# Chapter 7
# Phase Equilibria

In previous chapters, we have dealt with *simple systems* specified in Sect. 2.1 as *macroscopically homogeneous*. In this chapter, we remove this constraint and consider thermodynamics of *heterogeneous*[1] systems in which several *phases*[2] coexist in equilibrium. The homogeneous parts of a heterogeneous system are called phases. Using these terms, we can call simple thermodynamic systems considered earlier as homogeneous phases.

We can further precise the notion of phase; it is the spatially contiguous homogeneous part of a thermodynamic system where intensive variables (in equilibrium) are identical, independently of the spatial location within the phase. This means that intensive variables have usually different values in different phases; thus, they exhibit discontinuity at the phase boundaries. We could treat the phase boundaries as distinct phases whose extension in one direction is as small as the size of a few molecules. However, if the change of the extensive variables (except for the surface of the system) is negligible while changing the size of the phase boundaries, we do not consider them as distinct phases. Accordingly, we only consider *bulk phases* in this chapter; boundary (or surface) phases will be treated in a subsequent chapter. From the thermodynamic point of view, it is of no interest if the same phase is in a single contiguous part or in several fractions. For example, we consider liquid water and ice as two phases even if there are many pieces of ice floating in liquid water.

Within a phase, composition should be identical; thus, immiscible liquids, or solids of different chemical composition also form different phases. Within earthly conditions, it is possible to blend a liquid system consisting of ten vertically separated liquid phases. Gases always mix; thus, there is only one gas phase in a system if it is contained in a contiguous space accessible for the gas molecules

[1]The word *heterogeneous* comes from the Greek words ‘ετερος [heteros] =“other” and γενος [genos] = species. It refers to different origin of the parts of an entire system.

[2]The word *phase* comes from the Greek word φασις [phasis]. Originally, it meant different forms of a planet or star in the course of its change of luminosity (c.f. the phases of the Moon). In thermodynamics, it refers to different forms of the same substance.

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without any constraints. Solids usually form distinct phases unless melted, when they could mix into a homogeneous phase in case of miscibility, which then could become a homogeneous solid when freezing.

The number of chemical components is also relevant in the thermodynamic characterization of heterogeneous systems. It is important to emphasize that *component* in this sense means a *chemically independent* component. If, for example, chemical reactions can occur in a system leading to equilibrium, the condition of equilibrium written as constraint equations obviously diminishes the number of degrees of freedom. We take these constraints into account by diminishing the number of species. This has the consequence that the number of components within the same system might change depending on the actual conditions; changes in conditions can disable or enable some reactions. For example, pure water below 2000°C can be considered as one single component. However, at substantially higher temperatures, water dissociates into hydrogen and oxygen. In this case, we should subtract from 3 ($H_2O$, $H_2$, and $O_2$) the number of reactions ($H_2O \rightleftharpoons H_2 + ½\, O_2$) to get the number of components that becomes 2. Accordingly, if all the three species $H_2O$, $H_2$, and $O_2$ are present in the system, the number of components is 2 above 2000°C; but at room temperature, where neither formation nor dissociation of water occurs in the absence of suitable catalysts, the number of components is 3.

By summing up we can say that we should know the composition of all the phases of a heterogeneous system, and the number of components is considered as the minimum number of chemical species that must be available to form all the species in a chemical equilibrium within the given conditions.

The number of degrees of freedom in a heterogeneous system can readily be calculated from the number of components and phases. In Sect. 2.1, we have concluded from Postulate 1 that a simple system – i.e., one single phase – is completely characterized by its internal energy $U$, its volume $V$, and the amounts of the $K$ components $n_1$, $n_2$,...,$n_K$. We have expressed this in the form that a homogeneous phase has $K + 2$ *degrees of freedom*, meaning the number of independent variables. If we only need an *intensive characterization* of the system, i.e., the size of the system is of no interest, we can make use of the Gibbs–Duhem equation (2.36):

$$S\mathrm{d}T - V\mathrm{d}P + \sum_{i=1}^{K} n_i \mathrm{d}\mu_i = 0,$$

which will reduce the number of degrees of freedom by one, resulting in $K + 1$. (The Gibbs–Duhem equation is a constraint for the intensive variables; therefore, they are not independent.) As the entropy $S$, the volume $V$ and the amounts of components $n_i$ are different in each phase (as well as their molar values $s$, $v$, and $x_i$), in case of an equilibrium of several phases, *a different Gibbs–Duhem equation holds for each phase*. Consequently, each phase reduces the number of degrees of freedom by one. The corresponding formal statement is called the *Gibbs phase rule*:

$$F = K - P + 2. \tag{7.1}$$

As we shall see, this rule has some really useful applications. It is easy to remember; the number of components $K$ always increases, while the number of phases $P$ always decreases the number of degrees of freedom $F$. The number 2 refers to the two possible interactions of the *simple system* allowed with its surroundings: mechanical and thermal. (If there are further interactions allowed with the surroundings – e.g., magnetic, electric interactions, and elastic deformation – each interaction increases this number usually by one.)

## 7.1 Stability of Phases

We have stated in the introductory part of Chap. 5, when characterizing equilibria of a single homogeneous phase (a simple system), that entropy is a concave function of the extensive variables, but energy is a convex function of them. In the case of the entropy function, this concavity means that the $(K + 2)$-dimensional surface representing the function is such that its $(K + 1)$-dimensional tangent planes lie all *above* the surface. Similarly, tangent planes are situated all *below* the convex energy surface. Other energy-like functions characterizing equilibria within different conditions are also convex functions of their variables given in the respective fundamental equations. This property is reflected in the last column of Table 4.1 summarizing the stability conditions of equilibria.

The significance of stability can be analyzed with the help of the second differential. For a closed system (whose composition does not change), the second differential of the energy function can be given as follows:

$$\mathrm{d}^2U = \left(\frac{\partial^2 U}{\partial S^2}\right)_V (\mathrm{d}S)^2 + 2\left(\frac{\partial^2 U}{\partial S \partial V}\right) \mathrm{d}S\mathrm{d}V + \left(\frac{\partial^2 U}{\partial V^2}\right)_S (\mathrm{d}V)^2. \tag{7.2}$$

The condition of convexity requires that the second derivative with respect to $S$ and that with respect to $V$ be positive, and, in addition, $\mathrm{d}^2U$ itself should always be positive. This latter condition is fulfilled if the determinant of the symmetrical matrix containing the second derivatives

$$\begin{pmatrix} \dfrac{\partial^2 U}{\partial S^2} & \dfrac{\partial^2 U}{\partial S \partial V} \\ \dfrac{\partial^2 U}{\partial S \partial V} & \dfrac{\partial^2 U}{\partial V^2} \end{pmatrix}, \tag{7.3}$$

(the *Hessian matrix*) is always positive as well. These conditions imply that

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V > 0\,, \quad \left(\frac{\partial^2 U}{\partial V^2}\right)_S > 0 \quad \text{and} \quad \left(\frac{\partial^2 U}{\partial S^2}\right)_V \left(\frac{\partial^2 U}{\partial V^2}\right)_S - \left(\frac{\partial^2 U}{\partial S \partial V}\right)^2 > 0. \tag{7.4}$$

As the first derivative of the energy function $U(S, V)$ with respect to $S$ is the temperature $T$, we can use the definition of the heat capacity $c_V$ in (4.29) to express the first relation as

$$\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{n}\frac{1}{c_V} > 0. \tag{7.5}$$

Accordingly, the physical consequence of this stability condition implies that $c_V > 0$, as both $T$ and $n$ are positive. To analyze the second inequality, we make use of the fact that the first derivative of the function $U(S, V)$ with respect to $V$ is $-P$. If we differentiate this again with respect to $V$ to get the second derivative, we may relate it to the *adiabatic compressibility* that can be defined similarly to the isothermal compressibility given by (4.31):

$$\kappa_S \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S \tag{7.6}$$

From this we get the inequality condition $1/(V\kappa_S) > 0$, which is equivalent to $\kappa_S > 0$, as the volume $V$ is always positive. It is somewhat more tedious to express the third inequality in terms of measurable functions, but we can get the result using the above substitutions as follows:

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V \left(\frac{\partial^2 U}{\partial V^2}\right)_S - \left(\frac{\partial^2 U}{\partial S \partial V}\right)^2 = \frac{T}{V c_V \kappa_T} > 0. \tag{7.7}$$

By considering the previous condition that $c_V > 0$, this result is equivalent to the condition $\kappa_T > 0$, i.e., the isothermal compressibility should also be positive.

Let us discuss the physical meaning of the two conditions obtained. $c_V > 0$ implies that a stable system should become hotter if heated at constant volume. The conditions $\kappa_S > 0$ and $\kappa_T > 0$ imply that the pressure should increase if we compress the (adiabatic or isothermal) system. These conditions seem to be obvious and are certainly fulfilled, but they are sometimes disobeyed formally, when a particular phase is unstable and typically would form two stable phases. For example, it happens when we apply the van der Waals equation of state in a pressure and temperature region where the compressibility calculated from the equation happens to be negative. (See next section.)

It is easy to show that the above stability conditions cannot be violated. Let us imagine a phase of negative heat capacity in contact with a hotter stable phase (of positive heat capacity). Heat would be transferred from the hotter stable phase into the other, which would become colder and colder due to its negative heat capacity. This would enlarge the difference in temperature between the two phases, which in turn would lead to a higher rate of heat transfer to the phase that becomes colder. A similar unreal consequence follows from a negative compressibility. If such a phase with flexible boundaries is placed in a great container with rigid walls where

the pressure is higher but the compressibility is normal (positive), the negative-compressibility phase would inflate due to the higher external pressure, thus further increasing this pressure, which in turn would lead to further inflation of the negative-compressibility phase.

The energy of a phase as a function of composition cannot be concave either. The "response" of the system is phase separation in this case as well. This case will be treated in a later section after the equilibria of pure phases.

## 7.2 Phase Equilibria of Pure Substances

Let us begin the thermodynamic treatment of phase equilibria with the simplest heterogeneous systems containing only one single substance. As an example, let us examine the behavior governed by the equation of state of a van der Waals fluid while pressure and temperature change. To do this, we will first derive the van der Waals equation of state in terms of the principle of corresponding states described in Sect. 4.5, using the critical values of the state variables. Curves in Fig. 7.1 show

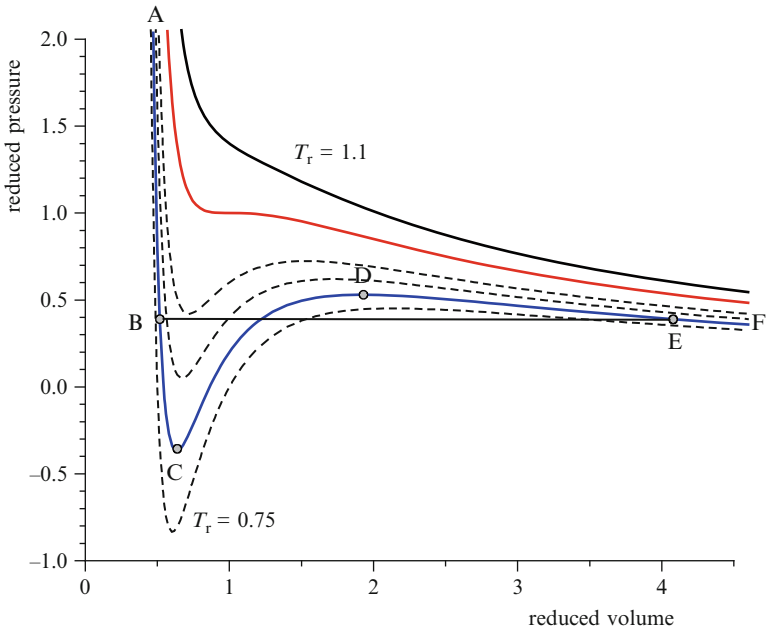



**Fig. 7.1** *P–V* diagram of a van der Waals fluid close to the critical point. Both pressure and temperature are scaled with the critical values, i.e. as reduced pressure $P/P_{cr}$ and reduced volume $V/V_{cr}$. Isotherms at reduced temperatures $T/T_{cr} = 0.75$, 0.8, 0.85, 0.9, 1.0, and 1.1 are plotted, of which the highest and the lowest are labeled in the diagram. The critical isotherm is the second thick solid line from the top

the behavior of the fluid at different temperatures. The top curve is markedly convex, the second from top has a *horizontal inflexion point*, and neither of the others below is convex as they all exhibit a maximum. The critical $P-V$ curve is the one having the horizontal inflexion. This divides the region of convex curves above and that of the nonconvex ones below, which have a minimum and a maximum as well. Using (2.56), it is easy to find the values of the critical variables as both the first and second derivatives of the $P(V, T)$ function are zero at the horizontal inflexion point:

$$\left(\frac{\partial P}{\partial V}\right)_T = +\frac{2an^2}{V^3} - \frac{nRT_c}{(V-bn)^2} = 0, \tag{7.8}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = -\frac{6an^2}{V^4} + \frac{2nRT_c}{(V-bn)^3} = 0. \tag{7.9}$$

Let us solve the two simultaneous equations for the variables $T$ and $V$ to get the critical temperature and volume:

$$T_{cr} = \frac{8}{27R}\frac{a}{b}, \tag{7.10}$$

$$V_{cr} = 3bn. \tag{7.11}$$

By substituting these results into the equation of state (2.56), the critical pressure is readily calculated:

$$P_{cr} = \frac{a}{27b^2}. \tag{7.12}$$

According to Sect. 4.5, we can use the *reduced pressure* $P_r$, the *reduced temperature* $T_r$, and the *reduced volume* $V_r$ expressed as

$$P_r = \frac{P}{P_{cr}}, \qquad T_r = \frac{T}{T_{cr}} \qquad \text{and} \qquad V_r = \frac{V}{V_{cr}},$$

to get the *reduced van der Waals equation of state*

$$P_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}, \tag{7.13}$$

which provides a fairly good approximation for the description of both the gas phase and the liquid phase in case of many substances. It is this latter property of the

van der Waals equation of state that enables us the thermodynamic analysis of the liquid–vapor equilibrium.

Figure 7.1 shows some typical curves in a $P$–$V$ diagram calculated from the reduced van der Waals equation of state in the vicinity of the critical point. (A function referring to constant temperature – or its graph – is sometimes called an *isotherm*.[3] In this case, it is the curve connecting equilibrium $P$–$V$ values at constant temperature. For the sake of brevity, we will use this expression during further discussion.) The top curve shows the isotherm at $T_\mathrm{r} = 1.1$, which completely obeys the condition of convexity; it is monotonically decreasing at all reduced volumes. This property is shared by all isotherms at $T_\mathrm{r} > 1$. The four bottom curves (one solid and three dashed curves) are not convex; they all contain locally concave parts. The transition between these two regions (strictly convex and partly concave) is the curve having a horizontal inflexion point, which is the second from top.

The stability of phases requires the isothermal compressibility $\kappa_T$ to be positive, which is equivalent to a monotonically decreasing $P(V)$ function. If we check this condition in Fig. 7.1 for the isotherm $T_\mathrm{r} = 0.8$, it is only fulfilled along the portion ABC and DEF, but not along CD where the derivative $(\mathrm{d}P/\mathrm{d}V)_T$ is positive. Consequently, the portion CD is mechanically unstable; thus, there are no possible equilibrium states along this portion of the curve. Though the portions BC and DE locally obey the condition $\kappa_T > 0$ as the derivative $(\mathrm{d}P/\mathrm{d}V)_T$ is negative along both of them, they also represent unstable states. We can prove this by calculating the chemical potential of the van der Waals fluid as a function of the volume at different temperatures. The chemical potential of a pure substance is its molar Gibbs potential $g$, as the (extensive) Gibbs potential in this case is simply given by

$$G = ng, \tag{7.14}$$

from which

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P} = \left(\frac{\partial (ng)}{\partial n}\right)_{T,P} = g. \tag{7.15}$$

The chemical potential $\mu$ as a function of pressure at constant temperature is given by (6.30):

$$\mathrm{d}\mu = V\mathrm{d}P.$$

[3]The word *isotherm* comes from the Greek words ισος [isos] = "itself" and θερμη [therme] = "heat", or "hotness". In thermodynamics, it means "at constant temperature". One should be careful about "isotherm" as the word could designate a function between *any* variables at constant temperature. In this particular case, both $P(V)$ and $\mu(V)$ can be called an isotherm.

Accordingly,

$$\mu(T_\mathrm{r}, P_\mathrm{r}) = \mu_0(T_\mathrm{r}, P_{\mathrm{r},0}) + \int_{P_{\mathrm{r},0}}^{P_\mathrm{r}} V \mathrm{d}P$$
$$= \mu_0(T_\mathrm{r}, V_{\mathrm{r},0}) + \int_{V_{\mathrm{r},0}}^{V_\mathrm{r}} V \left( \frac{6}{V^3} - \frac{24T_\mathrm{r}}{(3\,V-1)^2} \right) \mathrm{d}V, \tag{7.16}$$

where the integration variable has been changed from $P$ to $V$ by making use of the equality $\mu(T, P) = \mu(T, V(P))$, differentiating the van der Waals equation of state:

$$\mathrm{d}P = \frac{\mathrm{d}P}{\mathrm{d}V}\mathrm{d}V = \left( \frac{6}{V^3} - \frac{24T_\mathrm{r}}{(3\,V-1)^2} \right) \mathrm{d}V. \tag{7.17}$$

Let us perform the integration in (7.16):

$$\mu - \mu_0(T_\mathrm{r}, V_{\mathrm{r},0}) = \int_{V_{\mathrm{r},0}}^{V_\mathrm{r}} V \left( \frac{6}{V^3} - \frac{24T_\mathrm{r}}{(3\,V-1)^2} \right) \mathrm{d}V$$
$$= -\frac{6}{V_\mathrm{r}} + \frac{8T_\mathrm{r}}{3\,(3\,V_\mathrm{r}-1)} - \frac{8T_\mathrm{r}}{3} \ln(3\,V_\mathrm{r}-1). \tag{7.18}$$

The function $\mu - \mu_0$ at different temperatures is displayed in Fig. 7.2. Let us continue the discussion of stability based on this figure as well. Along the locally unstable portion CD, the system is separated into two (stable) phases. One of them is the liquid having smaller molar volume; the other is the vapor having larger molar volume. In equilibrium, both the condition of mechanical equilibrium (the equality of pressures) and that of the chemical equilibrium (the equality of chemical potentials) should hold, which requires that the end points of the horizontal lines in both Figs. 7.1 and 7.2, B and E, should be at the same reduced volumes, respectively. This condition can be written in the following two equations:

$$P_\mathrm{r}(T_\mathrm{r}, V_\mathrm{B}) = P_\mathrm{r}(T_\mathrm{r}, V_\mathrm{E}), \tag{7.19}$$

$$\mu\,(T_\mathrm{r}, V_\mathrm{B}) = \mu\,(T_\mathrm{r}, V_\mathrm{E}). \tag{7.20}$$

Let us substitute the corresponding variables into (7.13) and (7.18). By solving the simultaneous equations, we get the values of pressure and chemical potential at B and E. This result is displayed in Fig. 7.3, where the reduced volumes at the points B and E are identical with those shown in Figs. 7.1 and 7.2.

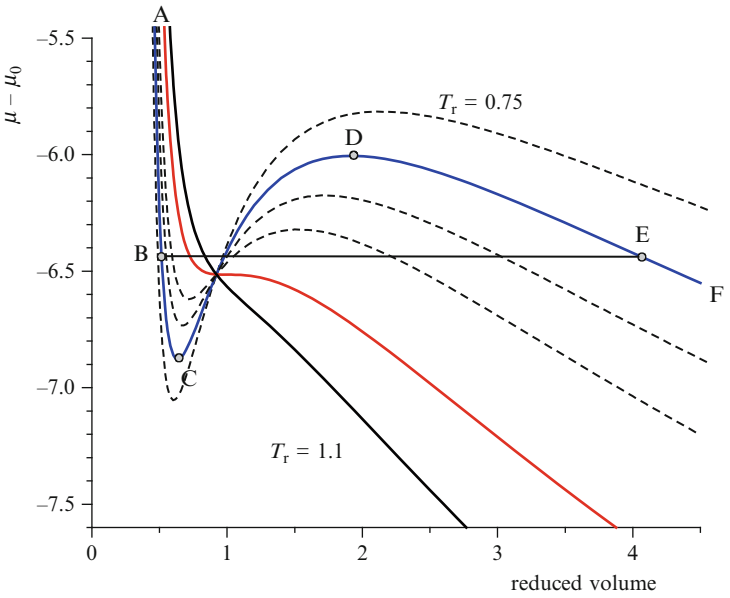



**Fig. 7.2** The chemical potential difference $\mu - \mu_0$ of a van der Waals fluid as a function of the reduced volume in the vicinity of the critical point. Isotherms at reduced temperatures $T/T_{cr} = 0.75$, 0.8, 0.85, 0.9, 1.0 and 1.1 are plotted, of which the highest and the lowest are labeled in the diagram. The critical isotherm at low volumes is the second thick solid line from the top, at high volumes it is the second from the bottom

The reduced volume values at points B and E can also be determined solely from the chemical potential condition, which is the same at the two points; $\mu_B = \mu_E$. According to (7.18), we can write for their difference

$$\mu_E - \mu_B = \int_{V_{r,B}}^{V_{r,E}} V \left( \frac{dP}{dV} \right) dV = 0, \tag{7.21}$$

which means that the integral of the isotherm in Fig. 7.1 between B and E is zero. In geometrical terms, the area between the curve BCDE and the straight line BE is such that the area above and that below the line are equal. This property of the isotherm was first described by Maxwell, so it is usually called the *Maxwell construction*. This construction and the solution of equations (7.19) – (7.20) yields the same results for the reduced volumes at B and E, as they are based on the same relations.

Figure 7.3 is usually called the *liquid–vapor phase diagram* (of a pure substance). Isotherms below the critical point in this diagram are such that the reduced volume of the liquid is never greater than the one which fulfills both the condition of mechanical and that of the chemical equilibrium. If the equation of state of the van

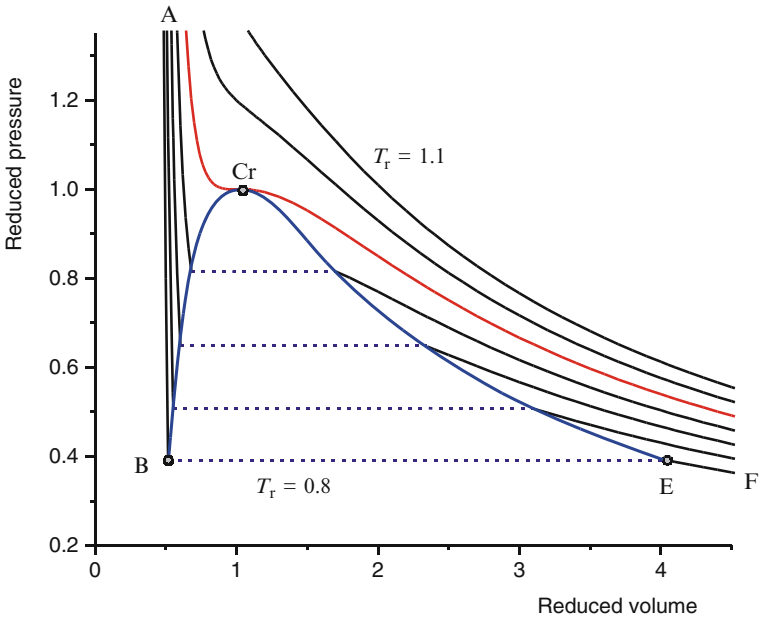



**Fig. 7.3** Equilibrium pressure of the van der Waals fluid as a function of the reduced volume in the vicinity of the critical point. Isotherms at reduced temperatures $T/T_{cr} = 0.75$, 0.8, 0.85, 0.9, 1.0, and 1.1 are plotted, of which the highest and the lowest are labeled in the diagram. The stable phases of a two-phase system are connected by the bell-shaped curve. Along the left portion of this curve, there is only liquid; along the right portion, there is only vapor. Below the curve, there are *no phases*; if two phases are present in equilibrium in the system, their respective states are interconnected by the *horizontal dotted lines*

der Waals fluid would predict a greater volume, the increase in volume will be achieved by the evaporation of part of the fluid, producing vapor whose state will be the one according to the least possible volume which is stable at the actual temperature. For example, in the case of the isotherm at $T_r = 0.8$, the substance is liquid all along the portion AB, but if its volume is further increased at B, part of the liquid will evaporate resulting vapor in a state according to E. As long as there is liquid left in the system, both pressure and chemical potential remain constant while the volume increases due to evaporation. If there is no more liquid left, further increase in volume can happen along the portion EF of the isotherm. There is no phase at any volume between B and E. If the mean volume of a two-phase system lies within this region, one part of it is always liquid (at point B) and the other part is vapor (at point E).

From the above considerations we can conclude that stable phases should not only obey the conditions $c_V > 0$ and $\kappa_T > 0$ – the *local stability conditions* – but also the *global stability conditions*, which means that the phases in equilibrium with each other should also satisfy (7.19) and (7.20). According to this, states along the portions BC and DE in Fig. 7.2 of the isotherm $T_r = 0.8$ are locally stable but not

globally stable. The physical consequence is interesting; if a pure liquid is expanded, and the volume becomes greater than $V_{r,B}$ corresponding to point B, in the absence of vapor and air, the metastable liquid can survive – even until point C where it becomes mechanically unstable and vapor will necessarily be formed. Within these circumstances, the evaporation cannot happen at the surface of the liquid, but bubbles should form for the vapor to appear. To form bubbles, energy should be concentrated at the site of the bubble to be formed, which needs large *fluctuations* in local energy. Until the occurrence of a large enough fluctuation, there will be no bubble formed, and the metastable (superheated) liquid phase survives. In a similar way, the vapor phase whose state lies along the isotherm between D and E is metastable; its molar volume is lower than that of the stable vapor at E. However, until droplets would be formed, the vapor cannot condense to liquid. Formation of the droplet also needs a relatively large fluctuation in energy; thus, the metastable (supercooled or supersaturated) vapor can also survive.

