9.1: Composition Variables

A **composition variable** is an intensive property that indicates the relative amount of a particular species or substance in a phase.

9.1.1 Species and substances

We sometimes need to make a distinction between a species and a substance. A **species** is any entity of definite elemental composition and charge and can be described by a chemical formula, such as H_2O, H_3O^+, NaCl, or Na^+. A **substance** is a species that can be prepared in a pure state (e.g., N_2 and NaCl). Since we cannot prepare a macroscopic amount of a single kind of ion by itself, a charged species such as H_3O^+ or Na^+ is not a substance. Chap. 10 will discuss the special features of mixtures containing charged species.

9.1.2 Mixtures in general

The **mole fraction** of species i is defined by

$$x_i \overset{\text{def}}{=} \frac{n_i}{\sum_j n_j} \qquad \text{or} \qquad y_i \overset{\text{def}}{=} \frac{n_i}{\sum_j n_j} \tag{9.1.1}$$

$(P{=}1)$

where n_i is the amount of species i and the sum is taken over all species in the mixture. The symbol x_i is used for a mixture in general, and y_i is used when the mixture is a gas.

The **mass fraction**, or weight fraction, of species i is defined by

$$w_i \overset{\text{def}}{=} \frac{m(i)}{m} = \frac{n_i M_i}{\sum_j n_j M_j} \tag{9.1.2}$$

$(P{=}1)$

where $m(i)$ is the mass of species i and m is the total mass.

The **concentration**, or molarity, of species i in a mixture is defined by

$$c_i \overset{\text{def}}{=} \frac{n_i}{V} \tag{9.1.3}$$

$(P{=}1)$

The symbol M is often used to stand for units of mol L^{-1}, or mol dm^{-3}. Thus, a concentration of $0.5\,\text{M}$ is 0.5 moles per liter, or 0.5 molar.

> Concentration is sometimes called “amount concentration” or “molar concentration” to avoid confusion with number concentration (the number of *particles* per unit volume). An alternative notation for c_A is [A].

A **binary mixture** is a mixture of *two* substances.

9.1.3 Solutions

A **solution**, strictly speaking, is a mixture in which one substance, the **solvent**, is treated in a special way. Each of the other species comprising the mixture is then a **solute**. The solvent is denoted by A and the solute species by B, C, and so on. (Some chemists denote the solvent by subscript 1 and use 2, 3, and so on for solutes.) Although in principle a solution can be a gas mixture, in this section we will consider only liquid and solid solutions.

We can prepare a solution of varying composition by gradually mixing one or more solutes with the solvent so as to continuously increase the solute mole fractions. During this mixing process, the physical state (liquid or solid) of the solution remains the same as that of the pure solvent. When the sum of the solute mole fractions is small compared to x_A (i.e., x_A is close to unity), the solution is called *dilute*. As the solute mole fractions increase, we say the solution becomes more *concentrated*.

Mole fraction, mass fraction, and concentration can be used as composition variables for both solvent and solute, just as they are for mixtures in general. A fourth composition variable, molality, is often used for a solute. The **molality** of solute species B is defined by

$$m_\text{B} \overset{\text{def}}{=} \frac{n_\text{B}}{m(\text{A})} \tag{9.1.4}$$

(solution)

where $m(\mathrm{A}) = n_\mathrm{A} M_\mathrm{A}$ is the mass of solvent. The symbol m is sometimes used to stand for units of mol kg^{-1}, although this should be discouraged because m is also the symbol for meter. For example, a solute molality of 0.6 m is 0.6 moles of solute per kilogram of solvent, or 0.6 molal.

9.1.4 Binary solutions

We may write simplified equations for a binary solution of two substances, solvent A and solute B. Equations 9.1.1–9.1.4 become

$$x_\mathrm{B} = \frac{n_\mathrm{B}}{n_\mathrm{A} + n_\mathrm{B}} \tag{9.1.5}$$
(binary solution)

$$w_\mathrm{B} = \frac{n_\mathrm{B} M_\mathrm{B}}{n_\mathrm{A} M_\mathrm{A} + n_\mathrm{B} M_\mathrm{B}} \tag{9.1.6}$$
(binary solution)

$$c_\mathrm{B} = \frac{n_\mathrm{B}}{V} = \frac{n_\mathrm{B}\rho}{n_\mathrm{A} M_\mathrm{A} + n_\mathrm{B} M_\mathrm{B}} \tag{9.1.7}$$
(binary solution)

$$m_\mathrm{B} = \frac{n_\mathrm{B}}{n_\mathrm{A} M_\mathrm{A}} \tag{9.1.8}$$
(binary solution)

The right sides of Eqs. 9.1.5–9.1.8 express the solute composition variables in terms of the amounts and molar masses of the solvent and solute and the density ρ of the solution.

