9.7: Activity of an Uncharged Species

The **activity** a_i of uncharged species i (i.e., a substance) is defined by the relation

$$a_i \overset{\text{def}}{=} \exp\!\left(\frac{\mu_i - \mu_i^\circ}{RT}\right) \tag{9.7.1}$$
$$\text{(uncharged species)}$$

or

$$\mu_i = \mu_i^\circ + RT \ln a_i \tag{9.7.2}$$
$$\text{(uncharged species)}$$

where μ_i° is the standard chemical potential of the species. The activity of a species in a given phase is a dimensionless quantity whose value depends on the choice of the standard state and on the intensive properties of the phase: temperature, pressure, and composition.

> Some chemists define the activity by $\mu_i = \mu_i^{\text{ref}} + RT \ln a_i$. The activity defined this way is not the same as the activity used in this e-book unless the phase is at the standard pressure.

The quantity a_i is sometimes called the *relative activity* of i, because it depends on the chemical potential relative to a standard chemical potential. An important application of the activity concept is the definition of equilibrium constants (Sec. 11.8.1).

For convenience in later applications, we specify that the value of a_i is the same in phases that have the same temperature, pressure, and composition but are at different elevations in a gravitational field, or are at different electric potentials. Section 9.8 10.1 will describe a modification of the defining equation $\mu_i = \mu_i^\circ + RT \ln a_i$ for a system with phases of different elevations, and Sec. 10.1 will describe the modification needed for a charged species.

9.7.1 Standard states

The standard states of different kinds of mixture components have the same definitions as those for reference states (Table 9.3), with the additional stipulation in each case that the pressure is equal to the standard pressure p°.

When component i is in its standard state, its chemical potential is the standard chemical potential μ_i°. It is important to note from Eq. 9.7.2 that when μ_i equals μ_i°, the logarithm of a_i is zero and the activity in the standard state is therefore unity.

The following equations in the form of Eq. 9.7.2 show the notation used in this e-book for the standard chemical potentials and activities of various kinds of uncharged mixture components:

$$\text{Substance } i \text{ in a gas mixture} \qquad \mu_i = \mu_i^\circ(\text{g}) + RT \ln a_i(\text{g}) \tag{9.7.3}$$

$$\text{Substance } i \text{ in a liquid or solid mixture} \qquad \mu_i = \mu_i^\circ + RT \ln a_i \tag{9.7.4}$$

$$\text{Solvent A of a solution} \qquad \mu_\text{A} = \mu_\text{A}^\circ + RT \ln a_\text{A} \tag{9.7.5}$$

$$\text{Solute B, mole fraction basis} \qquad \mu_\text{B} = \mu_{x,\text{B}}^\circ + RT \ln a_{x,\text{B}} \tag{9.7.6}$$

$$\text{Solute B, concentration basis} \qquad \mu_\text{B} = \mu_{c,\text{B}}^\circ + RT \ln a_{c,\text{B}} \tag{9.7.7}$$

$$\text{Solute B, molality basis} \qquad \mu_\text{B} = \mu_{m,\text{B}}^\circ + RT \ln a_{m,\text{B}} \tag{9.7.8}$$

9.7.2 Activities and composition

We need to be able to relate the activity of component i to the mixture composition. We can do this by finding the relation between the chemical potential of component i in its reference state and in its standard state, both at the same temperature. These two chemical potentials, μ_i^{ref} and μ_i°, are equal only if the mixture is at the standard pressure p°.

It will be useful to define the following dimensionless quantity:

$$\Gamma_i \overset{\text{def}}{=} \exp\!\left(\frac{\mu_i^{\text{ref}} - \mu_i^\circ}{RT}\right) \tag{9.7.9}$$

The symbol Γ_i for this quantity was introduced by Pitzer and Brewer (*Thermodynamics*, 2nd edition, McGraw-Hill, New York, 1961, p. 249). They called it *the activity in a reference state*. To see why, compare the definition of activity given by

$\mu_i = \mu_i^\circ + RT \ln a_i$ with a rearrangement of Eq. 9.7.9: $\mu_i^{\text{ref}} = \mu_i^\circ + RT \ln \Gamma_i$.

At a given temperature, the difference $\mu_i^{\text{ref}} - \mu_i^\circ$ depends only on the pressure p of the mixture, and is zero when p is equal to p°. Thus Γ_i is a function of p with a value of 1 when p is equal to p°. This e-book will call Γ_i the **pressure factor** of species i.

To understand how activity is related to composition, let us take as an example the activity $a_{m,\text{B}}$ of solute B based on molality. From Eqs. 9.5.18 and 9.7.8, we have

$$
\begin{aligned}
\mu_\text{B} &= \mu_{m,\text{B}}^{\text{ref}} + RT \ln\left(\gamma_{m,\text{B}} \frac{m_\text{B}}{m^\circ}\right) \\
&= \mu_{m,\text{B}}^\circ + RT \ln a_{m,\text{B}}
\end{aligned}
\tag{9.7.10}
$$

The activity is then given by

$$
\begin{aligned}
\ln a_{m,\text{B}} &= \frac{\mu_{m,\text{B}}^{\text{ref}} - \mu_{m,\text{B}}^\circ}{RT} + \ln\left(\gamma_{m,\text{B}} \frac{m_\text{B}}{m^\circ}\right) \\
&= \ln \Gamma_{m,\text{B}} + \ln\left(\gamma_{m,\text{B}} \frac{m_\text{B}}{m^\circ}\right)
\end{aligned}
\tag{9.7.11}
$$

$$
a_{m,\text{B}} = \Gamma_{m,\text{B}} \gamma_{m,\text{B}} \frac{m_\text{B}}{m^\circ}
\tag{9.7.12}
$$

The activity of a constituent of a condensed-phase mixture is in general equal to the product of the pressure factor, the activity coefficient, and the composition variable divided by the standard composition.

We are now able to write explicit formulas for Γ_i for each kind of mixture component. They are collected in Table 9.6.

Considering a constituent of a condensed-phase mixture, by how much is the pressure factor likely to differ from unity? If we use the values $p^\circ = 1\,\text{bar}$ and $T = 300\,\text{K}$, and assume the molar volume of pure i is $V_i^* = 100\,\text{cm}^3\,\text{mol}^{-1}$ at all pressures, we find that Γ_i is 0.996 in the limit of zero pressure, unity at 1 bar, 1.004 at 2 bar, 1.04 at 10 bar, and 1.49 at 100 bar. For a solution with $V_\text{B}^\infty = 100\,\text{cm}^3\,\text{mol}^{-1}$, we obtain the same values as these for $\Gamma_{x,\text{B}}$, $\Gamma_{m,\text{B}}$, and $\Gamma_{c,\text{B}}$. These values demonstrate that it is only at high pressures that the pressure factor differs appreciably from unity. For this reason, it is common to see expressions for activity in which this factor is omitted: $a_i = \gamma_i x_i$, $a_{m,\text{B}} = \gamma_{m,\text{B}} m_\text{B}/m^\circ$, and so on.

> In principle, we can specify any convenient value for the standard pressure p°. For a chemist making measurements at high pressures, it would be convenient to specify a value of p° within the range of the experimental pressures, for example $p^\circ = 1\,\text{kbar}$, in order that the value of each pressure factor be close to unity.