Chapter 6
Thermodynamics of Mixtures (Multicomponent Systems)

Chemistry typically deals with systems containing several components – called *mixtures* – whose composition can also change. For this reason, it is important to explore how thermodynamic properties depend on the composition. As we shall see, it is not a simple problem due to the great variety of components as well as the nature of their interactions in mixtures. For historical reasons, thermodynamic description of real mixtures is seemingly rather simple; a formal description based on the behavior of mixtures of ideal gases is adapted for them. The origin of this formalism is that early experiments on mixtures concentrated for finding simple relations of general validity, even if they were only approximately valid. This was an efficient method to formalize the theoretical basis, but this simple formalism has been conserved. The great advantage of this thermodynamic formalism is the simplicity and generality of relations concerning ideal gas mixtures. However, keeping this formalism for *real mixtures* necessitates to introduce (and understand) a complicated system of conventions. This feature makes chemical thermodynamics a rather special topic.

This chapter begins with describing the basic formalism on the example of a mixture of ideal gases, and then this description is extended for use in the case of real mixtures. As the most common and useful thermodynamic function in chemical applications is the chemical potential as a function of pressure and temperature, we shall concentrate on the dependence on composition of the chemical potential when the other variables are pressure and temperature.

6.1 Partial Molar Quantities

In earlier chapters, we have frequently used *molar quantities* to describe thermodynamic properties if the extent of the system was not important. We obtained these quantities by dividing the extensive quantities by the total amount of the system, which is the sum of the amounts of all the components. Let us consider an extensive thermodynamic property X as a function of the temperature T, the pressure P, and

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the composition given as the amounts of the K components $n_1, n_2, \ldots, n_K$. The molar quantity of X is calculated as

$$x = \frac{X}{\sum_{i=1}^{K} n_i}. \tag{6.1}$$

From this molar quantity x, we get back the extensive property when multiplying it by the total amount of substance $n = \sum_{i=1}^{K} n_i$:

$$X = nx \tag{6.2}$$

The function $X = X\,(T, P, n_1, n_2, \ldots, n_K)$ is homogeneous first order in the amounts $n_1, n_2, \ldots, n_K$. According to the Euler theorem for homogeneous first-order functions (see (2.31)):

$$X(T, P, n_1, n_2, \ldots, n_K) = \sum_{i=1}^{K} \left(\frac{\partial X}{\partial n_i}\right)_{T,P,n_{j\neq i}} n_i. \tag{6.3}$$

Partial derivatives in the above sum are called *partial molar quantities*. We shall denote them by the symbol X_i:

$$X_i = \left(\frac{\partial X}{\partial n_i}\right)_{T,P,n_{j\neq i}.} \tag{6.4}$$

Using this notation, (6.3) can be written in the form:

$$X = \sum_{i=1}^{K} n_i X_i. \tag{6.5}$$

We may interpret this result telling that the extensive quantity X can be calculated as the sum of the contributions of each component, where the individual contribution is the partial molar quantity multiplied by the amount of the component. Note that partial molar quantities are not independent of the composition. Being derivatives of the function $X\,(T, P, n_1, n_2, \ldots, n_K)$, they are functions of the same variables, i.e., of T, P, and the amounts $n_1, n_2, \ldots, n_K$. However – unlike the original extensive function – $X_i\,(T, P, n_1, n_2, \ldots, n_K)$ is homogeneous zero-order function in the amounts $n_1, n_2, \ldots, n_K$; thus, it is independent of the extent of the system, and the transformation of (2.12) holds:

$$X_i(T, P, \lambda n_1, \lambda n_2, \ldots, \lambda n_K) = X_i(T, P, n_1, n_2, \ldots, n_K) \tag{6.6}$$

By choosing the factor $\lambda = 1/n$, we get the transformed as a function of the variables n_i/n, i.e., of the mole fractions x_i:

$$X_i(T, P, x_1, x_2, \ldots, x_K) = X_i(T, P, n_1, n_2, \ldots, n_K) \tag{6.7}$$

It is important to note that the mole fractions x_i are not independent (cf. (2.10)); consequently, it is enough to specify $K - 1$ of them. (This is in accordance with the fact that the number of degrees of freedom in case of intensive characterization of the system is one less than in case of extensive characterization.)

Partial molar quantities have an important role in the thermodynamic description of mixtures. It is easy to show that relations between extensive variables also hold between the respective partial molar quantities.

6.1.1 Chemical Potential as a Partial Molar Quantity

Let us illustrate the properties of the general partial molar quantity X_i defined above on the example of the chemical potential of component i. It is obvious now that we can calculate it as the partial molar quantity of the Gibbs potential function $G\,(T, P, n_1, n_2, \ldots, n_K)$ (*cf.* (4.22)):

$$\mu_i(T, P, x_1, x_2, \ldots, x_K) = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} \tag{6.8}$$

(Note that the symbol μ_i will be used instead of G_i for this quantity and the corresponding function; thus, it differs from the usual notation of partial molar quantities in form of a subscripted capital letter.)

By derivating both sides of the equation $G = H - TS$ with respect to n_i (considering that the other variables $T, P,$ and the further amounts of components different from i are constant from the point of view of derivation), we get the equation:

$$\mu_i = H_i - TS_i. \tag{6.9}$$

The total differential of the function $\mu_i\,(T, P, x_1, x_2, \ldots, x_K)$ can be written formally as

$$\mathrm{d}\mu_i = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,\boldsymbol{x}} \mathrm{d}T + \left(\frac{\partial \mu_i}{\partial P}\right)_{T,\boldsymbol{x}} \mathrm{d}P + \sum_{i=1}^{K} \left(\frac{\partial \mu_i}{\partial x_i}\right)_{T,P,x_{j\neq i}} \mathrm{d}x_i, \tag{6.10}$$

where $\boldsymbol{x}$ denotes the composition vector $(x_1, x_2, \ldots, x_K)$. Based on (4.22):

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

we can identify the partial derivatives of the function $G(T, P, n_1, n_2, \ldots, n_K)$ as follows:

$$\left(\frac{\partial G}{\partial T}\right)_{P,\boldsymbol{n}} = -S \qquad \left(\frac{\partial G}{\partial P}\right)_{T,\boldsymbol{n}} = V \qquad \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \mu_i.$$

Accordingly, the two first partial derivatives of μ_i in (6.10) can be obtained as second partial derivatives of the function G:

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,\boldsymbol{n}} = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial T}\right)_{P,\boldsymbol{n}} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_{j\neq i}} = -S_i, \quad (6.11)$$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,\boldsymbol{n}} = \frac{\partial}{\partial P}\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial P}\right)_{T,\boldsymbol{n}} = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}} = V_i. \quad (6.12)$$

In the above derivations, we have made use of the rule that we get the same function irrespective of the order of derivation. Consequently, by analogy to (4.22), we can write the total differential of the function $\mu_i(T, P, x_1, x_2, \ldots, x_K)$ in the following form:

$$\mathrm{d}\mu_i = -S_i\,\mathrm{d}T + V_i\,\mathrm{d}P + \sum_{i=1}^{K}\left(\frac{\partial \mu_i}{\partial x_i}\right)_{T,P,x_{j\neq i}} \mathrm{d}x_i. \quad (6.13)$$

This result illustrates well that relations between extensive variables also hold between the respective partial molar quantities.

6.1.2 *Determination of Partial Molar Quantities from Experimental Data*

Mixtures of two components – usually called as *binary*[1] *mixtures* – are common in chemical practice. They occur not only in case of two chemical components in a mixture, but in a broader sense, also if one of the multiple components is considered as "solute," and all the remaining components as "solvent". Accordingly, we usually do not speak about mixtures but solutions. In a binary mixture, one concentration is enough to specify the composition, as the concentration of the other component is not independent; it can be calculated from the first component's concentration. We shall discuss the determination of partial molar quantities on the

[1]The word comes from the Latin *binarius* meaning "two things together". Its meaning in mathematics is the system of numbers consisting of two symbols, usually 0 and 1.

example of a binary mixture, which is, of course, applicable to a solute–multi-component solvent system as well.

As we shall extensively use the symbol x for the mole fraction, it is more appropriate to use V for the extensive variable instead of X to avoid confusion. Accordingly, we shall also call V as volume. Thus, we can state the aim of the following discussion: it is the determination of the partial molar volumes of the components from the measured molar volumes of a binary mixture at constant temperature and pressure. In case of two components, the molar volume of the mixture is

$$v = \frac{V}{n_1 + n_2}, \tag{6.14}$$

from which we obtain:

$$V = v\,(n_1 + n_2) \tag{6.15}$$

The partial molar volume of component 1 can be obtained from (6.4) as the partial derivative of the right-side product of (6.15). To simplify notation, we do not show the variables T and P as they are constant in the experiments:

$$V_1 = \left(\frac{\partial V}{\partial n_1}\right)_{n_2} = v + (n_1 + n_2)\left(\frac{\partial v}{\partial n_1}\right)_{n_2}. \tag{6.16}$$

To justify this result, we should take into account that the first term of the derivative of the product is $v\partial(n_1 + n_2)/\partial n_1$ and that $\partial n_1/\partial n_1 = 1$ and $\partial n_2/\partial n_1 = 0$. We would like to use the derivative of molar volume with respect to x_2 instead of n_1, which we can write using the chain rule as follows:

$$\left(\frac{\partial v}{\partial n_1}\right)_{n_2} = \left(\frac{\partial x_2}{\partial n_1}\right)_{n_2} \frac{\mathrm{d}v}{\mathrm{d}x_2} \tag{6.17}$$

(The function $v(x_2)$ is only a univariate function, which is the reason for not writing a partial derivative in $\mathrm{d}v/\mathrm{d}x_2$.) The partial derivative of the mole fraction x_2 with respect to n_1 is:

$$\left(\frac{\partial x_2}{\partial n_1}\right)_{n_2} = \frac{\partial}{\partial n_1}\left(\frac{n_2}{n_1 + n_2}\right) = \frac{(n_1 + n_2)\left(\frac{\partial n_2}{\partial n_1}\right) - n_2\left(\frac{\partial (n_1 + n_2)}{\partial n_1}\right)}{(n_1 + n_2)^2} = -\frac{n_2}{(n_1 + n_2)^2}. \tag{6.18}$$

Let us substitute the partial derivative calculated above into (6.16):

$$V_1 = v - \frac{n_2}{(n_1 + n_2)}\frac{\partial v}{\partial x_2} = v - \frac{\partial v}{\partial x_2}x_2 \tag{6.19}$$

This can be used to calculate the partial molar volume V_1. By rearranging this equation, we get an expression to graphically plot the result:

$$v = V_1 + \frac{\partial v}{\partial x_2} x_2 \tag{6.20}$$

This is the equation of a straight line whose intercept (the value at $x_2 = 0$) is the molar volume of component 1. The molar volume of the other component, V_2, can be given from (6.5) as follows:

$$v = (1 - x_2)V_1 + x_2 V_2. \tag{6.21}$$

As seen in Fig. 6.1, in a graphical representation the tangent line of the graph of the function at mole fraction x_2 can be used to determine the partial molar volumes. The intercept of the line at $x_2 = 0$ gives V_1, while the intercept at $x_2 = 1$ gives V_2.

