Homework 5 Solution

Exercise 1. Enthalpy of a binary mixture

In a binary mixture, enthalpy $H(p, S, n_A, n_B)$ is a homogeneous function of degree n=1.

a. Write down the equivalence of $H(p, S, n_A, n_B)$ in terms of its variables as a homogeneous function of degree n=1 (using the extra variable λ).
b. Write the fundamental equation for the enthalpy and identify its partial derivatives.
c. Write the full expression of the partial molar enthalpy of component n_A.

a. Any extensive variable is a homogeneous function of degree 1 of other extensive variables of the system.

$$H(p, \lambda S, \lambda nA, \lambda nB) = \lambda H(p, S, nA, nB)$$

b.

$$dH = Vdp + TdS + \mu_A dn_A + \mu_B dn_B$$

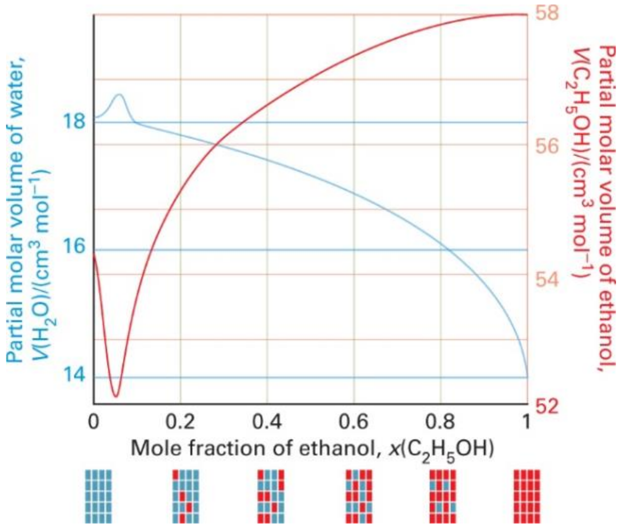
$$dH = \left(\frac{\partial H}{\partial p}\right)_{S,n_A,n_B} dp + \left(\frac{\partial H}{\partial S}\right)_{p,n_A,n_B} dS + \left(\frac{\partial H}{\partial n_A}\right)_{p,S,n_B} dn_A + \left(\frac{\partial H}{\partial n_B}\right)_{p,S,n_A} dn_B$$

c. Partial molar enthalpy of component A in a mixture at constant T and p:

$$\bar{H}_A = \left(\frac{\partial H}{\partial n_A}\right)_{\boldsymbol{p,T,n_B}}$$

Exercise 2. Partial molar volume of a salt-water mixture

Using the graph below, calculate the total volume of a mixture of 50 g of ethanol and 50 g of water at 25ºC and 1 atm. The molar masses of ethanol and water are 46.07 g mol-1 and 18.02 g mol-1 res.



First, we need to express the composition in terms of the mole fraction. The molar masses of CH2CH2OH and H20 are 46.07 g mol-1 and 18.02 g mol-1. Therefore the amounts present in the mixture are:

n eth=50/46.07=1.08 mol
n w=50/18.02=2.77 mol

For a total of 3.86 mol and hence

x eth=0.281 & x w=0.718

According to the figure at this composition: 56 and 18 so the total volume of the system is

V tot= 1.08x56 + 2.77x18 = 110cm-3

Exercise 3. Water-ethanol mixture

The difference between the volume of 1 mol of mixture of water and ethanol and the volume of its species taken separately at the same pressure and temperature (1atm, 20ºC), is given in terms of the mol fraction of ethanol, x_e, by the equation:

$$\frac{\Delta_{mix}V}{\sum n} = K_1x_e + K_2{x_e}^{3/2} + K_3{x_e}^2 + K_4{x_e}^{5/2} + K_5{x_e}^3$$

When volumes are expressed in cm^3, the coefficients are:

$$K_1 = 1.0, \quad K_2 = -52.0, \quad K_3 = 141.5, \quad K_4 = -141.0, \quad K_5 = 50.2$$

a. Calculate the molar volume of a solution at x_e=0.2
b. Provide a graphical representation of $\frac{\Delta_{mix}V}{\sum n}$ (you could do it in excel if you wish). Find the partial molar volumes of water and ethanol at x_e=0.2
c. Find the expressions for the partial molar volumes of water and ethanol and represent them graphical on the same plot as in question b.

