Homework 4

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.

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

The partial molar volume of $MgCl_2$ in a dilute solution of water is -1.4 cm^3/mol. Calculate the volume change when 0.2 mol of the salt is added to a large amount of water. Comment on the reason behind this behavior.

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:

$$\frac{\Delta_{mix}V}{\sum n} = K_1 x_e + K_2 {x_e}^{3/2} + K_3 {x_e}^2 + K_4 {x_e}^{5/2} + K_5 {x_e}^3$$

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

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

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

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 ($cm^3 mol^{-1}$)	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 $n_B = 1$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?