We shall see later that the partial molar volume of a component at its zero concentration is a quantity of interest. This is obviously not the molar volume of the pure solvent, but the extrapolated value of the function $v(x_2)$ to $x_2 = 0$. This extrapolation is easy to perform if we fit a power series to the experimental data. The constant term of this series gives the extrapolated partial molar volume of component 1, the sum of the constant term and the coefficient of the first-order term gives that of component 2 (both at $x_2 = 0$).

The procedure discussed above can, of course, be used not only in case of volume, but any other extensive quantities (*U, H, F, G, etc.*) to determine the corresponding partial molar quantity.

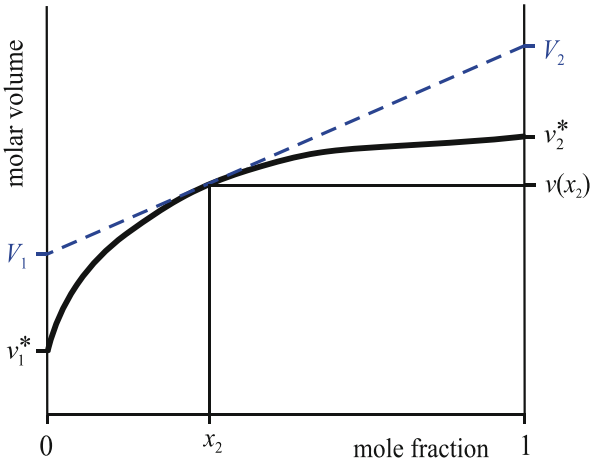

Fig. 6.1 Determining partial molar volume using the method of intercepts in a binary mixture. At the composition x_2 shown, the partial molar volume of component 1 is V_1, while that of component 2 is V_2

6.2 Thermodynamics of Ideal Mixtures

As already mentioned at the beginning of this chapter, the formalism used to describe thermodynamic properties of mixtures is based on the description of mixtures of ideal gases; thus, we begin this section by discussing these mixtures. Their practical importance is negligible in chemistry, but their characterization enables to understand the thermodynamic formalism used to describe real mixtures of practical importance.

6.2.1 Ideal Gas Mixtures

Mechanical properties of an ideal gas can be calculated using the equation of state given in (2.39):

$$V = \frac{nRT}{P}. \tag{6.22}$$

In an ideal gas, there is no interaction between molecules (apart from elastic collisions); thus, a mixture of different ideal gas species also behaves as an ideal gas. This means that the behavior of the mixture components is independent of the presence and concentration of other components. If we write individual components explicitly in (6.22), it becomes:

$$V = \frac{RT\sum_{i=1}^{K} n_i}{P}. \tag{6.23}$$

It is easy to calculate partial molar volumes from this form:

$$\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}} = V_i = \frac{RT}{P}. \tag{6.24}$$

This is exactly the same as the molar volume of the mixture. We can interpret this by saying that each component fills the whole volume accessible. A consequence of the equality of the molar volume for each component is that the total volume can be given as $V_i \sum_{i=1}^{K} n_i$. As the components behave independently, we can also associate with each of them the pressure which they would have if they were only alone in the whole volume, without the other components. From (6.22) and (6.24), this pressure is

$$p_i = \frac{n_i RT}{V}, \tag{6.25}$$

while the total pressure is

$$P = \frac{\sum_{i=1}^{K} n_i RT}{V}. \tag{6.26}$$

Comparing the two equations, we can deduce a simple expression:

$$p_i = \frac{n_i}{\sum_{i=1}^{K} n_i} P = x_i P. \tag{6.27}$$

Summing up we can say that the total pressure P of a mixture of ideal gases can be obtained as the weighted sum by the mole fractions x_i of the partial pressures p_i. The partial pressures p_i are also identical to the pressures which individual components would have if they were only alone in the whole volume V, without the other components. This relation is called *Daltons Law*, named after its first identifier.[2]

It is important to note that the partial pressure is always defined as

$$p_i = x_i P, \tag{6.28}$$

but, for a real gas, it is usually not the same as the pressure of the pure component being alone in the total volume of the mixture. It is also worth noting that the partial pressure p_i is *not a partial molar quantity*, as it is not the partial derivative of a function determining an extensive quantity.

Based on the above results, we can determine the chemical potential of the components of an ideal gas mixture as a function of the concentration. To do so, let us start from (6.13) writing it for a closed system ($\mathrm{d}x_i = 0, \forall i$) at constant temperature ($\mathrm{d}T = 0$):

$$\mathrm{d}\mu_i = V_i \, \mathrm{d}P \tag{6.29}$$

In accordance with the above results, let us conceive the mixture by expanding each component from the total pressure P to its actual partial pressure p_i in the mixture. (The total pressure is P, in accordance with (6.28)). The chemical potential of the components can be obtained by integration of the above equation:

$$\mu_i(T, p_i) = \mu_i(T, P) + \int_P^{p_i} V_i \, \mathrm{d}p. \tag{6.30}$$

[2]John Dalton (1766–1844) was an English chemist and physicist, one of the determining persons who established and made accepted the atomic theory in chemistry. His experimental studies on gases also contributed to the development of his atomic theory.

Substitute the volume of an ideal gas into the integrand:

$$\mu_i(T,p_i) = \mu_i(T,P) + \int_P^{p_i} \frac{RT}{p}\,\mathrm{d}p = \mu_i(T,P) + RT\ln\frac{p_i}{P}. \tag{6.31}$$

According to (6.28), we can substitute x_i for p_i/P:

$$\mu_i(T,p_i) = \mu_i(T,P) + RT\ln x_i. \tag{6.32}$$

As p_i uniquely determines x_i, this equation can be rewritten in the form:

$$\mu_i(T,P,x_i) = \mu_i(T,P) + RT\ln x_i \tag{6.33}$$

Equation (6.33) determines the chemical potential of the species i in an ideal gas mixture at a given temperature T and pressure P as a function of the concentration. Note that the function $\mu_i\ (T, P, x_i)$ depends only on the concentration of the species i and does not depend on the concentration of any other species.

6.2.2 Properties of Ideal Mixtures

Equation (6.33) has a particular importance in thermodynamic formalism of mixtures; the chemical potential of a component as a function of composition in any mixture is derived from this equation. The first step of this derivation is the definition of an *ideal mixture*. An ideal mixture is a hypothetical multicomponent system, for which the chemical potential of each component has the same functional form as in an ideal gas mixture:

$$\mu_{i,\text{mixture}}(T,P,x_i) = \mu_{i,\text{pure substance}}(T,P) + RT\ln x_i. \tag{6.34}$$

Following the usual simplified notation, we shall omit hereinafter the word "mixture" in the subscript of $\mu_{i,\,\text{mixture}}(T,P,x_i)$, and also the variable list T, P, x_i – unless it has a particular relevance. In a similar manner, the word "pure substance" in the subscript of $\mu_{i,\,\text{pure substance}}(T,P)$ and the variables T and P will also be omitted. Instead, we shall use an asterisk to indicate the chemical potential of the pure substance. The simplified equation commonly encountered is:

$$\mu_i = \mu_i^* + RT\ln x_i. \tag{6.35}$$

As the chemical potential p_i is given relative to μ_i^* – the chemical potential of the pure substance – this latter is called the chemical potential of the *reference state*. This means that the reference state is the pure substance at $x_i = 1$.

Let us discuss the properties of an ideal mixture on the basis of (6.35). We can do this by exploring the change of thermodynamic properties of the system when mixing takes place, i.e., a homogeneous mixture is formed from its pure, unmixed components of the appropriate proportions. (Alternatively, we can formulate it as in previous chapters on thermodynamic equilibria. We suppose internal constraints in the initial state that do not allow mixing. By removing these constraints, mixing occurs and a new equilibrium is achieved. We shall describe this new equilibrium state and compare it to the initial state.) These changes are called *properties of mixing*. Instead of a general definition, let us discuss some thermodynamically important quantities. We can start with the chemical potential itself, which we know it changes from μ_i^* to μ_i during mixing. The change due to mixing can be expressed from (6.35) as follows:

$$\Delta_{\text{mix}}\mu_i = \mu_i - \mu_i^* = RT \ln x_i \tag{6.36}$$

Of course, there is nothing new in this statement, but we can easily calculate the *Gibbs potential of mixing* from this equation. From (6.5), we know:

$$G = \sum_{i=1}^{K} n_i G_i = \sum_{i=1}^{K} n_i \mu_i. \tag{6.37}$$

Let us divide both sides of this equation by $n = \sum_{i=1}^{K} n_i$, the total amount of components. On the left side, we get the molar Gibbs potential of the mixture, while on the right side, we can write x_i in place of the amounts of components n_i:

$$g = \sum_{i=1}^{K} x_i \mu_i. \tag{6.38}$$

Thus, we can write for the Gibbs potential of mixing

$$\Delta_{\text{mix}} g = g - g* = \sum_{i=1}^{K} x_i(\mu_i^* + RT \ln x_i) - \sum_{i=1}^{K} x_i \mu_i^*, \tag{6.39}$$

which results in:

$$\Delta_{\text{mix}} g = RT \sum_{i=1}^{K} x_i \ln x_i. \tag{6.40}$$

In conclusion, we can state that – in constant-temperature and constant-pressure systems – the formation of a mixture from its pure components is accompanied by a decrease of the Gibbs potential. (The mole fractions x_i are all inferior to 1; thus, the logarithm of each of them is negative.) Based on our knowledge of thermodynamics, we can say that mixing is a spontaneous process.

The *entropy of mixing* can be calculated from (6.11) and the expression (6.35) of the chemical potential:

$$-S_i = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,\mathbf{n}} = \frac{\partial}{\partial T}(\mu_i^* + RT \ln x_i) = -S_i^* + R \ln x_i. \tag{6.41}$$

The result is easily obtained:

$$\Delta_{\text{mix}} s = -R \sum_{i=1}^{K} x_i \ln x_i. \tag{6.42}$$

According to this, mixing is always accompanied by an increase in entropy.

The partial molar volume can also be calculated as the partial derivative of the chemical potential function (*cf.* (6.12)):

$$V_i = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,\boldsymbol{n}} = \frac{\partial}{\partial P}(\mu_i^* + RT \ln x_i) = \left(\frac{\partial \mu_i^*}{\partial P}\right)_{T,\boldsymbol{n}} = V_i^*. \tag{6.43}$$

From this result, we can see that the molar volume does not change when the components are mixed. According to (6.5), it also means that the total volume of the system does not change either, when mixing occurs. We can conclude that the *volume of mixing* of ideal mixtures is zero.

