9.5: Activity Coefficients in Mixtures of Nonelectrolytes

An *activity coefficient* of a species is a kind of adjustment factor that relates the actual behavior to ideal behavior at the same temperature and pressure. The ideal behavior is based on a *reference state* for the species.

We begin by describing reference states for nonelectrolytes. The thermodynamic behavior of an electrolyte solution is more complicated than that of a mixture of nonelectrolytes, and will be discussed in the next chapter.

9.5.1 Reference states and standard states

A *reference state* of a constituent of a mixture has the same temperature and pressure as the mixture. When species i is in its reference state, its chemical potential μ_i^{ref} depends only on the temperature and pressure of the mixture.

If the pressure is the standard pressure p°, the reference state of species i becomes its *standard state*. In the standard state, the chemical potential is the *standard chemical potential* μ_i°, which is a function only of temperature.

Reference states are useful for derivations involving processes taking place at constant T and p when the pressure is not necessarily the standard pressure.

Table 9.3 describes the reference states of nonelectrolytes used in this e-book, and lists symbols for chemical potentials of substances in these states. The symbols for solutes include x, c, or m in the subscript to indicate the basis of the reference state.

9.5.2 Ideal mixtures

Since the activity coefficient of a species relates its actual behavior to its ideal behavior at the same T and p, let us begin by examining behavior in ideal mixtures.

Consider first an ideal gas mixture at pressure p. The chemical potential of substance i in this ideal gas mixture is given by Eq. 9.3.5 (the superscript "id" stands for ideal):

$$\mu_i^{\text{id}}(\text{g}) = \mu_i^\circ(\text{g}) + RT \ln \frac{p_i}{p^\circ} \tag{9.5.1}$$

The reference state of gaseous substance i is pure i acting as an ideal gas at pressure p. Its chemical potential is given by

$$\mu_i^{\text{ref}}(\text{g}) = \mu_i^\circ(\text{g}) + RT \ln \frac{p}{p^\circ} \tag{9.5.2}$$

Subtracting Eq. 9.5.2 from Eq. 9.5.1, we obtain

$$\mu_i^{\text{id}}(\text{g}) - \mu_i^{\text{ref}}(\text{g}) = RT \ln \frac{p_i}{p} \tag{9.5.3}$$

Consider the following expressions for chemical potentials in ideal mixtures and ideal-dilute solutions of nonelectrolytes. The first equation is a rearrangement of Eq. 9.5.3, and the others are from earlier sections of this chapter (in order of occurrence, Eqs. 9.4.8, 9.4.35, 9.4.24, 9.4.27, and 9.4.28).

$$\text{Constituent of an ideal gas mixture} \quad \mu_i^{\text{id}}(\text{g}) = \mu_i^{\text{ref}}(\text{g}) + RT \ln \frac{p_i}{p} \tag{9.5.4}$$

$$\text{Constituent of an ideal liquid or solid mixture} \quad \mu_i^{\text{id}} = \mu_i^* + RT \ln x_i \tag{9.5.5}$$

$$\text{Solvent of an ideal-dilute solution} \quad \mu_A^{\text{id}} = \mu_A^* + RT \ln x_A \tag{9.5.6}$$

$$\text{Solute, ideal-dilute solution, mole fraction basis} \quad \mu_B^{\text{id}} = \mu_{x,B}^{\text{ref}} + RT \ln x_B \tag{9.5.7}$$

$$\text{Solute, ideal-dilute solution, concentration basis} \quad \mu_B^{\text{id}} = \mu_{c,B}^{\text{ref}} + RT \ln \frac{c_B}{c^\circ} \tag{9.5.8}$$

$$\text{Solute, ideal-dilute solution, molality basis} \quad \mu_B^{\text{id}} = \mu_{m,B}^{\text{ref}} + RT \ln \frac{m_B}{m^\circ} \tag{9.5.9}$$

Note that the equations for the condensed phases have the general form

$$\mu_i^{\text{id}} = \mu_i^{\text{ref}} + RT \ln \left(\frac{\text{composition variable}}{\text{standard composition}} \right) \tag{9.5.10}$$

where μ_i^{ref} is the chemical potential of component i in an appropriate reference state. (The standard composition on a mole fraction basis is $x^\circ=1$.)

