are three two-phase regions $(\alpha + \mathrm{l}, \beta + \mathrm{l}, \alpha + \beta)$ along with the single-phase melt (l) and the mixed crystals (α, β).

Eutectic Mixture What happens when we cool a melt having a composition $x_\mathrm{B}^{\blacktriangle}$? When the temperature is lowered and the boundary of the two-phase region solid/liquid is reached, a very B-rich mixed crystal β begins to separate from the melt. Further cooling causes more and more solid substance to crystallize whereby the ratio of melt to mixed crystal is determined by the lever rule. In the process, the melt is constantly depleted of B because almost pure B (mixed only with a bit of A) precipitates. When the system reaches the temperature T_e and thereby the horizontal line, the residual melt with the composition x_B^e solidifies. The $\mu(x)$ curves (Fig. 14.11) are applied again here for the purposes of illustration.

At temperature T_e, the tangent touches the $\mu(x_\mathrm{B})$ curves at three points (once the μ_l curve and twice the μ_s curve). This means that the melt is in equilibrium with the

Fig. 14.10 Melting point diagram for a system of two components that show incompatible behavior in their solid states as well as application of the "lever rule".

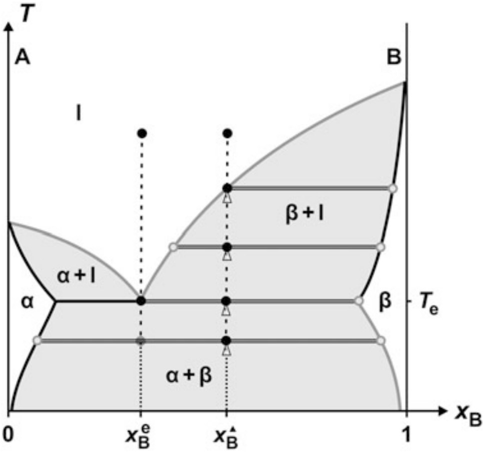
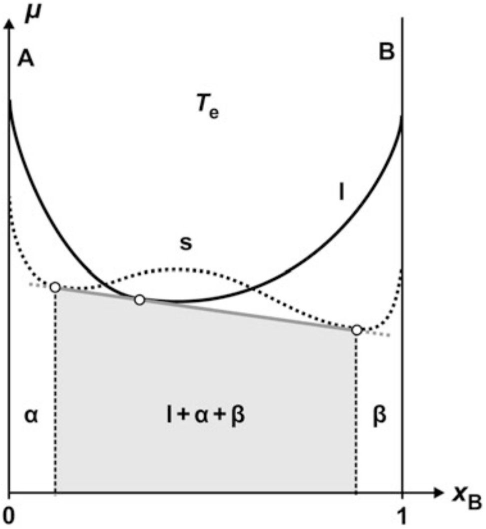
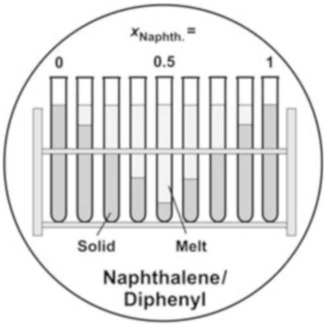


Fig. 14.11 Behavior of (average) chemical potential $\mu(x_B)$ for a system of two substances that are indifferent in their liquid states and incompatible in their solid states, at temperature T_e.



mixed crystal α and the mixed crystal β. At this point, a tangent can be plotted for the last time on the μ_l curve because at lower temperatures, the chemical potential of the melt is always greater than that of the solid state so the curve increasingly retracts upwards. T_e is therefore the lowest temperature at which the melt can exist. This temperature is known as *eutectic* temperature; the term "eutectic" (abbreviated e) comes from the Greek eutektos, meaning "easily melted."

Let us now return to the phase diagram. Beneath the eutectic temperature T_e lies a two-phase system of a very A-rich mixed crystal α and a very B-rich mixed crystal β. Further cooling alters the composition of the mixed crystals. The α mixed crystal



Experiment 14.2 *Melting point diagram of naphthalene and diphenyl*: The test tubes with the nine different mixtures are put in a boiling water bath in order to melt the mixtures. Subsequently, the mixtures are allowed to cool down in front of a black background. Starting with the test tubes on the ends the transparent melts begin to congeal and they become gradually white and more opaque. After a while, only the melts at the center are liquid. In the end, just about everything has solidified.

becomes continuously richer in A and the β mixed crystal becomes continuously richer in B. However, these changes in composition require an extremely long time.

Now what happens if a melt with a eutectic composition of x_B^e is cooled? A liquid with this composition will solidify as a whole at a single definite temperature (like a pure substance). This means that none of the components have separated out before. A heterogeneous mixture has been formed of simultaneously precipitated α and β mixed crystals that also exhibits a total composition of x_B^e (for simplicity, the lever rule is not drawn here). In contrast to all the others, the eutectic mixture does not need to be cooled slowly in order to have conditions for equilibrium and one obtains a uniform and very fine-grained structure (microcrystals).

