Chapter 13
Homogeneous and Heterogeneous Mixtures

In chemistry but also in everyday life, we are very often confronted with mixtures, be they homogeneous or heterogeneous. Think for example of hard liquor, basically a homogeneous mixture of ethanol and water, but also of fog, a heterogeneous mixture of air and minuscule water droplets. First, we concentrate on mixtures made up of two liquid components. We discuss the behavior of the chemical potential of one component in such mixtures and the reason for spontaneous mixing or demixing. For an adequate quantitative description, the concept of chemical potential has to be extended on substances in real solutions by introducing an extra potential $\overset{+}{\mu}$.

For the characterization of mixing processes, it is useful to assign an (average) chemical potential to a mixture of two components A and B (with the mole fractions x_A and x_B), as is done for pure substances. Depending on whether the resulting mixture is homogeneous or heterogeneous the concentration dependence of this average potential is different. On this basis, concepts such as miscibility gap and lever rule are discussed.

13.1 Introduction

To begin with, let us take a look at mixtures made up of two liquid components. A homogeneous mixture of ethanol and water (like it is found in hard liquor) can be preserved over long periods of time; we always observe only one single *phase*. (We were introduced to the concept of phase for a homogeneous region of matter in Sect. 1.5.) However, if we let a hot mixture of phenol and water cool down, it will split up into two separate parts (Experiment 13.1) meaning that *demixing* (phase separation) occurs.

A similar situation occurs with ether and water (Experiment 13.2).

If only a small amount of ether—colored brown with iodine—is added to water, a homogeneous brown-colored solution results as we have seen. This is because the

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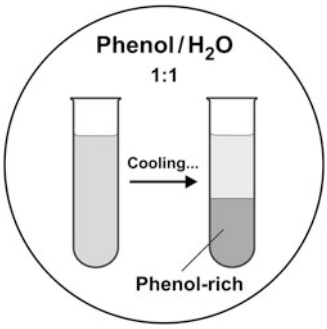
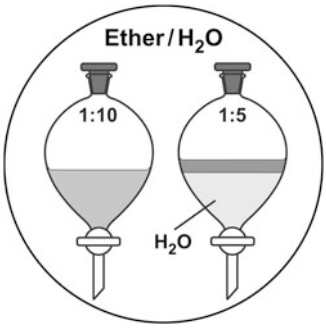
Experiment 13.1 *Demixing of phenol/water*: We let a hot mixture of phenol and water (at a ratio of 1:1) cool down in the air. After a while, demixing takes place thereby forming streaks. The phenol-rich phase settles to the bottom because of its higher density. The demixing becomes nicely visible when a tiny amount of methyl red is added to the original mixture. Because the dye is not soluble in water but is very soluble in phenol, it remains in the phase rich in phenol.



Experiment 13.2 *Mixing of ether with water*: We add a small amount of ether—colored brown with a bit of iodine—to water in a separating funnel (at a ratio of 10:1), and subsequently, we shake the funnel gently. A homogeneous brown-colored solution results. When the same amount of ether is added once more (ratio now 5:1) and we shake the funnel again, a large portion of the ether separates as a brown layer on top of the almost colorless water.



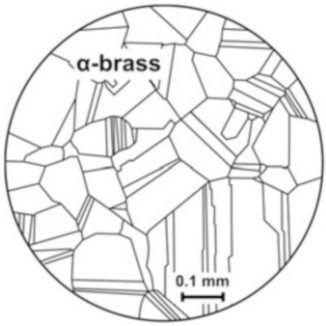
small amount of ether completely dissolves in the water and the iodine distributes through the water along with it. When the ratio of ether to water is 1:5, the ether separates as a brown layer on top of the water because water can only absorb about 10 % of its own volume in ether. Iodine can dissolve much better in ether than in water so it moves from the aqueous phase and collects in the layer of ether lying on top of it. This has been already discussed in Sects. 4.2 and 6.6.

Solid mixtures behave very similarly. For example, α-brass (an alloy of copper and up to 40 % zinc) can be preserved for just about any amount of time (Experiment 13.3).

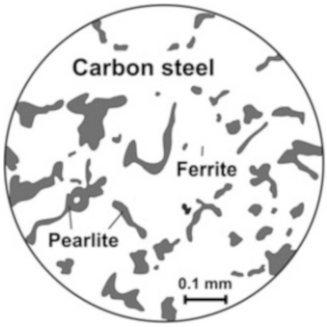
On the other hand, carbon steel made up of iron with a maximum of 2 % carbon separates more or less quickly—when cooled from its melted state—into two homogeneous but intricately entangled areas (Experiment 13.4).

Processes of this type can be discussed in the same way as chemical reactions. The constituents of the mixture assume the role of elements as basic substances whose amounts are conserved during transformation (see Sect. 1.2). The homogeneous and heterogeneous mixtures themselves, however, correspond to chemical compounds. Therefore, the composition of these mixtures can be given by a content formula but with the peculiarity that the content numbers are not necessarily integer

Experiment 13.3 *Polished cross section of brass*: A polished cross section studied under a light microscope after etching shows well-distinguishable grain boundaries that separate the variously oriented but otherwise identical regions of matter.



Experiment 13.4 *Polished cross section of carbon steel*: The *white areas* are ferrite (materials science term for α-Fe, i.e., (nearly) pure iron with a body-centered cubic crystal structure). The *dark gray areas*, however, are pearlite (a fine lamellar structure of ferrite and cementite, an iron–carbon compound with the formula Fe_3C).



numbers but can also be real. Normally, one chooses the numbers in such a way that their sum equals 1. The simplest case would be the mixing of two substances A and B resulting in a mixture with defined composition, for example, with a mole fraction x_B of B and therefore $x_A = 1 - x_B$ of A:

$$v_A A + v_B B \rightarrow A_{x_A} B_{x_B}.$$

One glance is enough to recognize that the conversion numbers v_i on the left side have to be identical with the content numbers g_i in the formula on the right side and hence with the mole fractions x_i in the mixture: $v_A = g_A = x_A$ and $v_B = g_B = x_B$. The content formula on the right describes only the fractions of the components, but no information is provided if the resulting mixture is homogeneous (such as water and alcohol) or heterogeneous (like sugar and flour when preparing a cake dough). However, the meaning of the formula on the right is usually clear from the context. We will first discuss homogeneous mixtures; in this case, the content formula on the right is sufficient for characterization. The situation is more complex for heterogeneous mixtures because their constituents have not to be pure substances but can also be homogeneous or even heterogeneous mixtures. But also in this case we basically need no new means for capturing the essence.

13.2 Chemical Potential in Homogeneous Mixtures

Why do certain mixtures split up when others do not? How are phases formed? To answer these questions, we will again refer to the chemical potential μ. Until now we have considered the situation as follows: If a region is inhomogeneous, the substances move more or less quickly along the potential gradient until the chemical potential for every substance is equal everywhere in that region. Although a homogeneous region is what would be expected as the final result, this is obviously not always the case. For clarity we will consider the $\mu(x)$ curve.