We have seen before that the same relations hold between partial molar quantities as between the corresponding extensive variables. (This is the reason behind the above expressions of S_i and V_i.) By making use of these relations, we can calculate further properties of mixing. From the relation

$$H_i = \mu_i + TS_i \tag{6.44}$$

it follows that

$$\Delta_{\text{mix}} h = \Delta_{\text{mix}} g + T \Delta_{\text{mix}} s, \tag{6.45}$$

Thus, the molar enthalpy of mixing is

$$\Delta_{\text{mix}} h = RT \sum_{i=1}^{K} x_i \ln x_i - TR \sum_{i=1}^{K} x_i \ln x_i = 0. \tag{6.46}$$

Accordingly, the enthalpy of the system does not change on mixing, i.e., mixing at constant pressure is accompanied neither by warming nor cooling.

The *molar internal energy of mixing* can be obtained from

$$U_i = \mu_i - PV_i + TS_i \tag{6.47}$$

as

$$\Delta_{\text{mix}} u = \Delta_{\text{mix}} g - P\Delta_{\text{mix}} v + T\,\Delta_{\text{mix}} s. \tag{6.48}$$

This is also zero; as according to (6.45), $\Delta_{\text{mix}} g + T\,\Delta_{\text{mix}} s$ is zero, and according to (6.43), $\Delta_{\text{mix}} v$ is also zero.By taking into account the equation

$$F_i = \mu_i - PV_i, \tag{6.49}$$

we can calculate the *molar free energy of mixing* as

$$\Delta_{\text{mix}} f = \Delta_{\text{mix}} g - P\Delta_{\text{mix}} v. \tag{6.50}$$

By considering (6.40) and the above result that $\Delta_{\text{mix}} v = 0$, we obtain the result:

$$\Delta_{\text{mix}} f = RT \sum_{i=1}^{K} x_i \ln x_i \tag{6.51}$$

In summary, we can state that – when mixing ideal mixtures from the pure components – volume, internal energy, and enthalpy do not change, but entropy is increased, while free energy and the Gibbs potential are decreased.

6.2.3 Alternative Reference States

The chemical potential of the components of an ideal mixture can be written in an alternative form of (6.31) as follows:

$$\mu_i(T, p_i) - \mu_i(T, P) = RT \ln \frac{p_i}{P}. \tag{6.52}$$

The method used in Sect. 6.1.1 to derive this equation leads to a similar result even if we chose another partial pressure as the initial pressure instead of the total pressure P. Thus, if the partial pressure of a component in the mixture changes from $p_{i,1}$ to $p_{i,2}$, (6.52) can be rewritten as follows:

$$\mu_i(T, p_{i,2}) - \mu_i(T, p_{i,1}) = RT \ln \frac{p_{i,2}}{p_{i,1}} \tag{6.53}$$

In an ideal gas mixture – according to (6.25) – we can write

$$p_i = \frac{n_i RT}{V} = \frac{n_i}{V} RT = c_i RT, \tag{6.54}$$

where c_i is the *molar concentration* expressed in the usual mol/dm^3 units. Consequently, (6.53) can also be written as follows:

$$\mu_i\big(T,P,c_{i,2}\big)-\mu_i\big(T,P,c_{i,1}\big)=RT\ln\frac{c_{i,2}}{c_{i,1}}. \tag{6.55}$$

Obviously, at constant pressure we can also write it in another form:

$$\mu_i\big(T,P,x_{i,2}\big)-\mu_i\big(T,P,x_{i,1}\big)=RT\ln\frac{x_{i,2}}{x_{i,1}}. \tag{6.56}$$

The above equations can be rewritten using a different notation:

$$\mu_i(T,x_i)=\mu_i\big(T,x_{i,\mathrm{ref}}\big)+RT\ln\frac{x_i}{x_{i,\mathrm{ref}}}, \tag{6.57}$$

$$\mu_i(T,p_i)=\mu_i\big(T,p_{i,\mathrm{ref}}\big)+RT\ln\frac{p_i}{p_{i,\mathrm{ref}}}, \tag{6.58}$$

$$\mu_i(T,c_i)=\mu_i\big(T,c_{i,\mathrm{ref}}\big)+RT\ln\frac{c_i}{c_{i,\mathrm{ref}}}. \tag{6.59}$$

In liquid mixtures, the *molality* m_i (the amount of component i per 1 kg solvent, expressed in $\mathrm{mol\,kg^{-1}}$ units) is also *nearly* proportional to a good approximation to the mole fraction, especially at low m_i values. (This is one of the reasons to speak about *dilute solutions*.) Thus, we can write a fourth equation:

$$\mu_i(T,P,m_i)=\mu_i\big(T,P,m_{i,\mathrm{ref}}\big)+RT\ln\frac{m_i}{m_{i,\mathrm{ref}}}. \tag{6.60}$$

The four equations above suggest that the chemical potential of a mixture component can be given relative to any reference state. The concentration of the reference state, as well as that of the actual state, can be given either as partial pressure, or mole fraction, or molar concentration, or molality. (Obviously, partial pressure is only relevant in gases, while molality in dilute solutions.) However, it is important to emphasize that the *definition* of an ideal mixture is (6.35), using *mole fraction* as concentration. Consequently, the other expressions above can only be used for accurate calculations if the concentration used is strictly *proportional* to the mole fraction. (As we have seen, in gas mixtures, the partial pressure p_i and the molar concentration c_i fulfill this condition.)

Let us check the general applicability of the concentrations c_i and m_i from this point of view. As to c_i, we can write the amount of component i in the numerator, while we can replace the volume V in the denominator by the total mass of the mixture divided by the density ρ. (The density is then written in the numerator. M_j is the molar mass of component j.) We can readily simplify by the total amount n:

$$c_i = \frac{\rho x_i n}{n \sum_{j=1}^{K} x_j M_j} = \frac{\rho x_i}{\sum_{j=1}^{K} x_j M_j}. \tag{6.61}$$

Let us rewrite the equation by separating component 1 from all the other components in the denominator and express the concentration of this component:

$$c_1 = x_1 \frac{\rho}{x_1 M_1 + \sum_{j=2}^{K} x_j M_j}. \tag{6.62}$$

Observing this result, we can see that c_i is only proportional to x_i if the density ρ does not change with the composition, and if the molar mass M_1 of component 1 is identical to the mean molar mass of the other components. Otherwise, c_1 is only proportional to a good approximation to x_1 if c_1 is small.

The molality m_i – which is the amount of component i dissolved in 1000 g of the solvent – is used to express concentration in liquid solutions. In many cases, the "solvent" means all the other components except for component 1; thus, we can write for the molality m_1:

$$m_1 = x_1 \frac{1000}{\sum_{j=2}^{K} x_j M_j}. \tag{6.63}$$

(The number 1000 in the numerator appears as a consequence of writing the molar masses M_j in *gram/mol units*.) Let us suppose that the composition of the solvent does not change; thus, we can treat it as a single component. By denoting its total amount by n_2, its mole fraction can be calculated as $x_2 = n_2/(n_1 + n_2)$. By taking into account that $x_2 = 1 - x_1$, we can rewrite the above equation as follows:

$$m_1 = \frac{1000}{M_2} \frac{x_1}{1 - x_1}. \tag{6.64}$$

From this result, we can see that the proportionality of m_1 to x_1 holds only to the same approximation as the proportionality of the ratio $x_1/(1 - x_1)$ to x_1 – which is a good approximation only if $x_1 \ll 1$, i.e., in dilute solutions.

By summing up the above results, we can say that the definition of an ideal mixture

$$\mu_i(T, P, x_i) = \mu_i^*(T, P) + RT \ln \frac{x_i}{1} \tag{6.65}$$

can be replaced in gaseous mixtures by

$$\mu_i(T, P, p_i) = \mu_i\left(T, P, p_{i,\mathrm{ref}}\right) + RT \ln \frac{p_i}{p_{i,\mathrm{ref}}} \tag{6.66}$$

to give exact results. In case of low concentrations of the species i, we can also use the following equations to a good approximation:

$$\mu_i(T,P,c_i) = \mu_i\left(T,P,c_{i,\mathrm{ref}}\right) + RT\ln\frac{c_i}{c_{i,\mathrm{ref}}}, \tag{6.67}$$

$$\mu_i(T,P,m_i) = \mu_i\left(T,P,m_{i,\mathrm{ref}}\right) + RT\ln\frac{m_i}{m_{i,\mathrm{ref}}}. \tag{6.68}$$

6.2.4 Activity and Standard State

Equations (6.65) – (6.68) are rather similar to each other; in each of them, the logarithm of the concentration ratio multiplied by RT is added to the chemical potential of the reference state. The concentration ratio can be related to the ratio of the activities. Activity is defined by the following equation:

$$\mu_i = RT\ln\lambda_i. \tag{6.69}$$

The quantity λ_i is called *absolute activity*. Obviously, the difference of the chemical potentials is related to the ratio of the absolute activities:

$$\mu_2 - \mu_1 = RT\ln\frac{\lambda_2}{\lambda_1}. \tag{6.70}$$

The particular ratio

$$a_i = \frac{\lambda_i}{\lambda_{i,\,\mathrm{ref}}} \tag{6.71}$$

is called the *relative activity with respect to the reference state*. In the light of this definition, (6.65)–(6.68) can be written in the same general form:

$$\mu_i = \mu_{i,\,\mathrm{ref}} + RT\ln a_i. \tag{6.72}$$

It is common practice to use $\mu_i^{\ominus}$ instead of $\mu_{i,\mathrm{ref}}$, which we will also adopt in this book.[3] If there is no ambiguity, this simple notation is used to formulate the composition-dependent chemical potential:

$$\mu_i = \mu_i^{\ominus} + RT\ln a_i \tag{6.73}$$

[3]The symbol $\ominus$ has been devised by Samuel Plimsoll (1825–1898) as a safe load line on ships to avoid overloading. Plimsoll was a liberal Member of Parliament and succeded to prescribe the safe load line in a bill. IUPAC introduced the "plimsoll sign" to denote the reference state in 1970, but it considers the sign $^{\ominus}$ and $^{\circ}$ as equally acceptable. In the rest of the book, we shall use $^{\ominus}$.

The quantity a_i is the ratio of the value of a composition variable (such as x_i, p_i, c_i, or m_i) and the value of the same variable in the reference state, which is identical to the respective ratio of absolute activities λ_i.

A more informative but not quite correct formulation contains the composition variable itself instead of the activity a_i, and we have to *imagine* a division by the value of the composition variable in the reference state. In other words, we can say that we consider the concentration (or partial pressure) of the reference state as unit and the concentration (or partial pressure) in the formula is the *measured value* on this scale – which is identical to the relative activity defined in (6.71). (Of course, this is only true if the concentration used is proportional to the mole fraction.) This formulation is quite commonly used; thus, we summarize different possibilities in Table 6.1. If there is no ambiguity, we shall use this simplified notation in this book.