Use $m_w = 18.0$ g, $m_e = 46.0$ g, $v_w = 18.0$ cm^3, and $v_e = 58.3$ cm^3

a. Using the given formula, it is possible to determine the difference of the volume of a mixed water-ethanol solution for $x_e = 0.2$:

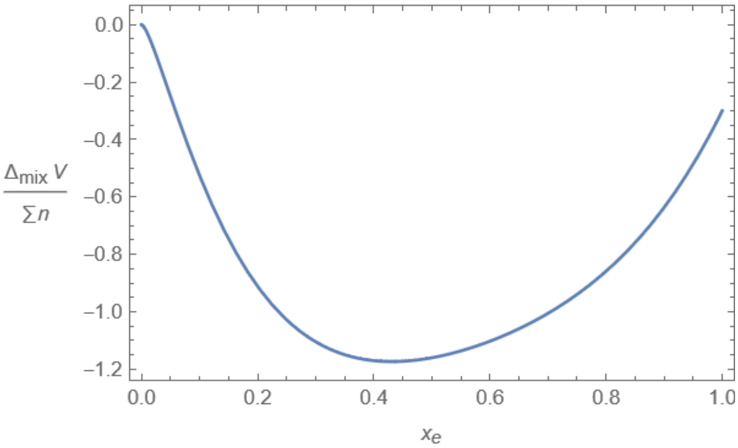
$$\Delta_{mix}V = \left(K_1x_e + K_2{x_e}^{\frac{3}{2}} + K_3{x_e}^2 + K_4{x_e}^{\frac{5}{2}} + K_5{x_e}^3\right) * \sum n = -0.912\ cm^3$$

It is then possible to determine the actual volume of the mixture, by determining the initial volume of both species taken separately and by adding the difference of the volume of a mixed water-ethanol solution. We remind here that, as we have a binary mixture, the mol fraction of water, knowing that $x_e = 0.2$, is $x_w + x_e = 1 \rightarrow x_w = 0.8$.

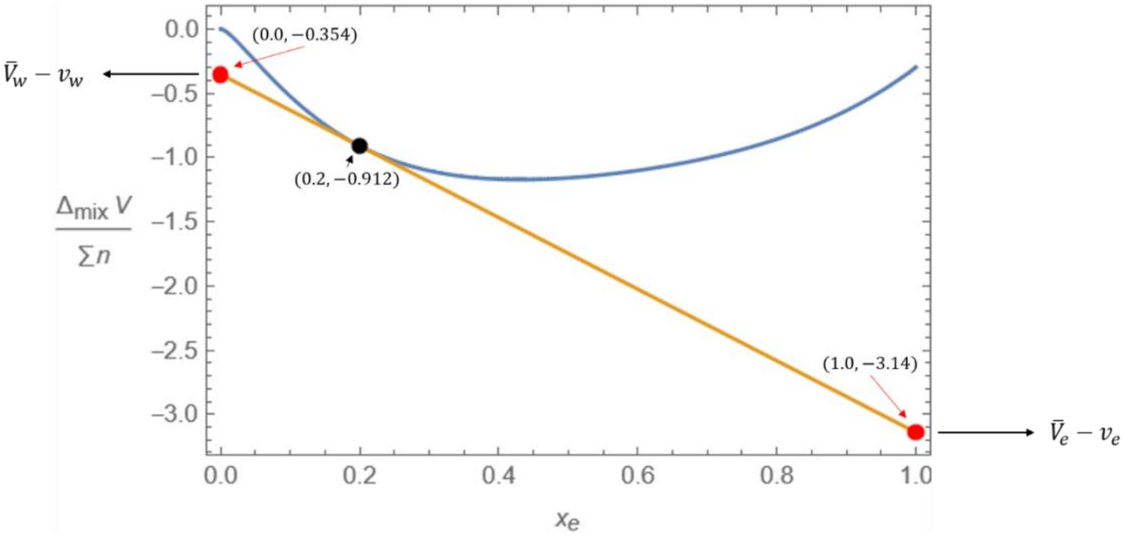
$$V_{mix} = V_{init} + \Delta_{mix}V = x_wv_w + x_ev_e + \Delta_{mix}V$$

$$= 0.8 \cdot 18.0 + 0.2 \cdot 58.3 - 0.912 = 25.15\ cm^3$$

b. A graphical representation of $\frac{\Delta_{mix}V}{\sum n}$ is presented below.