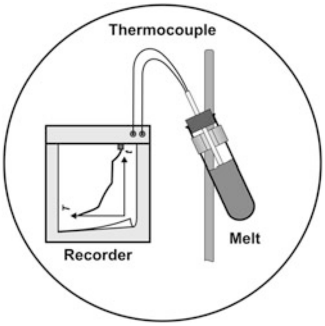
We will look at an experiment showing what happens when we cool down different mixtures of liquid naphthalene ($C_{10}H_8$) and diphenyl (phenylbenzene, $C_{12}H_{10}$) (Experiment 14.2).

In their solid states, naphthalene and diphenyl are completely incompatible. This means that they crystallize when cooled into an (almost) pure state (diagram on the far right in Fig. 14.9). (The infinite gradient of the tangent showing the impossibility of the existence of a pure substance has been mentioned in the last chapter.) Finally, only the melts with nearly eutectic compositions, namely $x_{\text{Naphthalene}} = 0.45$, are liquid.

Thermal Analysis *Thermal analysis* has proven to be especially suited to investigating phase diagrams. Samples of varying compositions have been melted and then cooled down again for this. During cooling, a thermocouple measures the mixture's temperature as a function of time and a *cooling curve* is recorded (Experiment 14.3).

Supplementary micrographs and structural investigations are often used as well.

Experiment 14.3 *Cooling curve of a mixed melt* (*using the example of a lead–tin alloy*): The lead–tin alloy (40 wt% Sn; so-called soft solder) in the test tube is slowly melted over a Bunsen burner. Subsequently, the sample is allowed to cool down. Using a thermocouple, the temporal change of temperature is recorded by a plotter or a computer.



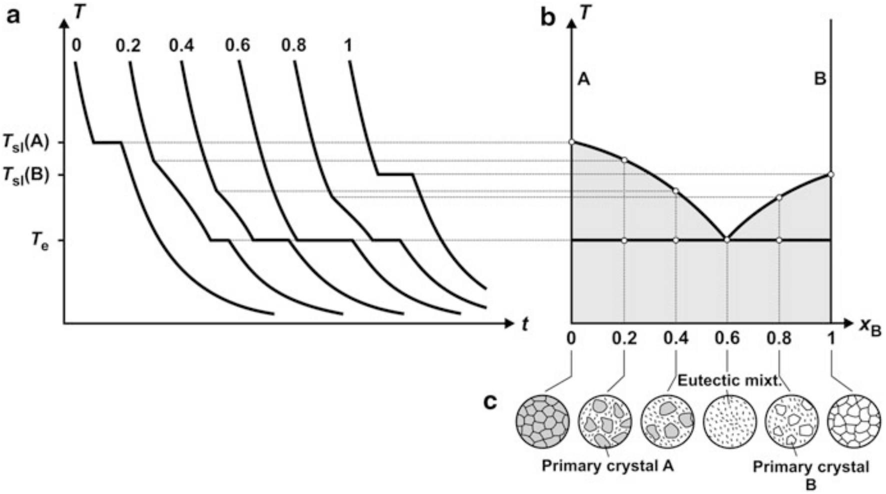


Fig. 14.12 (**a**) Cooling curves for a system of two substances A and B, which are completely incompatible in their solid states, (**b**) Melting point diagram constructed from the cooling curves, (**c**) Corresponding micrographs.

Figure 14.12 shows (idealized) cooling curves for various liquid mixtures of the two components A and B (which are completely incompatible in their solid states) as well as the schematic of the corresponding micrographs. These curves were used to construct the melting point diagram.

The pure substances (curves for $x_B = 0$ and $x_B = 1$) yield *arrest points* at the crystallization temperature T_{sl} because during the process of isothermal solidification, the cooling is "arrested" by the entropy emitted by crystallization. Only when the entire melt has solidified, does the temperature begin to drop again.

Let us now consider the process for a mixture with the mole fraction of $x_B = 0.2$. At first, this liquid system cools evenly until it reaches a temperature at which solid A begins to precipitate. During the continuous crystallization of A, meaning the phase transition liquid → solid, entropy is emitted steadily; therefore, the cooling of the system slows down considerably. Accordingly, an *inflection point* appears on the cooling curve where the phase field with solid A and the remaining melt is entered. When the system finally reaches the eutectic temperature T_e, A and B crystallize simultaneously. The rest of the sample solidifies without its composition changing. This is shown by an arrest point on the cooling curve comparable to what we have seen with pure substances. Initially, substance A crystallizes continuously during the cooling process and new substance grows on crystals already present, producing large primary A crystals. When the eutectic temperature is attained, the entire amount of B (as well as the remaining A) must freeze at once, thereby creating a great number of seed crystals. The micrograph of the solid mixture shows large A crystals imbedded in extremely fine-grained B and A crystals.