The instability of both the liquid and the vapor can be efficiently eliminated by the presence of electrically charged particles, which largely facilitate the formation of droplets as well as bubbles. (The early detection of ionizing particles was also based on this phenomenon in a bubble chamber or cloud chamber.) A similar effect is the condensation of vapor on tiny soot particles which leads to the formation of *contrails* (short for condensation trail), easily seen behind jet planes, especially in the morning or evening hours when the water vapor in the air is supercooled due to low air temperatures.

### 7.2.1 Phase Diagrams of Pure Substances

A phase diagram in general is a graph showing the existence region of phases in a heterogeneous system in equilibrium, as a function of the state variables. The actual form of this graph varies according to the function plotted and its variables. In case of pure substances, the most general phase diagram is the tridimensional plot of the function $P(V, T)$. In this diagram, we can find the already discussed liquid and vapor phases along with their transition region, but also different solid phases and the solid–liquid, solid–vapor, and eventual solid–solid transitions. As tridimensional surfaces are complicated to show, a more common type of the phase diagram is their two-dimensional projection, which is easier to show on a piece of paper (or on a screen). In a narrower sense, these two-dimensional representations are called phase diagrams.

One possible type of a $P(V, T)$ state surface or $P$–$V$–$T$ diagram is shown in Fig. 7.4. We can recognize on this surface the phase-free transition region of the liquid–vapor equilibrium with the liquid phase on the left and the vapor phase on the right edge. The critical point is labeled as Cr. At higher pressures and temperatures than the critical point, there is no phase separation and that is the reason for designating the phase in this region as *gas*. The name *vapor* is used only for states lying below the critical pressure and temperature, i.e., they can coexist

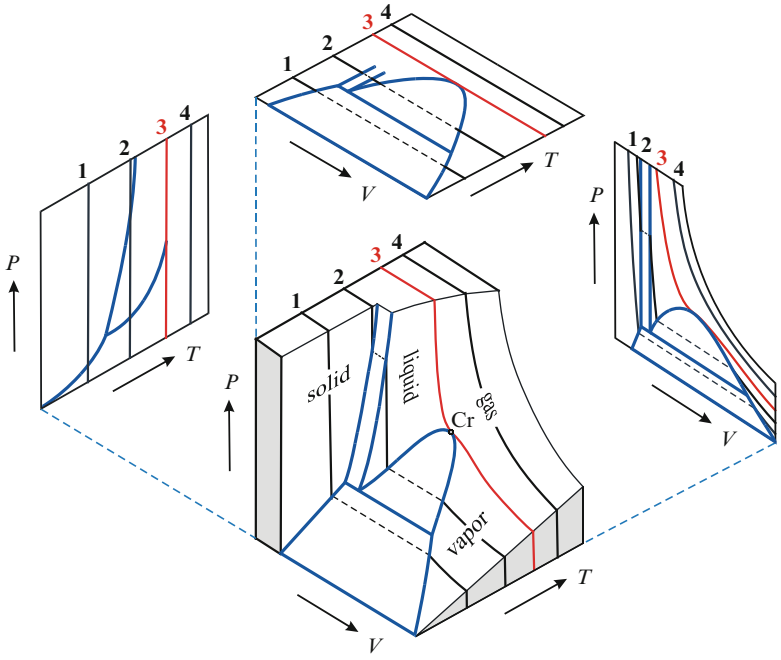



**Fig. 7.4** *P–V–T* diagram of a pure substance and its projections (phase diagrams) in case of a substance whose solid phase has a smaller molar volume than its liquid phase. Isotherms (curves at constant temperature) are marked by the numbers 1, 2, 3, and 4, on both the 3D surface and the 2D projections. There exist no phases between the solid lines (on the 3D surface as well as in the 2D projections) if the states of coexistent phases are interconnected by *dashed lines* (of constant temperature and pressure)

in equilibrium with a liquid at the same pressure and temperature. It is also readily seen from the figure that the solid phase is only stable at the lowest volumes, in equilibrium with the vapor at low temperatures and the liquid at higher temperatures.

There is a limiting line between the liquid–vapor and the solid–vapor transition area. The temperature and pressure of this line between the two no-phase areas are constant; thus, the three phases can only coexist at this particular temperature and pressure. The locus of the coexistence on the $P(V, T)$ surface and in the $T(V)$ and $P(V)$ projections is called the *triple line*, while its projection in the $P(T)$ plane is the *triple point*. It is easy to show that three phases of a single component can only coexist at fixed temperature and pressure. Applying the Gibbs phase rule (7.1), the number of degrees of freedom if there is one component and three phases is $F = K - P + 2 = 0$. This means that there is no possibility to determine any one of the intensive variables arbitrarily if all the three phases are present in the system; this can only happen at fixed temperature and pressure determined by the thermodynamic properties (the fundamental equation) of the substance. This temperature and pressure of the triple point can be calculated by solving the two simultaneous

equations for the equality of the chemical potentials of the three phases in equilibrium.

It is also straightforward to show that the projection of the $P(V, T)$ surface into the $P(T)$ plane consists only of simple (one-dimensional) curves, not of two-dimensional areas – contrarily to the case of the two other projections. In the $P(T)$ plane, each curve is a locus of points corresponding to the coexistence of two phases in equilibrium. According to the phase rule, these one-component two-phase systems have $1 - 2 + 2 = 1$ degree of freedom, which means that if we fix a given temperature $T$, all other (intensive) thermodynamic properties are fixed, the pressure $P$ among them. In other words, in the graph showing the coexistence of two phases, there is always one possible pressure at a given temperature. These three coexistence curves – as explained in the previous paragraph – should meet at a single point; the triple point having zero degrees of freedom.

An interesting consequence of the simple curves in the $P$–$T$ phase diagram is that the coexistence curve of the liquid and vapor phase *ends* at the critical point, as there is no phase separation beyond this point in the $P$–$V$–$T$ diagram; thus, there are not two phases present but one. The number of degrees of freedom is also 2 in this area; thus, both temperature and pressure are free to determine here, and the equilibrium state of the single phase follows these conditions. According to this, it is possible to change the state of the liquid into vapor without phase transition (i.e., without having both phases present in the system). To do so, changes of state should be performed bypassing the no-phase area while arriving into the single-phase region above the critical point and then changing the state again to bypass the no-phase area while reducing temperature and pressure to arrive into the range of vapor. The projected trajectory in the $P(T)$ plane goes around the critical point.

Both on the $P(V, T)$ surface and the projections, we can observe that the stability region of the liquid phase has not only an upper limit, but also a lower one; below the pressure of the triple line, there is no liquid phase but an equilibrium of solid and vapor. Accordingly, below the temperature of the triple point in the $P(T)$ plane, there is no liquid phase either. This can also be concluded from the behavior of the chemical potential as a function of pressure and temperature. At a given pressure and temperature, it is always the phase having the lowest chemical potential which is stable. (As it is stated in Sect. 3.3, the substance from the higher chemical potential region would flow to the lower chemical potential region.) According to (7.15), the chemical potential of a pure substance is its molar Gibbs potential, whose total differential can be written, following (4.22) as

$$\mathrm{d}\mu^{\alpha} = -s^{\alpha}\mathrm{d}T + v^{\alpha}\mathrm{d}P, \tag{7.22}$$

where $s^{\alpha}$ is the molar entropy and $v^{\alpha}$ is the molar volume of the phase $\alpha$. These two quantities can be given as the partial derivatives of the function $\mu(T, P)$:

$$-s^{\alpha} = \left(\frac{\partial \mu^{\alpha}}{\partial T}\right)_{P} \quad \text{and} \quad v^{\alpha} = \left(\frac{\partial \mu^{\alpha}}{\partial P}\right)_{T}. \tag{7.23}$$

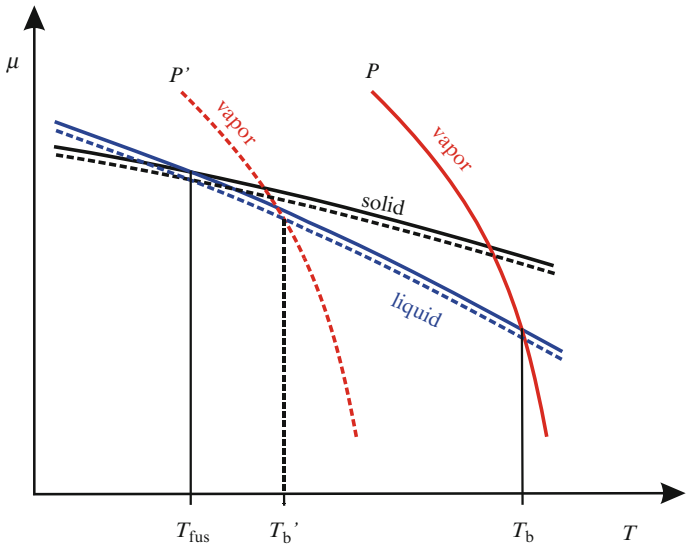



**Fig. 7.5** Chemical potential of different phases of a pure substance as a function of temperature. Solid curves show the chemical potentials at a given pressure $P$ and *dashed curves* at a lower pressure $P'$. When changing the pressure from $P$ to $P'$, the boiling point change from $T_b$ to $T_b'$ is much greater than the melting point change from $T_{fus}$ to $T'_{fus}$. This latter is so small that it cannot bee seen in the diagram

Accordingly, the slope of the chemical potential curve in a $\mu$–$T$ diagram is the molar entropy of the actual phase. As we can see in Fig. 7.5, the relation between the slopes of the chemical potential curves of different phases reflects the relation between the respective molar entropies:

$$s_v >> s_l > s_s, \tag{7.24}$$

i.e., the entropy of the vapor (far from the critical point) is much greater than that of the liquid, which is somewhat greater than that of the solid.

Figure 7.5 shows sections of the function $\mu(T, P)$ at constant pressure. The change of these functions $\mu(T)$ with pressure depends on the molar volume of the phases. As the molar volume of the vapor (far from the critical point) is much greater than that of the liquid or solid, the $\mu(T)$ curve of the vapor is shifted a lot compared to the $\mu(T)$ curve of the liquid or solid, if the pressure is reduced – as it can be seen in the figure. Further reduction of the pressure leads to regions where the chemical potential of the liquid is always higher than that of the vapor or the solid. At these pressures the solid would not melt but evaporate directly, which is called *sublimation*. In between the two regions, there exists a pressure at a certain temperature where the chemical potentials of the solid, the liquid, and the vapor coincide. This is the triple point where all the three phases can coexist.

An interesting and relatively rare group of substances has a somewhat different phase diagram than the one in Fig. 7.4. They exhibit the feature that their solid

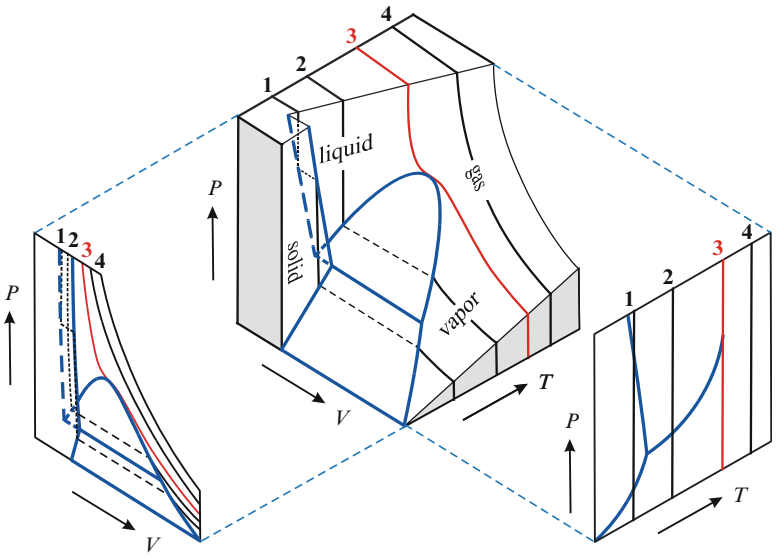



**Fig. 7.6** *P–V–T* diagram of a pure substance and its projections (phase diagrams) in case of a substance whose solid phase has a larger molar volume than its liquid phase. The notation is the same as in Fig. 7.4

phase in equilibrium with the liquid phase has a *larger* molar volume than the liquid phase; thus, they *dilate* at freezing, instead of contracting. A common example for this behavior is water, which breaks bottles and pipelines when freezing. In Fig. 7.6, in addition to the greater molar volume of the solid compared to the liquid, we can see another difference with respect to Fig. 7.4. As it can be seen from the projection $P(T)$, the melting point (equilibrium temperature between the solid and liquid phase) is reduced with increasing pressure. This property can be interpreted the following way. If the molar volume decreases while melting, higher pressure facilitates melting; thus, less energy is needed to melt the solid. (This behavior is also related to the stability of phases. Its general statement is called the *Le Châtelier–Braun principle*. A more detailed explanation of this principle is described in Chapter 8, in relation with chemical reactions.) The reason for sliding on the surface of ice is also this; by exercising pressure on ice, the melting point decreases and part of the ice will melt. Water formed this way lubricates the surface, largely decreasing friction.

### 7.2.2 *Calculation of the Quantity of Coexisting phases: the Lever Rule*

Phase diagrams can also be used to calculate the proportions between two phases in equilibrium. For this purpose, the independent variable of the plotted function

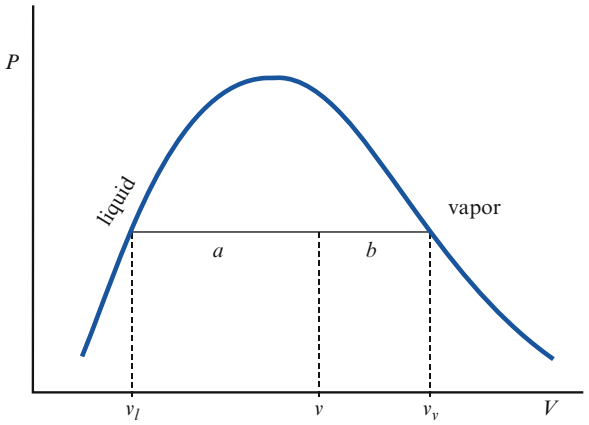



**Fig. 7.7** Notation used to calculate vapor quality in a *P*–*V* diagram

should be an extensive variable (or its molar value), as for example in a *P*–*V*, *T*–*V*, *T*–*S*, or *T*–*H* diagram. Let us consider the *P*–*V* diagram of Fig. 7.3, replotted in Fig. 7.7 for this purpose. The average molar volume of the system containing vapor and liquid is denoted by $v$. The molar volume of the vapor is $v_v$ and that of the liquid is $v_l$ in equilibrium at the pressure corresponding to the horizontal line. Along this line, the distance between the molar volume of the liquid and the average molar volume is $a$, between the average molar volume and that of the vapor is $b$.

The volume $V$ of the liquid–vapor system can be given in terms of the amounts of the liquid $n_l$ and that of the vapor $n_v$:

$$V = n_l v_l + n_v v_v = (n_l + n_v)\, v. \tag{7.25}$$

Let us substitute $v - a$ for $v_l$ and $v + b$ for $v_v$:

$$n_l(v - a) + n_v(v + b) = (n_l + n_v)\, v. \tag{7.26}$$

Let us perform the multiplications:

$$n_l v - n_l a + n_v v + n_v b = n_l v + n_v v. \tag{7.27}$$

By eliminating terms present at both sides of the equation, we get

$$n_v b = n_l a. \tag{7.28}$$

This relation is traditionally called the *lever rule*.[4] Using this rule, we can calculate the relative vapor content of the system:

[4]The name of the rule comes from the equation of balance of a first class lever where the condition of equilibrium is that the left weight multiplied by its distance from the fulcrum equals the right weight multiplied by its distance from the fulcrum.

$$\frac{n_v}{n_v + n_l} = \frac{n_v}{n_v + n_v(b/a)} = \frac{a}{a+b}. \tag{7.29}$$

To get this result, $n_l$ is expressed from the lever rule and then both numerator and denominator are multiplied by $a/n_v$. The relative vapor content of a liquid–vapor system is called *vapor quality* which is related in steam engines and turbines to the ability of vapor to do useful work.

The ratio of the amounts of two phases can be calculated similarly in other phase diagrams having an extensive variable (or its molar value) at the horizontal, and an intensive one at the vertical axis, for example, in a *T–V*, *T–S,* or *T–H* diagram.

### 7.2.3 Calculation of Equilibrium Temperature and Pressure; the Clausisus–Clapeyron Equation

If we are not interested in the amount of the coexisting phases, the projection of the $P(V, T)$ state surface into the *P–T* plane provides enough information for an intensive characterization of phase equilibria. Curves indicating the locus of points where two phases coexist in this diagram are easy to calculate from thermodynamic relations. To do these calculations, consider the phase diagram in Fig. 7.8.

The curves indicating the coexistence of the same pair of phases are continuous, without breakpoints. At a given temperature, there is only one point where the two phases can coexist. These curves can be constructed from the temperature and pressure dependence of the chemical potential. Two phases (say, $\alpha$ and $\beta$) are in equilibrium if their chemical potentials are equal:

$$\mu^{\alpha} = \mu^{\beta}. \tag{7.30}$$

This condition should be fulfilled at any point of the coexistence curves. Whenever the pressure changes, the temperature should also change in a way that

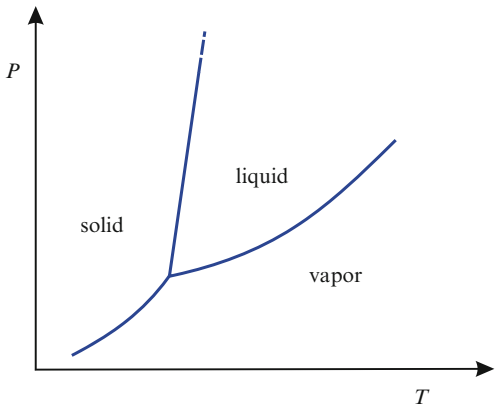



**Fig. 7.8** *P–T* phase diagram of a pure substance whose molar volume increases at melting

the chemical potentials of the two phases changed by $\mathrm{d}\mu^{\alpha}$ and $\mathrm{d}\mu^{\beta}$ should be equal again:

$$\mu^{\alpha} + \mathrm{d}\mu^{\alpha} = \mu^{\beta} + \mathrm{d}\mu^{\beta}. \tag{7.31}$$

The validity of the two above conditions require that

$$\mathrm{d}\mu^{\alpha} = \mathrm{d}\mu^{\beta}. \tag{7.32}$$

The total differentials of the chemical potentials as a function of the temperature and pressure can be given (cf. (7.22)) as follows:

$$-s^{\alpha}\mathrm{d}T + v^{\alpha}\mathrm{d}P = -s^{\beta}\mathrm{d}T + v^{\beta}\mathrm{d}P. \tag{7.33}$$

By rearranging this equation, we get

$$(v^{\beta} - v^{\alpha})\,\mathrm{d}P = (s^{\beta} - s^{\alpha})\,\mathrm{d}T. \tag{7.34}$$

The difference $\Delta_{\alpha}^{\beta}v = v^{\beta} - v^{\alpha}$ is the change in molar volume and $\Delta_{\alpha}^{\beta}s = s^{\beta} - s^{\alpha}$ is the change in molar entropy upon phase transition $\alpha \rightarrow \beta$. By substituting these symbols, the condition for coexistence becomes

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{\alpha}^{\beta}s}{\Delta_{\alpha}^{\beta}v}. \tag{7.35}$$

Solution of the above differential equation yields the function describing the coexistence curve. However, we can rewrite the equation making use that the chemical potential of the pure substance – the molar Gibbs potential – can be written as $\mu = h - Ts$. Let us rewrite the equality of the chemical potentials of the two phases as

$$h^{\alpha} - Ts^{\alpha} = h^{\beta} - Ts^{\beta}. \tag{7.36}$$

By rearranging, we can express the molar transition entropy $\Delta_{\alpha}^{\beta}s = s^{\beta} - s^{\alpha}$ with the molar transition enthalpy:

$$s^{\beta} - s^{\alpha} = \frac{h^{\beta} - h^{\alpha}}{T}. \tag{7.37}$$

Using the notation $\Delta_{\alpha}^{\beta}h = h^{\beta} - h^{\alpha}$, the differential equation for the coexistence curve is the following:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{\alpha}^{\beta}h}{T\,\Delta_{\alpha}^{\beta}v}. \tag{7.38}$$

This is called the *Clapeyron equation*.[5] (It is worth noting that if we would have written the equilibrium condition in terms of the entropy-representation intensive variable $\mu/T$ instead of $\mu$, we would directly obtain the Clapeyron equation.) This equation describes the coexistence of any two phases. Accordingly,

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{\mathrm{fus}} h}{T \Delta_{\mathrm{fus}} v} \tag{7.39}$$

is the equation of the *melting point curve* characterizing solid–liquid equilibrium.

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{\mathrm{b}} h}{T \Delta_{\mathrm{b}} v} \tag{7.40}$$

is the equation of the *boiling point curve* characterizing liquid–vapor equilibrium, and

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{\mathrm{sub}} h}{T \Delta_{\mathrm{sub}} v} \tag{7.41}$$

is the equation of the *sublimation point curve* characterizing solid–vapor equilibrium.

If one of the two phases is vapor, the change in molar volume upon phase transition is easy to calculate with a fairly good approximation. Far from the critical point, the molar volume of the condensed phases is negligible compared to that of the vapor; thus, the sublimation volume $\Delta_{\mathrm{sub}} v$ as well as the boiling (vaporization) volume $\Delta_{\mathrm{b}} v$ can be substituted by the volume of the vapor. (The volume of 1 mol solid or liquid water at room temperature is approximately 0.018 $\mathrm{dm}^3$, while that of the vapor is about 24 $\mathrm{dm}^3$. Neglecting 0.018 $\mathrm{dm}^3$ leads only to an error not greater than 0.08%.) Let us also suppose that the vapor behaves as an ideal gas and substitute $v = RT/P$ for its molar volume. By rewriting the Clapeyron equation by applying these approximations, we get

$$\frac{1}{P}\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{\mathrm{b}} h}{RT^2}, \tag{7.42}$$

which can be rewritten substituting $\mathrm{d} \ln P$ for $(1/P)\, \mathrm{d}P$ as

$$\frac{\mathrm{d} \ln P}{\mathrm{d}T} = \frac{\Delta_{\mathrm{b}} h}{RT^2}. \tag{7.43}$$

[5]Benoît Paul Émile Clapeyron (1799–1864) was a French engineer and physicist. He was responsible for the construction of the first French railway lines, but he also dealt with thermodynamics. He discovered Sadi Carnot's pioneering work two years after Carnot's death and reformulated it in simpler mathematical terms. He elaborated the theory of reversible processes and further developed the results of Clausius concerning entropy. This latter work led to the equation named after him and the one named after Clausius and him.

The above equation is called the *Clausisus–Clapeyron equation*.[6] A similar equation can also be derived for sublimation as well, writing the sublimation enthalpy $\Delta_{\text{sub}} h$ in place of $\Delta_{\text{b}} h$.

By integrating this equation, we can calculate the equilibrium vapor pressure at any temperature $T_2$ if we know it at another temperature $T_1$. The integration is easy to perform supposing that the sublimation or vaporization enthalpy does not change with temperature in the range from $T_1$ to $T_2$:

$$\int_{P_1}^{P_2} \mathrm{d} \ln P = \frac{\Delta_{\text{vap}} h}{R} \int_{T_1}^{T_2} \frac{1}{T^2} \mathrm{d}T \tag{7.44}$$

The result of the integration can be given in a form ready for vapor pressure calculations:

$$P_2 = P_1 \, e^{-\frac{\Delta_{\text{vap}} h}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}. \tag{7.45}$$

The equilibrium between two condensed phases is somewhat more complicated. Let us consider the Clapeyron equation for the solid–liquid equilibrium:

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_{\text{fus}} h}{T \Delta_{\text{fus}} v}.$$

Fusion is an endothermic process; thus, the numerator on the right-hand side is always positive. The sign of the denominator is also positive for the majority of substances; for those which dilate upon melting. As the molar volume change is usually little with respect to the enthalpy change during phase transition, the slope of the solid–liquid coexistence curve ($\mathrm{d}P/\mathrm{d}T$) is a large positive value. For substances such as water – which shrink upon melting – the slope is negative, but it has also a large absolute value. (To raise the melting point of water ice by 1°C, an increase of 140 kbar in pressure is needed.) As a consequence, the solid–liquid coexistence curve in a $P$–$T$ phase diagram is always very steep and its orientation is determined by the sign of the fusion volume $\Delta_{\text{fus}} v$. Similar conclusions can be drawn for the case of a solid–solid equilibrium.

### 7.2.4 First-Order and Second-Order Phase Transitions

As explained in Sect. 7.2.3, differences in the partial derivatives of the $\mu(T, P)$ function determine the shape of the coexistence curve in the phase diagram. These derivatives can be related to other thermodynamic quantities:

[6] Rudolf Julius Emmanuel Clausius (1822–1888) was a German physicist. He had a determining role in the development of thermodynamics. He introduced the notion of entropy and formulated the Second Law of thermodynamics in terms of it.

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -s, \tag{7.46}$$

$$\left(\frac{\partial \mu}{\partial P}\right)_T = v, \tag{7.47}$$

$$\left(\frac{\partial^2 \mu}{\partial T^2}\right)_P = -\left(\frac{\partial s}{\partial T}\right)_P = -\frac{c_P}{T}, \tag{7.48}$$

$$\left(\frac{\partial^2 \mu}{\partial P^2}\right)_T = \left(\frac{\partial v}{\partial P}\right)_T = -v\kappa_T. \tag{7.49}$$

In the case of phase transitions discussed so far, plots of chemical potential *vs.* temperature for different phases have different slopes at their intersection – as it can be seen in Fig. 7.5. This means that their derivatives are different in different phases. Molar entropy, for example, is always smaller in the phase stable at lower equilibrium temperature than that in the other phase, which is stable at higher equilibrium temperature. Molar volume is mostly also smaller in the phase stable at lower temperatures – though there are exceptions, as we have discussed before. As a consequence, the functions $s(T, P)$ and $v(T, P)$ should have a discontinuity at the equilibrium pressure and temperature.