To provide an example, we will now look at how the chemical potential μ of water depends upon its mole fraction x in various mixtures (Fig. 13.1).

On the right, all curves show the same slope RT in the vicinity of $x = 1$. On the left, they all approach negative infinity. The similar initial part of the curves on the right side is a consequence of indirect mass action which is the same for all substances (see Sect. 12.3). The similarities and differences for varying mixtures become even clearer when plotted logarithmically (Fig. 13.2).

In this representation, all curves end up on the left side in parallel straight lines with the slope RT. In Sect. 6.5 we set up the following equation to describe mass action [Eq. (6.28)]:

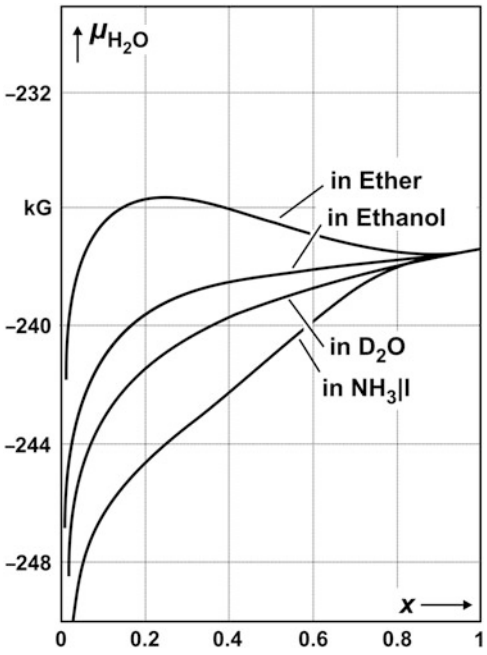


Fig. 13.1 Chemical potential of water in different mixtures as a function of its mole fraction (at a temperature of 298 K and a pressure of 100 kPa).

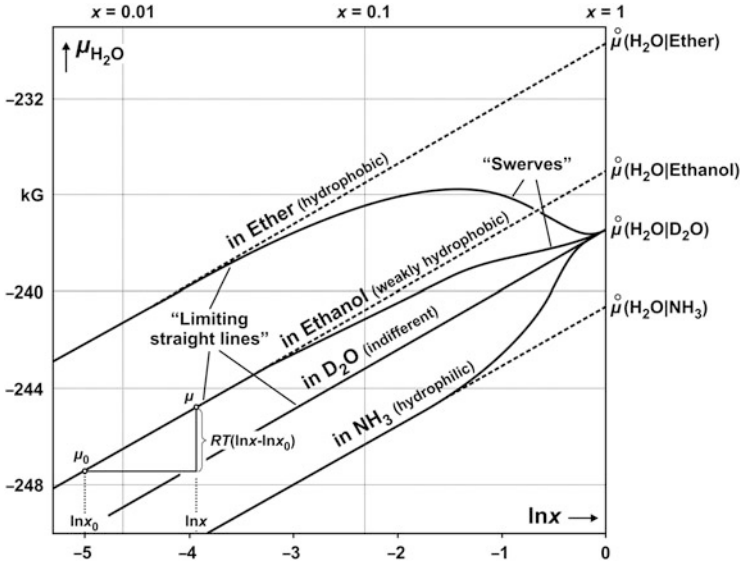


Fig. 13.2 Presentation of the chemical potential of water in different mixtures as a function of concentration on a logarithmic scale.

$$\mu = \mu_0 + RT\ln\frac{x}{x_0} \quad \text{for } x, x_0 \ll 1.$$

A logarithmic plot where μ is chosen to be the ordinate and $\ln x$ the abscissa, should result in a straight line with a slope of RT:

$$\begin{array}{l} \mu = \mu_0 + RT\underbrace{(\ln x - \ln x_0)}_{(x - x_0)}. \\ y = y_0 + m \cdot \end{array} \qquad \text{linear equation}$$

(As a reminder, the well-known equation you learned at school for a straight line with a slope of m through the point $(x_0; y_0)$ is given.)

A mixture is called *ideal* if this relation is not only valid for low mole fractions but in the whole range $0 \le x \le 1$ and in particular for $x_0 = 1$. If we write again $\mathring{\mu}$ for the chemical potential of the pure substance, the equation above simplifies to (cf. Sect. 12.3):

$$\mu = \mathring{\mu} + RT\ln x \quad \text{for } 0 \le x \le 1 \text{ in the ideal case.} \tag{13.1}$$

When we take the derivative of this function with respect to x at constant T, we obtain the value of RT at $x = 1$ as we should expect because of the indirect mass action:

$$\left(\frac{\partial \mu}{\partial x}\right)_T = \frac{RT}{x} \quad \text{and therefore} \quad \left(\frac{\partial \mu}{\partial x}\right)_T = RT \quad \text{for } x = 1.$$

However, only very similar substances that are *indifferent* to each other such as a homogeneous mixture of light water (H_2O) and heavy water (D_2O) show an ideal behavior. (The molecular rearrangement $H_2O + D_2O \rightarrow 2HDO$ which occurs easily is considered to be suppressed.).

A similar approach can be used to describe the behavior at low mole fractions. The $\mu(x)$ curves appear in Fig. 13.2 as straight lines parallel to that for the ideal case; they only differ from each other in the intercepts on the y-axis (vertical line at the far right in the figure). $\overset{\circ}{\mu}_x$ represents a special basic value (such as already $\overset{\bullet}{\mu}$) meaning a "basic contribution" independent from the composition. The index $_x$ can be omitted if it is clear from the context that the usual basic value specified in the concentration scale (i.e., the value for 1 kmol m^{-3}) is not meant. To avoid confusion, we can write $\overset{\circ}{\mu}_c$ instead of simply $\overset{\circ}{\mu}$ as before.

$\overset{\circ}{\mu}_x(B|A)$ or abbreviated $\overset{\circ}{\mu}(B|A)$ represents the chemical potential for a hypothetical state of the "pure" substance B in question (here water) in which the interaction of the substance (B) and the solvent molecules (A) (here ether, ethanol, etc.) determine the outcome, and not the interactions of the B molecules with each other. Naturally, each solvent leads to a different value (Table 13.1). We will take a short look at this again in the next section.

The substances' individual characteristics recede near $x = 1$ as well as $x = 0$ and general laws that are broadly independent of substance-specific quantities become valid. However, the form of the functions varies noticeably between the limits mentioned. But characteristic for all curves is the "swerve" from the straight line on the left with slope RT to the parallel straight line on the right.