If the melt has eutectic composition from the start (in our example, $x_B = 0.6$), it will continuously cool until it reaches the eutectic freezing temperature. When the mixture's temperature falls below this temperature, a simultaneous precipitation of A and B takes place until the entire sample has solidified. Correspondingly, the temperature remains constant over a longer period of time compared to other mixtures. A micrograph shows a heterogeneous mixture of A and B microcrystals of approximately the same size.

If there are enough cooling curves of mixtures with different compositions available, it is possible to construct the corresponding phase diagram.

14.4 Liquid–Gaseous Phase Diagrams (Vapor Pressure and Boiling Temperature Diagrams)

Finally, we will deal with phase diagrams for mixtures of two volatile liquids where we will initially assume an indifferent behavior.

Vapor Pressure Diagrams At a certain temperature, and in equilibrium, a saturation vapor pressure of $p^{\bullet}_{\mathrm{lg,A}}(T)$ develops over an easily evaporating liquid A (compare Sect. 12.5). (The symbol $^{\bullet}$ indicates again that the quantity refers to a pure phase.) In order to avoid an unattractive piling up of indices, we will use $p^{\bullet}_{\mathrm{A}}$ in the following. If an easily evaporating substance B is dissolved in A (Fig. 14.13), the chemical potential of A decreases as a result of dilution.

In Sect. 12.5, we were introduced to a similar situation that leads to lowering of vapor pressure over solutions. However, foreign substance B had low volatility so that the vapor phase was made up of only A (at least approximatively). In the case of two volatile components, reestablishment of equilibrium is caused by lowering of the partial pressure of A to p_{A} in the mixed vapor (above the liquid mixed phase):

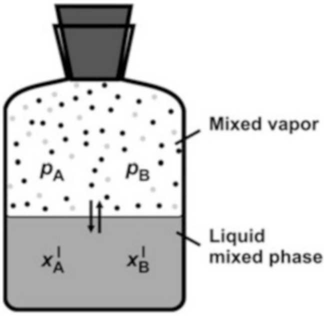


Fig. 14.13 Forming mixed vapor in equilibrium over a mixture of two indifferent liquid components A and B.

$$p_\mathrm{A} = x_\mathrm{A}^\mathrm{l} \cdot p_\mathrm{A}^\bullet. \tag{14.1}$$

The same is also valid for the second volatile component, the substance B:

$$p_\mathrm{B} = x_\mathrm{B}^\mathrm{l} \cdot p_\mathrm{B}^\bullet. \tag{14.2}$$

Here is a somewhat different formulation of Raoult's law: The partial pressure of every component *i* in a mixed vapor equals the product of the vapor pressure of the pure component and its mole fraction x_i^l in the liquid mixed phase. Ideal mixtures are subject to Raoult's law independent of chemical composition. Conversely, this law also represents a further experimental criterion for the indifferent behavior of the two components relative to each other.

If we assume ideal behavior in the gas phase as well, then according to Dalton's law, the total vapor pressure above the mixture is the sum of the partial pressures:

$$p = p_\mathrm{A} + p_\mathrm{B}. \tag{14.3}$$

The partial pressures

$$p_\mathrm{A} = \left(1 - x_\mathrm{B}^\mathrm{l}\right) \cdot p_\mathrm{A}^\bullet = p_\mathrm{A}^\bullet - p_\mathrm{A}^\bullet \cdot x_\mathrm{B}^\mathrm{l} \tag{14.4}$$

and

$$p_\mathrm{B} = p_\mathrm{B}^\bullet \cdot x_\mathrm{B}^\mathrm{l} \tag{14.5}$$

as well as the total pressure

$$p = p_\mathrm{A} + p_\mathrm{B} = p_\mathrm{A}^\bullet - p_\mathrm{A}^\bullet \cdot x_\mathrm{B}^\mathrm{l} + p_\mathrm{B}^\bullet \cdot x_\mathrm{B}^\mathrm{l} = p_\mathrm{A}^\bullet + \left(p_\mathrm{B}^\bullet - p_\mathrm{A}^\bullet\right) \cdot x_\mathrm{B}^\mathrm{l} \tag{14.6}$$

change linearly with the changing composition of the liquid mixture characterized by the mole fraction x_B^l (Fig. 14.14).

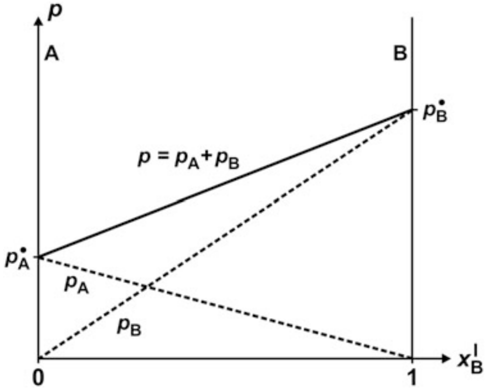


Fig. 14.14 Total pressure (*solid line*) and partial pressures (*dotted lines*) above a mixture of two indifferent components A and B at constant temperature.