To determine the partial molar volumes of water and ethanol at $x_e = 0.2$, we need to trace the tangent to the $\Delta_{mix}V/\Sigma n$ curve at the point of the composition of interest (i.e $x_e = 0.2$, see black point on the graph below). The value of this tangent at $x_e = 0.0$ (red point on the left of the graph below) will give the difference between the partial molar volume of the water and the molar volume of the water ($\bar{V}_w - v_w$). Similarly, the value of the tangent at $x_e = 1.0$ (red point on the right of the graph below) will give the difference between the partial molar volume of the ethanol and the molar volume of the ethanol ($\bar{V}_e - v_e$).

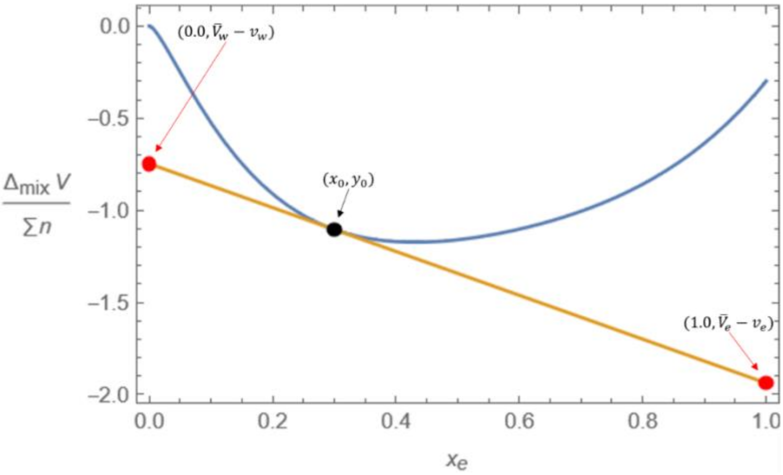


Therefore the partial molar volume at $x_e = 0.2$ are the following:

$$\bar{V}_w - v_w = -0.354\ cm^3 \rightarrow \bar{V}_w = -0.354 + 18.0 = 17.655\ cm^3$$

$$\bar{V}_e - v_e = -3.14\ cm^3 \rightarrow \bar{V}_e = -3.14 + 58.3 = 55.16\ cm^3$$

c. To determine the expressions for the partial molar volumes of water and ethanol, we want to repeat what we did in part b) but for an arbitrary concentration $x_e = x_0$. Thus, we want to define the tangent line to the curve $y = \Delta_{mix}V/\Sigma n$ at an arbitrary molar fraction (x_0, y_0).



The tangent line can be expressed by

$$y - y_0 = \left.\frac{dy}{dx_e}\right|_{x_e = x_0} (x_e - x_0) \rightarrow y = y_0 + \left.\frac{dy}{dx_e}\right|_{x_e = x_0} (x_e - x_0)$$

We remind here that

$$y_0 = K_1 x_0 + K_2 x_0^{\frac{3}{2}} + K_3 x_0^2 + K_4 x_0^{\frac{5}{2}} + K_5 x_0^3$$

and

$$\left.\frac{dy}{dx_e}\right|_{x_e = x_0} = K_1 + \frac{3}{2} x_0^{\frac{1}{2}} + 2K_3 x_0 + \frac{5}{2} K_4 x_0^{\frac{3}{2}} + 3K_5 x_0^2$$

To determine the difference between the partial molar volume of the water and the molar volume of the water $(\bar{V}_w - v_w)$, we need to determine the value of the tangent for $x_e = 0.0$. Thus, we have

$$\bar{V}_w - v_w = y_0 - \left.\frac{dy}{dx_e}\right|_{x_e = x_0} x_0$$

Therefore,

$$\bar{V}_w = v_w + y_0 - \left.\frac{dy}{dx_e}\right|_{x_e = x_0} x_0$$

$$\bar{V}_w = v_w - \frac{1}{2} K_2 x_0^{\frac{3}{2}} - K_3 x_0^2 - \frac{3}{2} K_4 x_0^{\frac{5}{2}} - 2K_5 x_0^3$$

$$\bar{V}_w = 18 + 26{x_0}^{3/2} - 141.5{x_0}^2 + 211.5{x_0}^{5/2} - 100.4{x_0}^3$$