Of the "substitutes" for relative activities shown in the table, there is no problem with the mole fraction x_i as it is a dimensionless quantity. In case of the molar concentration c_i or the molality m_i, the reference state is almost always 1 mol/dm^{-3} or 1 mol kg^{-1}; thus, the argument of the logarithm function is the measured value in mol dm^{-3} or mol kg^{-1} unit. In case of the partial pressure p_i, the situation is more complicated. The usual reference state is the pure gas at atmospheric pressure which, in SI units, is not 1 but 101 325 Pa. Thus, the correct value of the argument of the logarithm function is $p_i/p^{\ominus}$, i.e., "p_i" should be understood as p_i/101 325 Pa. (It should be noted that the reference pressure was originally *not* 101 325 Pa but 1 atm so that the partial pressure given in atm units was also simply the measured value in atm units.)

Reference state concentrations and pressure shown in Table 6.1 are particular values according to the 1970 recommendations of IUPAC. According to this recommendation, the pressure 101 325 Pa is called *standard pressure*, the concentration 1 mol dm^{-3} is called *standard concentration,* and the molality 1 mol kg^{-1} is called *standard molality*. The standard value of the mole fraction is of course 1. As to the pressure, IUPAC formulated a recommendation already in 1985 that the standard pressure should be changed from the "old" 1 atm (i.e., 101 325 Pa) to the simpler value of 1 bar = 10^5 Pa, but this recommendation has not really been

Table 6.1 Actual forms of the general equation $\mu_i = \mu_i^{\ominus} + RT \ln a_i$ in case of relative activities a_i defined in terms of different composition variables in *ideal mixtures*, and the respective reference states. The symbols p_i, c_i, and m_i always stand for the measured value of the respective quantity in units of the value of the reference state, i.e., for the ratios $p_i/p^{\ominus}$, $c_i/c^{\ominus}$, and $m_i/m^{\ominus}$

System	Equation	Meaning of $\mu_i^{\ominus}$	Comment
Every mixture	$\mu_i = \mu_i^{\ominus} + RT \ln x_i$	μ_i of the pure component	Always exact
Gas mixtures	$\mu_i = \mu_i^{\ominus} + RT \ln p_i$	μ_i of the pure component at pressure $p^{\ominus}$ ($p^{\ominus}$ is usually 101,325 Pa)	Always exact
Liquid solutions ideal gas mixtures	$\mu_i = \mu_i^{\ominus} + RT \ln c_i$	μ_i of the pure component at concentration $c^{\ominus}$ ($c^{\ominus}$ is usually 1 mol/dm^3)	Approximately valid in dilute solutions
Liquid solutions	$\mu_i = \mu_i^{\ominus} + RT \ln m_i$	μ_i of the pure component at concentration $m^{\ominus}$ ($m^{\ominus}$ is usually 1 mol kg^{-1})	Approximately valid in dilute solutions

implemented in practice. Anyway, we should be careful to check what is the standard pressure when referring to thermodynamic tables or databases.

The above-mentioned particular reference states are called *standard states*, and the symbol $\mu_i^{\ominus}$ refers to these states. This is the reason to call $\mu_i^{\ominus}$ the *standard chemical potential*. This name will have a more important role in case of real mixtures, but at the same time it loses its property of referring to a physically existing mixture. The property of the physical existence of the standard state holds only in ideal mixtures.

6.3 Thermodynamics of Real Mixtures

Similarly to ideal gases, ideal mixtures do not exist. However, as the fundamental equation of an ideal gas might be a good approximation of the thermodynamic properties of a real gas, the thermodynamic description of ideal mixtures can also be considered as an approximation. The ideal gas equation of state can be mathematically exact in limiting cases (e.g., at zero pressure). Similarly, there are limiting cases where thermodynamic formulae describing ideal mixtures are also mathematically exact. The analogy between an ideal gas and an ideal solution also extends to the actual treatment of real gases and real mixtures; on the analogy of fugacity correcting the ideal gas equation of state for real gases, a similar modification of activity corrects the formalism of ideal mixtures to describe the behavior of real mixtures. This modification is described in the next section.

6.3.1 Mixtures of Real Gases

Let us recall the expression for the chemical potential as a function of the partial pressure p_i in an ideal mixture, formulated in (6.30):

$$\mu_i(T, p_i) = \mu_i(T, P) + \int_P^{p_i} V_i \, \mathrm{d}p.$$

If component i does not behave as an ideal gas, its partial molar volume V_i is not identical to RT/p; thus, the equation found in Table 6.1,

$$\mu_i^{\mathrm{id}}(T, p_i) = \mu_i^{\ominus}(T, P^{\ominus}) + RT \ln \frac{p_i}{P^{\ominus}} \tag{6.74}$$

does not apply. Let us write equation (6.30) for both a real and an ideal mixture, and subtract the one for the real mixture from the other:

$$\mu_i(T,p_i) - \mu_i^{\mathrm{id}}(T,p_i) = \mu_i^{\ominus}(T,P^{\ominus}) - \mu_i^{\ominus\mathrm{id}}(T,P^{\ominus}) + \int_{P^{\ominus}}^{p_i} \left(V_i - \frac{RT}{p}\right) \mathrm{d}p. \quad (6.75)$$

The difference $\mu_i(T,p_i) - \mu_i^{\mathrm{id}}(T,p_i)$ is called *excess chemical potential* and is denoted by μ_i^{E}. This excess chemical potential can be considered as the "deviation from the ideal behavior". Let us fix the reference state of the real mixture concerning component i as the reference state of an ideal mixture; *i. e.* according to the identity $\mu_i^{\ominus}(T,P^{\ominus}) = \mu_i^{\ominus\mathrm{id}}(T,P^{\ominus})$. In this case, the deviation from the ideal behavior is fully accounted for by the integral in the last term of (6.75). We know of gases that the deviation from the ideal gas behavior diminishes as the pressure goes to zero, and we also expect this behavior in a gas mixture for all the components. Consequently, at small enough pressure, even a real gas mixture behaves as an ideal mixture. In the light of this limiting behavior, let us chose the pressure $P^{\ominus}$ of the reference state as zero. In this case, we can be certain that the values of $\mu_i^{\ominus}$ and $\mu_i^{\ominus\mathrm{id}}$ should be identical, their difference is zero, and the integration should be carried out from the lower limit of zero pressure:

$$\mu_i(T,p_i) - \mu_i^{\mathrm{id}}(T,p_i) = \int_0^{p_i} \left(V_i - \frac{RT}{p}\right) \mathrm{d}p. \quad (6.76)$$

The integral on the right-hand side is identical to the function $RT \ln \varphi_i$, which can be calculated using (4.95), where φ_i is the *fugacity coefficient*[4] of component i. Let us substitute into the above equation the expression of the chemical potential $\mu_i^{\mathrm{id}}(T,p_i)$ from (6.74) and replace the integral by $RT \ln \varphi_i$. By rearranging, we get:

$$\mu_i(T,p_i) = \mu_i^{\ominus}(T,\, P^{\ominus}) + RT \ln \frac{p_i}{P^{\ominus}} + RT \ln \varphi_i \quad (6.77)$$

This can be rewritten in the simpler form:

$$\mu_i(T,p_i) = \mu_i^{\ominus}(T,P^{\ominus}) + RT \ln \frac{\varphi_i p_i}{P^{\ominus}} \quad (6.78)$$

We should keep in mind that the above expression has been obtained by substitution of the chemical potential of an *ideal* mixture; thus, the standard chemical potential of the ideal mixture $\mu_i^{\ominus}(T,P^{\ominus})$ is "inherited". Accordingly, $\mu_i^{\ominus}(T,P^{\ominus})$ is the chemical potential of component i in a hypothetical *ideal mixture* at the given temperature and the reference pressure:

[4]Fugacity was introduced by the American chemist Gilbert Newton Lewis (1875–1946) in 1908 to calculate the chemical potential of components in gas mixtures. The quantity $f_i = \varphi_i\, p_i$ should properly be called as *partial fugacity* (in analogy to the partial pressure p_i) as the fugacity of a component in a mixture is typically not identical to the fugacity of the same pure component at the pressure p_i. However, this name is not used and we shall not use it either in this book. The word *fugacity* is coined from the Latin *fuga* = escape and the word *capacity* which is also of Latin origin, thus referring to the "capacity to escape" of the gas.

$$\mu_i^{\ominus}(T) = \lim_{p_i \to 0} \left[\mu_i(T, p_i, \varphi_i, x) - RT \ln \frac{\varphi_i p_i}{P^{\ominus}} \right]. \tag{6.79}$$

We may interpret this the following way. The actual partial pressure p_i in the numerator contains the corrected value $\varphi_i\, p_i$, and the standard chemical potential $\mu_i^{\ominus}(T)$ is to be understood so that, though it is the chemical potential at the pressure $\varphi_i\, p_i$ which is equal to $P^{\ominus}$ (as the fraction is 1 and the logarithm is zero in that case), its actual value reflects an ideal behavior of the gas mixture at the pressure $P^{\ominus}$. Due to the value of the standard at the limit of zero pressure, it does *not* depend on pressure, only on temperature – which is the reason not to show pressure as its argument. The value of the standard at any reference pressure $P^{\ominus}$ can be obtained by extrapolation to this pressure. The correction factor φ_i takes into account the deviation from the ideal behavior at any pressure. We can say that the standard chemical potential obtained at extremely low pressures is always extrapolated to the actual pressure $P^{\ominus}$ according to the expression valid for ideal mixtures. This interpretation is visualized in Fig. 6.2.

Following Lewis, the "effective (partial) pressure" $\varphi_i\, p_i$ is called *fugacity*, and it can be denoted also by f_i. Accordingly, the quantity φ_i is called the *fugacity coefficient*. If the existence of the limit at zero pressure and the possibility to calculate the fugacity coefficient using (4.95) are not to be proved, the chemical potential of a real gas mixture can more easily be derived. The chemical potential can be written as follows:

$$\mu_i(T, p_i) = \mu_i^{\mathrm{id}}(T, p_i) + \mu_i^{\mathrm{E}}(T, p_i) = \mu_i^{\ominus}(T) + RT \ln \frac{p_i}{P^{\ominus}} + \mu_i^{\mathrm{E}}(T, p_i). \tag{6.80}$$

Let us rewrite the excess chemical potential μ_i^{E} as $RT\ \ln\ \varphi_i$:

$$\mu_i(T, p_i) = \mu_i^{\ominus}(T) + RT \ln \frac{p_i}{P^{\ominus}} + RT \ln \varphi_i \tag{6.81}$$

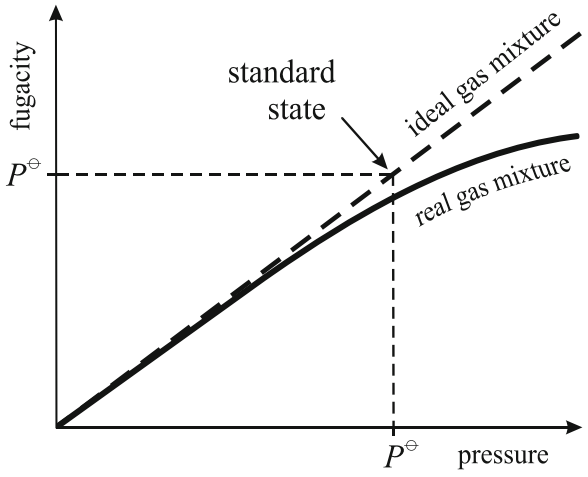

Fig. 6.2 Interpretation of the standard state if the chemical potential of a component in real gas mixtures is given as a function of fugacity

By rearranging the equation, we get:

$$\mu_i(T, p_i) = \mu_i^{\ominus}(T) + RT \ln \varphi_i \left(\frac{p_i}{P^{\ominus}}\right). \tag{6.82}$$

As we can see, we have kept *formally* (6.74) valid for ideal mixtures; we "only" inserted a correction factor. This "solution" only seems to be simple or elegant, as the correction factor φ_i should be calculated anyway, according to (6.76) and the standard chemical potential should also be calculated according to (6.79). However, *to write* equations is definitely simple this way; in (6.82), it is the ideal activity $p_i/P^{\ominus}$, which is simply multiplied by the correction factor φ_i. This is the only difference with respect to the expression of the ideal mixture. Formally, it is nothing but a mere multiplication of the relative activity in the expression of the chemical potential of an ideal mixture by the excess absolute activity λ_i^{E} defined as follows:

$$\mu_i^{\mathrm{E}}(T, p_i) = RT \ln \lambda_i^{\mathrm{E}}. \tag{6.83}$$

Obviously, λ_i^{E} is identical with the correction factor φ_i.