The behavior of the second derivatives is even more interesting; they are *infinite* at the coexistence of two phases. Consider, for example the transition ice → water. If a two-phase equilibrium system is heated, its *temperature would not change*, as the absorbed heat is used to melt some ice. As a consequence, the derivative $(\mathrm{d}Q/\mathrm{d}T)_P$ becomes infinite due to the zero increment in the denominator. The other way around; if we cool the ice–water system, its temperature would not change either, only part of the water will freeze. (This happens also in spring; while snow is melting during the day, air does not warm up. Similarly, it does not cool during the night until the melted water would freeze; thus, air temperature tends to be close to 0°C.) For this reason, enthalpy changes upon phase transitions are also called *latent heat.*[7]

In a similar manner, isothermal compressibility also becomes infinite at coexistence. In case of a liquid–vapor equilibrium, the pressure would not change upon compression of the system until vapor exists that can condense, thus keeping the equilibrium pressure constant. In this case, the derivative $(\mathrm{d}v/\mathrm{d}P)_T$ becomes infinite.

The behavior of the chemical potential function and its derivatives as a function of temperature is graphically shown in the upper diagrams of Fig. 7.9. The dashed vertical line with an upward arrow symbolizes infinite heat capacity. It is worth

[7]Until the late nineteenth century, the *substance of heat* was considered as a "subtle fluid" called *caloric*. Caloric was "filled" in a body upon heating, and "withdrawn" upon cooling. (This is still conserved in expressions like "heat capacity"). The theory interpreted that heat can be extracted at constant temperature from a system under phase transition as a "hidden" form of heat, which was termed *latent* after the Latin word of the same meaning *latens*.

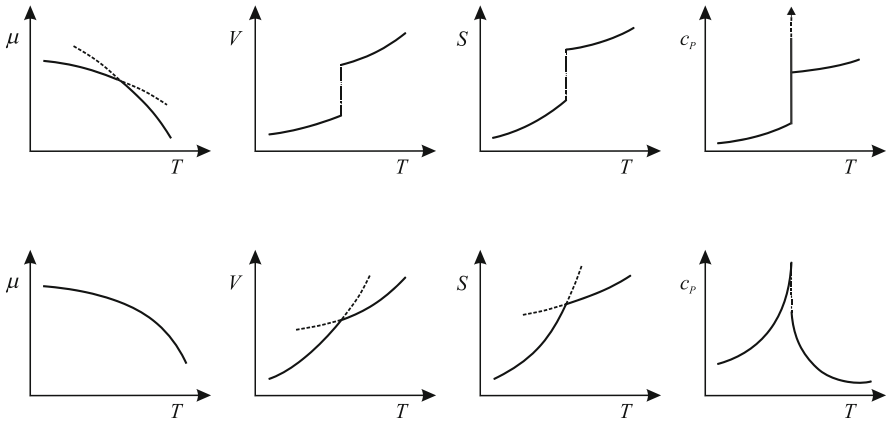



**Fig. 7.9** Plots of the chemical potential $\mu$, the volume $V$, the entropy $S$, and the heat capacity $c_P$ as a function of temperature in the vicinity of a phase transition. Upper diagrams: first-order phase transition; lower diagrams: second-order phase transition

noting that molar entropy is always increased upon transition to the phase which is stable above the transition temperature, while molar volume and heat capacity could increase but also decrease, depending on the nature of the substance.

Phase transitions discussed above all exhibit a latent heat of transition and are called *first-order* phase transitions. There exists another class discovered in the mid-twentieth century, which is called *second-order* or *continuous* phase transitions. They also exhibit well-defined transition temperature and pressure, but their chemical potential as a function of temperature is continuous and differentiable (does not have a breakpoint) at the transition temperature. However, the first derivatives of the chemical potential function – molar volume and molar entropy – do have a breakpoint similar to that of the chemical potential in case of first-order transitions. Consequently, the second derivatives – compressibility and heat capacity – exhibit discontinuity at the transition temperature. This is the origin of the name "second order".

By observing Fig. 7.9, in case of a first-order transition (upper diagrams), prior to the transition we cannot see any sign in the heat capacity that a transition is about to occur. The same is true for the compressibility as a function of pressure (not shown). The behavior of the first derivatives – molar volume and molar entropy – does not "forecast" the transition either. In contrast, the behavior of $c_P$ in case of a second-order phase transition "forecasts" the transition; the function turns into a huge increase. After the transition, it falls back steeply (but still continuously) to a "normal" slow change with increasing temperature. Researchers who discovered this kind of transition have seen the shape of the Greek letter $\lambda$ (lambda) in the plot of the $c_P$ function. That is the reason they are also called *lambda transition*.

Macroscopic (classical) thermodynamics is unable to provide satisfactory explanations for second-order phase transitions. Though a relation similar to the Clapeyron equation can be formulated for the *second* derivatives of the chemical potential functions, the phase rule cannot be applied for the equilibrium of these transitions, and the behavior of the second derivatives (the $\lambda$ shape) cannot be explained. Second-order phase transitions can only be interpreted at a molecular level, taking into account *fluctuations* around the local equilibrium state. Typical second-order phase transitions are the transition of solid $\beta$-brass or that of the solid salts of complex ions such as $NH_4^+$, $NO_3^-$, $SO_4^{2-}$, and $PO_4^{3-}$. Upon these transitions, it is not the crystal structure that would change but either the internal symmetry of the crystals or the mode of molecular movement of the complex ions.

The cubic $\beta$-brass crystal contains an equal number of Cu and Zn atoms. The two kinds of atoms are arranged as two interpenetrated cubic lattices where each Cu atom has eight Zn neighbors, and vice versa. At low temperatures, this minimum energy structure is stable, despite of its low entropy. With increasing temperature, large enough small-scale fluctuations enable some Cu and Zn neighbors to swap locations. But swapping locations needs higher energy than simple vibration of the atoms; thus, the heat capacity also increases with increasing temperature. As more and more atoms change location, further changes become easier from an energetic point of view, because the minimum energy structure is continuously destroyed. This "positive feedback" further increases the tendency of structure changes, also increasing the energy consumption and thus the heat capacity as well. The transition temperature (742 K) is in the state when the atoms' locations in the entire crystal become completely random. Heat capacity is restored to a "normal" low level at this temperature, as further heating only increases the vibrational energy of the atoms at the lattice points.

In case of some complex ions, the crystal structure at low temperatures does not enable rotation around all the rotational axes. As temperature rises, fluctuations lead to the onset of these "forbidden" rotations. At the $\lambda$-transition, all rotations can freely happen. Other types of $\lambda$-transitions are magnetic transitions of some metal crystals and conductor–semiconductor transitions. The liquid–vapor transition is also a second-order transition at the critical temperature.

## 7.3 Liquid–Vapor Equilibrium of Ideal Binary Mixtures

The condition of liquid–vapor equilibrium in a multicomponent system if all the components of the liquid evaporate in a detectable amount is the equality of chemical potentials in the two phases for each of the components:

$$\mu_{i,l} = \mu_{i,g}. \tag{7.50}$$

According to (6.36), the chemical potential can be given using the standard potential $\mu_i^*$ and the mole fraction $x_i$. This latter can be replaced by the quotient of

the partial pressure $p_i$ and the total pressure $p^{\ominus}$; thus, we can write the equilibrium condition as

$$\mu^*_{i,l} + RT \ln x_i = \mu^*_{i,g} + RT \ln \frac{p_i}{p^{\ominus}}. \tag{7.51}$$

For the pure component ($x_i = 1$) at the same temperature and pressure, we can write

$$\mu^*_{i,l} = \mu^*_{i,g} + RT \ln \frac{p^*_i}{p^{\ominus}}. \tag{7.52}$$

Subtracting the two equations results in:

$$RT \ln x_i = RT \ln \frac{p_i}{p^*_i}. \tag{7.53}$$

Obviously, the arguments of the two logarithms should be equal, which leads to the following equation valid for ideal mixtures:

$$p_i = x_i p^*_i. \tag{7.54}$$

This equation is the formal statement of *Raoult's Law*.[8] Using this equation, we can calculate the vapor pressure of ideal mixtures.

Let us calculate the vapor pressure $P_{\text{tot}}$ of ideal binary (i.e., containing two components) liquid mixtures. This can be given as the sum of the partial pressures of the two components:

$$P_{\text{tot}} = x_1 p^*_1 + x_2 p^*_2. \tag{7.55}$$

As $x_1$ and $x_2$ are not independent, we can substitute $(1 - x_1)$ in place of $x_2$:

$$P_{\text{tot}} = x_1 p^*_1 + (1 - x_1) p^*_2 = p^*_2 + x_1 (p^*_1 - p^*_2) \tag{7.56}$$

According to this result, the total vapor pressure of the binary liquid is a *linear* function of the concentration $x_1$, as it can be seen in Fig. 7.10.

The equilibrium vapor pressure can also be given as a function of the vapor composition. Mole fractions of the components $y_1$ and $y_2$ can be given with the help of the respective partial pressures:

$$y_1 = \frac{p_1}{P_{\text{tot}}} \qquad y_2 = \frac{p_2}{P_{\text{tot}}}. \tag{7.57}$$

[8] François-Marie Raoult (1830–1901) was a French chemist. He was the first to conduct experiments on the freezing point and vapor pressure depression of dilute solutions, which is the reason for naming the law of vapor pressure depression as Raoult's Law.

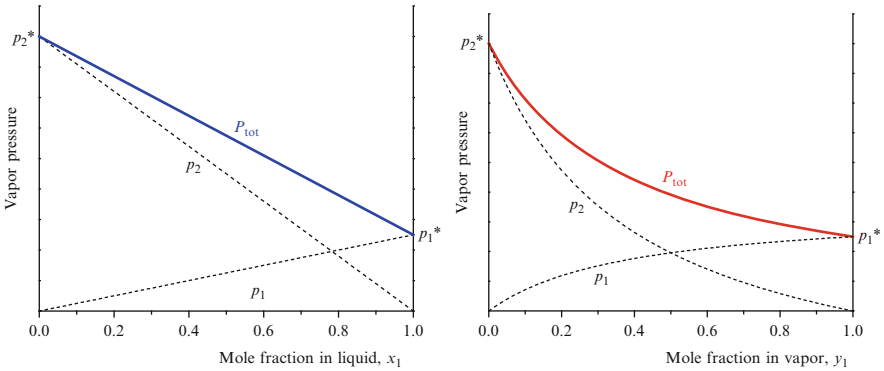



**Fig. 7.10** Vapor pressure of an ideal binary mixture as a function of the liquid and the vapor composition, respectively, at the same temperature

Based on Raoult's Law, the mole fraction $x_1$ in the liquid phase can be written as

$$x_1 = \frac{y_1 P_{\text{tot}}}{p_1^*}, \tag{7.58}$$

and this can be substituted into the expression (7.56) for the total pressure:

$$P_{\text{tot}} = p_2^* + \frac{y_1 P_{\text{tot}}}{p_1^*} p_1^* - y_1 P_{\text{tot}} \frac{p_2^*}{p_1^*}. \tag{7.59}$$

By rearranging, we can factor out $P_{\text{tot}}$:

$$P_{\text{tot}} \left( 1 - y_1 + y_1 \frac{p_2^*}{p_1^*} \right) = p_2^*. \tag{7.60}$$

Further rearrangement leads to an expression for the total pressure as a function of the mole fraction $y_1$:

$$P_{\text{tot}} = \frac{p_1^* p_2^*}{p_1^* + y_1 (p_2^* - p_1^*)}. \tag{7.61}$$

This expression has the form

$$P_{\text{tot}} = \frac{\text{constant}_1}{\text{constant}_2 + \text{constant}_3 \, y_1}, \tag{7.62}$$

which is a transformed hyperbola – as can be seen in Fig. 7.10.

In Fig. 7.11, the same curves are shown, with the regions of stability of the phases labeled. It is easy to interpret the two diagrams from a thermodynamic point

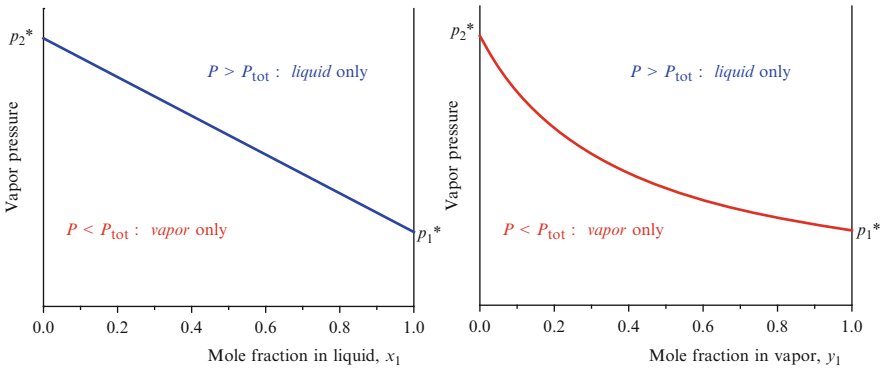



**Fig. 7.11** Stability regions of the liquid and vapor phases of an ideal binary mixture as a function of the liquid and the vapor composition, respectively, at the same temperature

of view. According to the phase rule, if there are two phases present in a two-component system, the number of degrees of freedom is $F = K + 2 - P = 2$. Thus, if temperature (which is the same in both diagrams) and composition are fixed, the system has a unique pressure – the *equilibrium vapor pressure* or *saturated vapor pressure*. This vapor pressure is determined by the equations (7.56) and (7.61), according to Raoult's Law. If the pressure is lower, the liquid is unstable; it completely evaporates. If the pressure is higher, the vapor is unstable; it completely condensates. Thus, the vapor pressure curve exactly shows the boundary between the regions of stability of the liquid and the vapor phases.

It is sensible to combine the two curves of Fig. 7.11 in a single diagram. The resulting diagram in Fig. 7.12 is called the *liquid–vapor phase diagram*. Of course, there is only one concentration scale on the horizontal axis; this denotes liquid composition in case of the upper straight line, but vapor composition in case of the lower hyperbolic curve. The upper line is still the *vapor pressure curve* (of the liquid mixture), but above this line – as discussed before – only the liquid phase is stable; therefore, it is also called the *liquid curve*. The lower curve shows the pressure (of the vapor mixture) where the vapor condenses (droplets of liquid are formed); therefore, it is called the *dew point curve*. However, as below this curve only the vapor phase is stable, it is also called the *vapor curve*.

The combination of the two diagrams and their concentration scales requires a slightly different interpretation concerning the stability range of the phases as was the case for the two distinct diagrams. If the liquid having a composition labeled $x_l$ evaporates, the vapor formed should have the composition labeled $x_v$, as this is in equilibrium with the liquid. (The two phases in equilibrium should have the same pressure.) According to this, there is no phase in between the two points L and V, along the horizontal solid line interconnecting these points. This is the case at any other pressure as well; thus, the area between the two curves is a *no-phase region*. If we would not take into account that the system contains two phases, but monitor

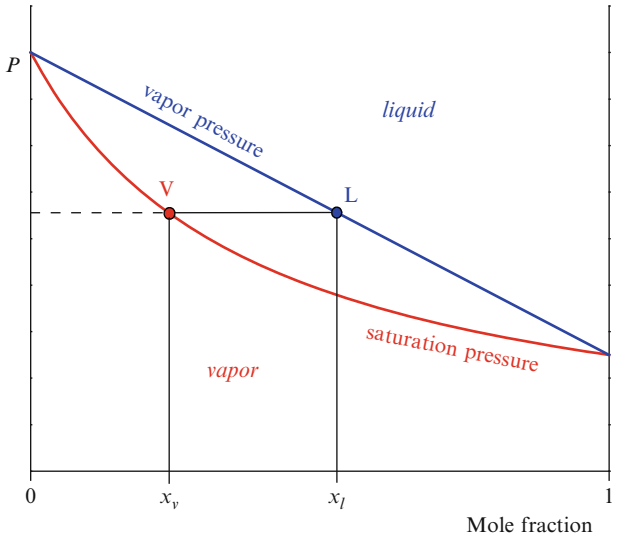



**Fig. 7.12** The pressure–composition liquid–vapor phase diagram of an ideal binary mixture

only the *overall composition* of the two-phase system, this should fall between $x_l$ and $x_v$. This is why the no-phase region is often called as *two-phase region*. However, this may be misleading, as *there is no stable phase between the two curves*; in the two-phase system, the vapor composition is on the vapor curve and the liquid composition is on the liquid curve.

The two points L and V indicating the composition of the phases in equilibrium at a given pressure are called *nodes* hence, the line interconnecting them (the *tie line* – solid line in the figure) is also called *conode*. In this phase diagram, the conode coincides with an *isobar*, i.e., a horizontal line indicating constant pressure.

Another useful liquid–vapor phase diagram is the one where the equilibrium temperature is shown as a function of the composition, at constant pressure. This also consists of two curves: the *boiling point curve* as a function of the liquid composition, and the *dew point curve* as a function of the vapor composition, and it is called the *temperature–composition phase diagram* or *T–x* phase diagram. The one corresponding to Fig. 7.12 is shown in Fig. 7.13. A major difference is that here the upper region (at higher temperatures) is the stability range of the vapor phase, while the liquid phase is stable below the dew point curve (at lower temperatures). Accordingly, the upper curve is the vapor curve and the lower one the liquid curve.

At the temperature indicated by the horizontal line, the liquid of composition $x_l$ could only form vapor whose composition is $x_v$, as this is in equilibrium with the liquid. (The two phases in equilibrium should have the same temperature.) Consequently, along the tie line interconnecting L and V, there cannot be any stable phase; thus, the area between the two curves is a no-phase region in this diagram as well. Note that the tie line coincides with an *isotherm*, i.e., a horizontal line indicating constant temperature.

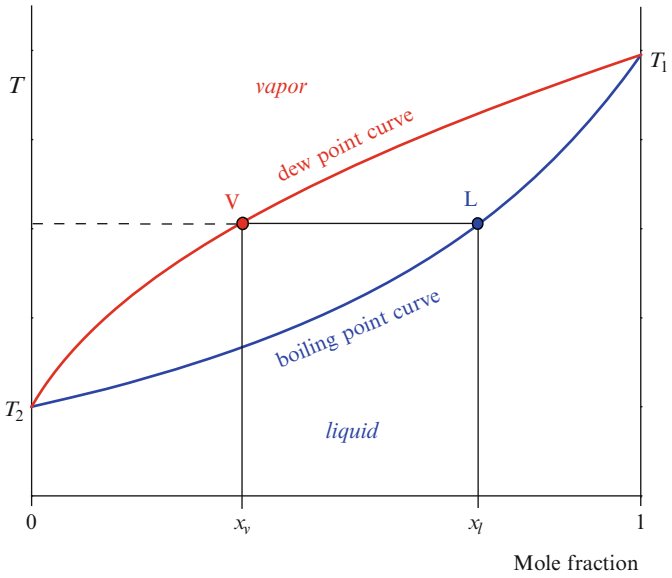



**Fig. 7.13** Temperature–composition (or $T$–$x$) liquid–vapor phase diagram of an ideal binary mixture

This phase diagram can be constructed the following way. It is a section of a tridimensional surface $x$–$T$–$P$ where the total pressure $P_{\text{tot}}$ is constant and can be given using (7.56) as the sum of the partial pressures of the two components. To calculate this, we need the equilibrium vapor pressures of the components, $p_1^*$ and $p_2^*$, between the boiling points of the two components, $T_2$ and $T_1$, which can be calculated using the integral form (7.45) of the Clausius–Clapeyron equation:

$$p_i^*(T) = p_i^*(T_2)\, e^{-\frac{\Delta_{\text{vap}} h_i}{R}\left(\frac{1}{T}-\frac{1}{T_2}\right)}. \tag{7.63}$$

Vapor pressures obtained this way can be substituted into (7.56), and the solution of the resulting equation yields the composition $x_1$ at a given temperature $T$ corresponding to the total pressure $P_{\text{tot}}$:

$$x_1 = \frac{P_{\text{tot}} - p_2^*(T)}{p_1^*(T) - p_2^*(T)}. \tag{7.64}$$

Once the liquid composition $x_1$ is known, the vapor composition $y_1$ is readily calculated using (7.57):

$$y_1 = \frac{x_1 p_1^*}{P_{\text{tot}}}. \tag{7.65}$$

In the $T$–$x$ phase diagram, the liquid curve (i.e., the boiling point curve) is no more a straight line but a convex curve, which is a consequence of the exponential nature of the Clausius–Clapeyron equation.

As discussed in Sect. 7.2.2, the ratio of the amounts of the two phases can be calculated based on phase diagrams having an extensive variable (or its molar value) at the horizontal, and an intensive one at the vertical axis. The $T$–$x$ diagram in Fig. 7.13 has mole fraction at the horizontal axis which is the molar value of the extensive amount of substance; i.e., the lever rule can be applied. The notation is shown in Fig. 7.14; along the horizontal line indicating equilibrium temperature, the overall composition is $x$ and that of the two phases $x_l$ and $x_v$, respectively. The distance between $x_v$ and $x$ is denoted by $a$ and that between $x_l$ and $x$ by $b$. The amount $n$ of the liquid–vapor system can be given in terms of the amounts of the liquid $n_l$ and that of the vapor $n_v$:

$$n = n_l x_l + n_v x_v = (n_l + n_v)\, x. \tag{7.66}$$

Let us substitute $x + b$ for $x_l$ and $x - a$ for $x_v$:

$$n_l(x + b) + n_v(x - a) = (n_l + n_v)\, x. \tag{7.67}$$

By performing the multiplications and combining terms we get the "lever rule"

$$n_v a = n_l b, \tag{7.68}$$

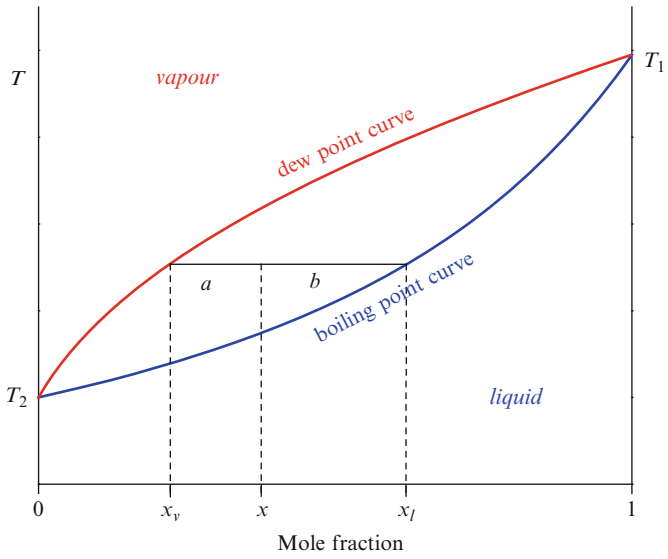



**Fig. 7.14** Notations for the calculation of the amount of liquid and vapor in a binary liquid–vapor phase diagram using the "lever rule". The overall mole fraction of component 1 is $x$ in the heterogeneous system containing both phases; it is $x_l$ in the liquid and $x_v$ in the vapor phase

which readily yields the ratio of vapor to liquid as

$$\frac{n_v}{n_l} = \frac{b}{a}. \tag{7.69}$$

## 7.4 Liquid–Vapor Equilibrium of Real Binary Mixtures

We cannot expect existing liquid mixtures to follow the ideal behavior described in the previous section. Though there exist some liquid mixtures with components whose molecules are closely related to each other, for example the benzene–toluene mixture, which follow the ideal behavior to a good approximation, the majority of real mixtures exhibit a large variety of deviation from this behavior. As molecular interactions depend on composition, the partial pressure of the components does not follow Raoult's law, and deviations also depend on composition. From the thermodynamics of mixtures, we already know that we can characterize these deviations by writing the nonideal chemical potential $\mu_{i,l}^* + RT \ln \gamma_i x_i$ into (7.51)–(7.54) leading to Raoult's law in a real mixture. This way, we get the nonideal equivalent of Raoult's law:

$$p_i = \gamma_i x_i p_i^*. \tag{7.70}$$

Let us consider the example of the ethanol–water mixture shown in Fig. 7.15. As it can be seen in the diagram, both components have higher partial pressures

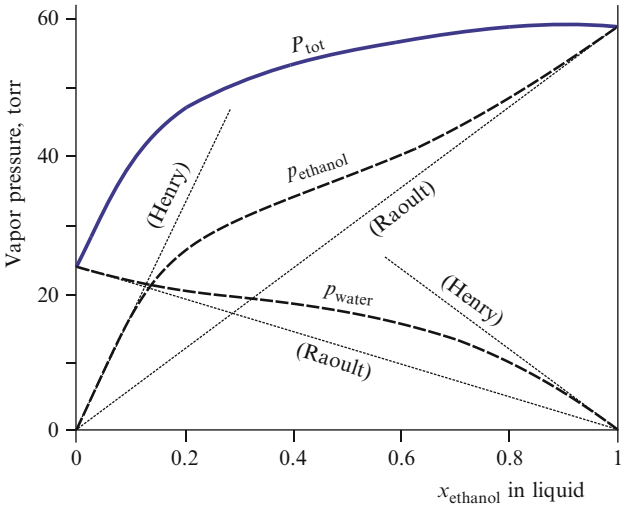



**Fig. 7.15** Vapor pressure vs. composition diagram of the binary mixture ethanol–water. *Thin dotted lines* show partial pressures according to Raoult's law and, at low concentrations of the components, partial pressures according to Henry's law

than could be calculated from Raoult's law. This is usually called a *positive deviation* from ideality, or from Raoult's law. (Similarly, a *negative deviation* means lower vapor pressures than predicted by Raoult's law. This is the case in acetone–chloroform or nitric acid–water mixtures.) Despite of deviations, at high concentrations (close to unit mole fraction) the partial pressures of concentrated ethanol or water are quite close to the one predicted by Raoult's law. Here we recall that the activity with respect to the pure substance reflects a behavior close to Raoult's law – as mentioned in connection with (6.86).

