9.3: Gas Mixtures

The gas mixtures described in this chapter are assumed to be mixtures of nonreacting gaseous substances.

9.3.1 Partial pressure

The **partial pressure** p_i of substance i in a gas mixture is defined as the product of its mole fraction in the gas phase and the pressure of the phase:

$$p_i \overset{\text{def}}{=} y_i p \qquad\qquad (9.3.1)$$
$$\text{(gas mixture)}$$

The sum of the partial pressures of all substances in a gas mixture is $\sum_i p_i = \sum_i y_i p = p \sum_i y_i$. Since the sum of the mole fractions of all substances in a mixture is 1, this sum becomes

$$\sum_i p_i = p \qquad\qquad (9.3.2)$$
$$\text{(gas mixture)}$$

Thus, the sum of the partial pressures equals the pressure of the gas phase. This statement is known as **Dalton's Law**. It is valid for any gas mixture, regardless of whether or not the gas obeys the ideal gas equation.

9.3.2 The ideal gas mixture

As discussed in Sec. 3.5.1, an ideal gas (whether pure or a mixture) is a gas with negligible intermolecular interactions. It obeys the ideal gas equation $p = nRT/V$ (where n in a mixture is the sum $\sum_i n_i$) and its internal energy in a closed system is a function only of temperature. The partial pressure of substance i in an ideal gas mixture is $p_i = y_i p = y_i nRT/V$; but $y_i n$ equals n_i, giving

$$p_i = \frac{n_i RT}{V} \qquad\qquad (9.3.3)$$
$$\text{(ideal gas mixture)}$$

Equation 9.3.3 is the ideal gas equation with the partial pressure of a constituent substance replacing the total pressure, and the amount of the substance replacing the total amount. The equation shows that the partial pressure of a substance in an ideal gas mixture is the pressure the substance by itself, with all others removed from the system, would have at the same T and V as the mixture. Note that this statement is only true for an *ideal* gas mixture. The partial pressure of a substance in a real gas mixture is in general different from the pressure of the pure substance at the same T and V, because the intermolecular interactions are different.

9.3.3 Partial molar quantities in an ideal gas mixture

We need to relate the chemical potential of a constituent of a gas mixture to its partial pressure. We cannot measure the absolute value of a chemical potential, but we can evaluate its value relative to the chemical potential in a particular reference state called the standard state.

The *standard state of substance i in a gas mixture* is the same as the standard state of the pure gas described in Sec. 7.7: It is the hypothetical state in which pure gaseous i has the same temperature as the mixture, is at the standard pressure p°, and behaves as an ideal gas. The standard chemical potential $\mu_i^\circ(\text{g})$ of gaseous i is the chemical potential of i in this gas standard state, and is a function of temperature.

By combining Eqs. 9.3.12 and 9.3.16, we obtain

$$\mu_i(p') = \mu_i^\circ(\text{g}) + RT \ln \frac{p_i'}{p^\circ} + \int_0^{p'} \left(V_i - \frac{RT}{p} \right) \mathrm{d}p \qquad\qquad (9.3.19)$$
$$\text{(gas mixture,}$$
$$\text{constant } T)$$

which is the analogue for a gas mixture of Eq. 7.9.2 for a pure gas. Section 7.9 describes the procedure needed to obtain formulas for various molar quantities of a pure gas from Eq. 7.9.2. By following a similar procedure with Eq. 9.3.19, we obtain the formulas for differences between partial molar and standard molar quantities of a constituent of a gas mixture shown in the second column of Table 9.1. These formulas are obtained with the help of Eqs. 9.2.46, 9.2.48, 9.2.50, and 9.2.52.

Equation of state

The equation of state of a real gas mixture can be written as the virial equation

$$pV/n = RT \left[1 + \frac{B}{(V/n)} + \frac{C}{(V/n)^2} + \cdots \right] \tag{9.3.20}$$

This equation is the same as Eq. 2.2.2 for a pure gas, except that the molar volume V_{m} is replaced by the mean molar volume V/n, and the virial coefficients $B, C, \ldots$ depend on composition as well as temperature.

At low to moderate pressures, the simple equation of state

$$V/n = \frac{RT}{p} + B \tag{9.3.21}$$

describes a gas mixture to a sufficiently high degree of accuracy (see Eq. 2.2.8). This is equivalent to a compression factor given by

$$Z \stackrel{\text{def}}{=} \frac{pV}{nRT} = 1 + \frac{Bp}{RT} \tag{9.3.22}$$

From statistical mechanical theory, the dependence of the second virial coefficient B of a binary gas mixture on the mole fraction composition is given by

$$B = y_{\mathrm{A}}^2 B_{\mathrm{AA}} + 2 y_{\mathrm{A}} y_{\mathrm{B}} B_{\mathrm{AB}} + y_{\mathrm{B}}^2 B_{\mathrm{BB}} \tag{9.3.23}$$
$$\text{(binary gas mixture)}$$

where B_{AA} and B_{BB} are the second virial coefficients of pure A and B, and B_{AB} is a mixed second virial coefficient. B_{AA}, B_{BB}, and B_{AB} are functions of T only. For a gas mixture with any number of constituents, the composition dependence of B is given by

$$B = \sum_i \sum_j y_i y_j B_{ij} \tag{9.3.24}$$
$$\text{(gas mixture, } B_{ij} = B_{ji} \text{)}$$

Here B_{ij} is the second virial of i if i and j are the same, or a mixed second virial coefficient if i and j are different.

If a gas mixture obeys the equation of state of Eq. 9.3.21, the partial molar volume of constituent i is given by

$$V_i = \frac{RT}{p} + B_i' \tag{9.3.25}$$

where the quantity B_i', in order to be consistent with $V_i = (\partial V/\partial n_i)_{T,p,n_{j \neq i}}$, is found to be given by

$$B_i' = 2 \sum_j y_j B_{ij} - B \tag{9.3.26}$$

For the constituents of a binary mixture of A and B, Eq. 9.3.26 becomes

$$B_{\mathrm{A}}' = B_{\mathrm{AA}} + (-B_{\mathrm{AA}} + 2 B_{\mathrm{AB}} - B_{\mathrm{BB}}) y_{\mathrm{B}}^2 \tag{9.3.27}$$
$$\text{(binary gas mixture)}$$

$$B_{\mathrm{B}}' = B_{\mathrm{BB}} + (-B_{\mathrm{AA}} + 2 B_{\mathrm{AB}} - B_{\mathrm{BB}}) y_{\mathrm{A}}^2 \tag{9.3.28}$$
$$\text{(binary gas mixture)}$$

When we substitute the expression of Eq. 9.3.25 for V_i in Eq. 9.3.18, we obtain a relation between the fugacity coefficient of constituent i and the function B_i':

$$\ln \phi_i = \frac{B_i' p}{RT} \tag{9.3.29}$$

The third column of Table 9.1 gives formulas for various partial molar quantities of constituent i in terms of B_i' and its temperature derivative. The formulas are the same as the approximate formulas in the third column of Table 7.5 for molar quantities of a *pure* gas, with B_i' replacing the second virial coefficient B.