The potential difference between $\overset{\circ}{\mu}(B|A)$ and $\overset{\bullet}{\mu}(B)$ can serve as measure for the compatibility of B with A. The higher the value $\overset{\circ}{\mu}(B|A)$ lies above that of $\overset{\bullet}{\mu}(B)$ the stronger the tendency of B to separate from A, the worser the compatibility between the substances. As long as one of the substances is added in small or very small amounts, it will always be tolerated. The situation can become critical when both components are present in comparable amounts. We call the substances "lowly compatible" when they do not yet separate from each other and "incompatible"

Table 13.1 Basic values of chemical potential of substances in several mixtures (at 298 K and 100 kPa).

Substance/solvent		$\overset{\circ}{\mu}_x$ (kG)
H_2O	Pure	−237.4
	In ether (hydrophobic)	−230
	In D_2O (indifferent)	−237.4
	In H_2SO_4 (hydrophilic)	−260
Hg	Pure	0
	In H_2O (lowly compatible)	+40
	In benzene (lowly compatible)	+30
	In liquid Na (highly compatible)	−150
Fe	Pure	0
	In Cu (lowly compatible)	+20

when they do. Also the opposite can occur meaning the value of $\overset{\circ}{\mu}(B|A)$ lies beneath that of $\overset{\bullet}{\mu}(B)$. In this case, A and B are better compatible among each other than each of the substances alone. We call substances showing this behavior "highly compatible."

In the case of a mixture of two "highly compatible" substances such as H_2O and NH_3 (in this special case also called a *hydrophilic* or "water-loving" substance), a downward deviation from the continuous straight line for indifferent substances can be observed. "Lowly compatible" substances like H_2O and Ethanol, however, show an upward deviation. The curve for a mixture of "incompatible" substances (such as H_2O and *hydrophobic* ether) shows a "swerve" raised to a maximum.

The varying behaviors of these mixtures are due to the different interactions of the components A and B at their molecular levels. If the attraction between particles of different types A and B is about equal to the average attraction between particles of the same type (A and A or B and B), the substances will behave *indifferently*. This holds for mixtures of substances that are chemically closely related such as H_2O/D_2O, hexane/heptane, benzene/toluene, etc. Dilute gases also behave indifferently toward each other because the attraction is almost nonexistent due to the large distances between the particles. For this reason,

- Non or weakly polar liquids: hexane, ether, carbon tetrachloride or
- Substances that form hydrogen bonds: water, ammonia, methanol, glycerol

are among each other more or less compatible.

If the attraction between particles A and B is stronger than that between the different types of particles themselves, one speaks of *highly compatible* substances. If, however, the attraction is considerably weaker, the substances are called *incompatible*. Incompatible ones are

- Polar and nonpolar liquids such as water in combination with organic solvents like benzene, hexane, or carbon tetrachloride,
- Metallic and nonmetallic liquids such as Hg/H_2O, Hg/benzene.

We can qualitatively interpret the demixing (separation) of a mixture like water and ether having a ratio of 1:1 ($x_{H_2O} = 0.5$) as follows (Fig. 13.3): A tiny arbitrary accumulation of H_2O molecules at some location in the mixture lowers the

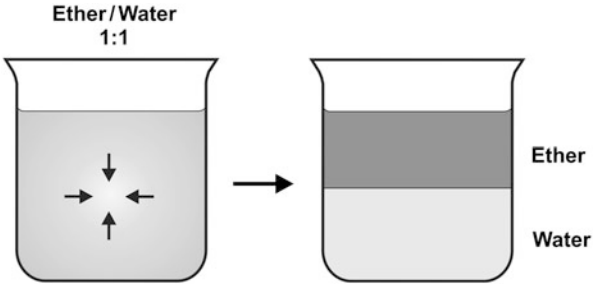
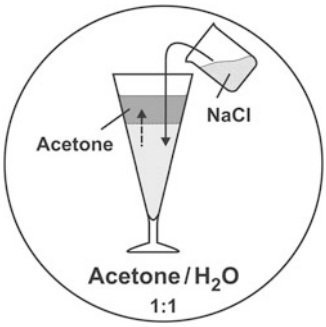


Fig. 13.3 Demixing of a mixture of ether and water into an upper ether-rich layer with 1 % water and a water-rich layer below with an ether fraction of 8 %.



Experiment 13.5 *Demixing of an acetone-salt water solution*: Acetone is colored with a little bit of methyl violet and the same amount of water is added. When table salt is added to the homogeneous mixture, a demixing takes place resulting in a deep violet acetone and a pale violet water layer.

chemical potential μ of the water there because it decreases with an increase of the mole fraction (compare Fig. 13.1). As a result, additional H_2O particles migrate into this spot from the area around it and it becomes gradually larger and richer in H_2O. This process continues until the surroundings are so depleted of water that the chemical potential there drops. The final state is a water-poor, lighter layer on top and a water-rich and heavier layer below.

The compatibility of two components A and B can be influenced by the addition of a third substance and the corresponding change of the concentrations of the components. For example, when table salt is added to a homogeneous mixture of water and acetone, a demixing takes place (Experiment 13.5). The reason for this is the low compatibility of the components which increases with the salt content of the water.

13.3 Extra Potential

When we were introduced to the ideal case for the potential μ of a substance in a homogeneous mixture, we learned about the following behavior:

$$\mu(x) = \overset{\bullet}{\mu} + RT\ln x \qquad \text{for } 0 \leq x \leq 1.$$

Deviations from this simple mass action equation can be explained by the fact that the chemical interactions between the particles upon each other are not taken into account. Corrections must therefore be made in order to describe the behavior correctly. This is most easily done by the addition of a correction term $\overset{+}{\mu}$, a so-called *extra potential*. This extra potential is not constant but is dependent upon the mole fraction x:

$$\mu(x) = \overset{\bullet}{\mu} + RT\ln x + \overset{+}{\mu}(x). \tag{13.2}$$

Substances such as light water and heavy water or dilute gases that are dissolved in each other follow the ideal curve, so the extra potential $\overset{+}{\mu}$ disappears. This means that $\overset{+}{\mu}(x) \equiv 0$. Otherwise, the extra potential would be either positive or negative.

For a strongly diluted substance, the change of $\overset{+}{\mu}$ with the mole fraction x is negligible compared to the strongly changing term $RT \cdot \ln x$, which in the limit tends toward $-\infty$ (compare Fig. 13.1). It is therefore possible to replace $\overset{+}{\mu}$ by the constant limiting value $\overset{+}{\mu}_{\emptyset}$ for "infinite" dilution meaning vanishingly low concentration (for better distinction we use a "slashed zero" as index):

$$\mu(x) = \underbrace{\overset{\bullet}{\mu} + \overset{+}{\mu}_{\emptyset}}_{\overset{\circ}{\mu}} + RT\ln x \quad \text{for small } x. \tag{13.3}$$

As we have seen in the previous section, when substances are indifferent to each other, both reference potentials are identical, $\overset{\circ}{\mu} = \overset{\bullet}{\mu}$. The extra potential vanishes in the entire range, $\overset{+}{\mu}(x) \equiv 0$, and so do all properties related to it.