At low concentrations (close to zero mole fractions), the partial pressures strongly deviate from that predicted by Raoult's law. However, in a certain range of low concentrations, they are linear functions of the composition. This follows from the nature of molecular interactions as described in Sect. 6.4 concerning dilute solutions. By diluting the binary mixture, a composition is sooner or later achieved where the solution is dilute enough that the structure of the solute molecules surrounded by the solvent molecules and their interaction will not change significantly with further dilution. The thermodynamic behavior of this "solvated component" is of course different than that of the nearly pure substance, which is reflected in the partial pressures obeying *Henry's law*.[9] This is why Henry's law is recalled in connection of the activity with respect to the infinitely dilute solution.

The liquid–vapor phase diagram of real binary mixtures can strongly deviate from the ideal behavior if molecular interactions are largely dependent on composition. In case of a positive deviation from Raoult's law, when molecules are less strongly bound together in the mixture than in the pure liquids, it also occurs that the vapor pressure of the mixture is superior to that of the more volatile pure liquid. In this case, the mixture evaporates easier than the more volatile pure component. Contrarily, if molecular interactions are stronger in the mixture than in the pure liquids, the vapor pressure of the mixture can be inferior to that of the less volatile pure liquid in a certain composition range. By depending on the molecular interactions, liquid–vapor phase diagrams of real mixtures are distorted with respect to the "cigar shape" of ideal mixtures seen in Fig. 7.13. If there exist mixtures whose vapor pressure is inferior or superior to that of one of the pure components, neither the boiling point curve nor the dew point curve is monotonous, but both exhibit extrema where the composition of liquid and vapor coincide. This is also the case for the ethanol–water mixture. Its $T$–$x$ phase diagram can be seen in Fig. 7.16 – though in a somewhat schematic way, as the temperature scale for part of the curve is magnified to see the detailed shape. It is worth noting that the composition of the minimum boiling point mixture coincides with that of the small vapor pressure maximum in Fig. 7.15.

[9]William Henry (1775–1836) was an English chemist. In a paper in 1803, he describes his experiments concerning the solubility of gases in water. According to these results, the partial pressure of the dissolved gas is proportional to its concentration: $p_i = x_i K_i$, which is called *Henry's law*. However, the proportionality factor $K_i$ is not the pressure of the pure component but a markedly different value characteristic of the gas.

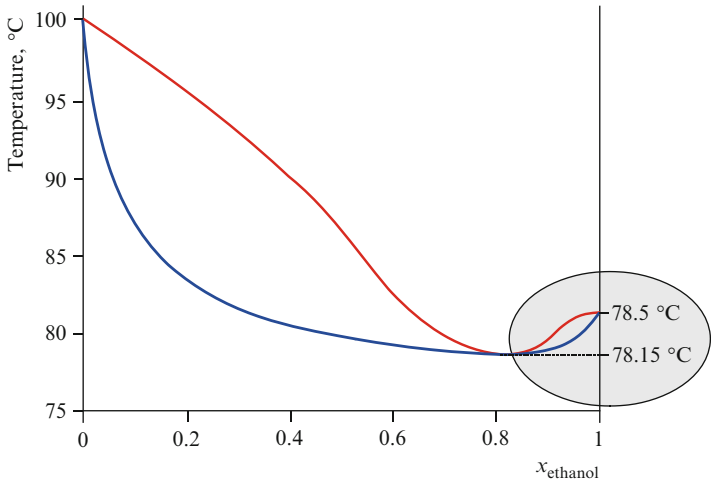



**Fig. 7.16** Composition–temperature phase diagram of the ethanol–water mixture. The temperature scale is expanded in the concentration range above the azeotrope concentration, indicated by the gray area, to better see details of the equilibrium curves

Mixtures which exhibit these extrema are called *azeotropes* (or *azeotropic mixtures*), and the composition at the extremum is called the *azeotropic composition*.[10] Using our thermodynamic knowledge, we can easily predict the shape of the liquid and the vapor curve of an azeotrope in the phase diagram. Let us write the Gibbs–Duhem equation for both phases in equilibrium:

$$S^v \mathrm{d}T - V^v \mathrm{d}P + n_1^v \mathrm{d}\mu_1 + n_2^v \mathrm{d}\mu_2 = 0, \tag{7.71}$$

$$S^l \mathrm{d}T - V^l \mathrm{d}P + n_1^l \mathrm{d}\mu_1 + n_2^l \mathrm{d}\mu_2 = 0. \tag{7.72}$$

These equations rely on the fact that the temperature $T$, the pressure $P$ and the chemical potentials of the components $\mu_1$ and $\mu_2$ should be the same in equilibrium. Let us rewrite the equations for 1 mol of the phases, i.e., divide both equations by the amount of the respective phases. As a result, we can write molar entropy and molar volume, along with mole fractions instead of the amounts of components. In a binary mixture, it is enough to write one of the two mole fractions, which we will denote by $x$, and the other component having a concentration of $1 - x$:

$$s^v \mathrm{d}T - v^v \mathrm{d}P + (1 - x^v)\mathrm{d}\mu_1 + x^v \mathrm{d}\mu_2 = 0, \tag{7.73}$$

$$s^l \mathrm{d}T - v^l \mathrm{d}P + (1 - x^l)\mathrm{d}\mu_1 + x^l \mathrm{d}\mu_2 = 0. \tag{7.74}$$

[10]The word *azeotrope* has Greek origin. It is the adjective formed from the verb $\zeta\varepsilon\omega$ = boil and the noun $\tau\rho o\pi\eta$ = change (or turn), with the prefix $\alpha$- denoting negation. The compound word $\alpha$-$\zeta\varepsilon\omega$-$\tau\rho o\pi\iota\kappa o\varsigma$ [a-zeo-tropikos] means "boils without change".

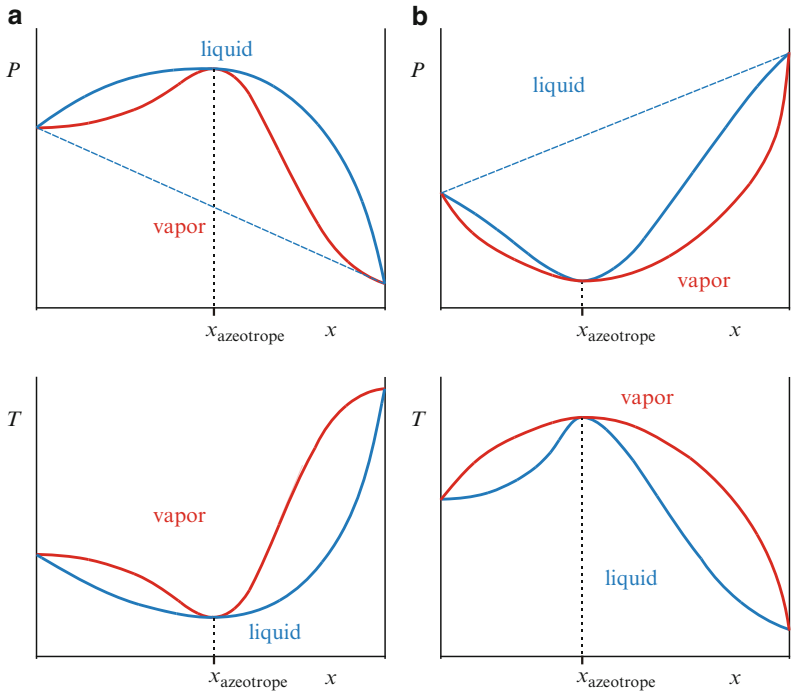



**Fig. 7.17** Schematic phase diagrams of azeotropes. (**a**) Minimum-boiling azeotrope where the vapor pressure of the mixture is superior to that of the more volatile pure component. (**b**) Maximum-boiling azeotrope where the vapor pressure of the mixture is inferior to that of the less volatile pure component. In the *P*–*x* diagrams, the dashed lines indicate the vapor pressure of an ideal mixture (according to Raoult's law)

By subtracting the two equations, we get:

$$(s^v - s^l)\mathrm{d}T - (v^v - v^l)\mathrm{d}P - (x^v - x^l)(\mathrm{d}\mu_1 - \mathrm{d}\mu_2) = 0. \tag{7.75}$$

At a fixed temperature ($\mathrm{d}T = 0$), the first term is zero, and the pressure and the chemical potentials can be treated as *univariate* functions of the composition variable $x$ – keeping in mind that the two-phase two-component binary system at fixed temperature has only one remaining degree of freedom. By making use of this and applying the chain rule, we can write:

$$-(v^v - v^l)\frac{\mathrm{d}P}{\mathrm{d}x}\mathrm{d}x = (x^v - x^l)\left(\frac{\mathrm{d}\mu_1}{\mathrm{d}x} - \frac{\mathrm{d}\mu_2}{\mathrm{d}x}\right)\mathrm{d}x \quad (\text{at constant } T). \tag{7.76}$$

The composition does not change during evaporation at the azeotropic composition; thus, we can write $x^v - x^l = 0$, which renders the right side of the equation zero. On the left side, neither $v^v - v^l$; nor $\mathrm{d}x$ is zero, which reduces the condition to

$$\frac{\mathrm{d}P}{\mathrm{d}x} = 0 \quad (\text{at constant } T). \tag{7.77}$$

By considering constant pressure ($\mathrm{d}P = 0$) and rewriting (7.75), we get similar results at the azeotropic composition:

$$(s^v - s^l)\frac{\mathrm{d}T}{\mathrm{d}x}\mathrm{d}x = (x^v - x^l)\left(\frac{\mathrm{d}\mu_1}{\mathrm{d}x} - \frac{\mathrm{d}\mu_2}{\mathrm{d}x}\right)\mathrm{d}x \quad (\text{at constant } P), \tag{7.78}$$

$$\frac{\mathrm{d}T}{\mathrm{d}x} = 0 \quad (\text{at constant } P). \tag{7.79}$$

In summary, both equilibrium curves (liquid and vapor) exhibit an extremum in the $T$–$x$, as well as in the $P$–$x$ diagram at the azeotropic composition, which can be either a minimum or a maximum. As the composition is the same in the vapor and the liquid, the two extrema coincide. This behavior is illustrated by the phase diagrams in Fig. 7.17, where the constant temperature in the $P$–$x$ diagram is the boiling point of the azeotrope, so the composition $x_{\text{azeotrope}}$ is the same in both diagrams of the same type. (As we would expect, the composition of the azeotrope depends on the pressure and temperature.)

## 7.5 Solid–Liquid Equilibrium of Ideal Binary Mixtures

In solids, the conditions of miscibility are more restricted than in liquids, due to the possible differences in the crystal structure of different substances that can hinder or even prevent the formation of *mixed crystals* (or *solid solutions*). Existing nearly ideal solid mixtures illustrate this principal; typical examples are, e.g., gold–platinum or gold–silver mixtures, where the crystal structure of the constituents is very close to each other. The $T$–$x$ phase diagram of such mixtures is shown in Fig. 7.18.

The calculation of the equilibrium curves is based in this case also on the equality of chemical potentials in the two phases. According to the notation in the diagram, component 1 has the higher melting point ($T_1$). The condition of equilibrium for this component at a temperature $T$, such that $T_1 > T > T_2$, is:

$$\mu^*_{1,s}(T) + RT\ln x_{1,s} = \mu^*_{1,l}(T) + RT\ln x_{1,l}. \tag{7.80}$$

By rearranging, we get:

$$\mu^*_{1,s}(T) - \mu^*_{1,l}(T) = RT\ln\frac{x_{1,l}}{x_{1,s}}. \tag{7.81}$$

A similar equation holds for the other component as well. If we know the temperature dependence of the chemical potentials $\mu^*_i(T)$, we can solve the

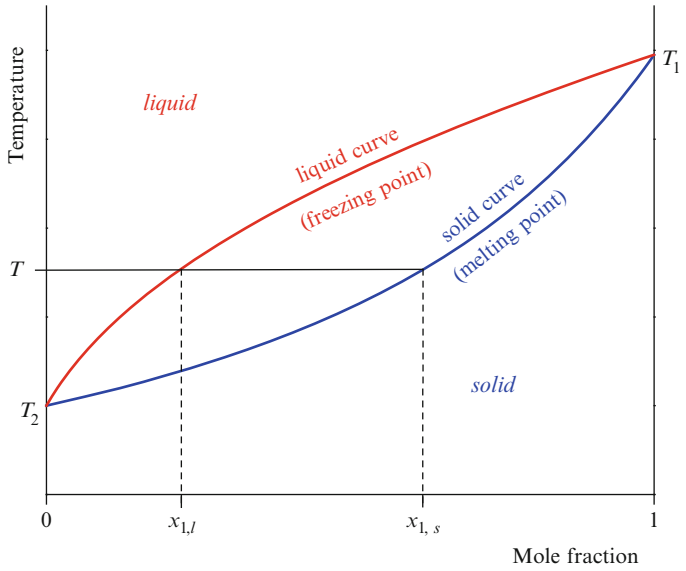



**Fig. 7.18** Temperature–composition solid–liquid phase diagram of an ideal binary mixture

simultaneous equations and get the compositions of the two phases in equilibrium. From the above equation, we can see that at lower temperatures than $T_1$ (the melting point of component 1) where the solid mixture melts, the solid phase of pure component 1 is stable. This means that $\mu^*_{1,s}(T) < \mu^*_{1,l}(T)$, which in turn requires $\ln(x_{1,l}/x_{1,s}) < 0$. Accordingly, even without solving the equations we can conclude that the relation $x_{1,l} < x_{1,s}$ holds. The actual shape depends on the chemical potential functions $\mu^*_i(T)$.

## 7.6 Equilibrium of Partially Miscible Binary Mixtures

As pointed out at the end of Sect. 7.1, if the energy of a phase as a function of composition is not convex, the "response" of the system is phase separation. At constant temperature and pressure, the Gibbs potential $G(T, P, \boldsymbol{n})$ is minimal in equilibrium. If we are interested in an intensive characterization of the system, it is the minimum of the *molar Gibbs potential* $g(T, P, \boldsymbol{x})$ which can be used as a criterion for equilibrium. This should be convex as a function of the molar extensive variables $x_i$.

According to (6.39), the molar Gibbs potential of an ideal mixture can be written as

$$g = \sum_{i=1}^{K} x_i(\mu^*_i + RT \ln x_i). \tag{7.82}$$

Let us write the sum for an ideal binary mixture:

$$g = x_1\mu_1^* + (1 - x_1)\mu_2^* + RT[x_1 \ln x_1 + (1 - x_1)\ln(1 - x_1)]. \tag{7.83}$$

By rearranging, we get:

$$g = \mu_2^* + x_1(\mu_1^* - \mu_2^*) + RT\,[x_1 \ln x_1 + (1 - x_1)\ln(1 - x_1)]. \tag{7.84}$$

It is easy to see from this equation that the molar Gibbs potential of the mixture as a function of the composition varies between the pure components' chemical potential $\mu_2^*(T)$ and $\mu_1^*(T)$ – which are the molar Gibbs potentials of the pure components. Due to the last term, $g$ is always convex, as both $x_1$ and $(1 - x_1)$ are less than unity. The actual shape of the curve depends on the ratio of $\mu_1^*(T)$ and $\mu_2^*(T)$ to the energy $RT$; as the sum $\mu_1^*(T) + \mu_2^*(T)$ becomes smaller with respect to $RT$, the shape will be more curved, and the minimum becomes deeper and closer to the location of the minimum of the term in square brackets which is at $x_1 = 0.5$.

It is worth noting that if the two components are immiscible, the molar Gibbs potential of the "mechanical dispersion" (or completely separated phases) is the linear combination of the chemical potentials of the two pure components, according to the first two terms of (7.83) and the straight line in Fig. 7.19. This also illustrates why substances mix; the molar Gibbs potential of the mixture is lower at all compositions than the sum of the molar Gibbs potentials of the components; thus, mixing leads to a decrease of the Gibbs potential.

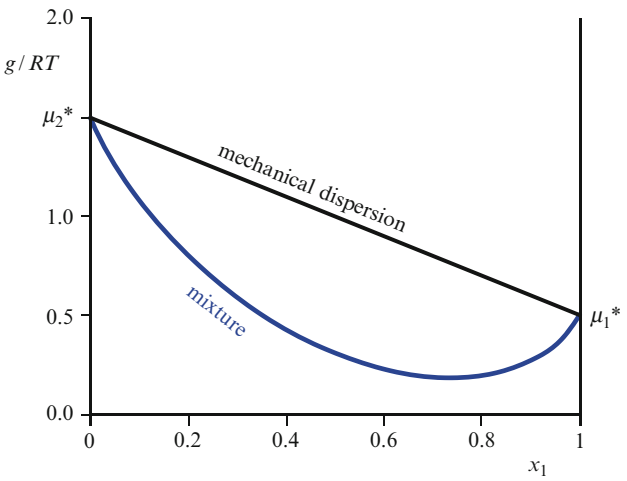



**Fig. 7.19** Molar Gibbs potential of an ideal binary mixture as a function of composition. The vertical (energy) scale is in $RT$ units. The molar Gibbs potentials of the components are $\mu_1^*(T) = 0.5\,RT$ and $\mu_2^*(T) = 1.5\,RT$. The line marked "mechanical dispersion" shows the molar Gibbs potential of immiscible components

Chemical potentials of the components in a real mixture may significantly deviate from that of an ideal mixture due to the dependence of molecular interactions on the composition. As a consequence, the molar Gibbs potential of real mixtures also deviates from the ideal behavior described by (7.82). However, the equation can readily be rewritten to take into account the actual behavior, using relative activities:

$$g = \sum_{i=1}^{K} x_i(\mu_i^* + RT \ln a_i). \tag{7.85}$$

### 7.6.1 Liquid–Liquid Phase Diagrams

The concentration dependence of the activities often leads to a calculated molar Gibbs potential according to (7.85) which is not convex; it also contains a concave region as illustrated in Fig. 7.20. The left-hand panel shows the calculated molar Gibbs potentials as a function of composition, at different temperatures. Above the curve marked by $T_{cr}$ (i.e., at lower temperatures than $T_{cr}$), the curves are convex; thus, the mixture phase is stable in the entire composition range. At higher temperatures than $T_{cr}$, the central part of the curves is unstable (concave), with adjacent metastable regions at both sides that only have local stability. Global stability is only possible if tangent lines of the entire curve always lie below the

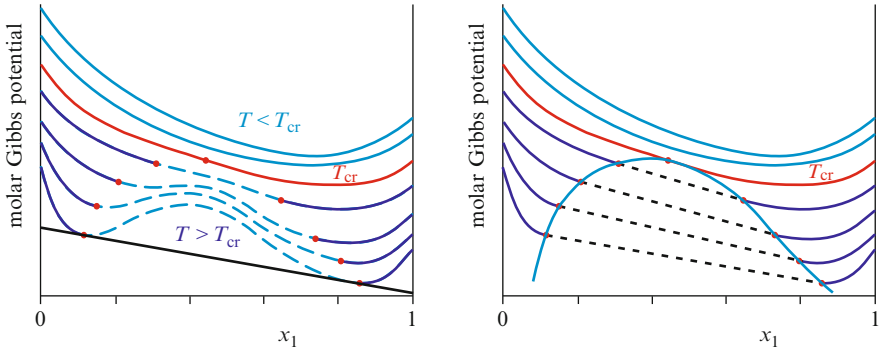



**Fig. 7.20** Molar Gibbs potential of a real binary mixture of limited miscibility as a function of composition. Curves from top to bottom are related to increasing temperature. The curve marked as $T_{cr}$ is related to the critical temperature; at lower temperatures (above this curve) the curves are convex, while at higher temperatures (below this curve) the curves are concave and exhibit two minima. The left-hand diagram shows the molar Gibbs potentials calculated using (7.85). Dashed parts of the curves between dots indicate the region of global instability. The limit of this region is shown in the right-hand diagram as a thin continuous line. Within this region, there is no stable phase but separation into two phases. The two phases are located at the points of contact of the tangent line and the calculated curve, as illustrated on the bottom curve in the left-hand diagram. Tangent points are interconnected by short-dashed lines in the right-hand diagram

curve. This condition can be fulfilled if the calculated molar Gibbs potentials in the unstable region are replaced by their lower lying tangent lines. (This principle is often referred to as the *rule of common tangents*, as the line is a common tangent of both minima.) In reality, the molar Gibbs potential according to the common tangent leads to phase separation, so that the two phases coincide with the points of contact of the tangent line and the calculated curve. The recalculated molar Gibbs potential is a linear combination of that of the two phases; thus, it exactly coincides with the common tangent. The relative quantity of the phases can be calculated from the overall composition using the lever rule (See Sect. 7.2.2).

The limit of miscibility is best visualized in a $T$–$x$ phase diagram where the locations of the dots in Fig. 7.20 are at the same composition but along a constant temperature line at the temperature of corresponding molar Gibbs potential curves. The points of common tangency in the molar Gibbs potential curves are called *nodes*; therefore, the miscibility limit curve in the $T$–$x$ phase diagram is referred to as *binodal* curve. The resulting phase diagram is illustrated in Fig. 7.21. An example for this behavior is the water–trimethylamine mixture with a *lower critical temperature* of 13 °C. Above this temperature, the mixture is separated into two phases.

It can be seen in Fig. 7.20 that there exist *locally stable* states in the vicinity of the points of tangency where global stability conditions do not hold. Similarly to the case of pure components where the metastable superheated liquid or supersaturated vapor can be formed (see end of Sect. 7.2), there is a possibility also in binary liquids to form locally stable but globally metastable states. In highly viscous mixtures, phase separation is largely hindered and the metastable one-phase

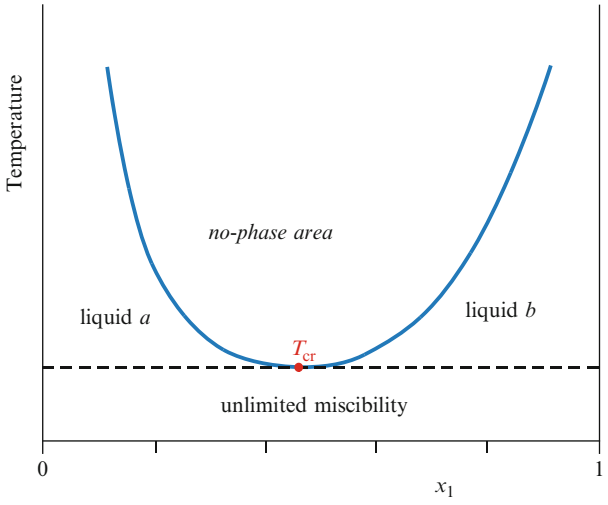



**Fig. 7.21** Temperature–composition phase diagram of the same partially miscible binary mixture as in Fig. 7.20. Below the dashed line drawn at the lower critical temperature $T_{cr}$, there is unlimited miscibility. At higher temperatures, the mixture is separated into two phases of compositions along the thick solid line. (Note that above the critical temperature of the liquid there is no phase separation either)

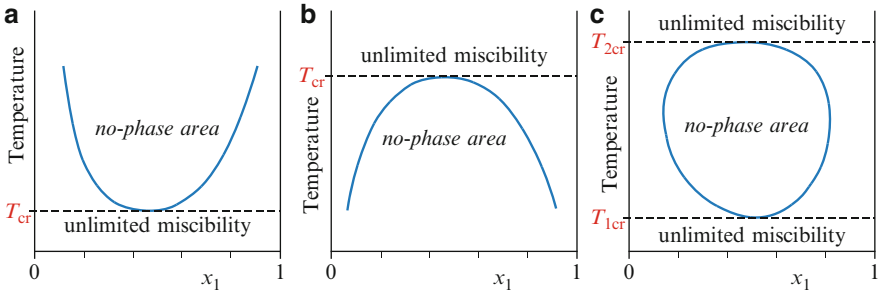



**Fig. 7.22** Possible types of temperature–composition phase diagrams of partially miscible binary mixtures. Diagram (**a**) illustrates a mixture with a lower critical temperature. Diagram (**b**) shows a mixture with an upper critical temperature. Diagram (**c**) shows a mixture with a lower and an upper critical temperature. Beyond the *dashed lines* indicating the critical temperatures, mixing is unlimited. If the overall concentration falls in between the solid curves, phase separation occurs resulting in two immiscible phases

mixture can survive for a long time. The metastable area is located between the points of tangency and the inflexion points marking the limits of local stability.

Figure 7.21 shows the temperature–composition phase diagram of the mixture shown in Fig. 7.20. Below the dashed line drawn at the lower critical temperature $T_{cr}$, there is unlimited miscibility, and above this line (up to the critical temperature of the liquid where no phase separation occurs), the mixture is separated into two phases whose compositions lie along the thick solid line.

Molecular interactions in binary mixtures can result in deviations from ideality leading to different situations from that illustrated in Figs. 7.20 and 7.21. It is also possible that phase separation occurs with decreasing temperature, below an *upper critical temperature*. This is the case for the phenol–water mixture, where the system separates into two phases below the critical temperature of 68.8°C. There exist also mixtures which separate into two phases within a finite temperature range; at both higher and lower temperatures outside this range, there is unlimited miscibility of the two components. A common example for this behavior is the water–nicotine mixture with a lower critical temperature of 61°C and an upper one at 210°C. Possible types of partially immiscible liquids are illustrated in Fig. 7.22. It is worth noting that in case of the panels b) and c) of these figures it is possible to include in the same diagram the liquid–vapor equilibrium curves as well. This way, the same phase diagram can show both the liquid–liquid and the liquid–vapor phase separation equilibria.