In further sections, we give a similar formula according to formal changes explained above for the chemical potential as a function of other composition variables.

6.3.2 The Chemical Potential in Terms of Mole Fractions

Partial molar quantities have an important role in the thermodynamic description of mixtures. According to (6.7), these quantities can be given as a function of the mole fractions x_i. Let us return our attention to the chemical potential as a function of the mole fraction. Following the procedure outlined at the end of the previous section, let us write the chemical potential based on a correction factor related to the excess chemical potential μ_i^{E} and define an appropriate standard chemical potential. Thus, we can write (6.35) for a real mixture in the following form:

$$\mu_i = \mu_i^* + RT \ln x_i + \mu_i^{\mathrm{E}}. \tag{6.84}$$

By substituting $\mu_i^{\mathrm{E}} = RT \ln \lambda_i^{\mathrm{E}}$ and denoting λ_i^{E} by f_i, we get the following equation:

$$\mu_i = \mu_i^* + RT \ln f_i x_i. \tag{6.85}$$

The quantity $a_i = f_i x_i$ is called *relative activity*, while f_i is called *relative activity coefficient*. (Unfortunately, the commonly used symbol f_i coincides with that of fugacity. One should be careful to distinguish between the two quantities.)

In fact, the term relative activity is used in a broader sense. The activity $f_i\ x_i$ defined in (6.85) can be called – in a more specific sense – as the *activity* (or f_i as the activity coefficient) *referenced to the pure substance*. (An alternative name – also specific for this case – is the *activity referenced to Raoults' s law*. The origin of this name is explained in Sect. 7.4.) It is obvious that the standard chemical potential μ_i^* in (6.85) is the chemical potential of the pure component at the given temperature and pressure; if the mole fraction x_i goes to 1, the mixture exhibits a behavior that is closer and closer to the ideal behavior; thus, the activity coefficient also goes to 1, and μ_i goes to the chemical potential of the pure substance.

It is important to note that the equation

$$\mu_i^{\mathrm{E}} = RT \ln f_i \tag{6.86}$$

can be used to calculate f_i if we know the fundamental equation of the system. From the fundamental equation we can calculate μ_i, and by rearranging (6.84) we directly obtain the excess chemical potential:

$$\mu_i^{\mathrm{E}} = \mu_i - \mu_i^* - RT \ln x_i. \tag{6.87}$$

Though (6.84) has a major importance in thermodynamic description of mixtures, its use is not always practical. In case of a mixture component which does not exist in the same physical state as the mixture, it is not sensible to use this equation. In case of ethanol–water mixtures, both components exist in the same state as the mixture (under ambient conditions both are liquid). However, dissolving oxygen or sucrose (table sugar) in water, the mixture is normally liquid, while pure oxygen is a gas and pure sugar is a solid. Obviously, it is not practical to give the chemical potential of these components referenced to the pure gas or the pure solid. To come around this problem, a practical solution is to reference the chemical potential to the concentration $x_i = 0$ instead of $x_i = 1$. This reference state is not to be interpreted as a "mixture" which does not contain the component in question; it rather refers to the chemical potential of the component in the mixture *extrapolated to zero concentration*. (This standard state is similar to that of the nonideal gas mixtures at zero pressure.) The chemical potential thus referenced can be written as follows:

$$\mu_i = \mu_{x,i}^{\ominus} + RT \ln \gamma_{x,i} x_i. \tag{6.88}$$

The quantity $a_i = \gamma_{x,i}\ x_i$ is frequently referred to as *rational activity*[5] while $\gamma_{x,i}$ is called *rational activity coefficient*. The mixture is considered as ideal concerning component i if it is infinitely dilute with respect to this component. The symbol $\mu_{x,i}^{\ominus}$ is the *hypothetical* chemical potential of the "pure" component i in a state which is identical to that of its state in an infinitely dilute solution (somewhat similar to the

[5]The name is based on the word *ratio*, referring to the mole fraction as a ratio of amounts.

case shown in Fig. 6.2.). It is obvious that such a liquid does not exist; this is the reason that the standard state is a hypothetical one. Mathematically, we can write an exact expression to calculate this standard chemical potential:

$$\mu_{i,x}^{\ominus}(T,P) = \lim_{x_i \to 0} [\mu_i(T,P,x_i) - RT \ln x_i]. \tag{6.89}$$

However, this simply means that writing the constant $\mu_{x,i}^{\ominus}$ in (6.88), it exactly yields the correct value of the chemical potential. Thus, $\mu_{x,i}^{\ominus}$ is not the chemical potential of the reference state (as such a state cannot be realized and does not exist). It is simply *a composition-independent constant* in (6.88) yielding the chemical potential. Despite this property, $\mu_{x,i}^{\ominus}$ is a state function. As we shall see later, it has a major role in describing equilibria in multicomponent systems.

6.3.3 The Chemical Potential in Terms of Solute Concentration

In the chemical praxis, there are many reactions that do not occur between pure substances but between substances dissolved in a solvent. The composition of these solutions is mostly given in terms of molar concentration or molality, instead of mole fractions, and the chemical potential as a function of these solute concentrations is usually preferred. As explained in Sect. 6.1.3, the molar concentration c_i depends also on the density (which in turn depends also on temperature), and its proportionality to the mole fraction only holds to an approximation depending on the ratio of the molar masses of components; thus, the molality m_i is more frequently used in thermodynamics.

To express the chemical potential in real mixtures as a function of molality, we can also use the "formal procedure" used before:

$$\mu_i(T,P,m_i,x) = \mu_{m,i}^{\ominus}(T,P) + RT \ln \frac{m_i}{m_i^{\ominus}} + \mu_i^{\mathrm{E}}(T,P,m_i,\boldsymbol{x}). \tag{6.90}$$

By omitting the variables T, P, m_i, and $\boldsymbol{x}$, and using $\gamma_{m,i}$ instead of λ_i^{E} in the expression $\mu_i^{\mathrm{E}} = RT \ln \lambda_i^{\mathrm{E}}$, we get:

$$\mu_i = \mu_{m,i}^{\ominus} + RT \ln \gamma_{m,i} \left(\frac{m_i}{m_i^{\ominus}} \right). \tag{6.91}$$

The product $\gamma_{m,i}\left(m_i/m_i^{\ominus}\right)$ is often called *practical activity*, while $\gamma_{m,i}$ is called *practical activity coefficient*. Another name is the activity (activity coefficient) *with respect to molality*. The standard state is *hypothetical* also in this case and can be given as the limit at zero concentration:

$$\mu_{m,i}^{\ominus}(T,P) = \lim_{m_i \to 0} \left[\mu_i(T,P,m_i) - RT \ln \frac{m_i}{m_i^{\ominus}} \right]. \tag{6.92}$$

The expression of the chemical potential as a function of molar concentration can be derived in a similar way. In the expression $\mu_i^{\mathrm{E}} = RT \ln \lambda_i^{\mathrm{E}}$, λ_i^{E} is then replaced by $\gamma_{c,i}$; thus, we get the following expression:

$$\mu_i = \mu_{c,i}^{\ominus} + RT \ln \gamma_{c,i} \left(\frac{c_i}{c_i^{\ominus}} \right). \tag{6.93}$$

Accordingly, the product $\gamma_{c,i}\left(c_i/c_i^{\ominus}\right)$ is often called *activity with respect to* (*molar*) *concentration*, while $\gamma_{c,i}$ is called *activity coefficient with respect to* (*molar*) *concentration*. The *hypothetical* standard state can be given as the limit at zero concentration:

$$\mu_{c,i}^{\ominus}(T,P) = \lim_{c_i \to 0} \left[\mu_i(T,P,m_i) - RT \ln \frac{c_i}{c_i^{\ominus}} \right]. \tag{6.94}$$

6.3.4 Activity and Standard State: An Overview

The use of activities as variables is inevitable in the thermodynamics of mixtures, but they should be used with care, as we can foresee from the above discussions. As we have seen, the short term activity is used for relative activities when the reference state is the pure substance, and also when it is the limiting value at zero concentration. In addition, molality and molar concentration can also be used as composition variable in addition to mole fraction, without changing the short term "activity". In many cases, there is no hint in the notation of the activity coefficient concerning the reference concentration, which is the same in case of the relative activity as well. In most cases, only a general form

$$\mu_i = \mu_i^{\ominus} + RT \ln a_i \tag{6.95}$$

is only given. Of course, we should always make it clear what are the actual reference concentration and the standard chemical potential. Let us summarize the most important characteristics of different activities in a table and explore their interrelations.