In Chap. 9, which dealt with cross relations, we learned that the volume and entropy demands of a substance in a mixture can be derived from the pressure coefficient β and the temperature coefficient α of chemical potential, meaning the derivatives of μ with respect to p and T at constant composition:

$$\beta = \left(\frac{\partial \mu}{\partial p}\right)_{T,n} = V_{\mathrm{m}} \quad \text{and} \quad \alpha = \left(\frac{\partial \mu}{\partial T}\right)_{p,n} = -S_{\mathrm{m}}.$$

Here, V_{m} and S_{m} are the molar volume and molar entropy, respectively. If we use the equation for the chemical potential above, $\mu(x) = \overset{\bullet}{\mu} + RT\ln x + \overset{+}{\mu}(x)$, as our starting point and abbreviate the derivatives of the terms $\overset{\bullet}{\mu}$, and $\overset{+}{\mu}$ correspondingly, we obtain

$$V_{\mathrm{m}} = \overset{\bullet}{V}_{\mathrm{m}} + \overset{+}{V}_{\mathrm{m}} \tag{13.4}$$

and, respectively,

$$S_{\mathrm{m}} = \overset{\bullet}{S}_{\mathrm{m}} - R\ln x + \overset{+}{S}_{\mathrm{m}}. \tag{13.5}$$

In the case of volume, the term $RT \cdot \ln x$ drops out because it is not dependent upon pressure. We call $\overset{+}{V}_{\mathrm{m}}(x)$ "molar extra volume" and $\overset{+}{S}_{\mathrm{m}}(x)$ "molar extra entropy." The extra quantities disappear in homogeneous mixtures of indifferent substances. While the volume demand V_{m} is independent of composition in this special case, this is not true for the entropy demand S_{m} which increases continually with falling mole fraction x. It tends toward $+\infty$ for $x \to 0$, but "extremely slowly."

13.4 Chemical Potential of Homogeneous and Heterogeneous Mixtures

Potential of Homogeneous Mixtures A process of mixing can be described as a "reaction" between two substances. When one-third ethanol and two-thirds water are mixed, the result is the mixed phase schnaps. This phase can be further put to use to produce a grog, for example (Experiment 13.6).

In order to describe these kinds of processes in the usual way, it is practical to assign an amount of substance and a chemical potential to a portion of a homogeneous mixture, too. The sum of the amounts n_A, n_B, n_C, ... of the pure substances A, B, C, ... that make up the homogeneous mixture M equals the amount of substance n_M of the mixture:

$$n_M = n_A + n_B + n_C + \dots \quad . \tag{13.6}$$

The weighted average of the chemical potentials of the components—weighted with the mole fractions x_A, x_B, x_C ...—is the chemical potential of the mixture, μ_M:

$$\mu_M = x_A\mu_A + x_B\mu_B + x_C\mu_C + \dots \quad . \tag{13.7}$$

μ_M is often called the *average* chemical potential (to keep in mind the averaging). It agrees nicely with the definition of chemical potential we learned earlier. We have seen that μ_i is the energy $dW_{\to n_i}$ (abbreviated dW_i) necessary for creating the substance i (no matter if the substance is pure or mixed with others; however, it is essential to avoid or subtract all energy contributions expended for any other purpose), per amount of substance n_i:

$$\mu_i = \frac{dW_{\to n_i}}{dn_i} = \frac{dW_i}{dn_i} .$$

The energy $dW_{\to n_M}$ (abbreviated dW_M) necessary for producing a homogeneous mixture M is simply the sum of the energies of formation of its components,

Experiment 13.6 *Mixing of a grog*: Two or three sugar cubes are put in a glass. Subsequently, we fill the glass halfway with boiling water, add the rum, and stir. A new mixed phase, the grog, has been produced from the two original mixed phases, the aqueous sugar solution and the rum.

$$\begin{aligned} dW_M &= \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \ldots, \\ &= \mu_A x_A dn_M + \mu_B x_B dn_M + \mu_C x_C dn_M + \ldots \ . \end{aligned}$$

Dividing this expression by the amount of the mixture n_M results in a quantity that we appropriately call the chemical potential of M:

$$\mu_M = \frac{dW_M}{dn_M} = x_A \mu_A + x_B \mu_B + x_C \mu_C + \ldots \ .$$

How does the (average) chemical potential change with the composition of the mixed phase? Let us consider the simple case of a so-called binary mixture of two pure components A and B that are indifferent to each other. The chemical potential of component A in the mixed phase is

$$\mu_A = \dot{\mu}_A + RT \ln x_A .$$

The relationship for component B can be formulated correspondingly. The chemical potential for the mixed phase is then

$$\mu_M = x_A \mu_A + x_B \mu_B = x_A \dot{\mu}_A + x_B \dot{\mu}_B + RT(x_A \cdot \ln x_A + x_B \cdot \ln x_B) \tag{13.8}$$

$$= \underbrace{(\dot{\mu}_B - \dot{\mu}_A) \cdot x_B + \dot{\mu}_A}_{\text{straight line}} + \underbrace{RT((1 - x_B) \cdot \ln(1 - x_B) + x_B \cdot \ln x_B)}_{\text{“drooping belly”}} . \tag{13.9}$$

We replaced x_A by $1 - x_B$ in the second step. Figure 13.4 illustrates the curve of μ_M (shaped as a “drooping belly”) as a function of x_B. At $x_B = 0$ as well as $x_B = 1$, the curve has vertical tangents, a fact that is not easy to recognize in the figure but that has important consequences which we will discuss later.

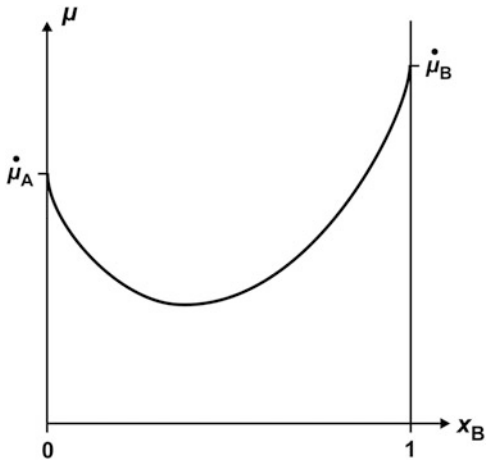


Fig. 13.4 The (average) chemical potential as a function of the composition of a homogeneous mixture of two indifferent substances A and B.