9.5.3 Real mixtures

If a mixture is *not* ideal, we can write an expression for the chemical potential of each component that includes an **activity coefficient**. The expression is like one of those for the ideal case (Eqs. 9.5.4–9.5.9) with the activity coefficient multiplying the quantity within the logarithm.

Consider constituent i of a gas mixture. If we eliminate $\mu_i^\circ(\text{g})$ from Eqs. 9.3.12 and 9.5.2, we obtain

$$
\begin{aligned}
\mu_i &= \mu_i^{\text{ref}}(\text{g}) + RT\ln\frac{f_i}{p} \\
&= \mu_i^{\text{ref}}(\text{g}) + RT\ln\frac{\phi_i p_i}{p}
\end{aligned}
\tag{9.5.11}
$$

where f_i is the fugacity of constituent i and ϕ_i is its fugacity coefficient. Here the activity coefficient is the fugacity coefficient ϕ_i.

For components of a condensed-phase mixture, we write expressions for the chemical potential having a form similar to that in Eq. 9.5.10, with the composition variable now multiplied by an activity coefficient:

$$
\mu_i = \mu_i^{\text{ref}} + RT\ln\left[(\text{activity coefficient of } i) \times \left(\frac{\text{composition variable}}{\text{standard composition}}\right)\right]
\tag{9.5.12}
$$

The activity coefficient of a species is a dimensionless quantity whose value depends on the temperature, the pressure, the mixture composition, and the choice of the reference state for the species. Under conditions in which the mixture behaves ideally, the activity coefficient is unity and the chemical potential is given by one of the expressions of Eqs. 9.5.4–9.5.9; otherwise, the activity coefficient has the value that gives the actual chemical potential.

This e-book will use various symbols for activity coefficients, as indicated in the following list of expressions for the chemical potentials of nonelectrolytes:

$$
\text{Constituent of a gas mixture} \quad \mu_i = \mu_i^{\text{ref}}(\text{g}) + RT\ln\left(\phi_i\frac{p_i}{p}\right)
\tag{9.5.13}
$$

$$
\text{Constituent of a liquid or solid mixture} \quad \mu_i = \mu_i^* + RT\ln(\gamma_i x_i)
\tag{9.5.14}
$$

$$
\text{Solvent of a solution} \quad \mu_A = \mu_A^* + RT\ln(\gamma_A x_A)
\tag{9.5.15}
$$

$$
\text{Solute of a solution, mole fraction basis} \quad \mu_B = \mu_{x,B}^{\text{ref}} + RT\ln(\gamma_{x,B} x_B)
\tag{9.5.16}
$$

$$
\text{Solute of a solution, concentration basis} \quad \mu_B = \mu_{c,B}^{\text{ref}} + RT\ln\left(\gamma_{c,B}\frac{c_B}{c^\circ}\right)
\tag{9.5.17}
$$

$$
\text{Solute of a solution, molality basis} \quad \mu_B = \mu_{m,B}^{\text{ref}} + RT\ln\left(\gamma_{m,B}\frac{m_B}{m^\circ}\right)
\tag{9.5.18}
$$

Equation 9.5.14 refers to a component of a liquid or solid mixture of substances that mix in all proportions. Equation 9.5.15 refers to the solvent of a solution. The reference states of these components are the pure liquid or solid at the temperature and pressure of the mixture. For the activity coefficients of these components, this e-book uses the symbols γ_i and γ_A.

> The IUPAC Green Book (E. Richard Cohen et al, *Quantities, Units and Symbols in Physical Chemistry*, 3rd edition, RSC Publishing, Cambridge, 2007, p. 59) recommends the symbol f_i for the activity coefficient of component i when the reference state is the pure liquid or solid. This e-book instead uses symbols such as γ_i and γ_A, in order to avoid confusion with the symbol usually used for fugacity, f_i.

In Eqs. 9.5.16–9.5.18, the symbols $\gamma_{x,B}$, $\gamma_{c,B}$, and $\gamma_{m,B}$ for activity coefficients of a nonelectrolyte solute include x, c, or m in the subscript to indicate the choice of the solute reference state. Although three different expressions for μ_B are shown, for a given solution composition they must all represent the same *value* of μ_B, equal to the rate at which the Gibbs energy increases with the amount of substance B added to the solution at constant T and p. The value of a solute activity coefficient, on the other hand, depends on the choice of the solute reference state.