The compositions of a liquid mixed phase and its corresponding mixed vapor need not be identical. In fact, we can expect the fraction of the more volatile component in the vapor to be higher. According to Dalton's law, the following is valid for the mole fraction x_B^g of component B in the vapor phase:

$$x_B^g = \frac{p_B}{p}. \tag{14.7}$$

Inserting Eq. (14.2) then yields

$$x_B^g = \frac{p_B^\bullet}{p} x_B^l. \tag{14.8}$$

If B in its pure state has a higher vapor pressure than A, then the following is valid: $p_B^\bullet/p > 1$ (compare Fig. 14.14) and therefore $x_B^g > x_B^l$. In fact, the vapor is enriched with the more volatile component B.

If the vapor pressure (as a function of the vapor composition) is inserted into a $p(x)$ diagram (*vapor pressure diagram* or boiling pressure diagram) along with the linear vapor pressure curve (function of the liquid's composition) (Fig. 14.15), the corresponding curve will always lie below the straight line. This is called the *dew point curve*, while the straight line is called the *boiling point curve*. Below the dew point curve, there is only the gas phase, and above the boiling point curve, there is only the liquid phase. Both curves delineate a two-phase region in which both vapor and liquid mixed phases are in equilibrium.

Tie-lines can again be used to determine the chemical compositions of coexisting phases. This can be done analogously to the approach used in $T(x)$ diagrams discussed earlier, but here the temperature is kept constant while the pressure is varied (Fig. 14.16). The lever rule can also be applied here to determine the ratio of amounts. For example, if we have a liquid mixture with the composition $x_B^\blacktriangle$ at pressure p_1, and slowly lower the pressure while keeping the temperature constant, it will begin to vaporize when it reaches the two-phase region at pressure

Fig. 14.15 Vapor pressure diagram of a system of two largely indifferent components A and B (at constant temperature).

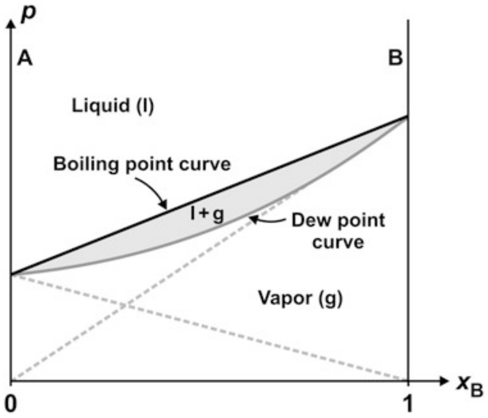
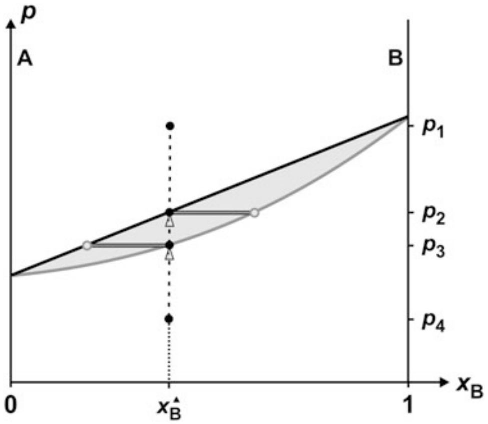


Fig. 14.16 Applying the "lever rule" in a vapor pressure diagram.



p_2. As we have already seen, the more volatile component is enriched in the vapor phase. As the pressure is lowered even more and the vaporizing continues, the liquid phase becomes increasingly depleted of this component. Finally, below pressure p_3, there is only vapor of the same composition as the initial liquid phase.

Boiling Temperature Diagrams Vaporization takes place much more often at constant pressure than at constant temperature. If we continue to assume the substances A and B to be indifferent to each other in the liquid as well as the gaseous phase, the corresponding $T(x)$ diagram (*boiling temperature diagram* or often also *boiling point diagram*) can be constructed analogously to the respective melting point diagram (Fig. 14.17). The *boiling point curve* in this case is nothing more than a plotting of the liquid mixture's boiling temperature (at constant pressure such as standard pressure) versus the mole fraction of one of the components. It delineates the homogeneous liquid phase's region of existence toward higher temperatures. The composition of the vapor phase, which is in equilibrium with the corresponding

Fig. 14.17 Boiling point diagram of a system with indifferent components (at constant pressure).

