Densities of ethanol/water solutions at 20 °C.†

Ethanol conc. (weight fraction)	ρ g/cm^3	Ethanol conc. (weight fraction)	ρ g/cm^3
0.00	1.0000	0.54	0.9049
0.10	0.9819	0.60	0.8911
0.20	0.9687	0.70	0.8676
0.30	0.9539	0.80	0.8436
0.40	0.9352	0.90	0.8180
0.50	0.9139	1.00	0.7893

†CRC Handbook of Chemistry and Physic, 60th ed. (New York: CRC Press, 1979), p. D-236. Physics

Solution The masses of ethanol and water in the solution are

$$M_E = V_E^{\text{tot}} \rho_E = (0.1\ \text{m}^3)(789.3\ \text{kg/m}^3) = 78.93\ \text{kg},$$

$$M_W = V_W^{\text{tot}} \rho_W = (0.1\ \text{m}^3)(1000\ \text{kg/m}^3) = 100\ \text{kg}.$$

The mass fraction of ethanol is

$$w_E = \frac{78.93}{78.93 + 100} = 0.441.$$

By interpolation in the above table, the density of the solution at $w_1 = 0.441$ is

$$\rho = 0.9267\ \text{g/cm}^3 = 926.7\ \text{kg/m}^3,$$

and the volume of the solution is

$$V^{\text{tot}} = \frac{M}{\rho} = \frac{178.93\ \text{kg}}{926.7\ \text{kg/m}^3} = 0.1931\ \text{m}^3.$$

Upon mixing the volume changes by:

$$\Delta V^{\text{tot}} = 0.1931 - 0.1 - 0.1 = -0.00692\ \text{m}^3.$$

To express this on a molar basis, we calculate the number of moles in the solution:

$$n_E = \frac{78.93\ \text{kg}}{46.07 \times 10^{-3}\ \text{kg/mol}} = 1713.26\ \text{mol},$$

$$n_W = \frac{100\ \text{kg}}{18.01 \times 10^{-3}\ \text{kg/mol}} = 5552.47\ \text{mol}.$$

The molar volume of mixing, also equal to the excess molar volume, is

$$V^E = \frac{-0.00692\ \text{m}^3}{(1713.26 + 5552.47)\ \text{mol}} = -0.952 \times 10^{-6}\ \text{m}^3/\text{mol} = -0.952\ \text{cm}^3/\text{mol}.$$

Comments When ethanol is mixed with water at 25 °C, the volume of the solution contracts relative to the volume of the pure components. In this example, the volume contracts by about 3.5%.

Example 12.2: Excess Volume

With the data of the previous example, plot the excess volume as a function of the mol fraction of ethanol and determine the partial molar volumes of the two components at ethanol mol fraction of 0.4.

Solution For every entry of the table in the previous example we calculate the molar volume of solution and the corresponding mol fraction of ethanol. The calculation is facilitated by choosing a basis of 1 kg of solution. The moles of each component are

$$n_E = \frac{w_E}{M_{mE}}, \quad n_W = \frac{1 - w_E}{M_{mW}},$$

where w_E is the weight faction of ethanol, and $M_{mE} = 46.07 \times 10^{-3}$ kg/mol and $M_{mW} =$ 18.01 kg/mol are the molar masses of ethanol and water, respectively. The molar volume of the solution is

18.01 times 10^-3

$$V = \frac{1}{\rho}\left(\frac{1 \text{ kg}}{n_E + n_W}\right).$$

Finally, the excess volume is calculated as

(1-xE) vW

$$V^{\mathrm{E}} = V - x_E v_E - (1 - x_E) v_W \cancel{)},$$

where $V_E = 0.05837$ m^3/mol and $V_W = 0.01801$ m^3/mol are the molar volumes of pure ethanol and water, calculated from the given data. These calculations are summarized in the table below:

x $(-)$	ρ (kg/m^3)	V (m^3/kg)	V^{E} (m^3/kg)	x $(-)$	ρ (kg/m^3)	V (m^3/kg)	V^{E} (m^3/kg)
0.000	1.0000	0.01801	0	0.315	0.9049	0.02966	−0.001048
0.042	0.9819	0.01953	−0.000158	0.370	0.8911	0.03185	−0.001077
0.089	0.9687	0.02117	−0.000432	0.477	0.8676	0.03619	−0.001076
0.143	0.9539	0.02310	−0.000700	0.610	0.8436	0.04164	−0.000989
0.207	0.9352	0.02546	−0.000893	0.779	0.8180	0.04873	−0.000708
0.281	0.9139	0.02834	−0.001017	1.000	0.7893	0.05837	0

