Department of Chemical and Process Engineering
Thermodynamics

Tutorial Sheet 9: Thermodynamics of mixtures

1. Consider a system of liquids A and B. At a given temperature and pressure, the molar volume of the mixture (cm^3/mol) varies with the mole fractions in the mixture by:

$$v = 100x_A + 80x_B + 5x_A x_B$$

(a) What are the molar volumes of the pure components A and B?

(b) Determine the expressions for the *partial molar volumes* of the two components.

Note that the partial molar volumes for components A and B are defined by:

$$\bar{v}_A = \left(\frac{\partial V}{\partial n_A}\right)_{P,T,n_B} \qquad \bar{v}_B = \left(\frac{\partial V}{\partial n_B}\right)_{P,T,n_A}$$

(c) Plot the variation of the molar volume of the mixture (v) and the two partial functions on a graph. Show that the two functions satisfy the Gibbs-Duhem equation for partial molar properties. As a hint to the solution, you should note that the total and molar volumes are related by:

$$V = v(n_A + n_B) \rightarrow V = v\, n_{total}$$

(d) What would the plot look like for an ideal mixture?

(e) For a particular batch process, 500 moles of component A are mixed with 500 moles of component B to provide a reactant mixture. Calculate the volume of the mixture (V) and the change in volume (ΔV_{mix}) caused by this mixing process.

2. Consider a system of two liquids, termed liquid A and liquid B. The densities at 20ºC and 1 atmosphere of the pure liquids are:

$$\rho_A = 700 \text{ kg/m}^3 \qquad \rho_B = 900 \text{ kg/m}^3$$

These liquids when mixed will form a single phase.

(a) What do you understand by an *ideal mixture* with respect to the volumes of the pure components?

(b) For an *ideal mixture*, write down the equation for the variation in the specific volume (v) of the mixture with mass fraction and the specific volume of the pure components.

(c) For an *ideal mixture*, derive an equation for the variation in mixture density (ρ) with mass fraction of the mixture. Show that the variation in density with mass fraction cannot be linear except where the densities of the pure-components are close.

(d) Assuming that the two liquids form an ideal mixture, calculate the density of a 50% by mass mixture of liquids A and B.

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1.

a) The molar volumes of the pure components A and B are given by substituting into the given expression, we know that for a pure component, the mole fraction of that component is one and that the sum of all mole fractions in the system must equal one. This means that the mole fractions of the other components must be zero giving;

$$\begin{aligned}
v &= 100x_A + 80x_B + 5x_A x_B \\
v_A^0 &= 100 \cdot 1 + \cancel{80 \cdot 0} + \cancel{5 \cdot 1 \cdot 0} \\
v_B^0 &= \cancel{100 \cdot 0} + 80 \cdot 1 + \cancel{5 \cdot 0 \cdot 1}
\end{aligned}$$

$$\boxed{v_A^0 = 100\ \frac{cm^3}{mol}\ ,\ v_B^0 = 80\ \frac{cm^3}{mol}}$$

b) We substitute $\frac{V}{n_A+n_B}$ in place of v in the given equation, as well as $x_i = \frac{n_i}{n_i+n_j}$. Then by multiplying through by the denominator of the left hand side, we obtain an expression for the total volume V. Partially differentiating this expression with respect to the number of moles of the different components yields relationships for the partial molar volumes $\bar{v}_A$ and $\bar{v}_B$ respectively.

$$\begin{aligned}
\frac{V}{n_A+n_B} &= \frac{100n_A}{n_A+n_B} + \frac{80n_B}{n_A+n_B} + \frac{5n_A n_B}{(n_A+n_B)^2} \\
V &= \frac{100n_A(n_A+n_B)}{n_A+n_B} + \frac{80n_B(n_A+n_B)}{n_A+n_B} + \frac{5n_A n_B(n_A+n_B)}{(n_A+n_B)^2} \\
V &= 100n_A + 80n_B + 5n_A n_B(n_A+n_B)^{-1} \\
\left(\frac{\partial V}{\partial n_A}\right)_{P,T,n_B} &= 100 + \frac{5n_B}{n_A+n_B} - \frac{5n_A n_B}{(n_A+n_B)^2} \\
\left(\frac{\partial V}{\partial n_B}\right)_{P,T,n_A} &= 80 + \frac{5n_A}{n_A+n_B} - \frac{5n_A n_B}{(n_A+n_B)^2}
\end{aligned}$$

$$\boxed{\bar{v}_A = 100 + \frac{5n_B^2}{(n_A+n_B)^2}}$$

$$\boxed{\bar{v}_B = 80 + \frac{5n_A^2}{(n_A+n_B)^2}}$$