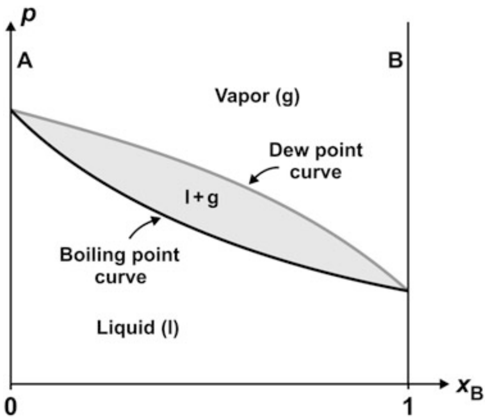
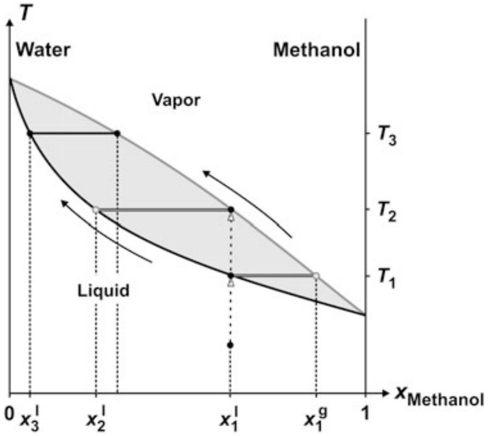


Fig. 14.18 Schematic boiling point diagram of the system water/methanol to show simple distillation.



liquid mixture at the respective boiling point, is indicated by the *dew point curve*. Above the dew point curve lies a homogeneous gas phase and between the two curves is the two-phase region. Usually, when there are two volatile liquids A and B, the one with the lower vapor pressure has the higher boiling temperature. Therefore, in the boiling point diagram the regions representing different states are exchanged compared to the ones in the vapor pressure diagram.

Distillation The differing compositions of the liquid mixed phase and its coexisting mixed vapor in the two-phase phase region can be utilized in separating the substances by means of *distillation*. First, though, we will take a look at the boiling process of a system of the (largely) indifferent components water and methanol (Fig. 14.18). When a mixture of composition x_1^l is heated at constant pressure until it boils, the vapor rising from it at boiling temperature T_1 will have the composition x_1^g. As a consequence, the methanol which has higher volatility (lower boiling temperature) becomes enriched in the vapor phase. Further heating causes a depletion of the methanol in the liquid which leads to a rise in boiling temperature: a slow raising of temperature changes it in the direction of T_2. At the same time, the methanol content in the vapor phase decreases and its composition shifts along the dew point curve in the same direction the liquid phase moves along the boiling point curve. Finally, at temperature T_2, the last drop of the (almost) completely vaporized liquid has the composition x_2^{l}, while the composition of the vapor phase is now the same as that of the initial mixture of the liquid.

Because of the enormous increase of volume during vaporization by a factor of about a thousand, this procedure is not practicable. The so-called *simple distillation* in which the liquid mixture is brought to a boil in a flask, the vapor condensed in a cooler, and the resulting condensate (distillate) collected in a receiver is the most common separation process in this context. Because methanol with its lower boiling temperature escapes preferably, the water with lower volatility is enriched in the flask. Therefore, the boiling temperature rises more and more—even over and above temperature T_2. When the distillation process is stopped near the boiling temperature T_3 of the component which has the higher boiling temperature, a mixture with composition x_3^{l} (water with little methanol) remains in the flask. The distillate in the receiver contains the more volatile component methanol with a reduced fraction of water in contrast to x_1^{l} (but higher compared to x_1^{g}).

The changes of the distillate in composition become more obvious when separate portions (fractions) of it are collected in interchangeable receivers (*fractional distillation*). The first fraction has, in fact, the composition x_1^{g} and is strongly enriched with methanol. The next fractions are increasingly poorer in methanol and therefore richer in water than the first one. The separation effect of fractional distillation can be improved by redistilling the individual fractions. In the process, the composition of the distillate moves along the dew point curve in the direction of pure methanol. After numerous repetitions, both components are just about pure. The disadvantage of this method is the low yield determined by the lever rule, which means that the distillation steps must be taken very often with continuously renewed initial mixture.

The tedious separate steps of vaporization and condensation are therefore combined in practice by the process of countercurrent distillation (rectification). In a *distillation column*, the ascending hotter vapor is flowing past the cooler *reflux*, i.e., a part of the condensate that is flowing back (Fig. 14.19). The close contact between the reverse flows favors a fast entropy and energy exchange. Temperature and composition are therefore close to the particular equilibrium (which depends upon the height in the column) but never reach it.

Let us take a closer look at this process using the water/methanol system as an example (Fig. 14.20). For describing the process, one imagines that the column is separated into (hypothetical) zones in which the equilibrium between liquid and vapor should have been established (*plate* or tray). When the initial liquid mixture with a mole fraction x_0 of methanol is heated in the flask, it begins to boil at temperature T_0. A part of the vapor condenses at the first plate, whereas the remaining vapor rises further to the next plate. At the same time, cooler condensate

Fig. 14.19 Sketch of a distillation column for use in laboratories.