Similarly, to determine the difference between the partial molar volume of the ethanol and the molar volume of the ethanol ($\bar{V}_e - v_e$), we need to determine the value of the tangent for $x_e = 1.0$. Thus, we have

$$\bar{V}_e - v_e = y_0 + \left.\frac{dy}{dx_e}\right|_{x_e=x_0} (1 - x_0)$$

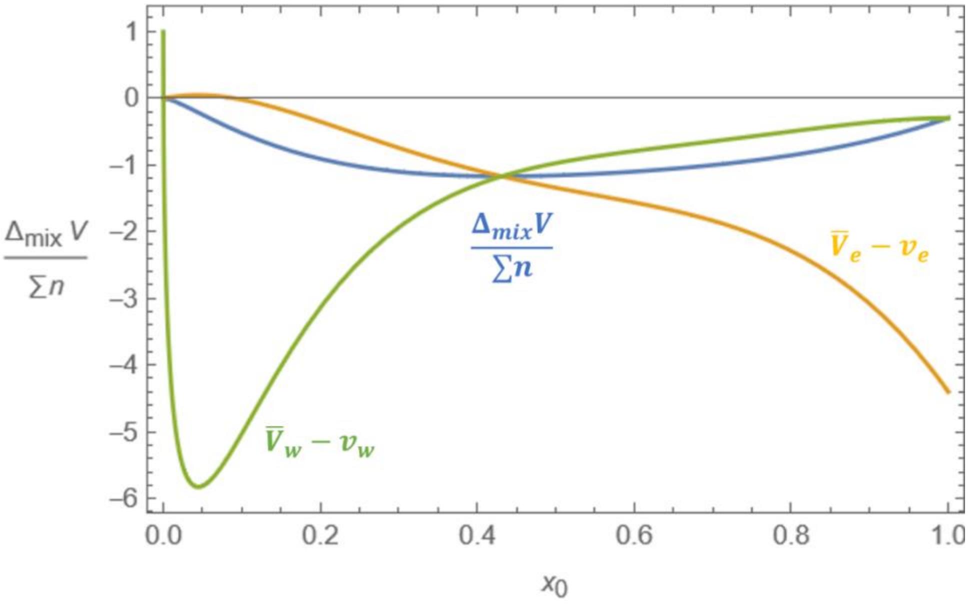
$$\bar{V}_e = v_e + y_0 + \left.\frac{dy}{dx_e}\right|_{x_e=x_0} (1 - x_0)$$

$$\bar{V}_e = v_e + K_1 + \frac{3}{2}K_2 x_0^{\frac{1}{2}} + 2K_3 x_0 + \left(\frac{5}{2}K_4 - \frac{1}{2}K_2\right) x_0^{\frac{3}{2}} + (3K_5 - K_3)x_0^2 - \frac{3}{2}K_4 x_0^{\frac{5}{2}} - 2K_5 x_0^3$$

$$\bar{V}_e = 58.3 + 1.0 - 78\sqrt{x_0} + 283x_0 - 326.5{x_0}^{3/2} + 9.1{x_0}^2 + 211.5{x_0}^{5/2} - 100.4{x_0}^3$$

In practice, it is probably more efficient to determine the functions $y_0, \left.\frac{dy}{dx_e}\right|_{x_e=x_0} x_0$ and $\left.\frac{dy}{dx_e}\right|_{x_e=x_0} (1 - x_0)$ directly with the informatic tool you are using (Excel, Python, Mathematica,…) and to plot $\bar{V}_w - v_w$ and $\bar{V}_e - v_e$ directly from them using the definition of the tangent mentioned above.

The partial molar volume of both water and ethanol are plotted below with the graphical representation of $\Delta_{mix}V/\Sigma n$ obtained in part b).



Exercise 4. Generalized Gibbs-Duhem equation

In this exercise, we are going to study a second method to compute the partial molar volume of a binary system at arbitrary concentrations using experimental data.

Consider a binary mixture of substances A = trichloromethane ($CHCl_3$) and B = propanone. The molar volume of the mixture at different concentrations (for 298K) are provided in the following table:

x ($CHCl_3$)	0	0.194	0.385	0.559	0.788	0.889	1.000
v (cm^3mol^{-1})	73.99	75.29	76.50	77.55	79.08	79.82	80.67
V (cm^3) (at constant n_B)							
n_A(mol)							

We now want to calculate the partial molar volumes $\bar{V}_A$, $\bar{V}_B$ and check that the values we get are consistent with the laws of thermodynamics.

a) We start by calculating $\bar{V}_A$. For this, we need the volume V and the number of moles of trichloromethane n_A at constant n_B. We can set $n_B = 1\text{mol}$. Try to express n_A as a function of the concentration $x_A = \frac{n_A}{n_A+n_B}$ and make a table of its values for the experimentally measured points (you can use the table above).

b) Derive a formula to calculate the volume V from either n_A or x_A and make a table of its values like for n_A.