Potential of Heterogeneous Mixtures A portion of a heterogeneous mixture $\mathcal{M}$ of several immiscible components A, B, C, ... can also be assigned an amount of substance n and an (average) chemical potential μ according to the same pattern used for homogeneous mixtures:

$$n_{\mathcal{M}} = n_{\mathrm{A}} + n_{\mathrm{B}} + n_{\mathrm{C}} + \ldots \tag{13.10}$$

and

$$\mu_{\mathcal{M}} = x_{\mathrm{A}}\mu_{\mathrm{A}} + x_{\mathrm{B}}\mu_{\mathrm{B}} + x_{\mathrm{C}}\mu_{\mathrm{C}} + \ldots \ . \tag{13.11}$$

There is, however, a fundamental difference: While in the case of homogeneous mixtures, the chemical potentials of the components are different in their mixed and unmixed state, μ_{A}, μ_{B}, μ_{C} ... always have the same values in heterogeneous mixtures whether A, B, C, ... are present in their mixed or unmixed states. In order to differentiate the chemical potential of a heterogeneous mixture from the chemical potential of a homogeneous mixture, we will label it with the index $\mathcal{M}$.

The following is then valid for a heterogeneous mixture of two pure components A and B:

$$\mu_{\mathcal{M}} = x_{\mathrm{A}}\dot{\mu}_{\mathrm{A}} + x_{\mathrm{B}}\dot{\mu}_{\mathrm{B}}. \tag{13.12}$$

Because $x_{\mathrm{A}} + x_{\mathrm{B}} = 1$, we obtain

$$\mu_{\mathcal{M}} = (1 - x_{\mathrm{B}})\dot{\mu}_{\mathrm{A}} + x_{\mathrm{B}}\dot{\mu}_{\mathrm{B}} = \underbrace{\left(\dot{\mu}_{\mathrm{B}} - \dot{\mu}_{\mathrm{A}}\right) \cdot x_{\mathrm{B}} + \dot{\mu}_{\mathrm{A}}}_{\text{straight line}}. \tag{13.13}$$

If the potential $\mu_{\mathcal{M}}$ of a heterogeneous mixture is plotted as a function of the mole fraction x_{B}, a straight line with the slope $\left(\dot{\mu}_{\mathrm{B}} - \dot{\mu}_{\mathrm{A}}\right)$ and the y-intercept $\dot{\mu}_{\mathrm{A}}$, which runs through points (0; $\dot{\mu}_{\mathrm{A}}$) and (1; $\dot{\mu}_{\mathrm{B}}$), appears in place of the "drooping" curve (Fig. 13.5).

"Lever Rule" An important fact to remember here is that the components themselves do not need to be pure substances but can be homogeneous mixtures of two (or more) components A and B. Let us assume that the entire system (homogeneous or heterogeneous mixture) characterized by $^{\blacktriangle}$, with a mole fraction $x_{\mathrm{B}}^{\blacktriangle}$ of B, is composed of two homogeneous mixtures M′ and M″ of which one (x_{B}') is poorer in B and the other (x_{B}'') is richer. If the system as a whole is made up of an amount of substance $n^{\blacktriangle}$, the balance for component B according to the general formula $n_{\mathrm{B}} = x_{\mathrm{B}} \cdot n$, applied to each mixed phase, yields:

$$x_{\mathrm{B}}'n' + x_{\mathrm{B}}''n'' = x_{\mathrm{B}}^{\blacktriangle}n^{\blacktriangle}.$$

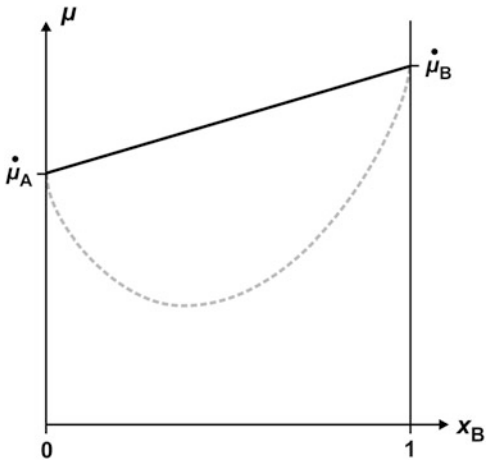


Fig. 13.5 The (average) chemical potential as a function of the composition of a heterogeneous mixture (*solid line*) (For comparison, the dotted curve for a homogeneous mixture is also included in the graphic.).

Because of $n' + n'' = n^{\blacktriangle}$, the following is valid:

$$x'_{\mathrm{B}} n' + x''_{\mathrm{B}} n'' = x^{\blacktriangle}_{\mathrm{B}} \cdot (n' + n'') \quad \text{and rearranged} \quad \left(x'_{\mathrm{B}} - x^{\blacktriangle}_{\mathrm{B}}\right) \cdot n' = \left(x^{\blacktriangle}_{\mathrm{B}} - x''_{\mathrm{B}}\right) \cdot n''.$$

Thus, the ratio of amounts of substance of the initial mixtures is

$$\frac{n'}{n''} = \frac{x''_{\mathrm{B}} - x^{\blacktriangle}_{\mathrm{B}}}{x^{\blacktriangle}_{\mathrm{B}} - x'_{\mathrm{B}}}. \tag{13.14}$$

This is the so-called "*lever rule*" (of the amounts of different phases). The name is borrowed from mechanics. The form

$$n' \cdot \left(x^{\blacktriangle}_{\mathrm{B}} - x'_{\mathrm{B}}\right) = n'' \cdot \left(x''_{\mathrm{B}} - x^{\blacktriangle}_{\mathrm{B}}\right)$$
$$\text{"load} \times \text{load arm} = \text{force} \times \text{force arm"}$$

brings a lever to mind that is supported at $x^{\blacktriangle}_{\mathrm{B}}$ and upon whose ends the two phases hang like two "weights" n' and n''. In this case, too, we see that the shorter the lever arm is that is oriented toward its corresponding phase, the greater the "weight" needs to be. In this case, the weight is the amount of substance.

In closing, let us take a look at the graphic representation of the potential of a heterogeneous mixture $^{\blacktriangle}$ of two homogeneous mixtures $'$ and $''$ (Fig. 13.6). The total potential is again defined by linear variation of the starting values. In this case, it lies upon the line connecting the two points (x'_{B}, μ') and $(x''_{\mathrm{B}}, \mu'')$.

Volume Demand and Entropy Demand The temperature coefficient α_{M} and the pressure coefficient β_{M} of chemical potential μ_{M} of a homogeneous mixture M are obtained by taking the derivative μ_{M} with respect to T or p. Based on the approach for a mixture of substances A, B, C, ...