You may find it helpful to interpret products appearing on the right sides of Eqs. 9.5.13–9.5.18 as follows.

- In other words, the value of one of these products is the value of a partial pressure or composition variable that would give the same chemical potential in an ideal mixture as the actual chemical potential in the real mixture. These effective composition variables are an alternative way to express the escaping tendency of a substance from a phase; they are related exponentially to the chemical potential, which is also a measure of escaping tendency.

A change in pressure or composition that causes a mixture to approach the behavior of an ideal mixture or ideal-dilute solution must cause the activity coefficient of each mixture constituent to approach unity:

9.5.4 Nonideal dilute solutions

How would we expect the activity coefficient of a nonelectrolyte solute to behave in a dilute solution as the solute mole fraction increases beyond the range of ideal-dilute solution behavior?

The following argument is based on molecular properties at constant T and p.

We focus our attention on a single solute molecule. This molecule has interactions with nearby solute molecules. Each interaction depends on the intermolecular distance and causes a change in the internal energy compared to the interaction of the solute molecule with solvent at the same distance.

In Sec. 11.1.5, it will be shown that roughly speaking the internal energy change is negative if the average of the attractive forces between two solute molecules and two solvent molecules is greater than the attractive force between a solute molecule and a solvent molecule at the same distance, and is positive for the opposite situation.

The number of solute molecules in a volume element at a given distance from the solute molecule we are focusing on is proportional to the local solute concentration. If the solution is dilute and the interactions weak, we expect the local solute concentration to be proportional to the macroscopic solute mole fraction. Thus, the partial molar quantities U_B and V_B of the solute should be approximately linear functions of x_B in a dilute solution at constant T and p.

From Eqs. 9.2.46 and 9.2.50, the solute chemical potential is given by $\mu_B = U_B + pV_B - TS_B$. In the dilute solution, we assume U_B and V_B are linear functions of x_B as explained above. We also assume the dependence of S_B on x_B is approximately the same as in an ideal mixture; this is a prediction from statistical mechanics for a mixture in which all molecules have similar sizes and shapes. Thus we expect the deviation of the chemical potential from ideal-dilute behavior, $\mu_B = \mu_{x,B}^{\mathrm{ref}} + RT \ln x_B$, can be described by adding a term proportional to x_B: $\mu_B = \mu_{x,B}^{\mathrm{ref}} + RT \ln x_B + k_x x_B$, where k_x is a positive or negative constant related to solute-solute interactions.

If we equate this expression for μ_B with the one that defines the activity coefficient, $\mu_B = \mu_{x,B}^{\mathrm{ref}} + RT \ln(\gamma_{x,B} x_B)$ (Eq. 9.5.16), and solve for the activity coefficient, we obtain the relation $\gamma_{x,B} = \exp(k_x x_B / RT)$. (This is essentially the result of the McMillan–Mayer solution theory from statistical mechanics.) An expansion of the exponential in powers of x_B converts this to

$$\gamma_{x,B} = 1 + (k_x / RT) x_B + \cdots \qquad (9.5.25)$$

Thus we predict that at constant T and p, $\gamma_{x,B}$ is a linear function of x_B at low x_B. An ideal-dilute solution, then, is one in which x_B is much smaller than RT/k_x so that $\gamma_{x,B}$ is approximately 1. An ideal mixture requires the interaction constant k_x to be zero.

By similar reasoning, we reach analogous conclusions for solute activity coefficients on a concentration or molality basis. For instance, at low m_B the chemical potential of B should be approximately $\mu_{m,B}^{\mathrm{ref}} + RT \ln(m_B / m^\circ) + k_m m_B$, where k_m is a constant at a given T and p; then the activity coefficient at low m_B is given by

$$\gamma_{m,B} = \exp(k_m m_B / RT) = 1 + (k_m / RT) m_B + \cdots \qquad (9.5.26)$$

The prediction from the theoretical argument above, that a solute activity coefficient in a dilute solution is a linear function of the composition variable, is borne out experimentally as illustrated in Fig. 9.10. This prediction applies only to a nonelectrolyte solute; for an electrolyte, the slope of activity coefficient versus molality approaches $-\infty$ at low molality.