TIP

Working with P°

It may be tempting to set $P^\circ = 1$ in the above equation and write $a_i = y_i \phi_i P$. *Don't do it!* This substitution produces an equation that is marginally simpler, but dimensionally incorrect, as the left-hand side is dimensionless whereas the right-hand side has units of pressure. Such equation is valid *only* if special units are used (bar, in this case) and this can lead to confusion and errors in the calculation. To avoid these problems, retain P° in your formulas until final numerical substitution. This recommendation applies to all formulas that involve P° or other constants of the reference state.

Activity of Liquid

To obtain an equation for the activity based on the liquid standard state, we use eq. (12.16) for the fugacity of component is solution,

$$f_i = \gamma_i x_i f_{i,\text{pure}}, \tag{12.16}$$

to write

$$a_i = \frac{f_i}{f_i^\circ} = \frac{\gamma_i x_i f_{i,\text{pure}}}{f_i^\circ}, \tag{14.18}$$

where $f_{i,\text{pure}} = f_{i,\text{pure}}(P, T)$ is the fugacity of the pure species i and $f_i^\circ = f_i(P^\circ, T)$ is the fugacity of the pure liquid at the standard state. The actual and the standard state are both at the same temperature but different pressures. Accordingly, the ratio of the corresponding fugacities is given by the Poynting factor,

$$\frac{f_{i,\text{pure}}}{f_i^\circ} = \exp\left(\frac{P - P^\circ}{RT} V_i\right), \tag{7.16}$$

where V_i is the liquid molar volume of pure component i. Combining these results the activity takes the form

$$a_i = \gamma_i x_i \exp\left(\frac{P - P^\circ}{RT} V_i\right). \tag{14.19}$$

This general equation can be put into simpler form in some special cases: *Low pressure*: At pressures not much higher than P°, the Poynting correction is negligible and the activity simplifies to

$$a_i = \gamma_i x_i. \tag{14.20}$$

Low pressure, ideal solution. With the additional assumption of ideal solution ($\gamma_i = 1$), the previous result gives

$$a_i = x_i. \tag{14.21}$$