c) Use the results of the previous exercises to graphically determine $\bar{V}_A$.

d) Repeat the same steps to calculate $\bar{V}_B$ from the same data. What is the partial molar volume of propanone in trichloromethane at $x = 0.5$?

e) Now, we want to make sure that our values are consistent with the laws of thermodynamics, because $\bar{V}_A$ and $\bar{V}_B$ are not independent! Write the generalized Gibbs–Duhem equation for the partial molar volume at constant pressure and temperature and show that $d\bar{V}_B = -\frac{n_A}{n_B} d\bar{V}_A$. Are the results obtained for the two partial molar volumes consistent with this equation?

f) Rewrite the above expression using the concentrations $x_A = \frac{n_A}{n_A+n_B}$ and $x_B = \frac{n_B}{n_A+n_B}$ instead. Show that the partial molar volume of the component B can be obtained if the partial molar volume of A is known for all compositions up to the one of interest by deriving this formula from part 1:

$$\overline{V_B} = v_B - \int_{v_A}^{\overline{V_A}} \frac{x_A}{1 - x_A} d\overline{V_A}$$

Is this expression consistent with the values of because $\bar{V}_A$ and $\bar{V}_B$ that we obtained?

Solution:

a) Using $n_B = 1\text{mol}$, we get

$$x_A = \frac{n_A}{n_A + 1} \quad \Rightarrow \quad n_A = \frac{x_A}{1 - x_A}$$

The obtained values are shown in the table below. Note that we have to exclude the point at $x_A = 1$ because that would mean that we have a pure trichloromethane (A) phase which is a contradiction to $n_B = 1\text{mol}$.

b) We can calculate the total volume either using n_A or x_A in the following way:

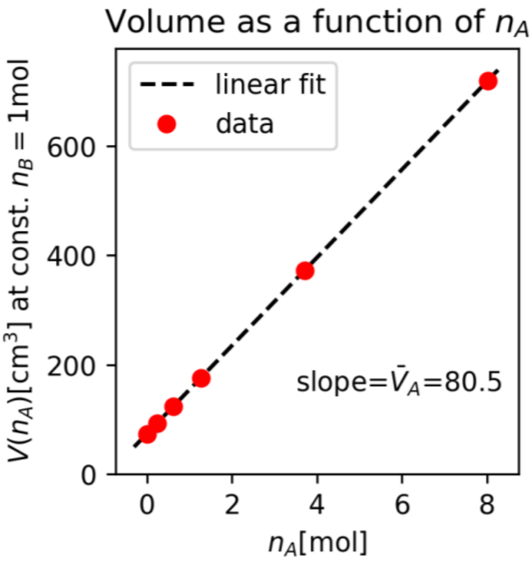
$$V = v * (n_A + 1) = v\left(\frac{x_A}{1 - x_A} + 1\right) = \frac{v}{1 - x_A}$$

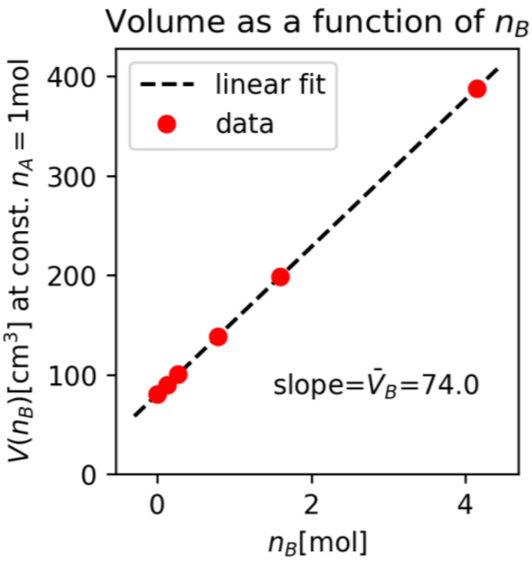
Again, the values obtained from the data are shown in the table.

x (CHCl3)	0	0.194	0.385	0.559	0.788	0.889	1.000
v (cm3mol−1)	73.99	75.29	76.50	77.55	79.08	79.82	80.67
V (cm3) (at constant n_B)	74.	93.4	124.4	175.9	373.	719.1	-
n_A(mol)	0.	0.24	0.63	1.27	3.72	8.01	-

c) We can now plot the volume V against n_A (at constant n_B). The slope of the data points is then the partial molar volume $\bar{V}_A = \left(\frac{\partial V}{\partial n_A}\right)_{n_B}$, see the figure below on the left.

