This section describes several methods by which activity coefficients of nonelectrolyte substances may be evaluated.

Section 9.6.3 describes an osmotic coefficient method that is also suitable for electrolyte solutes, as will be explained in Sec. 10.6.
9.6.1 Activity coefficients from gas fugacities

Suppose we equilibrate a liquid mixture with a gas phase. If component \(i\) of the liquid mixture is a volatile nonelectrolyte, and we are able to evaluate its fugacity \(\fug_i\) in the gas phase, we have a convenient way to evaluate the activity coefficient \(\g_i\) in the liquid. The relation between \(\g_i\) and \(\fug_i\) will now be derived.

When component \(i\) is in transfer equilibrium between two phases, its chemical potential is the same in both phases. Equating expressions for \(\mu_i\) in the liquid mixture and the equilibrated gas phase (from Eqs. 9.5.14 and 9.5.11, respectively), and then solving for \(\g_i\), we have:

\[
\begin{equation}
\mu_i^* + RT \ln \left( \g_i x_i \right) = \mu_i\rf\gas + RT \ln \left( \fug_i/p \right) \tag{9.6.1}
\end{equation}
\begin{equation}
\g_i = \exp \left[ \frac{\mu_i\rf\gas - \mu_i^*}{RT} \right] \times \frac{\fug_i}{x_i p} \tag{9.6.2}
\end{equation}
\begin{equation}
\g_i = C_i \frac{\fug_i}{x_i} \tag{9.6.3}
\end{equation}

where \(C_i\) is a factor whose value depends on \(T\) and \(p\), but not on the liquid composition. Solving Eq. 9.6.3 for \(C_i\) gives \(C_i = \g_i x_i / \fug_i\).

Now consider Eq. 9.5.20. It says that as \(x_i\) approaches 1 at constant \(T\) and \(p\), \(\g_i\) also approaches 1. We can use this limit to evaluate \(C_i\):

\[
\begin{equation}
C_i = \lim_{x_i \to 1} \frac{\g_i x_i}{\fug_i} = \frac{1}{\fug_i^*} \tag{9.6.4}
\end{equation}
\]

where \(\fug_i^*\) is the fugacity of \(i\) in a gas phase equilibrated with pure liquid \(i\) at the temperature and pressure of the mixture. Then substitution of this value of \(C_i\) (which is independent of \(x_i\)) in Eq. 9.6.3 gives us an expression for \(\g_i\) at any liquid composition:

\[
\begin{equation}
\g_i = \frac{\fug_i}{x_i \fug_i^*} \tag{9.6.5}
\end{equation}
\]

We can follow the same procedure for a solvent or solute of a liquid solution. We replace the left side of Eq. 9.6.1 with an expression from among Eqs. 9.5.15–9.5.18, then derive an expression analogous to Eq. 9.6.3 for the activity coefficient with a composition-independent factor, and finally apply the limiting conditions that cause the activity coefficient to approach unity (Eqs. 9.5.21–9.5.24) and allow us to evaluate the factor. When we take the limits that cause the solute activity coefficients to approach unity, the ratios \(\fugB/xB\), \(\fugB/cB\), and \(\fugB/mB\) become Henry’s law constants (Eqs. 9.4.19–9.4.21). The resulting expressions for activity coefficients as functions of fugacity are listed in Table 9.4.

Examples

![Figure 9.9 Liquid mixtures of ethanol (A) and H\(_2\)O at \(\{25\}\)](image)
Ethanol and water at \(25^\circ\text{C}\) mix in all proportions, so we can treat the liquid phase as a liquid mixture rather than a solution. A plot of ethanol fugacity versus mole fraction at fixed \((T)\) and \((p)\), shown earlier in Fig. 9.8, is repeated in Fig. 9.9(a). Ethanol is component A. In the figure, the filled circle is the pure-liquid reference state at \(x_A=1\) where \(f_A\) is equal to \(f_A^*\). The open circles at \(x_A=0.4\) indicate \(f_A\), the actual fugacity in a gas phase equilibrated with a liquid mixture of this composition, and \(x_A f_A^*\), the fugacity the ethanol would have if the mixture were ideal and component A obeyed Raoult’s law. The ratio of these two quantities is the activity coefficient \(\gamma_A\).

Figure 9.9(b) shows how \(\gamma_A\) varies with composition. The open circle is at \(x_A=0.4\) and \(\gamma_A=f_A/f_A^*\). Note how \(\gamma_A\) approaches \(1\) as \(x_A\) approaches \(1\), as it must according to Eq. 9.5.20.