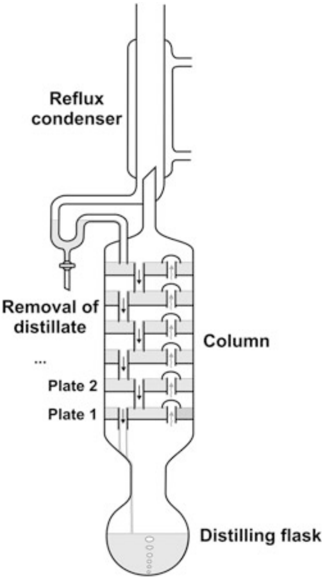
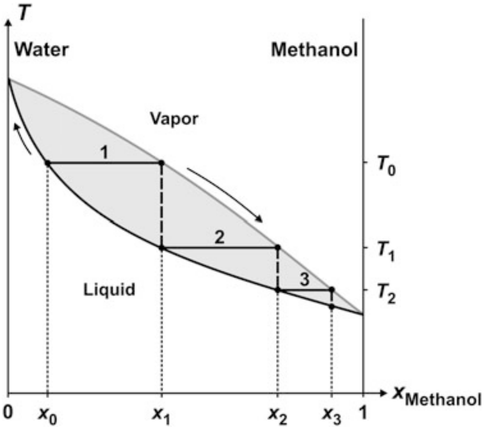


Fig. 14.20 Illustration of the process of rectification using the example of a mixture of water and methanol with an initial composition x_0.



from the plate above flows into this plate and warmer excess condensate leaves it. A liquid with temperature T_1 and composition $x_1 > x_0$ accumulates on the plate. It fills the plate until it flows over. In dynamic equilibrium, inflow and outflow of each component have to compensate each other on each plate.

Each plate can be seen as an isolated distillation unit. The assumption that liquid and vapor are in equilibrium on each plate requires that the corresponding parts of the step curve appear in Fig. 14.20 as tie-lines and therefore horizontal lines. The vertical parts of the curve in between imply that the exchange of substances between the plates takes place at constant composition. In the process, the portion of the more volatile component in the liquid and correspondingly in the vapor, $x_i = x_i^{\mathrm{l}}$ and x_i^{g}, increases from one plate to the next higher one, $x_0 \rightarrow x_1 \rightarrow x_2 \rightarrow \ldots$. At the same time, the temperature in the column falls, $T_0 \rightarrow T_1 \rightarrow T_2 \rightarrow \ldots$, thereby approaching that of pure methanol. A "step" in the boiling point diagram (a combination of a horizontal and a vertical line) is called a *theoretical plate*. The number of theoretical plates (our example shows three) indicates the efficiency of the distillation column, even if it contains a packing material (such as small glass helices) instead of true plates.

When there are enough plates and the separation efficiency of the column is therefore sufficient, the component boiling at lower temperature will be just about pure in the distillate. Instead of separate plates, columns in laboratories are mostly packed with a material which has a large surface, such as rings, helices, or small spheres made of glass, for example. Successive vaporization and condensation steps take place on these surfaces at increasing heights in the column. The number of theoretical plates for separating a homogeneous mixture of a given pair of substances can be determined by inserting the possible "equilibrium steps" between the initial composition and the composition of the distillate in the boiling point diagram. However, in practice one has to assume a slightly higher number of plates.

Distillation is one of the most important processes used in chemical laboratories for separating liquid mixtures. It has been in use since ancient times to extract essential oils such as attar of roses. An important industrial application is distilling of petroleum in oil refineries that produce the heavy and light gasoline used to fuel engines.

Azeotropes What we have discussed so far in this section is only valid for mixtures of components that behave indifferently toward each other in both their liquid and vapor states. However, the liquid state often exhibits differing behavior. If the two components are highly compatible, the stronger interaction of the particles in the liquid mixture relative to the pure state hinders the transition to the vapor phase. The partial pressures of the components are smaller than in the case of indifferent behavior and the vapor pressure curves show a negative deviation from Raoult's law. Compared to the behavior of indifferent substances, the curves appear more or less distorted. As long as the disturbance is small, the behavior can be described in a similar manner as before.

A strong disturbance results in a *vapor pressure minimum* for the total pressure in the vapor phase and therefore in the vapor pressure curve (or boiling point curve) (Fig. 14.21a).