These results are plotted in Figure 12-2. The excess partial molar volumes are indicated by the arrows and may be obtained by the graphical method. For a more accurate determination, the experimental excess volume is fitted to a polynomial, and the excess partial molar volumes are obtained by application of eqs. (12.8) and ~~(12.8)~~. The fitted polynomial for V^{E} is

$$V^{\mathrm{E}} = c_4 x_1^4 + c_3 x_1^3 + c_2 x_1^2 + c_1,$$

12.9

with

$$c_1 = -6.19944 \times 10^{-3}, c_2 = 1.1561 \times 10^{-2}, c_3 = -8.6877 \times 10^{-3}, c_4 = 3.32617 \times 10^{-3}.$$

Using the fitted equation we find the following values at $x_1 = 0.4$:

eliminate superscript E

$$V^{\mathrm{E}} = -1.101 \times 10^{-3}\ \mathrm{m^3/mol},$$

$$\bar{V}^{\mathrm{E}}_E = -1.262 \times 10^{-3}\ \mathrm{m^3/mol},$$

$$\bar{V}^{\mathrm{E}}_W = -9.932 \times 10^{-4}\ \mathrm{m^3/mol}.$$

These correspond to the three points on the tangent line in Figure 12-2.

NOTE

Fitting Excess Properties–Redlich-Kister Expansion

All excess properties of binary solution must go to zero at $x_1 = 0$ and $x_1 = 1$. One equation that satisfies this condition is

solutions

$$f = x_1(1 - x_1)\left(c_0 + c_1 x_1 + c_2 x^2 + \cdots\right),$$

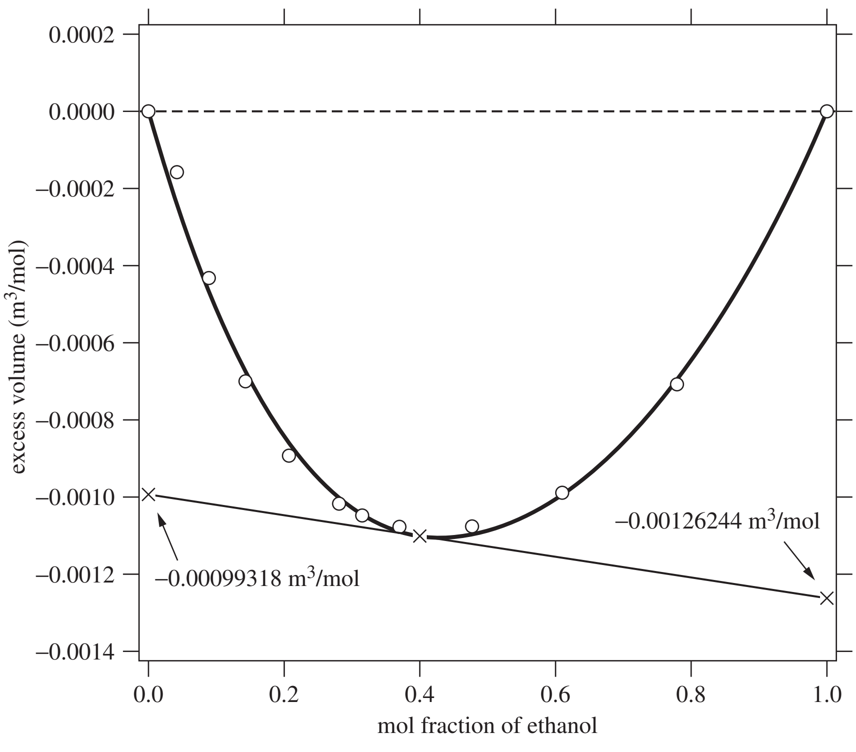

Figure 12-2: Excess volume of ethanol/water solutions at 20 °C (see Example 12.2).