The value of the chemical potential – being a state function – should be independent of the reference state and the unit of concentration. Thus, we can always write the equality of the chemical potentials in different reference systems if they refer to the mixture of the same composition. Let us consider first the equality based on (6.85) and (6.88):

$$\mu_i^*(T,P) + RT \ln f_i x_i = \mu_{x,i}^{\ominus}(T,P) + RT \ln \gamma_{x,i} x_i \tag{6.96}$$

Table 6.2 Characteristics of the activity a_i and the standard chemical potential $\mu_i^{\ominus}$ in the expression $\mu_i = \mu_i^{\ominus} + RT \ln a_i$ valid for real mixtures in case of different composition variables and reference states

Activity a_i	Name	Meaning of the standard $\mu_i^{\ominus}$	Condition
$f_i\, x_i$	Relative activity (activity referenced to Raoult's law)	$\mu_i^*(T,P)$ (chemical potential of the pure substance)	At any concentration $0 \le x_i \le 1$
$\gamma_{x,i} x_i$	Rational activity (activity referenced to Henry's law)	$\mu_{i,x}^{\ominus}(T,P) = \lim\limits_{x_i \to 0} \left[\mu_i(T,P,x_i) - RT \ln x_i\right]$ (chemical potential of the hypothetical pure substance in the state identical to that at infinite dilution)	At any concentration in existing mixtures
$\gamma_{m,i}\left(\frac{m_i}{m_i^{\ominus}}\right)$	Molality basis activity	$\mu_{m,i}^{\ominus}(T,P) = \lim\limits_{m_i \to 0} \left[\mu_i(T,P,m_i) - RT \ln \frac{m_i}{m_i^{\ominus}}\right]$ (chemical potential of the hypothetical ideal mixture at concentration $m_i^{\ominus} = 1\,\mathrm{mol\,kg^{-1}}$ in the state identical to that at infinite dilution)	In solutions
$\gamma_{c,i}\left(\frac{c_i}{c_i^{\ominus}}\right)$	Concentration basis activity	$\mu_{c,i}^{\ominus}(T,P) = \lim\limits_{c_i \to 0} \left[\mu_i(T,P,c_i) - RT \ln \frac{c_i}{c_i^{\ominus}}\right]$ (chemical potential of the hypothetical ideal mixture at concentration $c_i^{\ominus} = 1\,\mathrm{mol\,dm^{-3}}$ in the state identical to that at infinite dilution)	In solutions
$\varphi_i\left(\frac{p_i}{P^{\ominus}}\right)$	Fugacity	$\mu_i^{\ominus}(T) = \lim\limits_{p_i \to 0} \left[\mu_i(T,p_i,\varphi_i,x) - RT \ln \frac{\varphi_i p_i}{P^{\ominus}}\right]$ (chemical potential of the hypothetical ideal mixture at a reference pressure $\varphi_i p_i = P^{\ominus}$)	In every gaseous mixture

The difference of the standard chemical potentials μ_i^* and $\mu_{x,i}^{\ominus}$ can be expressed from this as follows:

$$\mu_i^* - \mu_{x,i}^{\ominus} = RT \ln \gamma_{x,i} x_i - RT \ln f_i x_i = RT \ln \frac{\gamma_{x,i}}{f_i}. \tag{6.97}$$

Both μ_i^* and $\mu_{x,i}^{\ominus}$ are independent of the concentration; thus, the ratio $\gamma_{x,i}/f_i$ is also *independent of concentration*; its value is always

$$\frac{\gamma_{x,i}}{f_i} = \mathrm{e}^{\frac{\mu_i^* - \mu_{x,i}^{\ominus}}{RT}}. \tag{6.98}$$

Based on the equation, we can say that, for a pure component (for which $x_i = 1$ and $f_i = 1$), the value of $\gamma_{x,i}$ is exactly the exponential on the right-hand side. Similarly, for an infinitely dilute solution (for which $x_i = 0$ and $\gamma_{x,i} = 1$), the value of f_i is the reciprocal of the exponential:

$$x_i = 1\text{:} \quad f_i = 1 \text{ and } \quad \gamma_{x,i} = \mathrm{e}^{\frac{\mu_i^* - \mu_{x,i}^{\ominus}}{RT}}; \quad x_i = 0\text{:} \quad \gamma_{x,i} = 1 \text{ and } \quad f_i = \mathrm{e}^{-\frac{\mu_i^* - \mu_{x,i}^{\ominus}}{RT}} \tag{6.99}$$

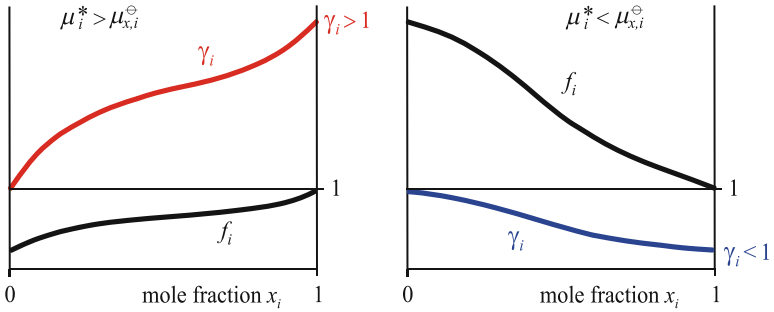

Fig. 6.3 Dependence of the activity coefficient f_i referenced to Raoult's law and that of γ_i referenced to Henry's law on concentration of the component i. The relative placement of the curves depends on the sign of the difference of the standard chemical potentials μ_i^* (of the pure component) and $\mu_{x,i}^{\ominus}$ (of the state of infinit dilution)

Thus, if $\mu_i^* - \mu_{x,i}^{\ominus}$ is positive, f_i is minimal at $x_i = 0$, and it increases with increasing concentration in case of a monotonical change until it reaches unit at $x_i = 0$. Accordingly, $\gamma_{x,i}$ starts from unit at $x_i = 0$, and it increases proportionally to f_i. This behavior is illustrated in the left panel of Fig. 6.3. In case of a negative $\mu_i^* - \mu_{x,i}^{\ominus}$, the concentration dependence of the activity coefficients is shown in the right panel of the figure.

Figure 6.4 shows more explicitly the meaning of $\gamma_{x,i}$ and f_i concerning the concentration dependence of the chemical potential. By rearranging (6.85) and (6.88), we obtain the following relations:

$$\mu_i - RT \ln x_i = \mu_i^* + RT \ln f_i; \qquad \mu_i - RT \ln x_i = \mu_{x,i}^{\ominus} + RT \ln \gamma_{x,i} \tag{6.100}$$

From these relations, it is obvious that the quantity $\mu_i - RT \ln x_i$ is obtained by adding $RT \ln \gamma_{x,i}$ to $\mu_{x,i}^{\ominus}$, and also by adding $RT \ln f_i$ to μ_i^*. As f_i happens to be less than or equal to unit ($f_i \leq 1$) in the illustration in Fig. 6.4, this addition diminishes the chemical potential with respect to μ_i^*, as it can be seen in the figure.

Summing up we can say that activities referenced to the pure component and to infinite dilution in case of a real mixture *are always different*, and the respective *standard chemical potentials are also different*. If the mixture exists in the entire concentration range (i.e., in case of unlimited miscibility), both standard chemical potentials can be determined from thermodynamic data. In this case, knowing one of the activity coefficients $\gamma_{x,i}$ and f_i, the other one can be determined using (6.98). However, in case of an ideal mixture, both $\gamma_{x,i}$ and f_i are identically unit; thus, $\mu_{x,i}^{\ominus} = \mu_i^*$ also holds.

Activities referenced to infinite dilution exhibit a similar behavior relative to activities referenced to the pure substance also if they are expressed on a molality or molar concentration basis instead of a mole fraction basis. As we know (cf. Sect. 6.2.3), standard concentrations are different in case of different concentration

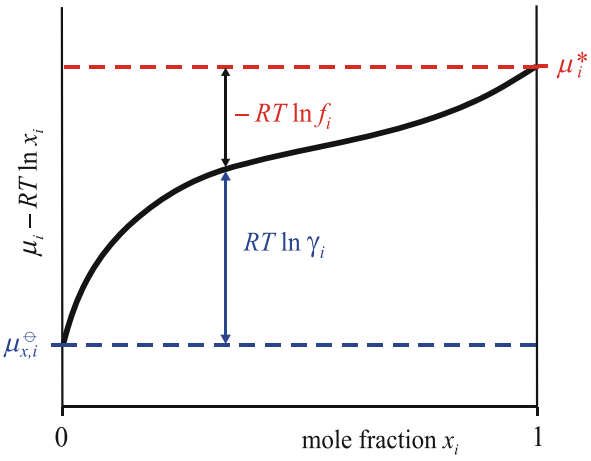

Fig. 6.4 A possible shape of the quantity $\mu_i - RT \ln x_i$ as a function of the mole fraction x_i, if $\mu_i^* > \mu_{x,i}^{\ominus}$. The difference of this quantity from μ_i^* – the chemical potential of the pure component – is $RT \ln f_i$, while from $\mu_{x,i}^{\ominus}$ – the chemical potential referenced to infinite dilution – it is $RT \ln \gamma_i$

bases if activities are referenced to infinite dilution. As neither molality nor molar concentration are strictly proportional to mole fraction, the activity coefficient of the same mixture will generally be different if expressed in different concentration bases. The principle of comparing them is still the same; the value of the chemical potential in an actual mixture is always the same, independently of the eventual form of the chemical potential function.

Applying this principle for activities on molality and mole fraction basis referenced to infinite dilution, we can write the equality based on (6.88) and (6.91):

$$\mu_{x,i}^{\ominus}(T,P) + RT \ln \gamma_{x,i} x_i = \mu_{m,i}^{\ominus}(T,P) + RT \ln \gamma_{m,i} \tilde{m}_i, \tag{6.101}$$

where $\tilde{m}_i$ is the molality divided by the standard molality $m_i^{\ominus}$, i.e., the *measured value* in units of the standard molality – which is identical to the relative activity defined in (6.91). By rearranging the above equation, we get:

$$RT \ln \frac{\gamma_{m,i} \tilde{m}_i}{\gamma_{x,i} x_i} = \mu_{x,i}^{\ominus}(T,P) - \mu_{m,i}^{\ominus}(T,P). \tag{6.102}$$

The difference of the two standard chemical potentials can be obtained by the limit $x_i \to 0$, i.e., in sufficiently dilute solutions where both $\gamma_{x,i}$ and $\gamma_{m,i}$ are identically unit; thus:

$$\mu_{x,i}^{\ominus}(T,P) - \mu_{m,i}^{\ominus}(T,P) = RT \ln \frac{\tilde{m}_i}{x_i}. \tag{6.103}$$

By applying this principle for activities on molality and mole fraction basis referenced to infinite dilution, we can write the equality based on (6.88) and (6.91):

By taking into account the relation of molality to mole fraction expressed in (6.63) as

$$m_1 = x_1 \frac{1000}{\sum_{j=2}^{K} x_j M_j},$$

the difference of the standard chemical potentials can be written as follows:

$$\mu^{\ominus}_{x,i}(T,P) - \mu^{\ominus}_{m,i}(T,P) = RT \ln \frac{1000}{\sum_{\forall j \neq i} x_j M_j}. \tag{6.104}$$

Let us consider the mixture to be a binary one and denote the solvent by the subscript 0. By taking into account that at infinite dilution $x_0 \to 1$, we can write the difference as follows:

$$\mu^{\ominus}_{x,i}(T,P) - \mu^{\ominus}_{m,i}(T,P) = RT \ln \frac{1000}{M_0} \tag{6.105}$$

(Though the mixture is binary here, with component i as solute and all other components as solvent, we still keep the subscript i to denote the solute component as it could be *any component*.)