The dew point curve must again lie below the boiling point curve—exactly as it does with indifferent behavior. The two curves touch each other at the vapor pressure minimum. This means that they have a common tangent at this point,

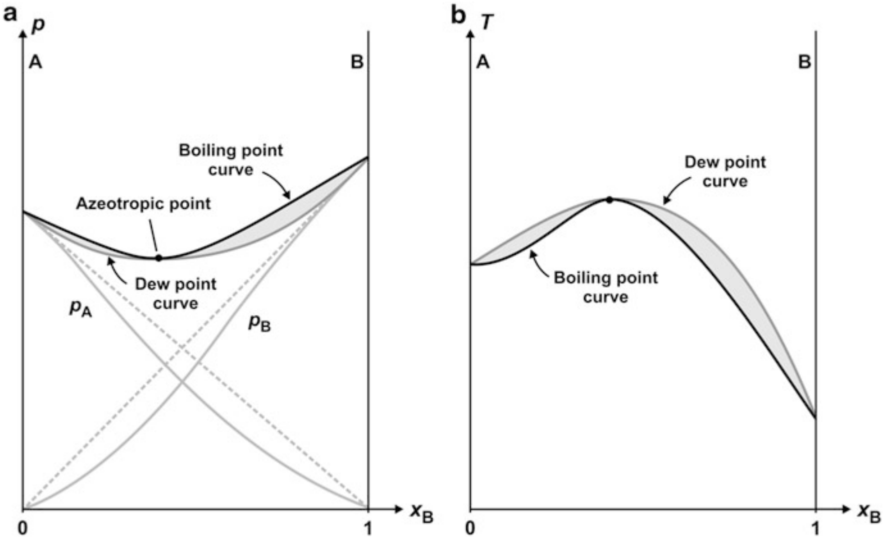


Fig. 14.21 (**a**) Vapor pressure diagram with azeotropic minimum of a binary system of two highly compatible substances, (**b**) Corresponding boiling point diagram with azeotropic maximum.

i.e., the liquid mixture is in equilibrium with a vapor of the same composition (!). This type of homogeneous mixture behaves just like a pure substance. This is called an *azeotropic mixture*, or an *azeotrope*. Its corresponding position in the vapor pressure diagram is called an *azeotropic point*. The word *azeotrope* is derived from the Greek words ζέειν (boil) and τρόπος (state) combined with the prefix α- (no) to give the overall meaning, “no change on boiling.” In the boiling point diagram, not only the phase regions are inverted compared with the vapor pressure diagram, but the vapor pressure minimum also becomes a *boiling point maximum* (Fig. 14.21b). Therefore, these azeotropes are called maximum-boiling azeotropes or minimum-pressure azeotropes, sometimes also negative azeotropes. Systems whose components show highly compatible behavior in their liquid states are chloroform/acetone or hydrogen chloride/water (hydrochloric acid).

Lowly compatible behavior by the components in the liquid state with weaker particle interactions leads to a positive deviation from Raoult’s law. Correspondingly, one can observe a *vapor pressure maximum* (Fig. 14.22a) as well as a *boiling point minimum* (Fig. 14.22b). Acetone/carbon disulfide and ethanol/water are examples of positive azeotropes (minimum-boiling or maximum-pressure azeotropes).

The appearance of azeotropic points has important consequences for the distillation of the mixtures concerned. First let us consider a system with a boiling point maximum (Fig. 14.23). A liquid mixture having the composition x_1^l boils at temperature T_1 and its corresponding vapor is enriched by the more volatile component B (x_1^g). If the vapor is removed continuously from equilibrium by simple distillation, meaning by condensation in a receiver, the composition of the

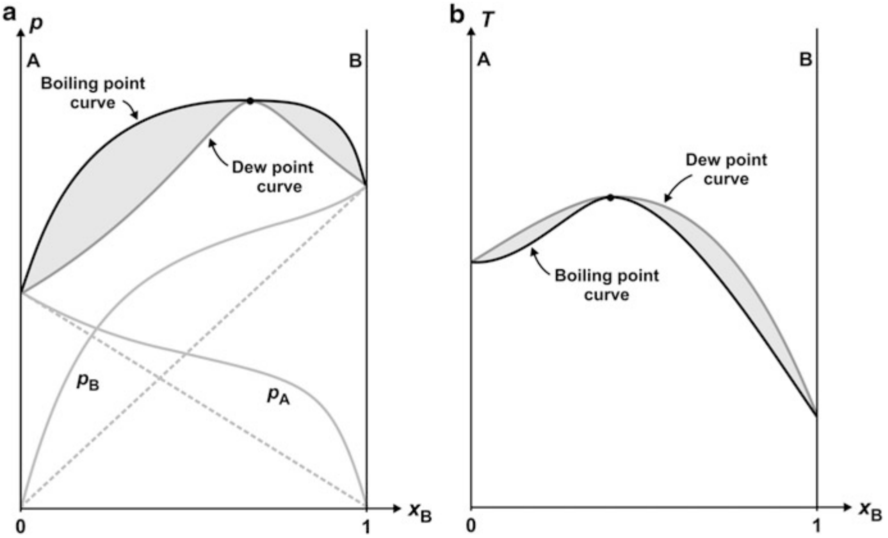
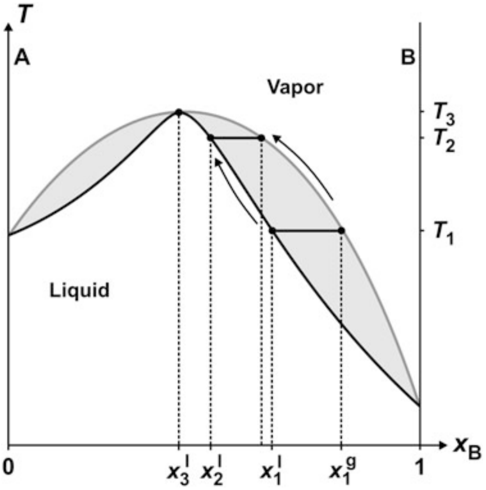
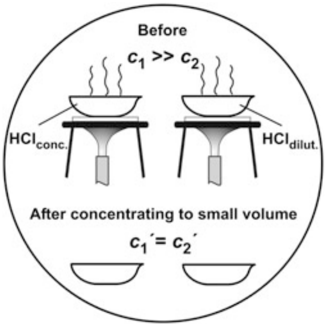