### *7.6.2 Solid–Liquid Phase Diagrams*

Binary systems with unlimited liquid miscibility often do not mix in solid phase, due to different crystal structures of the pure components. This is the case – among

others – for salts dissolved in water and a great number of metal alloys. When cooling these liquids, it is always one of the pure components that crystallizes at the freezing point. The freezing temperature as a function of the composition can be calculated from the chemical potentials of the components. It is clear – even without calculations – that the chemical potential of a component close to its unit mole fraction is always inferior to that of the pure component (see (6.86)). We can plot the temperature dependence of the chemical potentials of a component in the pure solid, in the pure liquid, and in the liquid mixture phase. Curves for the pure phases are identical with those in Fig. 7.5, and the chemical potential in the mixture phase will be lower than in the pure liquid. The lowering of the chemical potential increases monotonically with decreasing concentration – at least for nearly ideal mixtures. It is readily seen from Fig. 7.23 that the freezing point of the mixture also follows this lowering tendency. The same tendency applies for the other component as well; thus, the freezing point decreases with respect to the pure components when the concentration of this component decreases.

Accordingly, in the $T$–$x$ solid–liquid phase diagram, freezing points decrease from the pure substances toward the center of the diagram. The two curves intersect at the composition where the chemical potential of both mixture components are identical with that of the corresponding pure solid. At this composition and temperature the liquid mixture freezes without further composition change by crystallization of both components in a pure solid (micro)phase. The solid phase is a mixture of pure microcrystals of the components. The liquid phase at this composition has

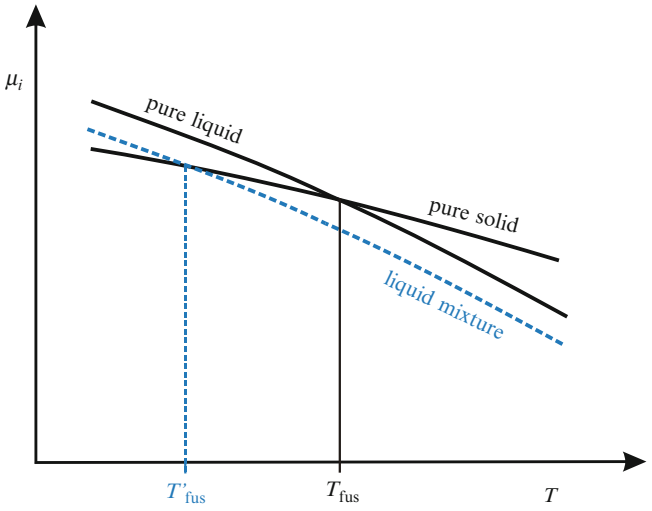



**Fig. 7.23** Chemical potential *vs.* temperature of the major component in the liquid binary mixture, in the pure solid (freezing out from the mixture) and in the corresponding pure liquid. It can be seen that the lowering of the component's chemical potential in the mixture results in an intersection with the pure solid's chemical potential at lower temperatures than that in case of the pure liquid. As indicated, melting points change accordingly

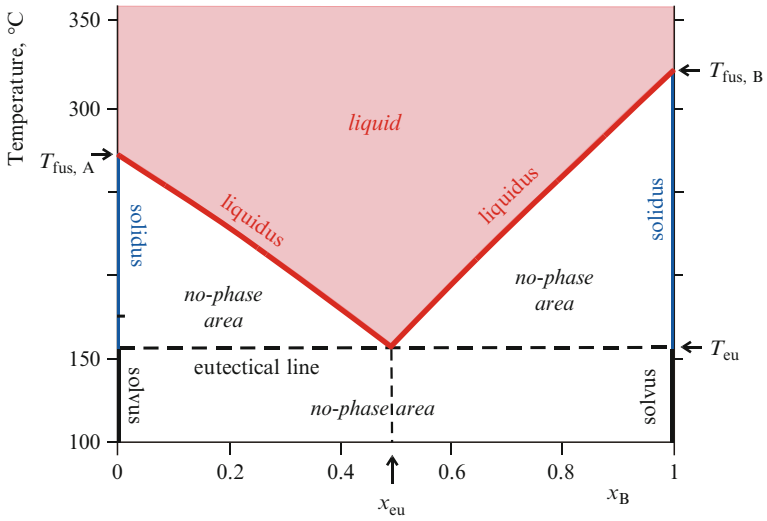



**Fig. 7.24** Phase diagram of a binary system with components of unlimited miscibility in the liquid phase and no miscibility in the solid phase, forming a eutectic. Actual data are those of bismuth (A) and cadmium (B); the calculated liquidus curves and the eutectical point were obtained using relations for an ideal mixture. The Cd–Bi phase diagram is only slightly different in reality. The upper shadowed area is the stability range of the liquid phase; the white one below is a no-phase area

the lowest freezing point and the mixture crystal of the same composition has the lowest melting point. For this reason, the mixture is called the *eutectic mixture*, the temperature of solidification the *eutectic point* and the solid formed is the *eutectic* or *eutectic solid*.[11]

A phase diagram illustrating the formation of a eutectic with no miscibility in the solid phase is shown in Fig. 7.24. Three phases may be seen in the diagram. Two of them are the pure solid substances at the left and the right edges, i.e. at $x_B = 0$ and $x_B = 1$, respectively. The third one is the liquid phase, stable above the two *liquidus curves* (or *freezing point curves*) in the entire composition range. This diagram can be constructed by calculating the liquidus curves from the condition of equilibrium. The liquidus curve indicates the composition of the liquid mixture in equilibrium with the corresponding pure solid at the given temperature. The equilibrium condition is, therefore, the equality of the chemical potential of the mixture component with that of the same component in the pure solid. By supposing an ideal mixture, let us write this equation for component A (at the left-hand side of the diagram):

$$\mu^*_{A,s}(T) = \mu_{A,l}(T, x_A) = \mu^*_{A,l}(T) + RT \ln x_A. \tag{7.86}$$

[11]The word originates from the Greek adverb $\varepsilon\upsilon$ = well and the verb $\tau\eta\kappa\omega$ = melt. The compound word $\varepsilon\upsilon\tau\eta\kappa\tau o\varsigma$ [eutektos] means: easily melting. The English word *eutectic* is a noun and an adjective as well.

We can express the logarithm of the composition variable $x_\mathrm{A}$ as

$$\ln x_\mathrm{A} = \frac{\mu^*_{\mathrm{A},s}(T) - \mu^*_{\mathrm{A},l}(T)}{RT} = \frac{\Delta_\mathrm{fus}\, h^*_\mathrm{A}(T)}{RT}. \tag{7.87}$$

The difference of the chemical potentials of the two pure phases is the molar Gibbs potential of fusion $\Delta_\mathrm{fus}\, g^*_\mathrm{A}(T)$ at the given temperature, which can be written as follows:

$$\Delta_\mathrm{fus}\, g^*_\mathrm{A}(T) = \Delta_\mathrm{fus}\, h^*_\mathrm{A}(T) - T\Delta_\mathrm{fus}\, s^*_\mathrm{A}(T). \tag{7.88}$$

At the melting point of the pure component, the chemical potential should be the same in both phases:

$$\mu^*_{\mathrm{A},s}(T^*_{\mathrm{fus,A}}) - \mu^*_{\mathrm{A},l}(T^*_{\mathrm{fus,A}}) = \Delta_\mathrm{fus}\, g^*_\mathrm{A}(T^*_{\mathrm{fus,A}}) = 0. \tag{7.89}$$

Based on this identity, we can express the molar entropy of fusion $\Delta_\mathrm{fus}\, s^*_\mathrm{A}(T^*_{\mathrm{fus,A}})$ with the help of the molar enthalpy of fusion, $\Delta_\mathrm{fus}\, h^*_\mathrm{A}(T^*_{\mathrm{fus,A}})$:

$$\Delta_\mathrm{fus} s^*_{\mathrm{A},s}(T^*_{\mathrm{fus,A}}) = \frac{\Delta_\mathrm{fus}\, h^*_\mathrm{A}(T^*_{\mathrm{fus,A}})}{T^*_{\mathrm{fus,A}}}. \tag{7.90}$$

Suppose that the dependence on temperature of both $\Delta_\mathrm{fus}\, h^*_\mathrm{A}$ and $\Delta_\mathrm{fus}\, s^*_\mathrm{A}$ is negligible between the temperatures $T^*_{\mathrm{fus,A}}$ and $T$; thus, we can replace $\Delta_\mathrm{fus}\, g^*_\mathrm{A}(T)$ by

$$\Delta_\mathrm{fus} h^*_\mathrm{A} - T\frac{\Delta_\mathrm{fus}\, h^*_\mathrm{A}}{T^*_{\mathrm{fus,A}}} = \Delta_\mathrm{fus} h^*_\mathrm{A}\left(1 - \frac{T}{T^*_{\mathrm{fus,A}}}\right). \tag{7.91}$$

Let us substitute this into (7.87):

$$\ln x_\mathrm{A} = \frac{1}{RT}\Delta_\mathrm{fus} h^*_\mathrm{A}\left(1 - \frac{T}{T^*_{\mathrm{fus,A}}}\right) = -\frac{\Delta_\mathrm{fus} h^*_\mathrm{A}}{R}\left(\frac{1}{T^*_{\mathrm{fus,A}}} - \frac{1}{T}\right). \tag{7.92}$$

This immediately yields the composition of the mixture in equilibrium with pure component A at temperature $T$:

$$x_\mathrm{A} = e^{-\frac{\Delta_\mathrm{fus} h^*_\mathrm{A}}{R}\left(\frac{1}{T^*_{\mathrm{fus,A}}} - \frac{1}{T}\right)}. \tag{7.93}$$

While deriving the above expression, our considerations were not specific for component A. Therefore, we can write the same formula for the composition of the mixture in equilibrium with the pure solid B at temperature $T$:

$$x_\mathrm{B} = e^{-\frac{\Delta_\mathrm{fus} h^*_\mathrm{B}}{R}\left(\frac{1}{T^*_{\mathrm{fus,B}}} - \frac{1}{T}\right)} \tag{7.94}$$

The phase diagram shown in Fig. 7.24 has been constructed using the two expressions above, and molar fusion enthalpies of bismuth and cadmium of 11.30 kJ/mol (at its melting point 271.4°C) and 6.19 kJ/mol (at its melting point 321.07°C), respectively. Liquidus curves calculated this way differ only negligibly from that based on measured equilibrium temperatures.

It is worth noting that the expressions obtained for the temperature-dependent solubility *do not contain* any specific data of the other component (the "solvent"). This can be generalized that if a substance forms an ideal mixture with several other substances, its solubility will be the same in all of them at the same temperature. (This is obvious at the molecular level; if the interaction of the solute molecules with those of the solvent is exactly the same as with their own molecules – which is the criterion to form an ideal mixture – then it is all the same from the point of view of mixture properties, what exactly the other molecules are.)

Phases of the diagram shown in Fig. 7.24 can be characterized as follows. Above the liquidus curves, there is only one phase, the liquid mixture. At constant pressure, the residual number of degrees of freedom is 2, which means that both temperature and pressure are free to determine to change state within this region. At the lower boundary of this region – on the liquidus curves – there are two phases in equilibrium; liquid mixture and one of the pure solids. Here, the residual number of degrees of freedom at constant pressure is only 1; therefore, we can freely choose either a temperature or a composition. At the bifurcation of the liquidus curves, there are three phases in equilibrium: liquid mixture and both pure solids, as these latter do not mix. This is a kind of "triple point" in the phase diagram having zero degrees of freedom. Consequently, the three phases coexist only at the unique *eutectic composition* and the unique *eutectic temperature*. Within the diagram, there are no other stable phases. The *no-phase area* completely fills the diagram below the liquidus curves, including the region below the eutectic temperature. This also means that the horizontal dashed line at this temperature – the *eutectic line* – is not a boundary between phases in equilibrium and only connects the compositions of the three phases in equilibrium. However, it delimits the regions of different *microcrystal structures* or *textures*. Above the line, the liquid mixture is in equilibrium with one of the pure solids, which is a homogeneous crystal. Below the line, there is a mixture crystal containing microcrystals of the two pure components.

If a liquid mixture of the eutectic composition is cooled, it is the mixture crystal of components A and B that solidifies at the eutectic temperature. If the composition of the liquid cooled is different, a pure component – A or B, depending on the actual composition – will form the solid phase first, until the composition of the liquid will become the eutectic composition. Upon further cooling, the eutectic mixture crystal structure will solidify onto the surface of the pure crystals formed before. In the completely frozen solid, there are grains of pure crystals embedded in the microcrystal structure. As a result, below the eutectic line there is always a mixture of the crystals of component A and B, while above there is always a pure component's crystal only.

The ratio of components A and B is unique for a given binary system, according to the eutectic composition. This fact can be interpreted by writing the following "stoichiometric equation":

$$\mathrm{A}_x\mathrm{B}_{1-x}(l) \rightleftharpoons x\mathrm{A}(s) + (1-x)\mathrm{B}(s). \tag{7.95}$$

This equation contains the liquid mixture on the left side as "reactant" and the two solids on the right side as "products". Thus, the general *eutectic reaction* can be written as follows:

$$\text{liquid} = \text{solid}_1 + \text{solid}_2. \tag{7.96}$$

We shall see similar reactions of isothermal equilibria concerning three phases later.

To calculate the eutectic temperature, we only have to make use of the fact that the two liquidus curves bifurcate at this temperature. Thus, the sum of the mole fractions of the liquid richer in A and that of the mixture richer in B is unit. Formally, we can write the equation

$$e^{-\frac{\Delta h^*_\mathrm{A}}{R}\left(\frac{1}{T^*_\mathrm{A}}-\frac{1}{T}\right)} + e^{-\frac{\Delta h^*_\mathrm{B}}{R}\left(\frac{1}{T^*_\mathrm{B}}-\frac{1}{T}\right)} = 1, \tag{7.97}$$

which yields as solution the eutectic temperature.

This equation is valid only in case of an ideal liquid solution, with the additional constraint that the enthalpy of fusion does not depend on temperature. However, we can readily take into account nonideality and the temperature dependence of the fusion enthalpy as well. Let us rewrite (7.87) for a real mixture:

$$\ln f_\mathrm{A} x_\mathrm{A} = \frac{\Delta_\mathrm{fus}\, g^*_\mathrm{A}(T)}{RT} \tag{7.98}$$

and substitute into it the temperature-dependent relative activity coefficient $f_\mathrm{A}$ and fusion enthalpy $\Delta_\mathrm{fus}\, g^*_\mathrm{A}(T)$. These data can be obtained either from detailed thermodynamic measurements or from the fundamental equation of the mixture. The modified equation provides the eutectic temperature for the real mixture.

There are binary mixtures of limited miscibility which mix to a certain degree in the solid phase as well. The difference with respect to the phase diagram shown in Fig. 7.24 is that solidus curves are not exactly at the pure components ($x_\mathrm{B} = 0$ and $x_\mathrm{B} = 1$) but "inside" the diagram, leaving space for the limited miscibility region in the solid phase at both edges. In metallurgy (where the two components are metals) and in mineralogy (where they are rock-forming substances), the solid solution richer in A is called $\alpha$ *crystal* and the one richer in B is called $\beta$ *crystal*. The structure of the $\alpha$ crystal is the same as that of the pure component A. Similarly, the $\beta$ crystal has the structure of the pure component B. They differ from the crystals of the pure components by containing the other component either in the lattice positions or between them.

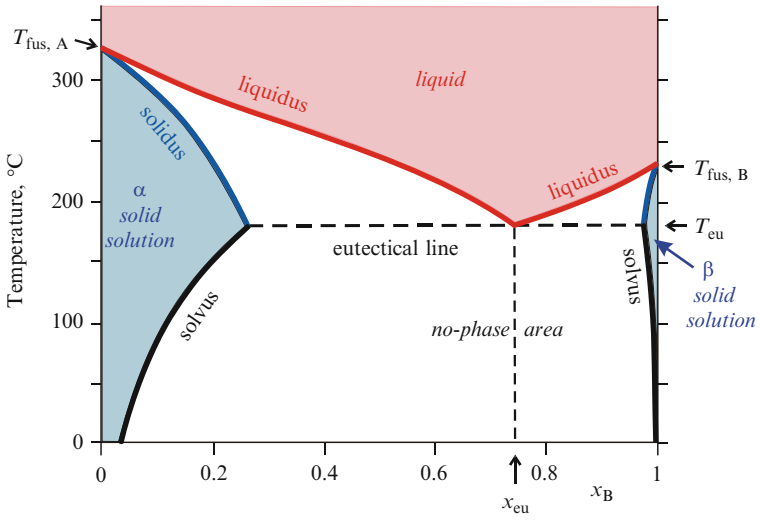



**Fig. 7.25** Phase diagram of a binary system with components of unlimited miscibility in the liquid phase and partial miscibility in the solid phase, forming a eutectic. This diagram shows the case of lead (A) and tin (B), forming the common *solder* as eutectic. Shadowed areas indicate the range of stable phases (liquid, lead-rich $\alpha$, tin-rich $\beta$); the white area below is a no-phase area. (Note that below 13°C, the $\beta$ phase is no more stable but pure tin – which is not discernable in the diagram)

In the phase diagram of such a system shown in Fig. 7.25, there are three phases; liquid mixture, solid solution $\alpha$, and solid solution $\beta$. (These latter are usually called simply as $\alpha$ *phase* and $\beta$ *phase*, respectively.) As the composition of the solids can vary within their stability range, the no-phase area is reduced compared to the case shown in Fig. 7.24. The actual composition of the solid in equilibrium with the liquid varies with temperature. The shapes of the two branches of the liquidus curve are similar to that in Fig. 7.24, and a eutectic solidifies when the composition of the liquid in equilibrium with the $\alpha$ phase is the same as the composition of the liquid in equilibrium with the $\beta$ phase. The texture of the eutectic exhibits a fine mixture of microcrystals of the $\alpha$ and the $\beta$ phase in a ratio corresponding to the eutectic reaction.

The equilibrium condition between the liquid and the solid solution is the equality of the chemical potentials of each component in the two phases. This condition is the basis to calculate the equilibrium temperature and concentration. We also know from earlier chapters (see e.g., Table 4.1) that the overall condition of equilibrium at constant temperature and pressure is the minimum of the Gibbs potential, or, in case of an intensive characterization only, the minimum of its molar value. The advantage of this method is that it can be used irrespective of the number of components and phases. It is easy to show that this condition is equivalent to the equality of the chemical potentials of the respective components in the phases in equilibrium.

Let us consider the Gibbs potential function $G(T, P, \boldsymbol{n}^{\varphi_1}, \boldsymbol{n}^{\varphi_2}, \ldots, \boldsymbol{n}^{\varphi_K})$ of a system consisting of $P$ phases and $K$ components, where the vectors $\boldsymbol{n}^{\varphi_j}$ describe the composition of the phase $\varphi_j$. A necessary condition of the minimum of $G$ is that its total differential be zero. At constant temperature ($\mathrm{d}T = 0$) and constant pressure ($\mathrm{d}P = 0$), the total differential contains only terms with nonzero increments of the composition variables:

$$\mathrm{d}G = \sum_{\varphi_j=1}^{P} \sum_{i=1}^{K} \mu_i^{\varphi_j} \mathrm{d}n_i^{\varphi_j} = 0. \tag{7.99}$$

This equation can be considered as the general equilibrium condition of a multicomponent multiphase system. Let us rewrite it for a binary system:

$$\mu_{\mathrm{A}}^{\alpha} \mathrm{d}n_{\mathrm{A}}^{\alpha} + \mu_{\mathrm{B}}^{\alpha} \mathrm{d}n_{\mathrm{B}}^{\alpha} + \mu_{\mathrm{A}}^{\beta} \mathrm{d}n_{\mathrm{A}}^{\beta} + \mu_{\mathrm{B}}^{\beta} \mathrm{d}n_{\mathrm{B}}^{\beta} = 0. \tag{7.100}$$

Let us make use of the constraint that the system is closed, i.e.,

$$\mathrm{d}n_{\mathrm{A}}^{\alpha} = -\mathrm{d}n_{\mathrm{A}}^{\beta} \quad \text{and} \quad \mathrm{d}n_{\mathrm{B}}^{\alpha} = -\mathrm{d}n_{\mathrm{B}}^{\beta}. \tag{7.101}$$

By substituting this into the previous equation, we get

$$(\mu_{\mathrm{A}}^{\alpha} - \mu_{\mathrm{A}}^{\beta})\, \mathrm{d}n_{\mathrm{A}}^{\alpha} + (\mu_{\mathrm{B}}^{\alpha} - \mu_{\mathrm{B}}^{\beta})\, \mathrm{d}n_{\mathrm{B}}^{\alpha} = 0. \tag{7.102}$$

As $\mathrm{d}n_{\mathrm{A}}^{\alpha}$ and $\mathrm{d}n_{\mathrm{B}}^{\alpha}$ are independent and nonzero, the equation holds only if

$$\mu_{\mathrm{A}}^{\alpha} = \mu_{\mathrm{A}}^{\beta} \quad \text{and} \quad \mu_{\mathrm{B}}^{\alpha} = \mu_{\mathrm{B}}^{\beta}, \tag{7.103}$$

which demonstrates the equivalence of the equality of the respective chemical potentials to the minimum of the (molar) Gibbs potential. The latter condition is usually easier to use in case of multicomponent systems.

To get the molar Gibbs potential, we only have to divide the extensive Gibbs potential by the total amount of the system; i.e., the total mole number. The temperature dependence of the molar Gibbs function of each phase is determined by its negative molar entropy:

$$\left(\frac{\mathrm{d}g}{\mathrm{d}T}\right)_{P,x} = -s. \tag{7.104}$$

Based on this identity, we can conclude that the molar Gibbs potential of the phases always increases with decreasing temperature. As the molar entropy of the liquid is always greater than that of the solid of the same composition, the molar Gibbs potential of the liquid increases in a greater extent compared to that of the solid of the same composition. Consequently, the molar Gibbs potential of the

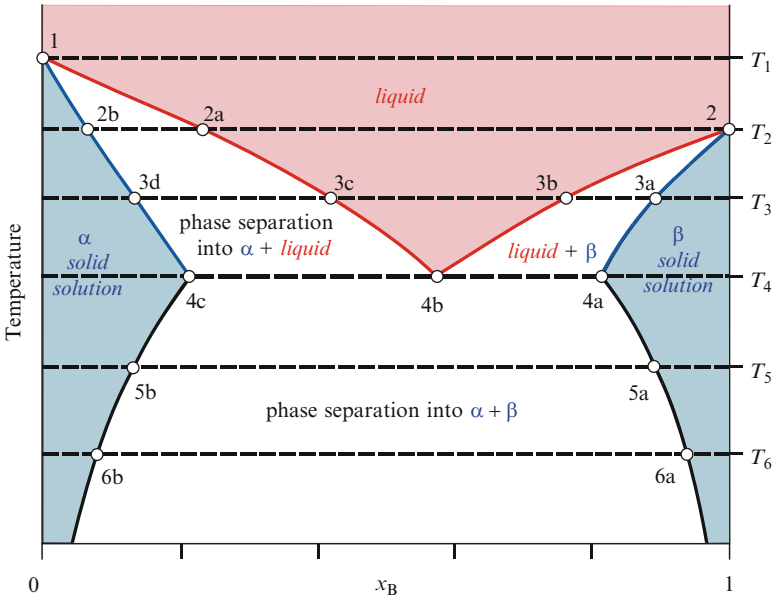



**Fig. 7.26** Phase diagram of a binary system with components of unlimited miscibility in the liquid phase and partial miscibility in the solid phase, forming a eutectic. Whenever the overall composition lies within the white (non-shaded) area, the system separates into two phases interconnected by the dashed lines. Molar Gibbs-potential curves of the relevant phases at temperatures $T_1$–$T_6$ are shown in Fig. 7.27

liquid as a function of composition shifts more and more upwards with increasing temperature compared to that of the corresponding solid. Let us analyze this behavior in a schematic phase diagram of the same type as the one in Fig. 7.25.

In Fig. 7.26, there are six different isotherms shown as horizontal dashed lines. These are conodes, interconnecting nodes representing phases in equilibrium at the given temperature, at the edges of the no-phase area. Figure 7.27 shows the molar Gibbs potentials of the phases at the same temperatures as a function of the composition. By inspecting the two figures, we can make the following observations.

At the temperature $T_1$, pure liquid A solidifies; the molar Gibbs potential of the solid formed (α phase) is equal to that of the liquid. As the equality holds only for pure substance A, the crystal also consists of pure A.

At a lower temperature $T_2$, it is the solid phase labeled 2b which is in equilibrium with the liquid mixture having the composition 2a. By inspecting the corresponding diagram in Fig. 7.27, we can see that, at compositions between 2a and 2b, the molar Gibbs potentials of both the liquid phase and the solid α phase are greater than that of the "mechanical dispersion" of the two phases, represented by the interconnecting line between the two points 2a and 2b. (Note that the calculation of the molar Gibbs potential of the mechanical dispersion is based on the lever rule

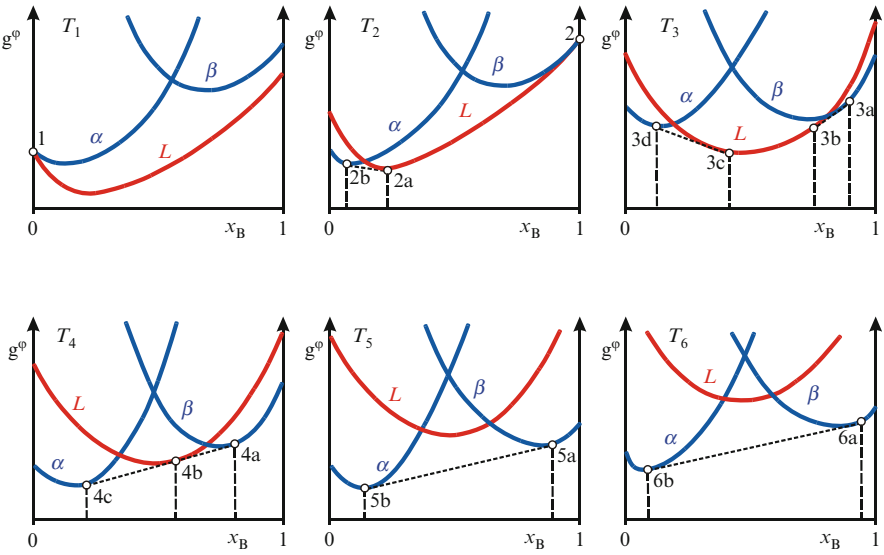



**Fig. 7.27** Molar Gibbs potential $g^{\varphi}$ of the phases in a binary system with components of unlimited miscibility in the liquid phase and partial miscibility in the solid phase, forming a eutectic, at temperatures shown in Fig. 7.26 as $T_1$–$T_6$. Phases are identified by labels above the curves ($\alpha$, $\beta$, and $L$ = liquid)

explained before.) This temperature is the melting point of pure B; thus, it also solidifies here, and the molar Gibbs potential of the liquid at point labeled 2 is identical to that of the $\beta$ phase, which is pure component B in this case.