To be able to relate the values of these composition variables to one another, we solve each equation for n_B and divide by n_A to obtain an expression for the mole ratio $n_\mathrm{B}/n_\mathrm{A}$:

$$\text{from Eq. 9.1.5} \qquad \frac{n_\mathrm{B}}{n_\mathrm{A}} = \frac{x_\mathrm{B}}{1 - x_\mathrm{B}} \tag{9.1.9}$$
(binary solution)

$$\text{from Eq. 9.1.6} \qquad \frac{n_\mathrm{B}}{n_\mathrm{A}} = \frac{M_\mathrm{A} w_\mathrm{B}}{M_\mathrm{B}(1 - w_\mathrm{B})} \tag{9.1.10}$$
(binary solution)

$$\text{from Eq. 9.1.7} \qquad \frac{n_\mathrm{B}}{n_\mathrm{A}} = \frac{M_\mathrm{A} c_\mathrm{B}}{\rho - M_\mathrm{B} c_\mathrm{B}} \tag{9.1.11}$$
(binary solution)

$$\text{from Eq. 9.1.8} \qquad \frac{n_\mathrm{B}}{n_\mathrm{A}} = M_\mathrm{A} m_\mathrm{B} \tag{9.1.12}$$
(binary solution)

These expressions for $n_\mathrm{B}/n_\mathrm{A}$ allow us to find one composition variable as a function of another. For example, to find molality as a function of concentration, we equate the expressions for $n_\mathrm{B}/n_\mathrm{A}$ on the right sides of Eqs. 9.1.11 and 9.1.12 and solve for m_B to obtain

$$m_\mathrm{B} = \frac{c_\mathrm{B}}{\rho - M_\mathrm{B} c_\mathrm{B}} \tag{9.1.13}$$

A binary solution becomes more dilute as any of the solute composition variables becomes smaller. In the limit of infinite dilution, the expressions for $n_\mathrm{B}/n_\mathrm{A}$ become:

$$\begin{aligned} \frac{n_\mathrm{B}}{n_\mathrm{A}} &= x_\mathrm{B} \\ &= \frac{M_\mathrm{A}}{M_\mathrm{B}} w_\mathrm{B} \\ &= \frac{M_\mathrm{A}}{\rho_\mathrm{A}^*} c_\mathrm{B} = V_{\mathrm{m,A}}^* c_\mathrm{B} \\ &= M_\mathrm{A} m_\mathrm{B} \end{aligned} \tag{9.1.14}$$
(binary solution at infinite dilution)

where a superscript asterisk (*) denotes a pure phase. We see that, in the limit of infinite dilution, the composition variables x_B, w_B, c_B, and m_B are proportional to one another. These expressions are also valid for solute B in a *multi*solute solution in which *each* solute is very dilute; that is, in the limit $x_\mathrm{A} \to 1$.

The rule of thumb that the molarity and molality values of a dilute aqueous solution are approximately equal is explained by the relation $M_\mathrm{A} c_\mathrm{B}/\rho_\mathrm{A}^* = M_\mathrm{A} m_\mathrm{B}$ (from Eq. 9.1.14), or $c_\mathrm{B}/\rho_\mathrm{A}^* = m_\mathrm{B}$, and the fact that the density ρ_A^*

of water is approximately 1 kg L^{-1}. Hence, if the solvent is water and the solution is dilute, the numerical value of c_{B} expressed in mol L^{-1} is approximately equal to the numerical value of m_{B} expressed in mol kg^{-1}.

9.1.5 The composition of a mixture

We can describe the composition of a phase with the amounts of each species, or with any of the composition variables defined earlier: mole fraction, mass fraction, concentration, or molality. If we use mole fractions or mass fractions to describe the composition, we need the values for all but one of the species, since the sum of all fractions is unity.

Other composition variables are sometimes used, such as volume fraction, mole ratio, and mole percent. To describe the composition of a gas mixture, partial pressures can be used (Sec. 9.3.1).

When the composition of a mixture is said to be *fixed* or *constant* during changes of temperature, pressure, or volume, this means there is no change in the relative *amounts* or *masses* of the various species. A mixture of fixed composition has fixed values of mole fractions, mass fractions, and molalities, but not necessarily of concentrations and partial pressures. Concentrations will change if the volume changes, and partial pressures in a gas mixture will change if the pressure changes.