We can see that the slope is almost constant. Thus, we can approximately say that the partial molar volume of A is independent of the concentration and takes the constant value $\bar{V}_A = 80.5\text{cm}^3/\text{mol}$ which is essentially the same as the molar volume of the pure substance at $x_A = 1$ shown in the original table.





d) Repeating the same steps with A and B reversed, we get the values of the volume V at constant n_A and n_B shown in the table below. Be careful not to forget that the variable x in the original table is actually x_A, so we need to use $x_B = 1 - x_A$instead. We can then use $n_B = \frac{x_B}{1-x_B}$ and $V = \frac{v}{1-x_B}$.

x (CHCl3) = x_A	0	0.194	0.385	0.559	0.788	0.889	1.000
$x_B = 1 - x_A$	1	0.806	0.615	0.441	0.212	0.111	0.
v (cm3mol−1)	73.99	75.29	76.50	77.55	79.08	79.82	80.67
V (cm3) (at constant n_A)	-	388.1	198.7	138.7	100.4	89.8	80.7
n_B(mol)	-	4.15	1.6	0.79	0.27	0.12	0.

By plotting V against n_B (at constant n_A), we again see that the slope is almost constant (see the figure above on the right). That slope is the partial molar volume $\bar{V}_B = 74.0\text{cm}^3/\text{mol}$ which is essentially the same as the molar volume of the pure substance at $x_A = 0$ shown in the original table.

e) For isothermal and isobaric conditions, dp=0 and dT=0. Therefore: $\sum_i n_i d\bar{X}_i = 0$ is the generalized Gibbs-Duhem relation which for the special case of a binary mixture of volume of A and B becomes: $n_A d\bar{V}_A + n_B d\bar{V}_B = 0$. Thus: $d\bar{V}_B = -\frac{n_A}{n_B} d\bar{V}_A$. This result is consistent with the partial molar volumes obtained in parts c) and d). Since both $\bar{V}_A$ and $\bar{V}_B$ are constant, plugging this into the above equation gives

$$d\bar{V}_B = 0 = -\frac{n_A}{n_B} \cdot 0 = -\frac{n_A}{n_B} d\bar{V}_A$$

which is a correct equation.

f) From $x_A = \frac{n_A}{n_A + n_B}$ as well as $x_B = \frac{n_B}{n_A + n_B}$ and using $x_A + x_B = 1$, we obtain:

$$d\bar{V}_B = -\frac{x_A}{1 - x_A} d\bar{V}_A$$

If one wants to know the partial molar volume $\bar{V}_B$ at the composition x_B, one can integrate from $x_B = 1$ to arbitrary x_B:

$$\int_{\bar{V}_B\ at\ x_B=1}^{\bar{V}_B\ at\ x_B=x_B} d\bar{V}_B = -\int_{\bar{V}_A\ at\ x_B=1}^{\bar{V}_A\ at\ x_B=x_B} \frac{x_A}{1 - x_A} d\bar{V}_A$$

$\bar{V}_B\ at\ x_B = 1$ is v_B. Therefore,

$$\bar{V}_B\big|_{at\ x_B=x_B} - v_B = -\int_{\bar{V}_A\ at\ x_B=1}^{\bar{V}_A\ at\ x_B=x_B} \frac{x_A}{1 - x_A} d\bar{V}_A$$

$$\bar{V}_B\big|_{at\ x_B=x_B} = v_B - \int_{\bar{V}_A\ at\ x_B=1}^{\bar{V}_A\ at\ x_B=x_B} \frac{x_A}{1 - x_A} d\bar{V}_A$$

$$\bar{V}_B\big|_{at\ x_B=x_B} = v_B - \int_{\bar{V}_A\ at\ x_A=0}^{\bar{V}_A\ at\ x_A=1-x_B} \frac{x_A}{1 - x_A} d\bar{V}_A$$

If the variation of $\bar{V}_A$ with x_A is known, then the integral on the right can be evaluated and hence a value found for $\bar{V}_B$. Since $\bar{V}_A = 80.5\ \mathrm{mol/cm^3}$ is constant with composition, the integral

$$\int_{\bar{V}_A\ at\ x_A=0}^{\bar{V}_A\ at\ x_A=0.5} \frac{x_A}{1 - x_A} d\bar{V}_A = 0$$

And thus $\bar{V}_B$ is constant as well. This is also consistent with the values derived for the partial molar volumes in parts c) and d).