### Table 9.4 Activity coefficients as functions of fugacity.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Activity coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substance (i) in a gas mixture</td>
<td>(\phi_i = \frac{f_i}{p_i})</td>
</tr>
<tr>
<td>Substance (i) in a liquid or solid mixture</td>
<td>(\gamma_i = \frac{f_i}{x_i f_i^*})</td>
</tr>
<tr>
<td>Solvent A of a solution</td>
<td>(\gamma_A = \frac{f_A}{x_A f_A^*})</td>
</tr>
<tr>
<td>Solute B, mole fraction basis</td>
<td>(\gamma_{x,B} = \frac{f_B}{k_{H,B} x_B})</td>
</tr>
<tr>
<td>Solute B, concentration basis</td>
<td>(\gamma_{c,B} = \frac{f_B}{k_{c,B} c_B})</td>
</tr>
<tr>
<td>Solute B, molality basis</td>
<td>(\gamma_{m,B} = \frac{f_B}{k_{m,B} m_B})</td>
</tr>
</tbody>
</table>
Water and 1-butanol are two liquids that do not mix in all proportions; that is, 1-butanol has limited solubility in water. Figures 9.10(a) and 9.10(b) show the fugacity of 1-butanol plotted as functions of both mole fraction and molality. The figures demonstrate how, treating 1-butanol as a solute, we locate the solute reference state by a linear extrapolation of the fugacity to the standard composition. The fugacity \( f_B \) is quite different in the two reference states. At the reference state indicated by a filled circle in Fig. 9.10(a), \( f_B \) equals the Henry’s law constant \( k_B \); at the reference state in Fig. 9.10(b), \( f_B \) equals \( k_m B m_B \). Note how the activity coefficients plotted in Figs. 9.10(c) and 9.10(d) approach \( 1 \) at infinite dilution, in agreement with Eqs. 9.5.22 and 9.5.24, and how they vary as a linear function of \( x_B \) or \( m_B \) in the dilute solution as predicted by the theoretical argument of Sec. 9.5.4.
9.6.2 Activity coefficients from the Gibbs–Duhem equation

If component B of a binary liquid mixture has low volatility, it is not practical to use its fugacity in a gas phase to evaluate its activity coefficient. If, however, component A is volatile enough for fugacity measurements over a range of liquid composition, we can instead use the Gibbs–Duhem equation for this purpose.

Consider a binary mixture of two liquids that mix in all proportions. We assume that only component A is appreciably volatile. By measuring the fugacity of A in a gas phase equilibrated with the binary mixture, we can evaluate its activity coefficient based on a pure-liquid reference state: \[ \ln \gamma_A = \frac{\text{fug}_A}{x_A \text{fug}_A^*} \] (Table 9.4). We wish to use the same fugacity measurements to determine the activity coefficient of the nonvolatile component, B.

The Gibbs–Duhem equation for a binary liquid mixture in the form given by Eq. 9.2.43 is

\[ x_A \text{d}\mu_A + x_B \text{d}\mu_B = 0 \]

where \( \text{d}\mu_A \) and \( \text{d}\mu_B \) are the chemical potential changes accompanying a change of composition at constant \( T \) and \( p \). Taking the differential at constant \( T \) and \( p \) of

\[ \text{d}\mu_A = \mu_A^{**} + RT \ln (\gamma_A x_A) \] (Eq. 9.5.14), we obtain

\[ \text{d}\mu_B = RT \text{d}\ln \gamma_B + \frac{RT}{x_B} \text{d}x_B = RT \text{d}\ln \gamma_B - \frac{RT}{x_B} \text{d}x_A \]

Substituting these expressions for \( \text{d}\mu_A \) and \( \text{d}\mu_B \) in Eq. 9.6.6 and solving for \( \text{d} \ln \gamma_B \), we obtain the following relation:

\[ \text{d} \ln \gamma_B = -\frac{x_A}{x_B} \text{d} \ln \gamma_A \]

Integration from \( x_B = 1 \), where \( \ln \gamma_B \) equals 0 and \( \ln \gamma_B \) equals 0, to composition \( x_B' \) gives

\[ \ln \gamma_B(x_B') = - \int_{x_B=1}^{x_B=x_B'} \frac{x_A}{x_B} \text{d} \ln \gamma_A \]

Equation 9.6.10 allows us to evaluate the activity coefficient of the nonvolatile component, B, at any given liquid composition from knowledge of the activity coefficient of the volatile component A as a function of composition.

