

5.7.1 Application of Gibbs-Duhem: rationalization of ϕ/x -curves

We now use the Gibbs-Duhem equation to calculate relations between ϕ_1 and ϕ_2 of a binary mixture. For the total derivatives we find

$$d\varphi_1 = \left(\frac{\partial\varphi_1}{\partial n_1}\right) dn_1 + \left(\frac{\partial\varphi_1}{\partial n_2}\right) dn_2 \quad \text{and} \quad d\varphi_2 = \left(\frac{\partial\varphi_2}{\partial n_1}\right) dn_1 + \left(\frac{\partial\varphi_2}{\partial n_2}\right) dn_2 \quad (5.22)$$

Using $\sum_i n_i d\varphi_i = 0$ we get

$$\begin{aligned} & \left[\left(\frac{\partial\varphi_1}{\partial n_1}\right) dn_1 + \left(\frac{\partial\varphi_1}{\partial n_2}\right) dn_2 \right] n_1 + \left[\left(\frac{\partial\varphi_2}{\partial n_1}\right) dn_1 + \left(\frac{\partial\varphi_2}{\partial n_2}\right) dn_2 \right] n_2 = 0 \\ \Rightarrow & \left[n_1 \left(\frac{\partial\varphi_1}{\partial n_1}\right) + n_2 \left(\frac{\partial\varphi_2}{\partial n_1}\right) \right] dn_1 + \left[n_1 \left(\frac{\partial\varphi_1}{\partial n_2}\right) + n_2 \left(\frac{\partial\varphi_2}{\partial n_2}\right) \right] dn_2 = 0 \end{aligned} \quad (5.23)$$

which must be true for all dn_i , so both terms of the sum must be zero, i.e.

$$\begin{aligned} \Rightarrow & n_1 \left(\frac{\partial\varphi_1}{\partial n_1}\right) + n_2 \left(\frac{\partial\varphi_2}{\partial n_1}\right) = 0 \quad \text{and} \quad n_1 \left(\frac{\partial\varphi_1}{\partial n_2}\right) + n_2 \left(\frac{\partial\varphi_2}{\partial n_2}\right) = 0 \\ \Rightarrow & x_1 \left(\frac{\partial\varphi_1}{\partial n_1}\right) = -(1-x_1) \left(\frac{\partial\varphi_2}{\partial n_1}\right) \quad \text{and} \quad x_1 \left(\frac{\partial\varphi_1}{\partial n_2}\right) = -(1-x_1) \left(\frac{\partial\varphi_2}{\partial n_2}\right) \end{aligned} \quad (5.24)$$

This implies that the slopes of φ_1 and φ_2 have opposite signs. Choosing $x_1 = 0.5$ we see that the absolute values of the slopes are equal. This is shown in Fig. 5.3 for 50 at% of the partial molar volume for water and ethanol.