Fig. 14.22 (**a**) Vapor pressure diagram with azeotropic maximum of a binary system of two lowly compatible substances, (**b**) Corresponding boiling point diagram with azeotropic minimum.

Fig. 14.23 Simple distillation using the example of a boiling point diagram with an azeotropic maximum.



remaining liquid shifts along the boiling point curve to higher mole fractions of A (x_2^l). At the same time, the boiling temperature (T_2) rises and the difference in the composition of the liquid and vapor phases becomes noticeably smaller. By continuing this process of distillation, the residual liquid finally reaches the azeotropic composition x_3^l. The boiling liquid and the vapor (or condensate as the case may be)



Experiment 14.4 *Azeotropic behavior of hydrochloric acid*: When diluted hydrochloric acid in a porcelain bowl is heated, it is primarily the water that evaporates until the residue reaches the azeotropic composition. Further separation is not possible any longer at this point, because only hydrochloric acid with 20 % HCl is distilled off. However, when concentrated hydrochloric acid is heated, it is mostly hydrogen chloride that evaporates until, again, the azeotropic point is reached. The residues in both cases exhibit identical concentrations of hydrochloric acid. This can be easily demonstrated by titration with sodium hydroxide solution.

Fig. 14.24 Fractional distillation using the example of a boiling point diagram with azeotropic minimum.

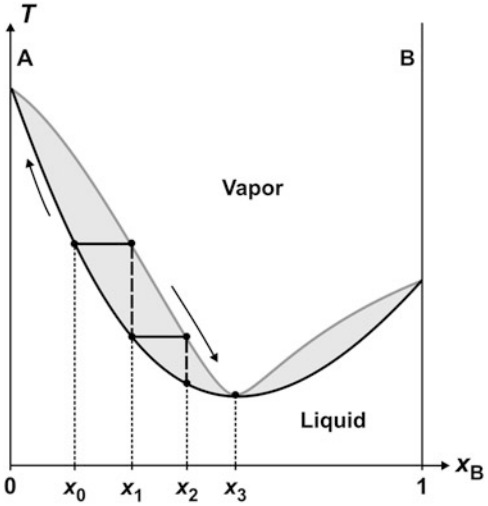


exhibit the same composition and further separation of the mixture is no longer possible.

An example of such a negative azeotrope is hydrochloric acid with a mass fraction $w_{\mathrm{HCl}} = 20\ \% (= 200\ \mathrm{g\ kg^{-1}})$ that boils at 382 K (at standard pressure) without its composition changing (Experiment 14.4).

No matter what the initial composition of a mixture is, a complete separation by distillation is not possible but only one of the substances can be obtained in pure form together with the azeotropic mixture. This is valid as long as the distillation is done at normal pressure, as is commonly the case. Because the azeotropic point changes with pressure, it is possible to finally separate such mixtures as well but only with a considerable effort.

In closing we will discuss the azeotropic behavior of a system with a boiling point minimum (Fig. 14.24). Let us assume we have begun a fractional distillation of a homogeneous mixture with a composition of x_0 and follow the composition of the vapor in the column. The fraction of the component that boils at higher temperatures decreases along the dew point curve in the direction $x_1 \rightarrow x_2$, etc., until the azeotropic point is reached. This point may not be exceeded, meaning that at the top of the column there is always a condensate with the azeotropic composition x_3. A well-known and technically relevant example is the ethanol/water system that has an azeotrope with an alcohol content of $w = 96\ \%$ ($= 960\ \text{g kg}^{-1}$) and a boiling temperature of 78 °C. The residue from this is almost pure water.