At the temperature $T_3$, below $T_2$, there exist systems of overall composition (in both regions richer in A and richer in B) where neither a liquid nor a solid of this composition is stable. Accordingly, between the overall compositions 3d and 3c, only the $\alpha$ phase having the composition 3d and liquid mixture having the composition 3c are stable. Similarly, between the overall compositions 3b and 3a, only the $\beta$ phase having the composition 3a and liquid mixture having the composition 3b are stable. The ratio of the coexisting phases can be calculated using the lever rule.

At the temperature $T_4$, the molar Gibbs-potential curves of the three phases have a common tangent. Accordingly, the solid richer in A consists of crystals of the $\alpha$ phase having the composition 4c and of eutectic mixture crystals containing $\alpha$ and $\beta$ microcrystals of compositions 4a and 4c. Similarly, at overall compositions richer in B than the eutectic mixture, the same eutectic is mixed with crystals of the $\beta$ phase having the composition 4a. At exactly the eutectic composition 4b, the system can exist as only liquid, or as a solid eutectic containing microcrystals of both solid phases, or all the three phases – $\alpha$, $\beta$, and liquid – can coexist. This is the only "triple point" in the phase diagram shown in Fig. 7.26.

At the temperature $T_5$ below the eutectic temperature $T_4$, the molar Gibbs potential of the liquid is greater at all compositions than that of the solid phases $\alpha$ and $\beta$ and also greater than the common tangent of the two curves of the solids.

Therefore, the liquid phase is no more stable at this temperature. To the left of point 5b only the $\alpha$ phase, while to the right of point 5a, only the $\beta$ phase is stable. If the overall composition lies between 5a and 5b – within the no-phase area – the system consists of a mixture crystal of the solid solutions $\alpha$ and $\beta$. At the still lower temperature $T_6$, the situation is in principle the same except that the stability range of the two solid solutions $\alpha$ and $\beta$ further shrinks. This can also be seen in Fig. 7.27 where the common tangent of the two curves extends to a greater interval between 6b and 6a. Within this composition range, we can find mixture crystals in the solid.

To calculate temperature-dependent molar Gibbs potentials of the phases shown in Fig. 7.27, we need to know the chemical potentials of the components in each phase – the terms in the second sum of (7.99) – as a function of temperature. To find the compositions of two (or three) phases in equilibrium, we have to find the tangency points of the common tangents on the molar Gibbs-potential curves. The necessary calculations can readily be made even in the case of more complicated phase diagrams. We shall only show a few common types of these diagrams without discussing the thermodynamic calculations.

There is also another way to construct binary phase diagrams; we can determine experimentally equilibrium temperatures and compositions in the diagram. This method is usually simpler than the thermodynamic description, which is the reason that most binary phase diagrams are known from experimental data. There are several experimental techniques providing the necessary data. Probably the most simple is the observation of cooling curves. A brief description of this method is shown in a solved problem at the end of the chapter.

It is worth while noting an interesting behavior of the binary systems characterized by the phase diagram in Fig. 7.26. Let us suppose that the liquid mixture of the corresponding composition is cooled until point 3b. Upon further cooling, it is first the solid of composition 3a that freezes out; thus, the composition of the liquid will be less and less rich in component B as we continue cooling, continuously changing along the liquidus curve toward 4b. Meanwhile, the composition of the solid also shifts along the solidus curve from 3a toward 4a. Accordingly, the first crystals formed will have the composition corresponding to 3a, but upon further cooling, the surface layers of the growing crystals will be richer and richer in component A. All layers of any composition solidified are stable until point 4a. However, as the temperature falls below $T_4$, layers (or grains of crystals) richest in A gradually lose stability as their composition falls within the no-phase area. For example, at the temperature $T_6$, the composition of the stable $\beta$ crystal rich in A cannot lie to the left of point 6a. To maintain stability, $\beta$ microcrystals or the surface layers of larger crystals formed at higher temperatures, richer in A, partly recrystallize forming $\alpha$ crystals of composition 6b. However, during this recrystallization the composition of the solid should change, which necessitates material transport. As diffusion in the solid state is slower by several orders of magnitude than that in the liquid state, this equilibrium is achieved only very slowly. $\alpha$ crystals formed this way are called *secondary crystals*. This name only refers to the process of their formation; from a thermodynamic or structural point of view, there is no difference

between them and the *primary crystals* (frozen out at temperatures higher than $T_4$) or eutectic microcrystals (frozen out as a mixture crystal at temperature $T_4$). Nevertheless, the texture – the arrangement of microcrystals and crystal layers – of these crystals of different specific history is usually different.

Another important type of binary solid–liquid phase diagrams is the case of components that form nearly ideal mixtures both at compositions rich in A and rich in B, except for the composition range where they form a compound. (The edges of the diagram at compositions rich in A and rich in B are quite similar to the shape shown in Fig. 7.18.) The compound formed does not mix with one of the components. The example shown in Fig. 7.28a) is a mixture which forms the

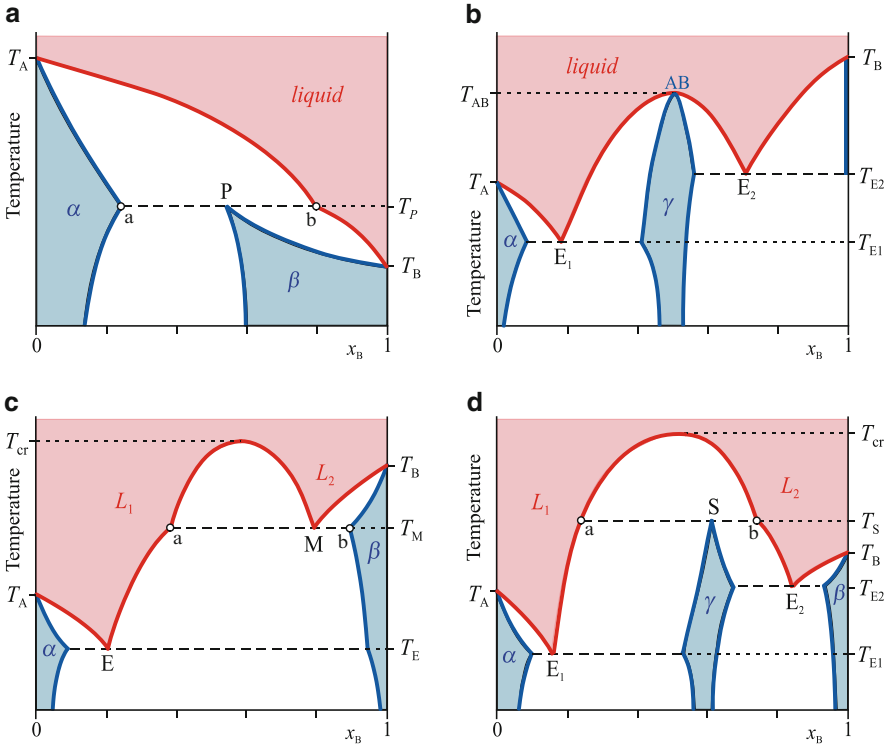



**Fig. 7.28** Some further types of phase diagrams of binary mixtures with partial miscibility in the solid phase. Shadowed areas indicate the range of stable phases; the white area is a no-phase area. (**a**) Two components of unlimited miscibility in the liquid phase with a peritectic reaction at the point P. (**b**) The two components form a compound AB which dissolves both components in a limited concentration in the solid ($\gamma$) phase. Component A can dissolve some B in the solid phase ($\alpha$), but B is immiscible with A in the solid phase. Both $\alpha$ and $\gamma$, and $\gamma$ and pure solid B, form eutectics. (**c**) The two components are also only partially miscible in the liquid phase with a monotectic reaction at the point M and a eutectic reaction at the point E. (**d**) The two components are also only partially miscible in the liquid phase with a syntectic reaction at the point S and eutectic reactions at points $E_1$ and $E_2$

compound $A_2B_3$. At the temperature $T_P$, it is a solid solution containing mostly this compound that is formed in a reaction between the liquid mixture ($L$) and the solid $\alpha$ phase. This is called a *peritectic*[12] *reaction* and can be written in a general form:

$$\text{liquid} + \text{solid}_1 \rightleftharpoons \text{solid}_2. \tag{7.105}$$

In the figure shown, $\text{solid}_1$ is the $\alpha$ phase and $\text{solid}_2$ is the $\beta$ phase. The liquidus curve is $T_A$−b−$T_B$ and the solidus curve is $T_A$−a. On cooling a liquid mixture of concentration $x_B$ to the left of point b, upon intersection of the liquidus, $\alpha$ phase will freeze out. (Its composition can be found by the intersection of the isothermal conode and the solidus.) As cooling continues, the liquid becomes richer in B, just like the new layers of the growing crystals, until the temperature $T_P$ is reached. At this temperature, the composition of the liquid corresponds to point b and the peritectic reaction occurs. During the reaction, part of the solid $\alpha$ phase and all the liquid is transformed into the solid $\beta$ phase consisting mostly of the compound $A_2B_3$. If the solvus curve delimiting phase stability below point P was vertical or was tending to the left with lowering temperature, its composition would remain the same upon further cooling. However, the change of activities with temperature in the figure is such that further cooling results in forming some $\alpha$ phase from the $\beta$ phase during recrystallization of a small fraction of the latter.

On cooling a liquid mixture of composition falling between the points P and b, the only difference is that at the completion of the peritectic reaction there is still some liquid remaining. Upon further cooling, its composition will change along the curve b−$T_B$ and the composition of the freezing solid along the curve P−$T_B$. The same happens also when cooling a liquid mixture of composition to the right of b. The horizontal line a−P−b (dashed in the figure) at temperature $T_B$ is called the *peritectic line*. This only delimits solids of different textures and not different phases, as is the case with the eutectic line. Binary mixtures exhibiting peritectic reactions are, for example, the Al–Ti and Fe–C systems and several water–salt systems forming water containing crystals.

In partially miscible binary systems, interaction of the molecules A–B might exceed significantly both interactions A–A and B–B, leading to strongly nonideal behavior. This may result in the formation of a stable compound between A and B, which is completely immiscible or partially immiscible with the pure components. The formation of the compound is a chemical reaction in the classical sense as stoichiometric coefficients in the equations are small integer numbers (e.g., AB, $AB_2$, $A_2B$, and $A_3B_2$). These compounds can directly crystallize from the liquid mixture according to the reaction

$$n\,\text{A}(l) + m\,\text{B}(l) \rightleftharpoons \text{A}_n\text{B}_m\,(s) \tag{7.106}$$

[12]The word has been coined by analogy with eutectic. The first part is the Greek preposition $\pi\varepsilon\rho\iota$ which means "around". The second part is the verb $\tau\eta\kappa\omega$ = melt. The compound word reflects the fact that the composition of the liquid in equilibrium with the two solid phases lies outside ("around") the interval determined by the compositions of the solids, not between them.

On the left-hand side, there is only the liquid phase, while on the right-hand side, there is only the solid phase. Accordingly, a usual simplification of the "reaction" can be written as

$$\text{liquid} \rightleftharpoons \text{solid}, \tag{7.107}$$

which reflects that the liquid corresponding to a ratio $n : m$ freezes out without any composition change. (This is also called *congruent freezing*.) At this temperature, the composition of the liquid and the solid are the same, while at slightly lower temperatures this is not the case. As it is shown in Sect. 7.4, both liquidus and solidus should have a maximum at this temperature, which means that their common tangent line is horizontal at this particular composition.

Among binary phase diagrams of components forming a compound, we can find cases where the compound does not mix at all with the pure components in the solid phase, and other cases where the solid compound dissolves some of the pure components. In the latter case, the stability range of the compound extends to the left and right of the composition of the compound (see Fig. 7.28b). Pure components A and B usually do not dissolve the compound as the compound does not "fit" into their crystal structure. Therefore, if an $\alpha$ or $\beta$ mixture phase appears close to the pure components, they usually contain pure B or pure A, respectively, instead of the compound. The example in Fig. 7.28b) shows the case where the (solid) compound AB dissolves both A and B to form the $\gamma$ phase. Component A can dissolve some B in the solid phase; thus, we can see a stability range of the $\alpha$ phase. Pure B cannot dissolve A; thus, there is no $\beta$ phase in the diagram; the solidus at the right edge is a vertical line representing pure B only.

Some binary mixtures exhibit partial miscibility not only in the solid but also in the liquid phase. Two types of such phase diagrams are shown in Fig. 7.28c and d, where the liquid separates into two phases below the critical temperature $T_{\text{cr}}$. In the diagram (c), there are only two solids $\alpha$ and $\beta$ that can freeze out from the liquid. In the diagram (d), a third solid $\gamma$ can also solidify from the two immiscible liquids $L_1$ and $L_2$. The $\gamma$ phase consists of the compound $A_2B_3$ and can dissolve some of both pure components.

At point M of diagram (c) a *monotectic reaction*[13] takes place, which can be written in a general form as follows:

$$\text{liquid}_2 \rightleftharpoons \text{solid}_2 + \text{liquid}_1. \tag{7.108}$$

In the diagram shown, $\text{solid}_2$ is the $\beta$ phase and the two liquids are $L_1$ and $L_2$. Upon cooling the liquid $L_2$ at point M, the monotectic reaction yields the $\beta$ phase of composition b and the liquid $L_1$ of composition a, until no $L_2$ remains. Upon further

[13]This word has also been coined by analogy with eutectic. The first part is the Greek adverb *μονο* [mono] which means "only (one)". The second part is the verb *τηκω* = melt. The compound word reflects the fact that one of the two liquids disappears during crystallization, another liquid and one solid survives.

cooling the composition of the liquid $L_1$ shifts along the liquidus curve toward point E, where a eutectic reaction takes place and the composition remains unchanged during solidification. The dashed horizontal line a-M-b at temperature $T_M$ is called the *monotectic line*.

At point S of diagram (d) a *syntectic reaction*[14] takes place, which can be written in a general form as follows:

$$\text{liquid}_1 + \text{liquid}_2 \rightleftharpoons \text{solid}. \tag{7.109}$$

In the diagram, solid$_2$ is the $\gamma$ phase and the two liquids are $L_1$ and $L_2$. Upon cooling, the liquid $L_1$ of composition a and the liquid $L_2$ of composition b yield the solid $\gamma$ phase of composition M at constant temperature $T_S$ until one of the two liquids is entirely transformed. Upon further cooling either $\alpha$ or $\beta$ phase freezes out, depending on the composition of the remaining liquid. During this process, the composition shifts either toward $E_1$ or $E_2$, respectively, where the liquid solidifies in the corresponding eutectic reaction. The dashed horizontal line a−S−b at temperature $T_S$ is called the *syntectic line*.

It is useful to comment on transitions of fixed temperature in the phase diagrams in Fig. 7.28. In the diagram (b), the solid compound AB is formed upon cooling and disintegrates upon heating, while both the solid AB and the liquid mixture are present. The rationale for constant temperature during congruent melting is that both solidus and liquidus have a maximum. The peritectic, monotectic, and syntectic reactions in case of the other three diagrams take place in the presence of three phases. The phase rule for two components in this case prescribes one degree of freedom, thus a unique temperature and composition at constant pressure – similarly to the eutectic reaction. It is worth mentioning that three of these reaction types have their analogues where the solution reaction partner is also a solid, instead of a liquid. These reactions are called *eutectoid, peritectoid,* and *monotectoid*.

There exist more complicated phase diagrams than the above-described types. Though they contain more solid phases, they can be constructed from the elements discussed before. Irrespective of the complexity of a binary solid–liquid phase diagram, its interpretation is relatively simple based on the principles explored in this chapter. We can summarize a few general rules that always apply.

– Starting from a pure component, moving toward the other component along an (horizontal) isotherm, the first phase is a stable one, followed by a no-phase area, then comes a stable phase again, then a no-phase area, etc. If the overall composition lies within the no-phase area, the system separates into the adjacent two stable phases. At the other edge of the diagram, there is also a stable phase. (The stable phase close to the pure component can be a vertical line

[14]This word has also been formed by analogy with eutectic; from the Greek preposition $\sigma\upsilon\nu$ which means "together" and the verb $\tau\eta\kappa\omega$ = melt. The compound word reflects the fact that the two liquid phases crystallize together and yield one solid phase.

corresponding to the pure component only.) The isotherm of a three-phase reaction is an exception from this rule; across the no-phase area, we can find a particular point where a third (stable) phase is also present.
- According to the phase rule, at the overall composition within a no-phase area, the maximum number of phases is three. Consequently, at any (overall) composition, the number of phases can be 1, 2, or 3. If we cross a curve delimiting the stability range of a phase (even if diagonally) in the phase diagram, the number of phases in equilibrium always changes by one. (It can increase or decrease by one.)
- The number of solidus–liquidus pairs (connected directly by isotherms as tie lines or conodes) equals the number of solid phases that can freeze out from the liquid mixture.
- Above the liquidus curve there is always a stable phase: the liquid mixture.
- Below the solidus curve there is always a stable phase: the solid solution.
- Below the eutectical line there is always a heterogeneous mixture of solid phases.
- Above the monotectical line there is always a no-phase area according to the equilibrium of two liquid phases.
- Above the peritectical line there is always a no-phase area according to the equilibrium of a liquid and a solid phase.

### 7.6.3 *Colligative Properties: Equilibrium of a Binary Mixture Phase and a Pure Phase Containing One of the Mixture Components*

There is a special type of phase equilibria where a binary mixture is in equilibrium with one of its pure components. If the mixture phase behaves ideally to a good approximation, a number of thermodynamic properties can be characterized in a similar way. This is the reason they are called *colligative properties*.[15] Prior to the thermodynamic characterization, let us overview these systems and their relevant properties. In the first column of Table 7.1, we can find the two phases in equilibrium, while the second column contains the property modified in the mixture phase with respect to the pure component.

It can be seen from the table that the boiling point of the liquid mixture is higher than that of the pure liquid, if the other component dissolved in the pure liquid does not evaporate; i.e., it is not present in the vapor phase. At the same time, the vapor pressure of the mixture also decreases relative to that of the pure liquid. The freezing point of the mixture phase is also lowered relative to the freezing point

[15]The word *colligative* originates from the Latin verb *colligo*, meaning to bind or fasten together. As the word has a figurative sense of "united in a class", it refers to the fact that the thermodynamic description of these properties is closely related; namely these properties depend on the molar concentration of the solute, irrespective of its chemical nature.

**Table 7.1** Different cases of equilibria of a mixture phase and a pure phase

| Phases in equilibrium | Property due to the equilibrium |
|---|---|
| Liquid mixture–pure vapor | Elevation of the boiling point; decrease of the vapor pressure |
| Solid mixture–pure vapor | Elevation of the sublimation point; decrease of the vapor pressure |
| Liquid mixture–pure solid | Depression of the freezing point |
| Liquid mixture–pure liquid (solvent) | Osmosis |
| Vapor mixture–pure vapor | Porous diffusion |

of the pure liquid. The vapor pressure of a solid mixture is also lower if only one of the components evaporates from the mixture, and its sublimation point will be elevated. The last two rows of the table refer to equilibria across *semipermeable* membranes. If two liquid phases are separated by a membrane through which only one of the components is able to diffuse but the other not, we speak of *osmosis*. If the two phases are gases, the phenomenon is called *porous diffusion*.

Even in the absence of a semipermeable membrane, other cases shown in the table also refer to equilibria where only one of the two components can freely move between the two phases. Consequently, the equilibrium condition is the same as already stated in Sect. 3.3; the freely moving component should have the same chemical potential in equilibrium in both phases. By supposing that component A is present in both phases, the general equation describing colligative properties can be written as follows:

$$\mu^*_{\mathrm{A,pure}}(T,P) = \mu_{\mathrm{A,mixture}}(T,P,x_{\mathrm{A}}). \tag{7.110}$$

Let us recall that two cases included in the table – the decrease of the vapor pressure and the depression of the freezing point – are already discussed in previous sections. To calculate the decrease of the vapor pressure, in analogy of (7.51), we can start with the equilibrium condition

$$\mu^*_{\mathrm{A,vapor}}(T,p^*) + RT\ln\frac{p_{\mathrm{A}}}{p*} = \mu^*_{\mathrm{A,liquid}}(T,p^*) + RT\ln x_{\mathrm{A}}, \tag{7.111}$$

where $p^*$ is the equilibrium vapor pressure of the pure liquid at temperature $T$. We can write a similar equation for the equilibrium of the pure liquid and its vapor:

$$\mu^*_{\mathrm{A,vapor}}(T,p^*) = \mu^*_{\mathrm{A,liquid}}(T,p^*). \tag{7.112}$$

By subtracting this from the previous equation, we get the vapor pressure of pure component A in equilibrium with the liquid mixture of composition $x_{\mathrm{A}}$:

$$p_{\mathrm{A}} = x_{\mathrm{A}}p^*. \tag{7.113}$$

As expected, the result is the same as Raoult's Law stated in (7.54); this is also the partial pressure of component A in the vapor. The only difference is that, in this case, $p_A$ is also the total pressure of the liquid, as the other component does not evaporate.

The depression of the freezing point can also be calculated from the previously used condition of (7.86). The resulting (7.92) has been used to calculate the composition at the freezing point of the liquid; now we want to calculate the freezing point from the known composition. To do this, let us rewrite (7.92):

$$\frac{1}{T^*_{\mathrm{fus,A}}} - \frac{1}{T} = -\frac{R}{\Delta_{\mathrm{fus}} h^*_{\mathrm{A}}} \ln x_{\mathrm{A}}. \tag{7.114}$$

In addition to the approximations used to get this equation (the dependence on temperature of $\Delta_{\mathrm{fus}} h^*_{\mathrm{A}}$ is negligible between the melting point $T^*_{\mathrm{fus,A}}$ of pure component A and that of the mixture, $T$), let us suppose that the concentration $x_{\mathrm{A}}$ is close to unity. This enables us to approximate the logarithm of the concentration expressed with the other component's mole fraction, $1 - x_{\mathrm{B}}$ by the first-order term of its power series:

$$\ln x_{\mathrm{A}} = \ln(1 - x_{\mathrm{B}}) \cong -x_{\mathrm{B}}. \tag{7.115}$$

The difference of the inverse temperatures can be approximated on the same basis; if $x_{\mathrm{A}}$ is close to unity, then the difference of the inverse of $T^*_{\mathrm{fus,A}}$ and $T$ is close to zero, and the product of $T^*_{\mathrm{fus,A}}$ and $T$ in the denominator can be replaced by $T^*_{\mathrm{fus,A}}$ squared:

$$\frac{1}{T^*_{\mathrm{fus,A}}} - \frac{1}{T} = \frac{T - T^*_{\mathrm{fus,A}}}{T\, T^*_{\mathrm{fus,A}}} \approx \frac{T - T^*_{\mathrm{fus,A}}}{\left(T^*_{\mathrm{fus,A}}\right)^2}. \tag{7.116}$$

Let us write the depression of the freezing (melting) point as $\Delta_{\mathrm{fus}} T = T^*_{\mathrm{fusA}} - T$. Using the two additional approximations, we can rewrite (7.114) as

$$\Delta_{\mathrm{fus}} T = \frac{R \left(T^*_{\mathrm{fus,A}}\right)^2}{\Delta_{\mathrm{fus}} h^*_{\mathrm{A}}} x_{\mathrm{B}}. \tag{7.117}$$

The depression of the freezing point expressed this way was used to determine the molar mass of a new compound until the mid-twentieth century. In order to use the above equation for this purpose, we can transform it into a more "user-friendly" form using molality instead of mole fraction. To do this, let us use another approximation; when calculating the mole fraction, let us neglect the amount of $n_{\mathrm{B}}$ in the denominator based on the fact that it is much less than $n_{\mathrm{A}}$:

$$x_{\mathrm{B}} = \frac{n_{\mathrm{B}}}{n_{\mathrm{A}} + n_{\mathrm{B}}} \approx \frac{n_{\mathrm{B}}}{n_{\mathrm{A}}}. \tag{7.118}$$

This approximation is equivalent to the supposition that $x_B$ moles of component B are dissolved in 1 mol of component A, which in turn is equivalent to $m_B = x_B/M_A$ moles of B dissolved in 1 kg of A. ($M_A$ is the molar mass of the solvent A, while $m_B$ is the molality of the solute B.) Thus, let us write $x_B = m_B/M_A$ into the expression of the freezing point depression, and let us use a simplified notation:

$$\Delta_{\text{fus}} T = \frac{R\,(T_o^*)^2 M_o}{\Delta_{\text{fus}} h_o^*} m. \tag{7.119}$$

In this expression, the subscript o refers to the (pure) solvent and $\Delta_{\text{fus}}T$ is proportional to the molality $m$ of the solvent. According to this "user-friendly" formula, we measure a given mass of an unknown substance in 1 kg of solvent, and we can get the result from measuring the depression of the freezing point of this solution that this mass is $m$ moles. The molar mass of the unknown substance can readily be calculated from these results.

We can again see from the above expression that the depression of the freezing point does *not* depend on the nature of the *dissolved component* but is simply proportional to its molality. It is also clear that the proportionality coefficient depends on the nature of the *solvent*; on its enthalpy of fusion, molar mass, and melting point. This is in accordance with the statement of the depression of freezing point of components immiscible in the solid phase already given in Sect. 7.6.2.; in an ideal mixture, the freezing point of the mixture *does not depend* on any specific data of the solute, only on its concentration.

It will turn out that all the colligative properties depend only on the nature of the solvent and not on that of the solute. A common textbook error is to say that they depend on the *quantity* of the solute, but this is not correct, as if the "quantity" of the solute (i.e., its concentration) changes, the concentration of the solvent also changes. The correct statement is that *colligative properties depend on the nature and concentration of the solvent only*, but do not depend on the nature of the solute.

