ECHE 363 – Thermodynamics of Chemical Systems
Homework #8

100 points total. Complete the following problems and upload your solutions to the Canvas assignment dropbox by the due date/time.

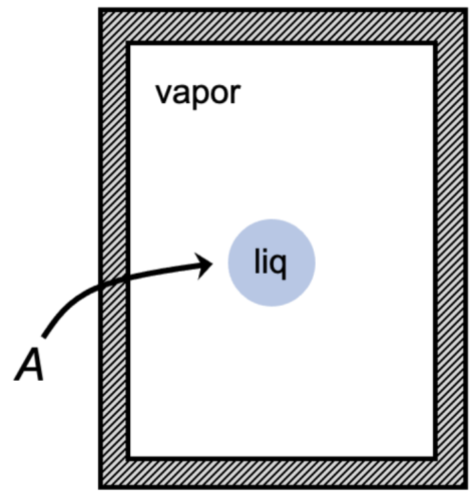
You are strongly encouraged to collaborate with your classmates on the homework, but each student is required to come up with a unique solution to the homework problems. For full credit, you must show all work. This includes showing all steps involving algebra and/or calculus. Your calculator can only be used for the final evaluation of numerical answers and may not be used for solving algebraic equations and/or integrals.

1. You need to find the enthalpy of sublimation of solid A at 300 K. The following equilibrium vapor pressure measurements have been made on pure A: (1) at 250 K, the pressure is 0.258 bar and (2) at 350 K, the pressure is 2.00 bar. The following heat capacity data are known:

$$c_{\mathrm{p,m}}^{\mathrm{sol}} = 40 \quad [\mathrm{J/mol\text{-}K}]$$
$$c_{\mathrm{p,m}}^{\mathrm{vap}} = 40 + 0.1T \quad [\mathrm{J/mol\text{-}K}]$$

   a) Calculate the enthalpy of sublimation, assuming $\Delta h_{\mathrm{m}}^{\mathrm{sub}}$ is constant.
   b) Calculate $\Delta h_{\mathrm{m}}^{\mathrm{sub}}$, now accounting for the temperature variation of $\Delta h_{\mathrm{m}}^{\mathrm{sub}}$.
   c) Estimate the error in the constant T assumption.

2. Consider a two-phase, vapor–liquid equilibrium. In this case, we will assume the liquid is a spherical droplet with volume V, surface area A, and radius, r. We have an isolated system (there is no gravity).



The vapor phase can be described as in class, but since the droplet has surface tension, there is an additional work term: $\delta W^{\mathrm{L}} = -P^{\mathrm{L}} dV^{\mathrm{L}} + \gamma dA^{\mathrm{L}}$ for a reversible process, where γ is the surface tension. Thus, $dU^{\mathrm{L}} = T^{\mathrm{L}} dS^{\mathrm{L}} - P^{\mathrm{L}} dV^{\mathrm{L}} + \mu^{\mathrm{L}} dn^{\mathrm{L}} + \gamma dA^{\mathrm{L}}$. This is the form of the Fundamental Equation for systems where surface tension is important (usually only for very small droplets). Note that A in this problem is the surface area of the droplet, <u>not</u> the Hemholtz free energy.

a) Given that $V = \frac{4}{3}\pi r^3$ and $A = 4\pi r^2$ for a sphere, find an equation $dA^{\mathrm{L}} = f(r) dV^{\mathrm{L}}$.

b) Using the equation developed in part (a), find $T^{\mathrm{L}} - T^{\mathrm{vap}}$, $P^{\mathrm{L}} - P^{\mathrm{vap}}$, and $\mu^{\mathrm{L}} - \mu^{\mathrm{vap}}$. What is different about the pressure term as compared to phase equilibria problems where surface tension is not included?

   Hint: Consider the following relationships at equilibrium: dS^{vap} and dS^{L}, dV^{vap} and dV^{L}, dn^{vap} and dn^{L}.

3. The molar enthalpy of a ternary mixture of species a, b, and c can be described by the following expression:
   a. $h_{\mathrm{m}} = -5000x_{\mathrm{a}} - 3000x_{\mathrm{b}} - 2200x_{\mathrm{c}} - 500x_{\mathrm{a}}x_{\mathrm{b}}x_{\mathrm{c}}$ [J/mol]
   b. Come up with an expression for $\overline{H}_{\mathrm{a}}$.
   c. Calculate $\overline{H}_{\mathrm{a}}$ for a solution with 1 mole a, 1 mole b, and 1 mole c.
   d. Calculate $\overline{H}_{\mathrm{a}}$ for a solution with 1 mole a but with no b or c present.
   e. Calculate $\overline{H}_{\mathrm{b}}$ for a solution with 1 mole b but with no a or c present.

4. The molar enthalpy of a binary liquid mixture of species 1 and 2 is given by:

$$h_{\mathrm{m}} = x_1\left(275 + 75T\right) + x_2\left(125 + 50T\right) + 750x_1x_2 \left[\frac{\mathrm{J}}{\mathrm{mol}}\right]$$

where T is the temperature in [K].

   a. What is the enthalpy of mixing, ΔH_{mix} in [J], of a mixture with 2 mol of 1 and 3 mol of 2 at 20°C?

   b. Consider the adiabatic mixing of a stream of pure 1 flowing at 2 mol/s with a stream of pure 2 flowing at 3 mol/s. Both inlet streams are at 20°C. What is the exit temperature of the mixture?

5. The partial molar volume of benzene (1) in cyclohexane (2) at 30℃ is given by the following equation:

$$\bar{V}_1 = 92.6 - 5.28x_1 + 2.64x_1^2 \ \ [\mathrm{cm^3/mol}]$$

Find an expression for the partial molar volume of cyclohexane. The density of cyclohexane at 30℃ is 0.769 g/cm^3.

6. Answer the following reflection questions (5 points):

   a. What about the way this class is taught is helping your learning?

   b. What about the way this class is taught is inhibiting your learning?