According to (6.102), we can write:

$$RT \ln \frac{\gamma_{m,i}\, \tilde{m}_i}{\gamma_{x,i}\, x_i} = RT \ln \frac{1000}{M_0}. \tag{6.106}$$

This can be rearranged to

$$RT \ln \frac{\gamma_{m,i}}{\gamma_{x,i}} = RT \ln \frac{1000 x_i}{\tilde{m}_i M_0}. \tag{6.107}$$

We can substitute m_i from (6.64), changing the notation accordingly, to get:

$$\frac{\gamma_{m,i}}{\gamma_{x,i}} = 1 - x_i. \tag{6.108}$$

From this result we can see that – for dilute solutions, until we accept the approximation that x_i is much smaller than 1 – the activity $\gamma_{m,i}$ on molality basis and the activity $\gamma_{x,i}$ on mole fraction basis (both referenced to infinite dilution) are approximately equal. However, if x_i is not small enough to be neglected compared to one, this equality does not hold. Furthermore, we can state that, if a mixture is *ideal* according to the thermodynamic definition (i.e. if the concentration is expressed in mole fraction), at concentrations not negligible compared to one, the

activity coefficient $\gamma_{m,i}$ on molality basis is *not unit*. Thus, "ideality" on a mole fraction basis does not coincide with "ideality" on molality basis.

Similarly to the above comparison, we can write for the activities on molarity basis and that on mole fraction basis, accordingly to (6.88) and (6.93):

$$\mu^{\ominus}_{x,i}(T,P) - \mu^{\ominus}_{c,i}(T,P) = RT \ln \frac{\gamma_{c,i}\,\tilde{c}_i}{\gamma_{x,i}\,x_i}, \tag{6.109}$$

Here, $\tilde{c}_i$ is the molarity divided by the standard molarity $c_i^{\ominus}$, i.e., the *measured value* in units of the standard molarity – which is identical to the relative activity defined in (6.93). At the limit $x_i \to 0$, i.e., in sufficiently dilute solutions where both $\gamma_{x,i}$ and $\gamma_{m,i}$ are identically unit:

$$\mu^{\ominus}_{x,i}(T,P) - \mu^{\ominus}_{c,i}(T,P) = RT \ln \frac{\tilde{c}_i}{x_i}. \tag{6.110}$$

By substituting

$$c_i = x_i \frac{\rho}{x_i M_i + \sum\limits_{\forall j \neq i}^{K} x_j M_j}$$

from (6.62), we get:

$$\mu^{\ominus}_{x,i}(T,P) - \mu^{\ominus}_{c,i}(T,P) = RT \ln \frac{\rho}{x_i M_i + \sum\limits_{\forall j \neq i}^{K} x_j M_j}. \tag{6.111}$$

By considering the mixture as a binary one and using the notation already applied in (6.105), this can be rewritten as

$$\mu^{\ominus}_{x,i}(T,P) - \mu^{\ominus}_{c,i}(T,P) = RT \ln \frac{\rho}{(1-x_0)M_i + x_0 M_0}, \tag{6.112}$$

which provides the difference of the two standard chemical potentials at the limit of infinite dilution ($x_0 \to 1$):

$$\mu^{\ominus}_{x,i}(T,P) - \mu^{\ominus}_{c,i}(T,P) = RT \ln \frac{\rho}{M_0}. \tag{6.113}$$

By inserting this in (6.109), upon substitution of the ratio

$$\frac{x_i}{c_i} = \frac{(1-x_0)M_i + x_0 M_0}{\rho}, \tag{6.114}$$

we get the following result for the ratio of $\gamma_{x,i}$ and $\gamma_{c,i}$:

$$\frac{\gamma_{c,i}}{\gamma_{x,i}} = \frac{\rho}{M_0}\frac{x_i}{c_i} = \frac{M_i}{M_0}x_i + (1 - x_i). \tag{6.115}$$

We can see that the two activity coefficients are in general not equal, except for the case if the molar mass of the solute is identical to the (mean) molar mass of the solvent. If this is not the case, the activity $\gamma_{x,i}$ and $\gamma_{c,i}$ are only approximately equal in dilute solutions where x_i is small enough to be neglected compared to one. We can also state here what has been stated for the activity coefficient on the molality base; at concentrations not negligible compared to one, the activity coefficient $\gamma_{c,i}$ on molarity base is, in general, *not unit*. It is worth noting that the use of molarity is further complicated by the fact that this concentration also depends on temperature, through its density dependence.

From the above comparisons of different reference systems, we can conclude that the use of mole fraction best suits to thermodynamic purposes; it is in accordance with the very definition of ideal mixtures and it does not change either with pressure or with temperature. If – for practical purposes – we use solute concentrations different from mole fraction, molality is to be preferred as it does not depend on density; thus, it is independent of temperature as well.

Note that thermodynamic quantities referenced to infinite dilution – such as the standard chemical potential $\mu_i^{\ominus}$ – *depend also on the concentration of components other than component i*. Therefore, it is important to know what "solvent composition" the given standard quantity and the derived activity is referenced to. In practical problems, the standard solvent may be rather complex; an example is blood serum, a frequently used solvent in medical practice.

6.3.5 Thermodynamic Properties of a Real Mixture

As already stated when writing (6.84), real mixtures can reasonably be characterized by *excess thermodynamic properties*. Similarly to (6.84), we can write the following for any partial molar property X_i:

$$X_i = X_i^{\mathrm{id}} + X_i^{\mathrm{E}} \tag{6.116}$$

Let us take the Gibbs potential as an example to show the calculation of excess properties in case of a real mixture. The partial molar Gibbs potential is, by definition, the chemical potential, which can be written in the following form:

$$\mu_i = \mu_i^{\ominus} + RT \ln \gamma_i x_i. \tag{6.117}$$

From this, we can write

$$\mu_i^{\mathrm{id}} = \mu_i^{\ominus} + RT \ln x_i, \tag{6.118}$$

Thus, the excess chemical potential is

$$\mu_i^{\mathrm{E}} = RT \ln \gamma_i. \tag{6.119}$$

(Note that we get the same result in case of other standard concentrations – like c_i or m_i – as well.) From this relation, the excess Gibbs potential as a function of composition is

$$G^{\mathrm{E}} = RT \sum_{i=1}^{K} n_i \ln \gamma_i, \tag{6.120}$$

while the molar excess Gibbs potential is

$$g^{\mathrm{E}} = RT \sum_{i=1}^{K} x_i \ln \gamma_i. \tag{6.121}$$

Using common thermodynamic relations, we can easily derive the molar excess entropy:

$$s^{\mathrm{E}} = -\left(\frac{\partial g^{\mathrm{E}}}{\partial T}\right)_{P,\boldsymbol{n}} = -R \sum_{i=1}^{K} x_i \ln \gamma_i - RT \sum_{i=1}^{K} x_i \left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{P,\boldsymbol{n}}. \tag{6.122}$$

Similarly, the molar excess volume can be written as follows:

$$v^{\mathrm{E}} = \left(\frac{\partial g^{\mathrm{E}}}{\partial P}\right)_{T,\boldsymbol{n}} = RT \sum_{i=1}^{K} x_i \left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,\boldsymbol{n}}. \tag{6.123}$$

As the molar volume of mixing in ideal mixtures is zero, the above expression also provides the molar volume of mixing for real mixtures.

The molar excess enthalpy can be calculated using the relation

$$h^{\mathrm{E}} = g^{\mathrm{E}} + Ts^{\mathrm{E}} \tag{6.124}$$

as follows:

$$h^{\mathrm{E}} = -RT^2 \sum_{i=1}^{K} x_i \left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{P,\boldsymbol{n}}. \tag{6.125}$$

This expression also provides the molar enthalpy of mixing for real mixtures, as the molar enthalpy of mixing in ideal mixtures is zero.

Any other excess thermodynamic property can be calculated similarly, applying the corresponding thermodynamic relations to excess properties. These calculations are not really important from a practical point of view. The inverse problem is much more important; if we know excess thermodynamic properties from experiments, activity coefficients can be determined. For example, if the heat capacity of a mixture along with the heat capacities of all the pure components are known from calorimetric measurements, we can calculate the enthalpy and the entropy of mixing. Knowing these two quantities, the Gibbs potential of mixing can also be derived at a given temperature. By comparing this result to the calculated Gibbs potential of mixing of an ideal mixture, the excess Gibbs potential can be calculated. By knowing this quantity as a function of composition, we can also calculate its partial molar value, the excess chemical potential (cf. Sect. 6.1.2), from which the activity coefficient can be obtained using (6.119).

We can get the temperature and pressure dependence of the activity coefficient in a similar way. Based on (6.119), using the Gibbs–Helmholtz equation (A2.23), we can write:

$$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{P,\boldsymbol{n}} = \frac{\partial}{\partial T}\left(\frac{\mu_i^{\mathrm{E}}}{RT}\right) = -\frac{H_i^{\mathrm{E}}}{RT^2} \tag{6.126}$$

(Note that – as stated previously – the Gibbs–Helmholtz equation interrelating G and H also holds for the interrelation of the corresponding partial molar properties.) Accordingly, the pressure dependence can be given by the following equation:

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,\boldsymbol{n}} = \frac{\partial}{\partial P}\left(\frac{\mu_i^{\mathrm{E}}}{RT}\right) = \frac{V_i^{\mathrm{E}}}{RT}. \tag{6.127}$$

From the above equations, we can see that to describe the temperature dependence of the activity coefficient, the knowledge of partial molar excess enthalpy is sufficient. Similarly, the partial molar excess volume provides sufficient information to describe its pressure dependence.

If we want to know the properties of a mixture as a function of temperature and pressure, in addition to the composition-dependence, we need to know the temperature and pressure dependence of the standard chemical potential $\mu_i^{\ominus}$. This can be obtained from (6.11) and (6.12) as

$$\left(\frac{\partial \mu_i^{\ominus}}{\partial T}\right)_{P,\boldsymbol{n}} = -S_i^{\ominus} \tag{6.128}$$

and

$$\left(\frac{\partial \mu_i^{\ominus}}{\partial P}\right)_{T,\boldsymbol{n}} = V_i^{\ominus}, \tag{6.129}$$

i.e. from the standard partial molar entropy and the standard partial molar volume. In case of the rational and practical activity coefficients, these properties can be obtained from the molar quantities of the corresponding mixtures by calculating the limiting values at $x_i \to 0$, as described in Sect. 6.1.2. In case of the relative activity coefficient, these are the molar quantities of the pure component i.

6.4 Ideal Solutions and Ideal Dilute Solutions

As it has already been emphasized at the beginning of Sect. 6.3, ideal mixtures do not exist, it is only a formally simple approximation. The applicability of the approximation depends on the extent of the error we allow in the thermodynamic calculations. We have seen that for exact results without approximation, we only need to multiply the mole fraction in the expression of the composition-dependent chemical potential by the activity coefficient f_i, thus keeping the validity of simple formulae valid for ideal mixture. We can accordingly hope that *the formal validity of thermodynamic relations describing ideal mixtures holds if we write relative activity* (referenced to the pure substance) *in place of the mole fraction*. As we shall see in subsequent chapters, this hope is fulfilled in most of the cases.

However, referencing to the pure component is often not reasonable. For example, if we are dealing with dilute solutions only, it is reasonable to restrict thermodynamic description only to the low concentration region we are interested in. Another practical reason is the fact that in the same phase as the solution (liquid or solid), the solute does not exist within the given circumstances, or its solubility is rather low so that only dilute solutions can be made. In these cases, referencing to infinitely dilute solutions – as described in Sect. 3.3.4 – is more convenient. It must be noted, however, that the standard chemical potential is then also different from that of the pure substance.