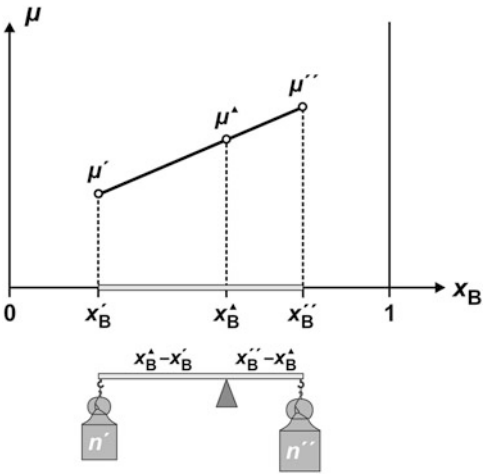


Fig. 13.6 Applying the "lever rule" to a heterogeneous mixture.

$$\mu_M = x_A\mu_A + x_B\mu_B + \ldots \quad \text{with} \quad \mu_A = \overset{\bullet}{\mu}_A + RT\ln x_A + \overset{+}{\mu}_A, \ldots,$$

this results in the desired equations for α_M and β_M. We forgo writing down these equations and select instead a more well-known version by replacing α with molar entropy S_m (but pay attention to the different algebraic sign), $\alpha = -S_m$, and β with molar volume V_m, $\beta = V_m$:

$$S_M = x_A S_A + x_B S_B + \ldots \quad \text{with} \quad S_A = \overset{\bullet}{S}_A - R\ln x + \overset{+}{S}_A, \ldots,$$

$$V_M = x_A V_A + x_B V_B + \ldots \quad \text{with} \quad V_A = \overset{\bullet}{V}_A + \overset{+}{V}_A, \ldots,$$

where S_A is the molar entropy of a substance A, S_B that of a substance B, ... The same applies to the molar volume.

The ellipses (three points) at the end of the last two lines signify the corresponding expressions for the substances B, C, ..., etc., which only differ by the index from the previous one.

13.5 Mixing Processes

Indifferent Substances The chemical potential of homogeneous mixtures can be applied so that reactions between mixed phases can be treated exactly like reactions between pure substances. As an example the chemical drive $\mathcal{A}_{mix}$ for the mixing process of two substances that are indifferent to each other should be determined. Because the conversion numbers ν_A and ν_B coincide with the mole fractions x_A and x_B, the conversion formula simplifies to

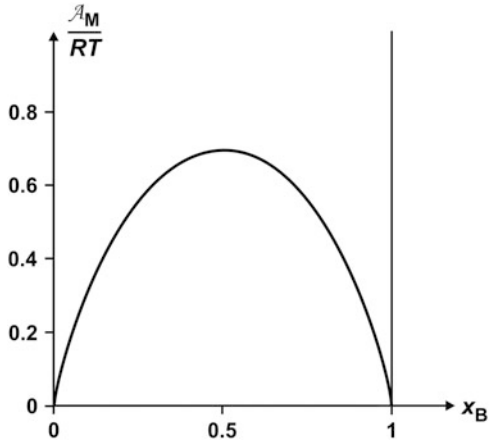


Fig. 13.7 Chemical drive of mixing $\mathcal{A}_{mix}$ as a function of the composition of a homogeneous mixture of two indifferent substances.

$$x_A A + x_B B \rightarrow A_{x_A} B_{x_B}.$$

As usual, the chemical drive corresponds to the potential drop from reactants to products. When we calculate the potential μ_M of the homogeneous mixture $M = A_{x_A} B_{x_B}$ in the manner discussed in the last section [see Eq. (13.7)],

$$\mathcal{A}_{mix} = x_A \dot{\mu}_A + x_B \dot{\mu}_B - \mu_M$$
$$= x_A \dot{\mu}_A + x_B \dot{\mu}_B - \left[x_A \dot{\mu}_A + x_B \dot{\mu}_B + RT(x_A \cdot \ln x_A + x_B \cdot \ln x_B)\right]$$

we obtain:

$$\mathcal{A}_{mix} = -RT(x_A \cdot \ln x_A + x_B \cdot \ln x_B).$$

Figure 13.7 shows the "chemical drive of mixing" $\mathcal{A}_{mix}$ as a function of the composition of the mixture. Notice that the drive for any arbitrary composition is invariably positive because the mole fractions x_A and x_B are always smaller than 1 so that the two logarithms are always negative ($\ln x < 0$ for $x < 1$). This means that two substances that are indifferent to each other mix spontaneously in any proportion.

Side Effects in the Ideal Case Changes of volume and entropy in mixing processes work just like those of chemical processes discussed in Chap. 8. Let us again consider a homogeneous mixture of two indifferent substances A and B. Because the extra quantities, in this case $\overset{+}{V}_m(x)$ and $\overset{+}{S}_m(x)$, disappear, the molar volume of mixing $\Delta_{mix}V$ and the molar entropy of mixing $\Delta_{mix}S$ turn out to be

$$\Delta_{mix}V = V_M - x_A \dot{V}_A - x_B \dot{V}_B = \underbrace{(x_A V_A + x_B V_B)}_{\dot{V}_A \quad \dot{V}_B} - x_A \dot{V}_A - x_B \dot{V}_B \qquad \text{meaning}$$

$$\Delta_{mix}V = 0 \tag{13.15}$$

and

$$\Delta_{\text{mix}}S = S_{\text{M}} - x_{\text{A}}\overset{\bullet}{S}_{\text{A}} - x_{\text{B}}\overset{\bullet}{S}_{\text{B}} = \underbrace{(x_{\text{A}}S_{\text{A}}}_{\overset{\bullet}{S}_{\text{A}} - R\ln x_{\text{A}}} + \underbrace{x_{\text{B}}S_{\text{B}})}_{\overset{\bullet}{S}_{\text{B}} - R\ln x_{\text{B}}} - x_{\text{A}}\overset{\bullet}{S}_{\text{A}} - x_{\text{B}}\overset{\bullet}{S}_{\text{B}} \qquad \text{meaning}$$

$$\Delta_{\text{mix}}S = -R\cdot(x_{\text{A}}\cdot\ln x_{\text{A}} + x_{\text{B}}\cdot\ln x_{\text{B}}). \tag{13.16}$$

When substances that are indifferent to each other (such as dilute gases and light and heavy water) are mixed, the volume does not change. They neither try to absorb entropy from the surroundings nor emit it and their temperatures remain constant. This is just as if different parts of one and the same substance were mixed. For this reason, such mixtures are called "*ideal*." In fact, it is $\Delta_{\text{mix}}V = 0$, but not $\Delta_{\text{mix}}S$, because the term $-R(x_{\text{A}}\cdot\ln x_{\text{A}} + x_{\text{B}}\cdot\ln x_{\text{B}})$, which is always positive because of $x < 1$, remains in the expression. The total required entropy has become greater so that the mixture would have to cool down if entropy cannot flow in from outside. However, this is not the case because energy is released as a result of the substances going through a potential difference during the mixing process. Exactly as much entropy is generated as is needed. The energy released by a small conversion $\mathrm{d}\xi$ and subsequently dissipated results in $\mathrm{d}W_{\text{b}} = \mathcal{A}_{\text{mix}}\cdot\mathrm{d}\xi$ and therefore the generated entropy is $\mathrm{d}S_{\text{g}} = \mathrm{d}W_{\text{b}}/T$ which is exactly equal to $\Delta_{\text{mix}}S\cdot\mathrm{d}\xi$:

$$\mathrm{d}S_{\text{g}} = \frac{\mathcal{A}_{\text{mix}}\mathrm{d}\xi}{T} = \frac{-RT(x_{\text{A}}\cdot\ln x_{\text{A}} + x_{\text{B}}\cdot\ln x_{\text{B}})}{T}\mathrm{d}\xi = -R(x_{\text{A}}\cdot\ln x_{\text{A}} + x_{\text{B}}\cdot\ln x_{\text{B}})\mathrm{d}\xi.$$

Indifferent behavior occurs on the molecular level when the interactions between particles (such as in dilute gas mixtures) are nonexistent or when they are of the same size independently of the type of particles.