The equilibrium resulting in the elevation of the boiling point can be treated similarly as the case of the freezing-point depression. The condition of equilibrium between the corresponding phases is

$$\mu_{\text{A},\,g}^*(T) = \mu_{\text{A},l}(T, x_A) = \mu_{\text{A},l}^*(T) + RT \ln x_A. \tag{7.120}$$

Similarly to (7.87), this can also be written as

$$\ln x_A = \frac{\mu_{\text{A},g}^*(T) - \mu_{\text{A},l}^*(T)}{RT} = -\frac{\Delta_{\text{vap}}\, g_A^*(T)}{RT} \tag{7.121}$$

and further rewritten, in analogy to (7.92), as follows:

$$\left(\frac{1}{T_{\text{boil, A}}^*} - \frac{1}{T}\right) = -\frac{R}{\Delta_{\text{vap}}\, h_A^*} \ln x_A. \tag{7.122}$$

By applying similar approximations as for the calculation of the freezing-point depression (the dependence on temperature of $\Delta_{vap} h^*_A$ is negligible between the boiling point $T^*_{boil,A}$ of pure component A and that of the mixture, $T$; the concentration $x_A$ is large enough to approximate the logarithm of $1 - x_B$ by the first-order term of its power series, $-x_B$; and $T^*_{boil,A}$ and $T$ are only negligibly different to replace $T^*_{boil,A} T$ by $(T^*_{boil,A})^2$), the elevation of the boiling point is given by

$$\Delta_{boil} T = \frac{R\,(T^*_{boil,A})^2}{\Delta_{vap} h^*_A} x_B. \tag{7.123}$$

This expression can also be transformed into a "user friendly" form to calculate the molar mass of an unknown substance from the elevation of the boiling point. Based on the low value of $x_B$ (close to zero), using the approximation of (7.118) we get

$$\Delta_{boil} T = \frac{R\,(T^*_o)^2 M_o}{\Delta_{vap} h^*_o} m. \tag{7.124}$$

The subscript o refers to the (pure) solvent with its boiling point $T^*_o$ and $\Delta_{vap}\ T$ is proportional to the molality $m$ of the solvent.

By comparing the above equation with (7.119), we can see that, in addition to a very similar thermodynamic description, final results for the depression of the freezing point and for the elevation of the boiling point are very much similar. The coefficients of the molality $m_B$ in both formulae depend only on the properties of the solvent; thus, we can find them for many solvents in thermodynamic tables. They also have distinct names; $\frac{R\,(T^*_o)^2 M_o}{\Delta_{fus} h^*_o}$ is called the *cryoscopic constant*[16] and $\frac{R\,(T^*_o)^2 M_o}{\Delta_{vap} h^*_o}$ is called the *ebullioscopic constant*.[17]

For the elevation of sublimation point, we can get a formally equivalent relation as for the elevation of boiling point; the two equilibria differ only in the physical state of the mixture, which is solid in case of sublimation. Consequently, the emerging formula contains data related to sublimation instead of evaporation. The elevation of sublimation point is less important in practice than other equilibria considered before.

All the approximations applied deriving the previous results are justified if the concentration of the solution does not exceed about 0.01 mol/dm$^3$. In this case, the use of only the first term in the series of the logarithm, and the simplification of the calculation of mol fraction do not result in a significant error; the

[16]The word was coined from the Greek noun $\kappa\rho\upsilon o\varsigma$ = freeze and the verb $\sigma\kappa\omega\pi\varepsilon\omega$ = look or investigate. Accordingly, *cryoscope* is the apparatus to measure the freezing point and *cryoscopic constant* gives the depression of freezing point relative to unit molality.

[17]The word *ebullioscope* was coined in analogy of cryoscope from the Latin verb *ebullire* = boil, a derivative of the noun *bulla* = bubble. It is the apparatus to measure the boiling point. Similarly, *ebullioscopic constant* gives the elevation of boiling point relative to unit molality.

equilibrium temperature difference is also small enough to use the square of the respective equilibrium temperature for the pure component, and the temperature dependence of the transition enthalpies can also be neglected. All calculations can, of course, be performed without any approximations using actual activities instead of the mole fraction $x_A$, taking into account the temperature dependence of transition enthalpies and avoiding approximations used to calculate the logarithm and the molar concentration.

Besides the ancient method to determine the molar mass of unknown substances, there are a number of practical applications related to colligative properties. On preparing dishes, we often boil food in water to make it easily digestible but also more valuable from a gastronomic point of view. Salting the water not only improves taste but increases the boiling point, thus shortening cooking time. Spreading salt in snowy roads decreases the melting point, thus eliminating freezing. However, it has a side effect in addition to pollution and corrosion; by decreasing the vapor pressure, drying of the road is slowed down; thus, the road remains moist longer than without salt. (Snow removal is more efficient.)

Osmosis[18] also has plenty of practical applications, but let us first discuss its thermodynamics. It is an equilibrium between two liquid phases separated by a semipermeable membrane through which only one of the components – the solvent – is able to diffuse but the other – the solute – not. If the container of the mixture and the membrane is not flexible, the solvent will diffuse into the mixture across the membrane until the elevation of the pressure renders the chemical potential of the solvent in the mixture equal to that of the pure solvent. (A flexible membrane would be deformed until all of the pure solvent would diffuse into the mixture.) The condition of equilibrium is the equality of the chemical potential of the solvent across the membrane, achieved by the extra pressure $\pi$ due to the osmosis:

$$\mu_o^*(T, P) = \mu_o(T, P + \pi, x_o) = \mu_o^*(T, P + \pi) + RT \ln x_o. \tag{7.125}$$

Let us write the pressure dependence of $\mu_o^*$, the chemical potential of the pure solvent, explicitly into the equation. This can be done using (6.13), which can be written at constant temperature as follows:

$$\mathrm{d}\mu_o^*(T) = V_o^* \, \mathrm{d}P. \tag{7.126}$$

Accordingly, the pressure dependence can be calculated by the integral

$$\mu_o^*(T, P + \pi) = \mu_o^*(T, P) + \int_P^{P+\pi} V_o^* \mathrm{d}p. \tag{7.127}$$

[18]The Greek noun $\omega\sigma\mu o\varsigma$ = thrust is a derivative of the verb $\omega\theta\varepsilon\omega$ = push. It refers to the inreased tension of the mixture as a consequence of diffusion across the semipermeable membrane.

Supposing $V_o^*$ – the molar volume of the pure solvent – to be independent of pressure between $P$ and $P + \pi$, the result of the integration is $\pi V_o^*$ and (7.125) can be written as

$$-RT \ln x_o = \pi V_o^*. \tag{7.128}$$

We could already express the *osmotic pressure* $\pi$ from the above equation, but we can also apply approximations used to describe other colligative properties. Supposing that the mole fraction $x$ of the solvent is small enough to approximate the logarithm $\ln x_o = \ln (1 - x)$ with the first term of the power series $-x$, we can write:

$$\pi \cong \frac{RT}{V_o^*} x. \tag{7.129}$$

We can also approximate the mole fraction $x = n/(n + n_o)$ by the ratio $n/n_o$, and the molar volume $V_o^*$ by the ratio $V/n_o$. $V$ is the volume of the *solvent*, but it is not much different from the volume of the *solution*. As a result, we get

$$\pi \cong \frac{nRT}{V} = cRT. \tag{7.130}$$

Within the approximations used, the osmotic pressure can be considered to be proportional to the molarity $c$ of the solvent. The left-side equality is called the *van't Hoff equation*. It suggests that the solute in an ideal mixture behaves as if it were an ideal gas filling in the volume of the solution.

It is worth recalling that the approximations leading to this simple formula are valid to a reasonable precision if the concentration is below of about 0.01 mol/dm$^3$. In this case, the use of only the first term in the series of the logarithm and the simplification of the calculation of the mole fraction do not result in a significant error, the solution behaves nearly ideally, and the pressure dependence of the molar volume can also be neglected when performing the integration. Of course, the calculations can be performed without any approximations using actual activities instead of the mole fraction $x$, taking into account the pressure dependence of the molar volume (using compressibility data) and avoiding approximations used to calculate the logarithm and the molar concentration. Thus, it is also feasible to calculate the osmotic pressure of highly concentrated solutions. Osmotic pressure measurements compared to calculations for an ideal mixture can be used to determine deviations from the ideal behavior, which enables to calculate activity coefficients. The corresponding apparatus is called an *osmometer*.

Results obtained above for one single solute in an ideal solution are valid also for multiple solute components if they cannot diffuse across the membrane, as colligative properties depend only on the *concentration* of the solute, not on its chemical nature. Thus, using the *total mole fraction* of the solutes in a multicomponent system, the osmotic pressure with the ideal approximation can be calculated.

Osmotic pressure plays a major role in cell viability. Cells in an aqueous environment having smaller molar concentration of solutes than the liquid inside the cell (this is called a *hypotonic* solution) are swelled due to osmosis, or they can eventually burst. In a *hypertonic* solution – having higher molar concentration of the solutes than the medium inside the cell – cells shrink and become wrinkled due to the outward diffusion of water. The same phenomenon can be observed in case of macroscopic membranes in living organisms. Fruits conserved in hypertonic sugar solutions become raisined. Contrarily, if the sugar solution is hypotonic, fruits swell and eventually burst. Conservation in sugar solution is also due to osmosis; cells of bacteria and fungi get "dryed out" in the concentrated solution and they die. Cell membranes are semipermeable not only for water but for a number of other compounds, depending on the cell. Regulation of the membrane permeability is an important means of normal physiological functionality of the cell. Coming back to cooking; it is useful to boil food in salted water also in order to avoid leaking out of minerals, thus retaining more natural taste of vegetables and meat. (Salt can also diffuse into the boiled food if membranes allow this transport.)

The above-described natural direction of osmosis can also be reversed; applying a greater pressure on the solution than the equilibrium osmotic pressure, the chemical potential of the solvent becomes greater than in the pure solvent. As a consequence, the solution becomes more concentrated and pure solvent diffuses across the membrane. This is called *reverse osmosis* and can be used, e.g,. to concentrate fruit juices without heating them or for desalinating seawater to get drinking water.

Porous diffusion does not have an important practical impact. Pressure differences occurring between a gas mixture and a pure gas across a membrane can be calculated similarly as in the case of osmosis.

## 7.7 Phase Diagrams of Multicomponent Systems

The phase diagram of a single component containing most information is a three-dimensional $P$–$V$–$T$ surface. Usual phase diagrams are two-dimensional projections of this surface; most of the time into the $P$–$T$ plane (cf. Figs. 7.4 and 7.6). In case of a binary system, this reduced $P$–$T$ plot is no more suitable to display the stability areas in two dimensions, as there is a third variable: composition. Accordingly, binary phase diagrams discussed in Sects. 7.3–7.6 are sections of a three-dimensional surface; either $P$–$x$ diagrams at constant temperature or $T$–$x$ diagrams at constant pressure. In case of three components (in a *ternary* mixture), even the composition cannot be displayed on a single axis. There is a possibility to maintain the concentration of one of the components constant, which enables to scale an axis with one of the remaining concentrations which also determines the third concentration. The resulting phase diagram is similar to a binary phase diagram, but only at one single value of the third component's concentration. A more common practice is to plot the concentrations of all the three components in a plane. There are several

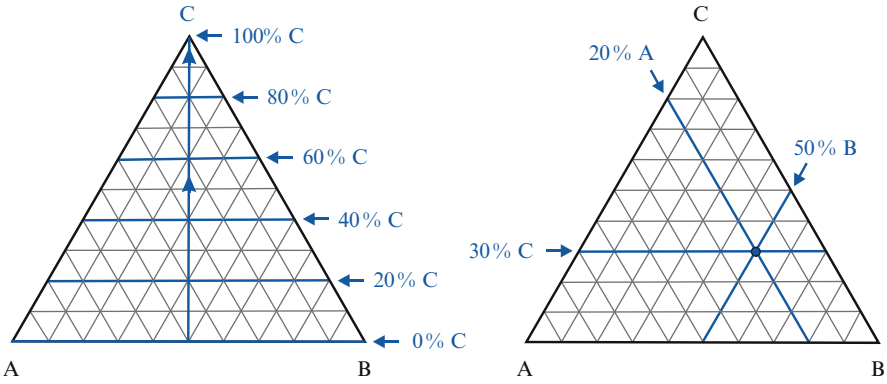



**Fig. 7.29** Composition of three-component systems in an equilateral triangular diagram. The concentration scale of component C is shown in the left diagram. *Arrowheads* along the altitude of the triangle show the direction of increasing concentrations. A mixture containing 20% of A, 50% of B, and 30% of C is shown as a dot at the intersection of scaling lines in the right diagram

possibilities to do this, of which the most frequent is an equilateral triangle in which each apex represents a pure component. Figure 7.29 illustrates this kind of plot.

At the left-hand side, the concentration scale of component C is shown. The apex labeled C corresponds to 100% of C, i.e., it is pure component C. Points on the edge opposite to C contain 0% of C; here we find binary mixtures containing A and B only. The concentration of C increases linearly along the altitude connecting the base AB with the apex C. (Arrow heads along the altitude indicate the direction of increasing concentrations.) Note that the concentration scale can also be associated with the edges adjacent to the apex C, i.e., to AC and BC. Actual values are at the intersection of the lines parallel to the base AB with the respective edges. (The scale is indicated along the edge BC.) We can similarly interpret the concentration of the other two components by rotating the altitude and the lines perpendicular to it. This is the reason to use the equilateral triangle instead, e.g., a right-angled isosceles triangle; concentrations of all the three components are equivalently treated.

To construct a constant-pressure ternary $T$–$x$ phase diagram, we can use a uniform triangular prism where the vertical axis perpendicular to the base equilateral triangle is the temperature. Figure 7.30 shows the liquid–vapor phase diagram of an ideal ternary mixture in this coordinate system. The complete tridimensional $T$–$x$ diagram can be seen in panel (a) along with a constant temperature plane and the projection of the section by this plane to the base of the prism. The projection of this constant temperature section is depicted separately in an equilateral triangular diagram (same as the base of the prism) in panel (b).

Inspecting the tridimensional diagram we can find on both sides above AB and BC – representing the corresponding binary mixtures – the well-known boiling point curve and dew point curve characteristic of ideal binary mixtures, similar to the system shown in Fig. 7.13. (Were it not hidden, we could see the same curves above AC as well.) Along the edges of the prism, boiling points of the three pure

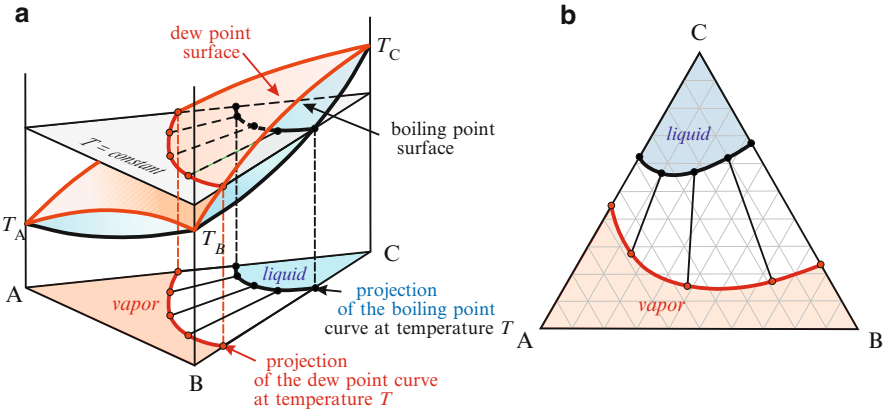



**Fig. 7.30** Phase diagram showing liquid–vapor equilibrium in the ternary system of components A, B, and C. (**a**) Composition is given in an equilateral triangle; temperature scale is along the vertical axis. The upper (concave) surface shows the equilibrium temperature as a function of the vapor composition, and the lower (convex) surface as a function of the vapor composition. The section made by a plane of constant temperature is projected onto the base of the diagram. (**b**) Plot of the constant temperature section in a triangular diagram. The lower shadowed area is the stability range of the vapor phase; the upper one is that of the liquid phase. The white region between them is a no-phase area. A few conodes (or tie lines) connecting the compositions of phases in equilibrium are shown in both diagrams (**a**) and (**b**)

components ($T_A$, $T_B$ and $T_C$) are marked. The *boiling point surface* is the lower (convex) surface spanned by the binary boiling pint curves on the faces. Similarly, the upper (concave) *dew point surface* is spanned by the binary dew point curves found on the vertical faces. In between these two surfaces, there is a no-phase area. Below the boiling point surface, liquid mixtures are stable; above the dew point surface, vapor mixtures are stable. If we are only interested in constant temperature equilibria, sections similar to the one shown in panel (b) are enough to know, which are easy to draw in two dimensions.

The same principles can be used to construct a phase diagram of partially miscible ternary liquids. In Fig. 7.31, two pairs of components (A and C, B and C) are completely miscible, while the pair A and B is only partially miscible. The concave surface in diagram (a) shows the equilibrium temperature as a function of composition. Homogeneous liquid mixtures are outside of the surface, while the inside is a no-phase area. Diagram (b) is a section at constant temperature, where a few points indicating the equilibrium concentrations of separated A-rich and B-rich mixtures (small circles) are interconnected by conodes (or tie lines). The continuous solid line is the locus of these equilibrium concentration *node pairs*, whence it is called a *binodal curve*. In case of an overall composition lying within the binodal curve, the mixture separates into an A-rich and a B-rich phase.

Figure 7.32 shows a ternary solid–liquid $T$–$x$ phase diagram with the three components forming eutectics pairwise, and partially mixing also in the solid phase. On the front face of the triangular prism, we can recognize the binary

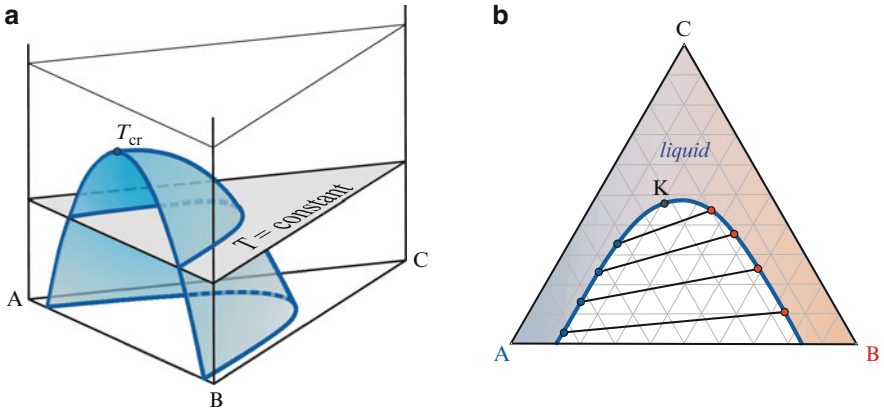



**Fig. 7.31** Phase diagram of a ternary liquid with partial miscibility of components A and B, and complete miscibility of the other two pairs of components. (**a**) Composition is given in an equilateral triangle; temperature scale is along the vertical axis. The concave surface shows the equilibrium temperature of the separated phases as a function of composition. Homogeneous liquid mixtures are outside of the surface, while the inside is a no-phase area. The three components are completely miscible above the critical temperature $T_{cr}$. A constant temperature plain is also shown. (**b**) A constant temperature section shown in a triangular diagram. The upper shaded area is the stability range of the liquid phase; the white one is the no-phase area; point K is the critical composition (cf. Fig. 7.22). Below the critical composition, there is a phase separation. A few conodes (or tie lines) connecting the compositions of liquid phases in equilibrium are also shown. (For the sake of clarity, there are no conodes shown in the tridimensional diagram)

phase diagram A–B similar to the tin–lead mixture. The other two faces are also alike. The three "lobes" of the tridimensional *liquidus surface* (or freezing point surface) is spanned by the binary systems' liquidus curves. As the three components mutually dissolve each other partially, we find stability ranges of solid solutions along the lateral edges of the prism. The limiting surfaces of these ranges are the *solidus surfaces* (or melting point surfaces) at temperatures where the solid is in equilibrium with a liquid mixture. At lower temperatures (below the freezing point) solid phases are in equilibrium with each other lying on the limiting surfaces, which are called *solvus surfaces*.

We can find ternary eutectics along the short-dashed curves at the intersection of the liquidus "lobes," starting from the eutectic points of the binary mixtures on the three lateral faces of the prism, and joining in a single point in the middle of the diagram. At this point, there are four phases in equilibrium: liquid mixture, and the solid solutions $\alpha$, $\beta$, and $\gamma$. According to the phase rule, the residual number of degrees of freedom at constant pressure is zero here; thus, this point occurs at a unique temperature and composition.

In the triangular diagram (b), we can see the section at the constant temperature indicated by the horizontal plane in the tridimensional diagram (a). This section is a convenient means to show the stability range of different phases at a given temperature. Solid phases are delimited by the solidus curves and the liquid phase by the

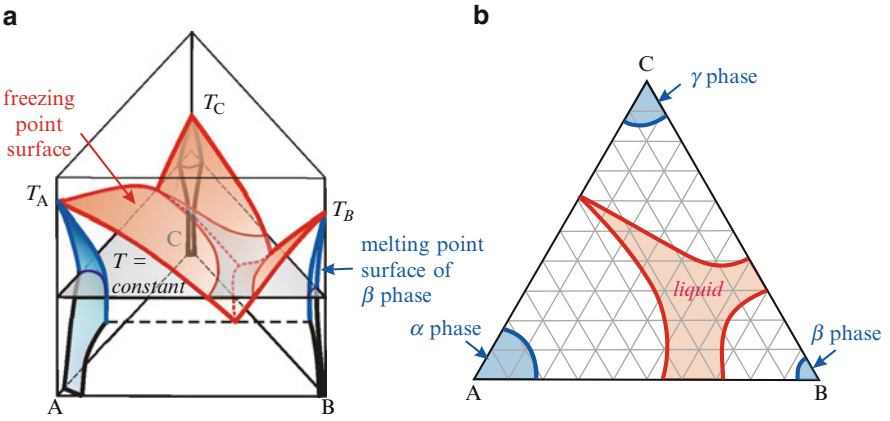



**Fig. 7.32** Phase diagram of a ternary system with components of unlimited miscibility in the liquid phase and partial miscibility in the solid phase, forming ternary eutectics. (**a**) Composition is given in an equilateral triangle; temperature scale is along the vertical axis. The contiguous surface on top is the freezing point of liquid mixtures, i.e., the solid–liquid equilibrium temperature as a function of liquid composition. Surfaces close to the lateral edges below show the melting point of the corresponding solid phases above the eutectical surface, i.e., the solid–liquid equilibrium temperature as a function of solid composition. Below the eutectical surface, they mark the boundaries of stability of the solid phases. (**b**) Plot of the constant temperature section shown in panel (**a**) in a triangular diagram. Shaded areas in the corners show the stability ranges of the solid phases, while that of the liquid phase is the central shaded area. White surfaces in between are no-phase areas

liquidus curves. Between these two curves, there is a no-phase area. Similar sections are useful to characterize the ternary phase equilibrium at constant temperatures.

If we are interested in changes of the stability regions as a function of temperature, projections of the tridimensional surfaces into a triangular diagram can be constructed instead of sections. As an example, the projection of the liquidus surface of the phase diagram in Fig. 7.32a) is shown in Fig. 7.33b). Panel (a) in this figure also shows the tridimensional phase diagram along with seven curves resulting from the intersections of seven planes at different constant temperatures. The projection of these curves onto the base triangle of the prism yields the triangular diagram of panel (b).

Contour lines represent decreasing equal temperatures of freezing points from the apexes inward. We can readily follow the change of composition of the two-phase eutectics, denoted by the dashed curves (which are not equitemperature curves). These start from the eutectical points of binary mixtures $E_{AB}$, $E_{AC}$, and $E_{BC}$ found at the edges of the triangle, and join at the composition of the three-phase eutectic $E_3$. This point is unique (invariant); i.e., it has zero degrees of freedom. Similar projections of the solidus surfaces can also be constructed where we can follow the change of melting points with composition.

In case of more than three components, the visualization of a phase diagram is not an easy task. The four-component equivalent of tracing the three-component

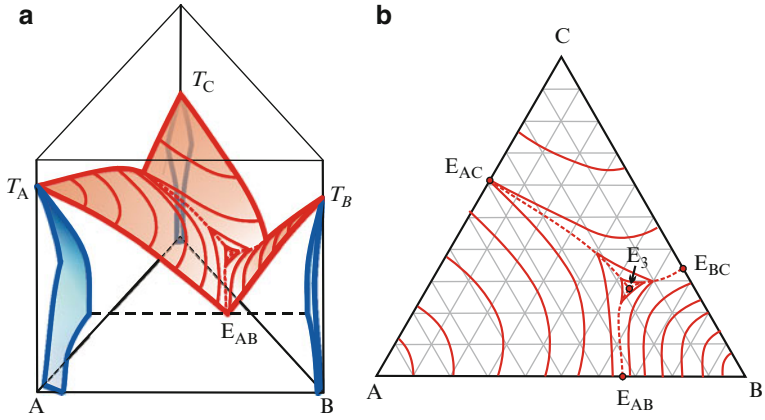



**Fig. 7.33** (**a**) Phase diagram of a ternary system with components of unlimited miscibility in the liquid phase and partial miscibility in the solid phase, forming ternary eutectics. The contiguous surface on top is the freezing point of liquid mixtures, i.e., the solid–liquid equilibrium temperature as a function of liquid composition. (**b**) The projection of this surface shown as equitemperature lines (same as in the tridimensional plot) in a triangular diagram. Eutectical points of binary mixtures $E_{AB}$, $E_{AC}$ and $E_{BC}$ are found at the edges of the triangle. Dashed curves show the composition according to two-phase ternary eutectics, which join at the composition of the three-phase eutectic $E_3$

composition in a triangle diagram was a tetrahedron diagram. Its apexes were the pure components, while the concentration would change linearly along the heights of the tetrahedron. However, to show equilibrium temperatures (or pressures) would need a fourth dimension which is almost impossible to trace. The projection of the phase boundaries into the tetrahedron is also hopeless to show. A usual practice is, therefore, to keep the concentration of all the components but two constant, thus showing a "quasi-two-component" phase diagram, or to keep the concentration of all the components but three constant, thus showing a "quasi-three-component" phase diagram. These are in fact sections of multicomponent phase diagrams. If a practical usage of some kind of – usually two-dimensional – projections of the multidimensional surface is useful, then these projections are shown. Many multicomponent phase diagrams in the field of mineralogy or metallurgy are traced this way.