Next consider a binary liquid mixture in which component B is neither volatile nor able to mix in all proportions with A. In this case, it is appropriate to treat B as a solute and to base its activity coefficient on a solute reference state. We could obtain an expression for \( \ln \gamma_B \) similar to Eq. 9.6.10, but the integration would have to start at \( x_B = 0 \) where the integrand \( x_A/x_B \) would be infinite. Instead, it is convenient in this case to use the method described in the next section.

9.6.3 Activity coefficients from osmotic coefficients

It is customary to evaluate the activity coefficient of a nonvolatile solute with a function \( \phi_m \) called the osmotic coefficient, or osmotic coefficient on a molality basis. The osmotic coefficient of a solution of nonelectrolyte solutes is defined by

\[ \phi_m \defn \frac{\mu_A^{**} - \mu_A}{RT M_A \sum_{i \ne A} m_i} \]

The definition of \( \phi_m \) in Eq. 9.6.11 has the following significance. The sum \( \sum_{i \ne A} m_i \) is the total molality of all solute species. In an ideal-dilute solution, the solvent chemical potential is \( \mu_A = \mu_A^{**} + RT \ln x_A \). The expansion of the function \( \ln x_A \) in powers of \( (1-x_A) \) gives the power series \( \ln x_A = -(1-x_A) - 3x_A - 12x_A^2 - \ldots \). Thus, in a very dilute solution we have \( \ln x_A \approx -(1-x_A) = -\sum_{i \ne A} \ln(x_A)x_i \). In the limit of infinite dilution, the mole fraction of solute \( i \)
becomes \( \ln x = \ln M - \sum_i m_i \) (see Eq. 9.1.14). In the limit of infinite dilution, therefore, we have:

\[
\ln x = -M \sum_i m_i \tag{9.6.12} \text{cond}(\text{infinite dilution}) \]

and the solvent chemical potential is related to solute molalities by:

\[
\mu = \mu^* - RTM \sum_i m_i \tag{9.6.13} \text{cond}(\text{infinite dilution}) \]

The deviation of \( \phi_m \) from unity is a measure of the deviation of \( \mu \) from infinite-dilution behavior, as we can see by comparing the preceding equation with a rearrangement of Eq. 9.6.11:

\[
\mu = \mu^* - \phi_m RTM \sum_i m_i \tag{9.6.14} \]

The reason \( \phi_m \) is called the osmotic coefficient has to do with its relation to the osmotic pressure \( \Pi \) of the solution: The ratio \( \Pi/m \) is equal to the product of \( \phi_m \) and the limiting value of \( \Pi/m \) at infinite dilution (see Sec. 12.4.4).

### Evaluation of \( \phi_m \)

Any method that measures \( \mu^* - \mu \), the lowering of the solvent chemical potential caused by the presence of a solute or solutes, allows us to evaluate \( \phi_m \) through Eq. 9.6.11.

The chemical potential of the solvent in a solution is related to the fugacity in an equilibrated gas phase by:

\[
\mu = \mu^* + RT \ln \left( \frac{f_{\text{g}}}{p} \right) \tag{9.6.15} \]

which allows us to evaluate \( \phi_m \) from fugacity measurements.

Osmotic coefficients can also be evaluated from freezing point and osmotic pressure measurements that will be described in Sec. 12.2.

### Use of \( \phi_m \)

Suppose we have a solution of a nonelectrolyte solute B whose activity coefficient \( \gamma_m \) we wish to evaluate as a function of \( m_B \). For a binary solution, Eq. 9.6.11 becomes:

\[
\phi_m = \frac{\mu^* - \mu}{RTM m_B} \tag{9.6.16} \text{cond}(\text{binary nonelectrolyte solution}) \]

Solving for \( \mu \) and taking its differential at constant \( \ln x \) and \( p \), we obtain:

\[
d\mu = -RT d(\phi_m m_B) = -RT \phi m_B d\ln m_B + m_B d\phi_m \tag{9.6.17} \]

From \( \ln m_B = \ln m_B^* + RT \ln \left( \frac{\gamma_m m_B}{m^*_B} \right) \) (Eq. 9.5.18), we obtain:

\[
d\ln m_B = RT \left( d\ln \gamma_m + \frac{d m_B}{m_B} \right) \tag{9.6.18} \]