Real Mixtures Let us now turn to real mixtures where interactions cannot be ignored any longer and the extra potential $\overset{+}{\mu}$ must be taken into account. The (average) chemical potential of a homogeneous mixture of two components A and B will be equal to:

$$\mu_{\text{M}} = x_{\text{A}}\mu_{\text{A}} + x_{\text{B}}\mu_{\text{B}} = \underbrace{x_{\text{A}}\overset{\bullet}{\mu}_{\text{A}} + x_{\text{B}}\overset{\bullet}{\mu}_{\text{B}}}_{\overset{\circ}{\mu}_{\text{M}}} + \underbrace{RT(x_{\text{A}}\cdot\ln x_{\text{A}} + x_{\text{B}}\cdot\ln x_{\text{B}})}_{\overset{\times}{\mu}_{\text{M}}} + \underbrace{x_{\text{A}}\overset{+}{\mu}_{\text{A}} + x_{\text{B}}\overset{+}{\mu}_{\text{B}}}_{\overset{+}{\mu}_{\text{M}}}.$$

When the chemical potential is plotted as a function of the composition of the mixture (characterized by the mole fraction x_{B}, Fig. 13.8), the three cases discussed above can again be distinguished: highly compatible, lowly compatible, and incompatible. For clarity, the graphic also includes the relation for indifferent behavior. The curve corresponding to highly compatible substances droops the most compared to the ideal case, while the curve corresponding to lowly compatible substances is more compressed. The curve for incompatible substances exhibits a noticeable "dent" upward.

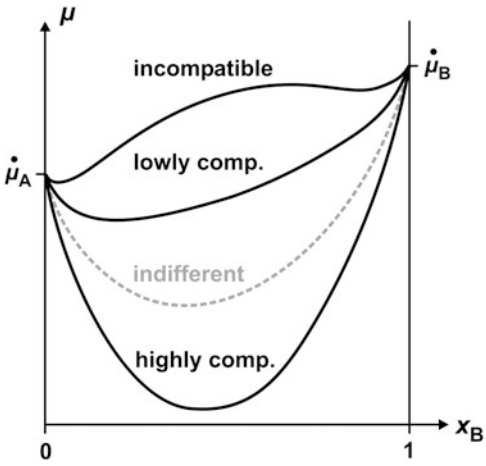


Fig. 13.8 (Average) chemical potentials for mixtures of two substances A and B of varying compatibility, as functions of concentration.

Just as in the case of a single substance, the chemical potential μ_M of a homogeneous mixture is divided into three contributions: "basic term" $\overset{\circ}{\mu}_M(x_B)$, "mass action term" $\overset{\times}{\mu}_M(x_B)$, and "extra term" $\overset{+}{\mu}_M(x_B)$. Figure 13.8 illustrates the effect of the three contributions. The first term results in a straight connection between the "pivot points" $(0, \dot{\mu}_A)$ and $(1, \dot{\mu}_B)$, and the second one is responsible for the formation of the "drooping belly" in between (dotted) which begins and ends with a vertical tangent. At last, the third term deforms the "belly," but the vertical tangents at the borders are always preserved no matter how strong this deformation in upward direction is. The $\overset{+}{\mu}_M(x_B)$ curve begins and ends in the "pivot points." The simplest approach would be a parabolic arc described by an equation such as

$$\overset{+}{\mu}_M(x_B) = a \cdot x_B(1 - x_B).$$

We have to choose an appropriate coefficient a which itself can be dependent on temperature. Negative a means high compatibility, positive a low compatibility, or even incompatibility when $a > 2\,RT$.

Demixing In closing, we will deal in more detail with the behavior of incompatible substances. To do so, we will take a closer look at the process of demixing (the reverse process of mixing):

$$M^{\blacktriangle} \rightarrow \nu' M' + \nu'' M''.$$

This means that the initial homogeneous mixture $M^{\blacktriangle}$ need not separate into the starting components A and B, but can also separate into two homogeneous mixtures M' and M'', of which one is richer in B than the initial mixture and the other one poorer. Because of $n'' = n^{\blacktriangle} - n'$, the balance for component B, for example, results in

$$x_B^{\blacktriangle} n^{\blacktriangle} = x'_B n' + x''_B n'' = x'_B n' + x''_B (n^{\blacktriangle} - n') = x''_B n^{\blacktriangle} - \left(x''_B - x'_B\right) n', \text{ meaning}$$

$$n' = \frac{x''_B - x_B^{\blacktriangle}}{x''_B - x'_B} \cdot n^{\blacktriangle} \quad \text{and finally} \quad v' = \frac{n'}{n^{\blacktriangle}} = \frac{x''_B - x_B^{\blacktriangle}}{x''_B - x'_B}.$$

v'' can be deduced accordingly or follows more simply from the condition $v' + v'' = 1$:

$$v'' = 1 - v' = \frac{x_B^{\blacktriangle} - x'_B}{x''_B - x'_B}.$$

The demixing process occurs spontaneously when its chemical drive $\mathcal{A}$ is positive, i.e., $\mathcal{A} = \mu^{\blacktriangle} - v'\mu' - v''\mu'' > 0$ or, put another way, when

$$\mu^{\blacktriangle} > v'\mu' + v''\mu''.$$

Let us now consider the $\mu(x_B)$ curve for incompatible substances (Fig. 13.9). Mixture $M^{\blacktriangle}$ separates into two homogeneous mixtures M′ and M″ if its chemical potential $\mu^{\blacktriangle}$ has a higher value than the chemical potential $\mu_{\mathcal{M}}$ of the heterogeneous mixture, which is made up of M′ with the fraction v' and M″ with the fraction v''. The potential $\mu_{\mathcal{M}}$ lies on the gray straight line connecting the points (x'_B, μ') and (x''_B, μ'') and is therefore noticeably lower than $\mu^{\blacktriangle}$.