We can easily elucidate this by simple molecular reasoning. In pure substances, there are only the same molecules; thus, their environment only consists of the same molecules. As long as the number of molecules dissolved in the pure substance (the solvent) is small, the interaction of the molecules does not change much. For this reason, we can consider the solvent – to some approximation – as an ideal component, and its chemical potential can be described by (6.35) using, as standard, the chemical potential of the pure substance. If we do not accept the approximation of ideal mixture, we can substitute the relative activity $a_i = f_i\, x_i$ in place of the mole fraction. As to the solute molecules in dilute solutions, their molecular surroundings do not consist of the same molecules but mostly of solvent molecules. Diluting the solution, we can arrive sooner or later to a concentration where the solution is dilute enough for that the molecular surrounding (solvent shell) of the solute molecules would not change any more in a detectable manner.

Thermodynamic behavior of this "solvated species" naturally differs from that of the pure species. The standard chemical potential referenced to infinite dilution truly reflects this difference. If it is expressed on mole fraction basis, we can imagine it as the chemical potential of a "pure substance" in the same state as if it were still solvated. (Of course, such substance cannot exist.) If it is expressed on molality or molarity basis, it can be interpreted as the chemical potential of unit molality or molarity – expressed in units of the standard concentration – of a "fully solvated substance". (Such a solution cannot exist either.)

Thus, standard chemical potentials referenced to different states are necessarily different. The extent of the difference depends on differences between interactions of solvent molecules and that of the solute molecules. If we can calculate the fundamental equation of the mixture based on a molecular model, we can also derive the respective standard chemical potentials. If a suitable model cannot be conceived, standard chemical potentials as well as activity coefficients can be calculated from experimental data.

In summary, we can state that, in dilute solutions, it is reasonable to reference the chemical potential of the *solvent to the pure substance*, while that of the *solute to the limit at infinite dilution* – as described in Sect. 6.3. However, if we accept the approximation that the mixture is ideal, there is no problem with the solute either; the activity coefficient becomes unit and we get back the simple formulae of the ideal mixture.

In analogy to the ideal mixture, it is common practice to consider *ideally dilute solutions*. According to this, the chemical potential of a solute is given by relations where the activity coefficient referenced to infinite dilution is supposed to be unit. However, it is important to emphasize that these solutions are *not ideal* in the sense of the thermodynamic definition. As it is discussed in Sect. 6.3, while the activity coefficient γ_i is unit, the identity $f_i = 1$ is, in general, not valid, apart from some special cases. Therefore, if we deal with the thermodynamic description of ideally dilute solutions, it is crucial to clarify what are the concentrations whose ratio defines the relative activity, and what is the standard chemical potential. If this is clear, we can write the usual simplified expressions containing only concentrations. (Cf. Table 6.2.) We shall also keep in mind that the symbol for concentration written in the simple notation means the ratio of the actual concentration to the standard concentration. Following this simple notation in this book, we shall also drop the *tilde* sign ˜ indicating the measured value of the concentration, thus writing only the following simplified expressions in case of ideally dilute solutions:

$$\mu_i = \mu_i^{\ominus} + RT \ln \gamma_i x_i, \tag{6.130}$$

$$\mu_i = \mu_i^{\ominus} + RT \ln \gamma_i m_i, \tag{6.131}$$

$$\mu_i = \mu_i^{\ominus} + RT \ln \gamma_i c_i. \tag{6.132}$$

As we can see, the activity coefficient γ_i as well as the standard chemical potential $\mu_i^{\ominus}$ in these cases is related to unit value of the concentration written in the argument of the logarithm function.

It is also important to know that activity coefficients γ_i on different concentration bases would not be approximately unit within the same error tolerance. Consequently, if a solution is considered ideally dilute due to unit activity coefficient, e.g., on a molality basis, the activity coefficient on a molarity or mole fraction basis is not necessarily unit as well. Thus, the solution cannot be considered generally as ideally dilute in case of other reference concentrations. If we do not allow for approximations but use the exact activity coefficients different from unit, these differences occur naturally.

In following chapters, when discussing actual equilibrium problems, we shall frequently use the approximation of an ideal solution, less frequently the ideally dilute solution approximation. Results obtained this way usually are easy to change so that they become valid for real mixtures as well; we should simply insert the proper activity coefficient as a multiplicative factor of the concentration ratio. This is the reason that we do not always discuss the applicability of thermodynamic relations obtained for ideal mixtures in case of real mixtures.

The notion of ideally dilute solution can be justified with additional arguments. We can calculate the partial molar volume and the partial molar entropy of the solute using (6.43) and (6.44). Though these values are not identical with the corresponding properties of the pure substance prior to mixing (*i.e.* the volume and entropy of mixing are nonzero), but both of them are *independent of concentration*, as long as the approximation of the ideally dilute solution holds on the actual concentration basis.

Problems

1. The densities of two aqueous NaCl solutions were determined at 25°C by using a pycnometer. The density of the 60 g/dm^{-3} concentration solution was found to be 1.0315 g cm^{-3} and that of the 82.5 g/dm^3 concentration solution was 1.0463 g cm^{-3}. Calculate the partial molar volume of NaCl and that of water in the solution.

Solution: The molar volume of the solution can be expressed in terms of the partial molar volumes and mole fractions of the two components, according to (6.5) and (6.21):

$$v = \sum_{i=1}^{2} x_i V_i = x_{\mathrm{H_2O}} V_{\mathrm{H_2O}} + x_{\mathrm{NaCl}} V_{\mathrm{NaCl}}$$

Dividing both sides of the equation by v yields:

$$1 = \frac{x_{\mathrm{H_2O}}}{v} V_{\mathrm{H_2O}} + \frac{x_{\mathrm{NaCl}}}{v} V_{\mathrm{NaCl}}. \tag{6.133}$$

The mole fraction x_i can be expressed with the help of the mass fraction w_i in the following way:

$$x_i = \frac{n_i}{n} = \frac{m_i/M_i}{m/M} = \frac{m_i}{m}\,\frac{M}{M_i} = \frac{w_i M}{M_i}\,.$$

As the density ρ of the solution is the ratio of the molar mass M (of the solution) to the molar volume v (of the solution), we can substitute ρv in place of M. After rearrangement we get:

$$\frac{x_i}{v} = \frac{\rho w_i}{M_i}\,.$$

By substituting this into (6.133), we get the following relation:

$$1 = \frac{\rho w_{\mathrm{H_2O}}}{M_{\mathrm{H_2O}}}\,V_{\mathrm{H_2O}} + \frac{\rho w_{\mathrm{NaCl}}}{M_{\mathrm{NaCl}}}\,V_{\mathrm{NaCl}}$$

We can replace $w_{\mathrm{H_2O}}$ by $1 - w_{\mathrm{NaCl}}$, and the mass fraction $w_{\mathrm{H_2O}}$ can be expressed by dividing the mass per volume concentration by the density of the solution; $w_{\mathrm{H_2O}} = c_{\mathrm{H_2O}}/\rho$; thus, we get:

$$1 = \frac{\rho\left(1 - \frac{c_{\mathrm{NaCl}}}{\rho}\right)}{M_{\mathrm{H_2O}}}\,V_{\mathrm{H_2O}} + \frac{c_{\mathrm{NaCl}}}{M_{\mathrm{NaCl}}}\,V_{\mathrm{NaCl}}$$

By rearranging the above equation, we can express ρ as a linear function of the mass per volume concentration of NaCl:

$$\rho = \frac{M_{\mathrm{H_2O}}}{V_{\mathrm{H_2O}}} + \left(1 - \frac{V_{\mathrm{NaCl}} M_{\mathrm{H_2O}}}{V_{\mathrm{H_2O}} M_{\mathrm{NaCl}}}\right) c_{\mathrm{NaCl}}$$

Substituting experimental data into this equation results in a system of two equations containing two unknown quantities, $V_{\mathrm{H_2O}}$ and V_{NaCl}. Solving this system of equations yields $V_{\mathrm{H_2O}} = 18.14\ \mathrm{cm^3\,mol^{-1}}$ and $V_{\mathrm{NaCl}} = 20.18\ \mathrm{cm^3\,mol^{-1}}$.

2. The two compartments of a gas container are filled at room temperature with 1 g of helium and 1 g of hydrogen, respectively. We let the two gases mix by opening the valve separating the two compartments. Calculate the change of entropy. (Consider the atomic masses to be 1 and 4 g/mol and both gases as ideal.)

Solution: By taking into account the molar masses, the amounts of the gases are $n_{\mathrm{H_2}} = 0.5$ mol and $n_{\mathrm{He}} = 0.25$ mol, summing up to a total amount of 0.75 mol; thus, $x_{\mathrm{H_2}} = 2/3$ and $x_{\mathrm{He}} = 1/3$. Since the two gases are ideal, their mixture is also an ideal mixture, and the entropy of mixing can be calculated using (6.42) as follows:

$$\Delta_{\mathrm{mix}} S = -\frac{3}{4} R \left(\frac{2}{3}\,\ln\frac{2}{3} + \frac{1}{3}\,\ln\frac{1}{3}\right) = 0.4774\,R$$

3. In a binary thermodynamic system of components A and B, $x_A = 0.1$. In the temperature range not much different from $T = 25°C$, the relative activity coefficients of the components are given by the empirical formulae

$$\ln \gamma_A = -935.111\, x_A T^{-3/2} \quad \text{and} \quad \gamma_A = -0.003.$$

Calculate the molar excess quantities of entropy, enthalpy, and Gibbs potential of the system at 25°C.

Solution: At the temperature of 25°C = 298.15 K – based on the formula given – $\ln \gamma_A = -0.0182$; thus, the molar excess Gibbs potential of the system can be calculated using (6.121):

$$g^E = RT(x_A \ln \gamma_A + x_B \ln \gamma_B) = -11.1953 \text{ J mol}^{-1}.$$

To calculate the molar excess enthalpy using (6.125), we need to know the partial derivatives of the logarithms of the activity coefficients with respect to temperature:

$$\left(\frac{\partial \ln \gamma_A}{\partial T}\right)_{P,\boldsymbol{n}} = 140.267\,\text{K}^{1.5} T^{-2.5} = 9.13838 \cdot 10^{-5}\text{K}^{-1}; \quad \left(\frac{\partial \ln \gamma_B}{\partial T}\right)_{P,\boldsymbol{n}} = 0.$$

Thus, the molar excess enthalpy can be calculated as

$$h^E = -RT^2\left[x_A\left(\frac{\partial \ln \gamma_A}{\partial T}\right)_{P,\boldsymbol{n}} + x_B\left(\frac{\partial \ln \gamma_B}{\partial T}\right)_{P,\boldsymbol{n}}\right] = -6.7538 \text{ J mol}^{-1}.$$

The molar excess entropy can be calculated by rearranging (6.124):

$$s^E = \frac{h^E - g^E}{T} = -0.0145 \text{ J/(mol K)}$$

Further Reading

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