We substitute these expressions for \( d\mu \) and \( d\ln m_B \) in the Gibbs–Duhem equation in the form given by Eq. 9.2.26, \( n \mu = n^* \mu + n \ln \gamma m_B + m_B \ln m_B \). Make the substitution \( n A M_A = n B m_B \), and rearrange to:

\[
d\ln \gamma m_B = d\phi_m + \frac{\phi_m - 1}{m_B} d m_B \tag{9.6.19} \]

We integrate both sides of this equation for a composition change at constant \( \ln x \) and \( p \) from \( m_B = 0 \) (where \( \ln x_B \) is \( 0 \)) to any desired molality \( m_B \), with the result:

\[
\ln \gamma m_B(m_B) = \ln \gamma_B(m_B^-1) + \ln(\phi_m - 1)(m_B) \tag{9.6.20} \text{cond}(\text{binary}) \]

When the solute is a nonelectrolyte, the integrand \( (\phi_m - 1)/m_B \) is found to be a slowly varying function of \( m_B \) and to approach a finite value as \( m_B \rightarrow 0 \).

Once \( \phi_m \) has been measured as a function of molality from zero up to the molality of interest, Eq. 9.6.20 can be used to evaluate the solute activity coefficient \( \gamma m_B \) at that molality.

(a) Integrand of the integral in Eq. 9.6.20 as a function of solution composition.

(b) Solute activity coefficient on a molality basis.

(c) Product of activity coefficient and molality as a function of composition. The dashed line is the extrapolation of ideal-dilute behavior.

Figure 9.11(a) shows the function \(\frac{(\phi_m - 1)}{m}\) for aqueous sucrose solutions over a wide range of molality. The dependence of the solute activity coefficient on molality, generated from Eq. 9.6.20, is shown in Fig. 9.11(b). Figure 9.11(c) is a plot of the effective sucrose molality \(\g mB mB\) as a function of composition. Note how the activity coefficient becomes greater than unity beyond the ideal-dilute region, and how in consequence the effective molality \(\g mB mB\) becomes considerably greater than the actual molality \(mB\).

### 9.6.4 Fugacity measurements

Section 9.6.1 described the evaluation of the activity coefficient of a constituent of a liquid mixture from its fugacity in a gas phase equilibrated with the mixture. Section 9.6.3 mentioned the use of solvent fugacities in gas phases equilibrated with pure solvent and with a solution, in order to evaluate the osmotic coefficient of the solution.

Various experimental methods are available for measuring a partial pressure in a gas phase equilibrated with a liquid mixture. A correction for gas nonideality, such as that given by Eq. 9.3.16, can be used to convert the partial pressure to fugacity.

If the solute of a solution is nonvolatile, we may pump out the air above the solution and use a manometer to measure the pressure, which is the partial pressure of the solvent. Dynamic methods involve passing a stream of inert gas through a liquid mixture and analyzing the gas mixture to evaluate the partial pressures of volatile components. For instance, we could pass dry air successively through an aqueous solution and a desiccant and measure the weight gained by the desiccant.
The isopiestic vapor pressure technique is one of the most useful methods for determining the fugacity of H\(_2\)O in a gas phase equilibrated with an aqueous solution. This is a comparative method using a binary solution of the solute of interest, B, and a nonvolatile reference solute of known properties. Some commonly used reference solutes for which data are available are sucrose, NaCl, and CaCl\(_2\).

In this method, solute B can be either a nonelectrolyte or electrolyte. Dishes, each containing water and an accurately weighed sample of one of the solutes, are placed in wells drilled in a block made of metal for good thermal equilibration. The assembly is placed in a gas-tight chamber, the air is evacuated, and the apparatus is gently rocked in a thermostat for a period of up to several days, or even weeks. During this period, H\(_2\)O is transferred among the dishes through the vapor space until the chemical potential of the water becomes the same in each solution. The solutions are then said to be isopiestic. Finally, the dishes are removed from the apparatus and weighed to establish the molality of each solution. The H\(_2\)O fugacity is known as a function of the molality of the reference solute, and is the same as the H\(_2\)O fugacity in equilibrium with the solution of solute B at its measured molality.

The isopiestic vapor pressure method can also be used for nonaqueous solutions.

Contributors

- Howard DeVoe, Associate Professor Emeritus, University of Maryland from Thermodynamics and Chemistry