

9.6: Evaluation of Activity Coefficients

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 f_i in the gas phase, we have a convenient way to evaluate the activity coefficient γ_i in the liquid. The relation between γ_i and f_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 μ_i in the liquid mixture and the equilibrated gas phase (from Eqs. 9.5.14 and 9.5.11, respectively), and then solving for γ_i , we have

$$\mu_i^* + RT \ln(\gamma_i x_i) = \mu_i^{\text{ref}}(\text{g}) + RT \ln(f_i/p) \quad (9.6.1)$$

$$\gamma_i = \exp \left[\frac{\mu_i^{\text{ref}}(\text{g}) - \mu_i^*}{RT} \right] \times \frac{f_i}{x_i p} \quad (9.6.2)$$

On the right side of Eq. 9.6.2, only f_i and x_i depend on the liquid composition. We can therefore write

$$\gamma_i = C_i \frac{f_i}{x_i} \quad (9.6.3)$$

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 $C_i = \gamma_i x_i / f_i$.

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

$$C_i = \lim_{x_i \rightarrow 1} \frac{\gamma_i x_i}{f_i} = \frac{1}{f_i^*} \quad (9.6.4)$$

Here f_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 γ_i at any liquid composition:

$$\gamma_i = \frac{f_i}{x_i f_i^*} \quad (9.6.5)$$

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 f_B/x_B , f_B/c_B , and f_B/m_B 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 9.11(a) shows the function $(\phi_m - 1)/m_B$ 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 $\gamma_{m,B} m_B$ 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 $\gamma_{m,B} m_B$ becomes considerably greater than the actual molality m_B .

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_2O 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_2O 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_2O fugacity is known as a function of the molality of the reference solute, and is the same as the H_2O 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.

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