## 7.8 Separation of Components Based on Different Phase Diagrams

Separation of mixtures is a common task in the laboratory as well as in the chemical industry. To accomplish this task, the knowledge of phase equilibria is often useful. We will consider some examples for the separation of mixtures using the information offered by different phase diagrams.

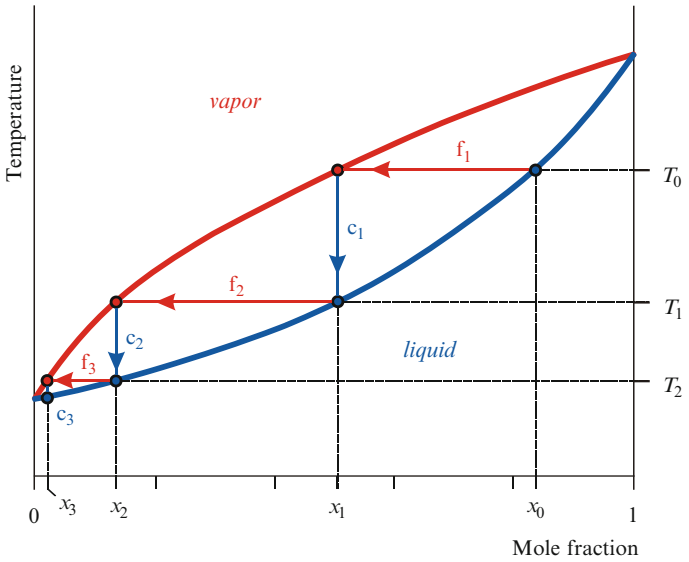



**Fig. 7.34** Distillation of a nearly ideal binary mixture illustrated in a $T - x$ phase diagram

A frequently used separation method is *distillation*.[19] This works best in case of an ideal (or nearly ideal) binary mixture, the vapor–liquid phase diagram of which is similar to that of Fig. 7.13. The separation of such a mixture using *fractional distillation* can be followed considering Fig. 7.34. When the liquid mixture of composition $x_0$ is heated to its boiling point $T_0$, the composition of the emerging vapor mixture $x_1$ is obtained along the tie line $f_1$ on the dew point curve. By condensation of this vapor, we get a liquid of the same composition along the vertical line $k_1$. Boiling of this liquid (at temperature $T_1$) leads to the emergence of a vapor mixture of composition $x_2$ along the tie line $f_2$. By condensation of this vapor, we get the liquid mixture of the same composition along the line $k_2$. Boiling this liquid and condensating its vapor (along tie line $f_3$ and vertical line $k_3$ – this latter hardly visible in the diagram) we get a liquid of composition $x_3$. As we can read off from the diagram, the concentration of the more volatile (that with the lower boiling point) component $1 - x_0$ is 16% before the first boiling, and it increases to 50% after the first, 86% after the second, and 98% after the third boiling and condensation. We can readily conclude that after a few further boiling and condensation cycles – the traces would not be visible on the figure anymore – we could get the more volatile component as pure as desired.

A crucial point of the above-described separation procedure is that the vapor condensed always has the equilibrium composition at the boiling point. This can be maintained if we condense only a tiny amount of the vapor – as the concentration of

[19]The English version of the Latin word *destillation*, which can be derived from the Latin noun *stilla* = drop, by adding the prefix *de-* = down from (something); meaning "dropping down".

the more volatile component in the vapor would decrease on further boiling. One possibility for an efficient separation would be a simple *multistage distillation* when only a small amount were boiled and condensed in the first step, then new distillations were performed in a similar manner until the desired purity would be achieved – in very little quantity. However, there is a more effective method; *fractional distillation*, usually called *rectification*.[20] This can be achieved in a distillation column by the interchange of matter between rising vapor and falling liquid, in a *countercurrent* process.

The first industrial columns contained *plates* or *trays* arranged vertically, each of them serving as a distillation step in a multistage process. Vapor arising from the boiler of temperature $T_0$ at the bottom of the column arrives through a tube covered by a *bubble cap* or *bubble valve* above the first plate and condenses. Condensation keeps the temperature at the dew point $T_1$ of the vapor, while the released condensation heat keeps the condensed liquid boiling. The emerging vapor passes (through the tube and bubble cap or bubble valve above the first plate) to the second plate, where it condenses at its dew point $T_2$. Excess liquid from the first plate flows back to the boiler through an overflow tube, ending below the liquid level to avoid the passage of vapor. Similarly, emerging vapor from the second plate passes to the third plate and condenses at temperature $T_3$, while excess liquid flows down to the first plate. The process continues in every plate further upwards, and the evaporating liquid in the boiler is continuously filled up. As a result, the liquid in the boiler has a steady-state composition $x_0$ and boils at temperature $T_0$. Composition in the first plate is $x_1$ and the temperature is $T_1$; in the second plate, it is $x_2$ and $T_2$, etc. Thus, a rectifying column hosts one boiling-condensation step of Fig. 7.34 in each plate – if equilibrium is maintained, which occurs if the feeding rate of the liquid into the boiler is low. As a result, we get an enriched mixture in the more volatile component, equivalent to the product of a multistage distillation described above. If equilibrium is maintained throughout the column, the result is the same as if we made a fractional distillation of as many stages as the number of plates. Accordingly, the efficiency of a rectifying column can be characterized by the number of plates.

As the enriched mixture is continuously removed at the top of the column, a continuous feed of the liquid to be separated is also necessary. To maintain the equilibrium concentration and temperature at the plates, the flow rate within the column should be greater than the rate of feed and removal. To this purpose, the condensed liquid at the top of the column (distillate or top product) is not completely removed; part of it is reintroduced into the top plate. This part is called the *reflux*. Some part of the liquid from the boiler should also be removed; this is called the *bottom product*, which is enriched in the less volatile component. If the purpose of rectification is only the separation of the pure more volatile product, fresh mixture is feeded into a lower plate near the boiler. If the less volatile component is also needed, feed is introduced near the middle of the column.

[20]Rectification is derived from the Latin adjective *rectus* = right, or simple. It refers to the isolation of the simple ("right") material from the composite mixture.

Equilibrium within the plates below the feed occur at compositions and temperatures which can be traced as perpendicular lines between the boiling point and dew point curves on the right of the phase diagram, toward increasing temperatures. This downward flow of the liquid results in gradual enrichment from plate to plate of the less volatile component.

The construction of valves and overflow tubes is rather expensive and their setup cannot be changed. A widely used alternative is a *packed column*: a hollow pipe filled with large-surface packing. The packing can consist of small pieces of tubes, beads, rings, or other objects that provide a great surface for liquid–vapor contact and control the flux of downstream liquid and upstream vapor so that a near-equilibrium state is achieved throughout the column at the actual top product and bottom product removal rate. The separation efficiency of a packed column is given as the *number of theoretical plates*, referring to an equivalent traditional column with the same number of discrete stages. The efficiency of the packing is determined as the *height equivalent to one theoretical plate* (HETP) which is the packing height equivalent to a theoretical equilibrium stage – a horizontal and a subsequent vertical line in Fig. 7.34. (Smaller HETP means greater separation efficiency.)

It is clear from Fig. 7.34 and the above discussion that the vapor is always enriched in the *more volatile* component; thus, separation by distillation is limited in case of azeotropes. Components of a maximum-boiling azeotrope can be completely separated by distillation, while in case of a minimum-boiling azeotrope; only the azeotrope mixture having the minimal boiling point can be separated. In either case, mixtures having exactly the azeotrope composition cannot be separated at all by distillation. (A common example is a 96 volume % ethanol–water mixture having a minimal boiling point of 78.15 °C.) One possibility to separate binary azeotropes is to prepare a ternary azeotrope in which the azeotrope concentration of the component to be enriched is higher than in the binary azeotrope. For example, rectification of the ternary azeotrope benzene–ethanol–water leads to almost pure ethanol. As the azeotrope concentration is pressure-dependent, a rectified azeotrope distilled at atmospheric pressure might be considerably enriched at another pressure. In case of the ethanol–water mixture, there is no azeotrope concentration below the pressure of 11.5 Pa.

From a thermodynamic point of view, solid–liquid equilibrium can be used in a similar manner as distillation to separate components if the liquid and solid mixtures are nearly ideal; i.e., neither the freezing-point nor the melting-point curve exhibits an extremum. By considering the phase diagram in Fig. 7.18, we can see that the concentration of the lower melting point component in the melted mixture ($x_{1,l}$) is greater than in the solid ($x_{1,s}$) in equilibrium with this mixture. Freezing a small quantity of the melt, the higher melting point component is enriched in the crystals formed. Melting the separated crystals and freezing a small portion of the melt again, further enrichment occurs. After a finite number of such *recrystallizations* we can get an almost pure component.

There exists a continuous version of this multistage recrystallization called *zone melting*. The liquid metal is filled in a thin tube whose material does not mix with the metal (neither with its impurities) and melts at higher temperature than the

metal. The tube is fitted inside a heater which heats only a small disc-like portion at one end of the tube. The metal inside melts and impurities having a lower melting point than the metal itself get enriched in the melt. The heater is slowly swept toward the other end of the tube. At the cooling end of the melt from where the heater is leaving, solid crystals in equilibrium with the melt freeze out, while at the front where the heater moves on, solid metal is melting (along with impurities). While the heater is sweeping along the tube, impurities "accumulate" in the melted zone as they freeze out in a lower concentration behind the zone. At the end of the tube, the melt is completely frozen and the disc containing a high concentration of impurities is detached from the metal rod. The procedure can be repeated several times to get purer and purer metal. Instead of sweeping several times with the same heater (usually back and forth), several heaters can be swept one after another at the same time so that the metal would refreeze between them. This latter technique obviously results in multiple recrystallizations in a much shorter time. Zone melting to remove impurities can be applied also in the case of eutectic phase diagrams of the types shown in Figs. 7.24 and 7.25, as well as in cases of the phase diagrams shown in Fig. 7.28, for in all these cases "impurity" B is always enriched near compositions of the pure component A.

Recrystallization is an efficient means of separation if the components do not mix in the solid phase, as for example in case of a phase diagram of Fig. 7.24. In this case, one of the pure components crystallizes, depending on the actual composition. Common examples are aqueous salt solutions, resulting in pure salt crystals when cooled. However, at exactly the eutectic composition, there is no separation of the components. When cooling mixtures of other compositions, their remaining liquid also reaches the eutectic composition sooner or later, when a mixture crystal begins to freeze out. Recrystallization should be halted before this event.

Immiscible liquids also offer an alternative for separation. A common separation method based on this kind of phase equilibrium is *steam distillation*. It is mostly used to separate mixtures of organic compounds immiscible with water, e.g., fragrances or spices (essential oils) extracted from natural raw material using oils. To boil the oil containing the extract would require high temperatures where the dissolved compound would decompose, which is avoided by steam distillation. On the other hand, the low-temperature steam distillation is also simpler and less energy-consuming. Let us consider the water-insoluble oily phase a binary mixture, e.g., wax distributed on glass plates containing an essential oil extracted from flowers placed onto the wax layer. The wax component has a negligibly low vapor pressure even at the boiling point of water, compared to the vapor pressure $p_i$ of the essential oil and $p^*_{\text{water}}$ of pure water. Therefore, the equilibrium vapor pressure over the immiscible water and the oily phase is the sum of these two pressures:

$$P = p^*_{\text{water}} + p_i. \tag{7.131}$$

This will be the overall vapor pressure, independently of the ratio of the two phases, until the liquids are stirred to have a great enough surface where they can

evaporate. As we can see, the boiling point of the stirred mixture is *lower* than that of the pure water, for it is not necessary that the vapor pressure of water reaches the atmospheric pressure $P$ to boil; it is enough that it reaches the lower value of $P - p_i$. Consequently, both stirring and boiling can be maintained by introducing water vapor into the two-phase liquid through a tube from an external boiler. The emerging vapor mixture is condensed, and the distillate consists of essential oil and pure water in separated phases, their molar ratio being equal to the ratio of the vapor pressures. (In case of – usually small – miscibility, water will contain some essential oil and the essential oil will also contain a small amount of water.) The quantity of the essential oil distilled this way can be obtained from the equation

$$n_i = n_{\text{water}} \frac{p_i}{p^*_{\text{water}}}. \tag{7.132}$$

Steam distillation is widely applied to the purification of temperature-sensitive organic compounds. By substituting the mass of the compounds divided by their molar mass into the above equation, we can express the mass yield of the organic component:

$$m_i = m_{\text{water}} \frac{M_i}{M_{\text{water}}} \frac{p_i}{p^*_{\text{water}}}. \tag{7.133}$$

As we can see, the small molar mass of water increases the amount of greater molar mass organic compounds, thus compensating for an eventual low partial pressure.

Another separation method based on immiscibility of liquids is *liquid–liquid extraction*.[21] An example is the separation of two completely miscible liquids of which one component is miscible with a third liquid, but the other component is only partially miscible. The separation procedure can be demonstrated in Fig. 7.35.

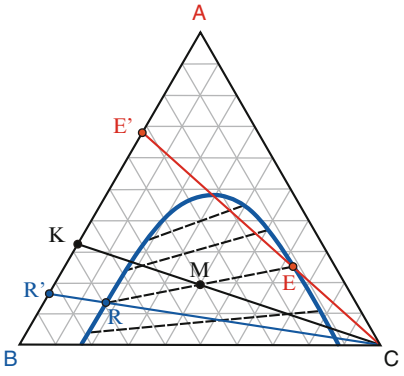



**Fig. 7.35** Extraction of component B from a binary mixture A–B using solvent C. K: initial binary mixture; M: overall composition of the ternary mixture after having added component C, which separates into two phases of compositions R and E. After complete evaporation of component C from both phases, the extract E′ and the raffinate R′ are obtained

[21]This word originates from the Latin verb *extraho* = draw out. The English verb is extract.

The *solvent* C is added to the binary mixture of composition K in a quantity that results in the *mixture* composition M. This ternary mixture of the overall composition M separates along the tie line passing through M into two phases at the intersection of the tie line and the equilibrium curve of the miscibility boundaries. The phase of composition E (*extract*) and that of composition R (*raffinate*) can physically be separated in a *settling vessel* due to their density difference. By evaporating the solvent C from both the extract and the raffinate, we get the binary extract E' and the raffinate R'. (Note that the molar ratio of components A and B is constant along the lines passing through the apex C.) The extract can further be enriched in component A by subsequent distillation of the binary extract.

Though extraction can also be carried out in a multi-stage extractor, increasing the rate of enrichment, but a pure component A cannot usually be obtained; it is typically provided by a subsequent distillation. Extraction is a good choice if the binary mixture is an azeotrope and the mixture of composition K cannot be separated by distillation, but the extract E' can be. It is also advantageous as a preenrichment method if energy consumption of the distillation is markedly higher than that of the extraction.

The efficiency of extraction can be characterized by the *partition ratio* (also called *distribution constant*), which can be derived from the thermodynamic characterization of the partition equilibrium. According to this, the chemical potential of component A should be the same in equilibrium in both phases of compositions R and E in Fig. 7.35. A formal statement of this condition is:

$$\mu_{\mathrm{B}}^{\ominus} + RT \ln \gamma_{x,\mathrm{B}}\, x_{\mathrm{B}} = \mu_{\mathrm{C}}^{\ominus} + RT \ln \gamma_{x,\mathrm{C}}\, x_{\mathrm{C}}. \tag{7.134}$$

In this equation, subscript B denotes the phase richer in component B, and subscript C the phase richer in component C. By rearranging, we get the ratio of the activities of component A in the two phases:

$$\frac{a_C}{a_B} = \frac{\gamma_{x,\mathrm{C}}\, x_{\mathrm{C}}}{\gamma_{x,\mathrm{B}}\, x_{\mathrm{B}}} = \mathrm{e}^{\frac{\mu_{\mathrm{B}}^{\ominus} - \mu_{\mathrm{C}}^{\ominus}}{RT}}. \tag{7.135}$$

As neither $\mu_{\mathrm{B}}^{\ominus}$ nor $\mu_{\mathrm{C}}^{\ominus}$ depends on the composition, the exponential is independent of concentration. Consequently, the distribution constant

$$K_D = \frac{a_C}{a_B} = \frac{x_{\mathrm{C}}}{x_{\mathrm{B}}} \frac{\gamma_{x,\mathrm{C}}}{\gamma_{x,\mathrm{B}}}, \tag{7.136}$$

is also independent of the composition. If both $x_{\mathrm{B}}$ and $x_{\mathrm{C}}$ are small enough that both liquids can be considered as ideal mixtures concerning component A, the ratio $\gamma_{x,\mathrm{C}}/\gamma_{x,\mathrm{B}}$ can be approximated as unit; thus, $K_D$ gives the ratio of concentrations. (The mixture B–C is of course *not* ideal, as the two components do not mix.)

There exist solvents used for extraction which do not mix in a measurable quantity with the solvent of the component to be extracted from a binary mixture, but the solute has a high solubility in them. This is the case if iodine is distributed between water and chloroform; iodine dissolves well in the moderately polar chloroform but rather purely in water. The partition ratio between chloroform and water is about 130, so that iodine can be efficiently separated from its aqueous solution by using a *separation funnel*. (A separation funnel is used in the laboratory practice, which is well shaken after the two phases are filled in. Equilibrium is achieved quickly by shaking, and the two phases separate quickly if the funnel stands still.) In addition to extraction, many chromatographic techniques are also based on the distribution of components between two immiscible phases.

**Problems**

1. The equilibrium vapor pressure of a single component liquid at 300 K was found to be 0.2 bar. The heat of vaporization of the liquid is 40 kJ/mol. Assume the vapor to be an ideal gas, its density to be much less than that of the liquid. Estimate the temperature at which the equilibrium vapor pressure is doubled.

*Solution*: The logarithmic form of (7.45) – the solution of the Clausius–Clapeyron equation – can be used in the following form:

$$\ln \frac{P_1}{P_2} = \frac{\Delta_{\text{vap}} h}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right).$$

Solution of the equation inserting $P_1/P_2 = 2$ yields 313.55 K at which the vapor pressure is doubled.

2. The triple point of methanol is at $T = 175.610$ K and $p = 0.0002$ Pa. Sketch the phase diagram at the vicinity of the triple point, using the following data: $\Delta_{\text{vap}}\, h = 35.2$ kJ/mol, $\Delta_{\text{fus}}\, h = 3.173$ kJ/mol, $\rho_l = 0.7918$ g/cm$^3$ and $\rho_s = 0.7802$ g/cm$^3$. Suppose the shape of the coexistence curves to be linear within the range of the sketch and the vapor as an ideal gas.

*Solution*: The slope of each line is given by the Clapeyron equation (7.38) as

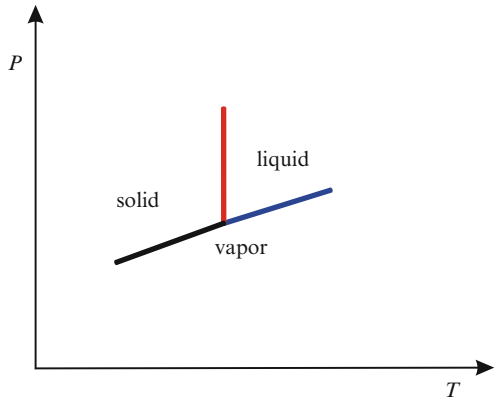
$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta_\alpha^\beta h}{T\ \Delta_\alpha^\beta v}.$$

The missing heat of sublimation can be calculated based on the state function property of enthalpy as $\Delta_{\text{sub}}\, h = \Delta_{\text{vap}}\, h + \Delta_{\text{fus}}\, h$. Molar volumes of solid and liquid methanol can be calculated from the densities as $v = M\ /\rho$, and the missing molar volume from the ideal gas equation of state. Using these quantities, the slopes of the three coexistence curves are the following:

$$v/l : 27.45\,\mu\text{Pa/K};\ \ v/s : 29.93\,\mu\text{Pa/K};\ \ l/s : -30.07\,\text{kPa/K}.$$

Using these quantities as the slopes of linear portions of coexistence curves, the sketch looks like the one below. Note that the solid/liquid coexistence line looks completely vertical at a scale (shown) where the vapor/liquid and vapor/solid lines

are not looking completely horizontal. However, the solid/liquid coexistence line is tilted to the left – similarly to that of water.




3. The boiling temperature of a binary solution of A and B of concentration $x_A = 0.45$ is 100°C at 1.016 atm. At this temperature, the vapor pressures of pure A and B are 120.1 and 89.0 kPa, respectively. Prove that the solution is ideal and calculate the composition of the vapor when boiling begins.

*Solution*: The equilibrium partial pressures of the components of an ideal mixture can be calculated using Raoult's law:

$$P_{\text{tot}} = x_A p_A^* + (1 - x_A) p_B^* = 102.955 \text{ kPa}.$$

As 1.016 atm = 102.9462 kPa, the solution can be considered as ideal. The composition of the vapor is easy to determine from the above data using the equations for the mole fractions in the vapor

$$y_A = \frac{p_A}{p_A + p_B} \quad \text{and} \quad y_B = \frac{p_B}{p_A + p_B}.$$

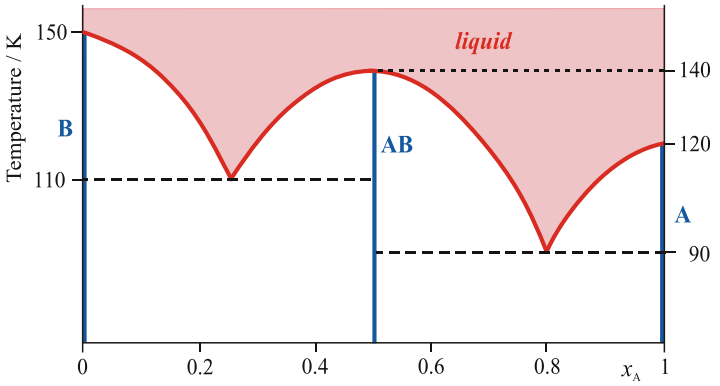
After substitution, we get $x_A = 0.52$ and $x_B = 0.48$.

4. The melting points of the pure compounds A and B are 120 and 150 K, respectively. The two substances undergo a chemical reaction to form a solid compound AB:

$$A(l) + B(l) \rightleftharpoons AB(s).$$

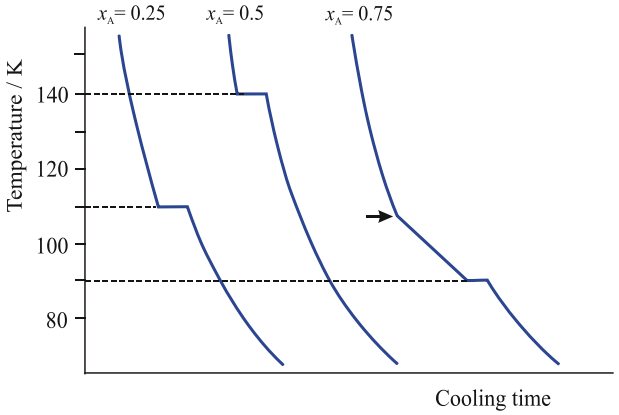
The melting point of the compound AB is 140 K. The system has two eutectic points at atmospheric pressure: one at the mole fraction 0.25 of component A (110 K) and another at 0.80 (90 K). Sketch the phase diagram of this system, and another diagram of the cooling curves at the three mole fraction values 0.25, 0.50, and 0.75 of A. Mark the temperatures given in the text and assign phases. Explain the shapes of the cooling curves.

*Solution*: The sketch of the phase diagram according to the data given looks like the one below.




Stable phases are liquid (shaded upper area), pure solid B (left edge below 150 K), pure solid A (right edge below 120 K), and the solid compound AB (vertical line at $x_A = 0.5$, below 140 K). Eutectical lines at 90 K and 110 K are marked dashed.

Cooling curves at the given three mole fractions are sketched below.




At $x_A = 0.25$, there is a eutectic point. Thus, the liquid cools down until the eutectic temperature of 110 K, where it solidifies. The cooling rate slightly decreases with decreasing melt temperature until 110 K, but the temperature remains constant at this value during solidification. Once the entire system becomes a solid eutectic microcrystalline mixture, cooling down is continued again with a decreasing cooling rate.

At $x_A = 0.5$, there is a reaction forming the compound AB at solidification. Thus, the liquid cools down until the solidification temperature of the compound at 140 K, where it solidifies, while the temperature remains constant. When the entire system becomes the solid compound AB, cooling down is continued again with a decreasing cooling rate.

At $x_A = 0.75$, the liquid begins to solidify at approximately 107 K (as it can be read from the phase diagram); thus, the cooling rate is abruptly slowed down due to the release of the heat of freezing. (The breakpoint is marked by an arrow. The solid formed is the compound AB). During this freezeout, the concentration continuously changes toward the eutectic concentration of $x_A = 0.8$, where the eutectic microcrystals are formed at the constant temperature 90 K, again without cooling. As soon as the remaining liquid mixture becomes a solid eutectic microcrystalline mixture, cooling down is continued again with a decreasing cooling rate.

Note that this cooling behavior makes it possible to experimentally determine the phase diagram from cooling curves. A congruent freezing (where the composition of the solid formed is identical to the composition of the liquid) is always accompanied by a horizontal (constant temperature) portion of the cooling curve, while an abrupt change of the slope of the cooling curve (but with continuing cooldown) indicates the onset of formation of a solid phase when composition changes continuously. By determining the constant temperatures and the breakpoint temperatures at different mixture concentrations, we can construct the phase diagram.

## Further Reading

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