The lever rule is again valid for the ratio of the two coexisting phases:

$$\frac{n'}{n''} = \frac{v'}{v''} = \frac{x''_B - x_B^{\blacktriangle}}{x''_B - x'_B} : \frac{x_B^{\blacktriangle} - x'_B}{x''_B - x'_B} = \frac{x''_B - x_B^{\blacktriangle}}{x_B^{\blacktriangle} - x'_B}.$$

Miscibility Gap Figure 13.9, however, does not yet represent the final situation. Further connecting lines that lie beneath the gray one—and therefore meaning lower potentials $\mu_{\mathcal{M}}$—are also conceivable. The lowest possible $\mu_{\mathcal{M}}$ value can be

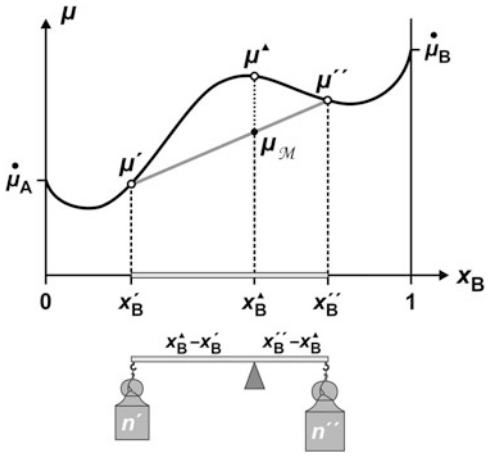


Fig. 13.9 Application of the "lever rule" to a mixture of two incompatible components A and B.

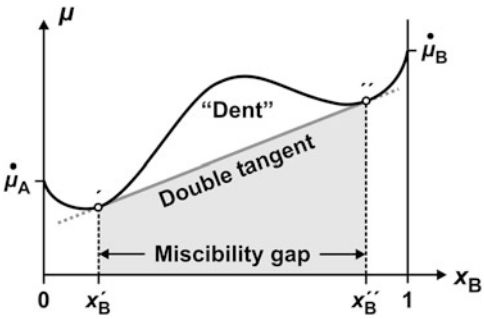


Fig. 13.10 Illustration of the double tangent rule as well as the appearance of a miscibility gap.

found by connecting the points of contact $'$ and $''$ of the common tangents on the "dented" curve, creating a double tangent (Fig. 13.10). These two points limit the so-called *miscibility gap*. For compositions $x_B^{\blacktriangle}$ which lie in the range of the gap, no homogeneous mixture is stable. Instead, it spontaneously separates more or less rapidly into a heterogeneous mixture $\mathcal{M}$ of the two homogeneous mixtures M$'$ and M$''$ with the compositions x'_B and x''_B at the left and right border of the miscibility gap.

If the heterogeneous mixture is liquid, differences in density are responsible for a further separation which often takes place in the gravitational field. The mixture with higher density collects at the bottom, the one with lower density at the top. Such systems of substances which are still connected by shared interfaces and in which pressure and temperature are still uniform can be regarded as *heterogeneous mixtures in a wider sense* because they can be described in the same manner as the systems which are usually considered as heterogeneous mixtures. When a differentiation should be necessary we will call such unusual heterogeneous mixtures *degenerate*.

13.6 More Phase Reactions

In addition to mixing, there are a lot of other processes that can be considered "reactions" between phases and described using the (average) chemical potential. An example of this might be the solidification of magma into mica, feldspar, and quartz.

For every state of an A–B mixture (vapor, melt, and every form of crystal), there is a corresponding (average) chemical potential μ_M, just as there is a chemical potential μ_B for each state of an individual substance B. The most stable state of a phase is the one with the lowest chemical potential, be it a pure phase or a mixed phase. Let us consider as a simple example the behavior of two substances A and B, which are completely miscible in both their solid and liquid states (indifferent behavior, Fig. 13.11). In this case, a gap appears as well, meaning there is a two-phase area. However, this time there is a melt 1 with the composition x_B^1 and a solid phase

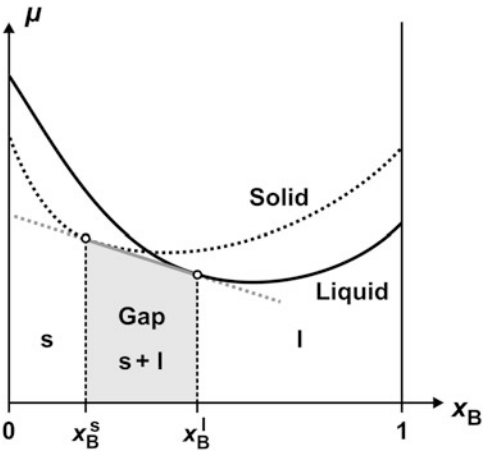


Fig. 13.11 The (average) chemical potential $\mu(x_B)$ as a function of concentration for mixtures of two components that show indifferent behavior in both their solid and liquid states.

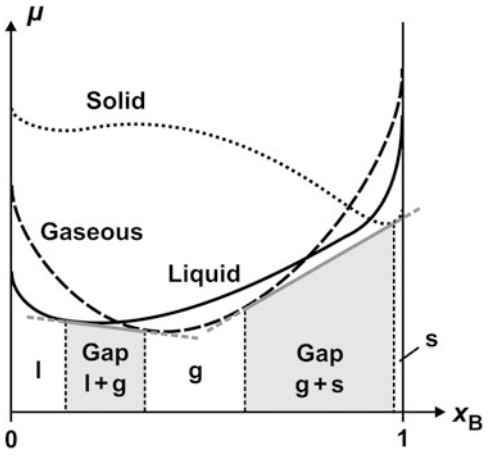


Fig. 13.12 The (average) chemical potential $\mu(x_B)$ as a function of concentration for mixtures of two components that show varying compatibility in their gaseous, liquid, and solid states.

s with the composition x_B^s coexisting with it. Between the points of contact, the double tangent lies everywhere below the $\mu_l(x_B)$ or $\mu_s(x_B)$ curves and therefore exhibits smaller values for the potential $\mu_{\mathcal{M}}$ of the heterogeneous mixture $\mathcal{M}$ which consists partly of mixed crystals M′ with the composition x_B^s and partly of a mixed melt M″ with the composition x_B^l. The separation of the phases is facilitated by the positive chemical drive.

Even more complex circumstances can be treated in this manner. Figure 13.12 shows $\mu(x_B)$ for two substances A and B, which

- As gases, are indifferent as usual,
- As liquids, are lowly compatible ("compressed drooping belly"),
- As solids, are incompatible ("dent upward").

In this case two gaps appear. Because each of the curves shows a vertical tangent on the left side at $x_B = 0$ and on the right side at $x_B = 1$, the gap can never exactly extend so far with the result that there is a narrow sometimes no longer recognizable region in which A and B are miscible.

Based on this, we can now construct phase diagrams just as we did in the case of single-component systems (Chap. 11). This will be discussed extensively in the next chapter.