

Homework Assignment Number Two

Problem 1.

Consider the Peng-Robinson Equation of state as given below. The critical temperature and pressure of oxygen are also given below. Each root of this equation is a molar volume. Find all of the roots of the Peng-Robinson equation for oxygen at the temperatures given below and for a pressure of 1.0 atmosphere.

(a) $T = 98.0 \text{ K}$

(b) $T = 298.0 \text{ K}$

(For those of you who have not had thermodynamics, there can only be one phase above the critical temperature.)

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)}$$

where, $R = 8.314 \text{ J/mol/K}$, and $a(T) = 0.45724 \frac{R^2 T_c^2}{P_c} \alpha(T)$, $b = 0.07780 \frac{RT_c}{P_c}$,

$$\alpha(T) = \left[1 + \kappa \left(1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \text{ where, for the oxygen molecule } \kappa = 0.4069, T_c = 154.6 \text{ K, and}$$

$$P_c = 5.046 \cdot 10^6 \text{ Pa.}$$

Problem 2.

Consider the van der Waals equation of state.

$$p = \frac{RT}{V-b} - \frac{a}{V^2}$$

Vapor-liquid equilibrium (VLE) at a given temperature, T , occurs at a specific pressure, the vapor pressure, p_{vap} . Therefore, we can consider the vapor pressure our unknown. However, you can't calculate the vapor pressure without knowing the molar volumes of the vapor, V_{vap} , and liquid, V_{liq} , phases. Therefore, in a standard VLE problem, we have three unknowns: p_{vap} , V_{vap} and V_{liq} . These three variables require three equations. The first equation is the relationship between p_{vap} , V_{vap} or V_{liq} , given by the equation of state,

$$f_1(p_{\text{vap}}, V_{\text{vap}}, V_{\text{liq}}) = \frac{RT}{V_{\text{vap}} - b} - \frac{a}{V_{\text{vap}}^2} - p_{\text{vap}} = 0$$

The second equation is the thermodynamic constraint establishing mechanical equilibrium,

$$f_2(p_{\text{vap}}, V_{\text{vap}}, V_{\text{liq}}) = p_{\text{vap}} - p_{\text{liq}} = \left(\frac{RT}{V_{\text{vap}} - b} - \frac{a}{V_{\text{vap}}^2} \right) - \left(\frac{RT}{V_{\text{liq}} - b} - \frac{a}{V_{\text{liq}}^2} \right) = 0$$

The third equation is the thermodynamic constraint establishing chemical equilibrium,

$$f_3(p_{\text{vap}}, V_{\text{vap}}, V_{\text{liq}}) = \mu_{\text{vap}} - \mu_{\text{liq}} = 0$$

where the chemical potential for a van der Waals gas is given by

$$\mu = -RT \left[\ln \left(\frac{V-b}{\Lambda^3} \right) - \frac{b}{V-b} + \frac{2a}{VRT} \right]$$

This expression for the chemical potential of a van der Waals gas introduces a new constant, the thermal de Broglie wavelength, Λ , but we don't need it because it drops out when we equate chemical potentials.

$$\begin{aligned} \mu_{liq} - \mu_{vap} &= -RT \left[\ln \left(\frac{V_{liq} - b}{\Lambda^3} \right) - \frac{b}{V_{liq} - b} + \frac{2a}{V_{liq}RT} \right] + RT \left[\ln \left(\frac{V_{vap} - b}{\Lambda^3} \right) - \frac{b}{V_{vap} - b} + \frac{2a}{V_{vap}RT} \right] \\ &= -RT \left[\ln(V_{liq} - b) - \frac{b}{V_{liq} - b} + \frac{2a}{V_{liq}RT} \right] + RT \left[\ln(V_{vap} - b) - \frac{b}{V_{vap} - b} + \frac{2a}{V_{vap}RT} \right] \end{aligned}$$

If we so choose, we could solve the VLE problem by finding the roots to these three equations. This requires good guesses for all three unknown variables.

Here is a better alternative solution approach. Solving a system of three equations and three unknowns is much harder than solving a system of equations with one equation and one unknown. Therefore, a useful trick in this problem is to recognize that the van der Waal's equation of state is a cubic equation of state and the roots of a cubic equation of state are easily obtained using the Matlab "roots" function.

$$pV^3 - (pb + RT)V^2 + aV - ab = 0$$

Therefore, we can pose the solution of the VLE problem of the van der Waals fluid as a single equation with a single equation, in which we guess the vapor pressure, use the roots command to solve for the V_{vap} and V_{liq} , and substitute them into the equation stating that the chemical potentials are equal.

So, in order to solve this problem as a single nonlinear algebraic equation with a single variable, p_{vap} , we have an equation,

$$f(p_{vap}) = \mu_{liq} - \mu_{vap} = 0$$

where we solve for the molar volumes each iteration and then substitute their values into the function above.

Find the vapor pressure of Argon at $T=77$ K. The van der Waals constants for argon are $a=0.1381 \text{ m}^6/\text{mol}^2$ and $b=3.184 \times 10^{-5} \text{ m}^3/\text{mol}$. The gas constant is $R=8.314 \text{ J/mol/K}$. Also report the liquid and vapor molar volumes.

Problem 3.

Find the solution to the following system of nonlinear algebraic equations near (1,1,1).

$$f_1 = x_1 + 2x_2 + 3x_3 - 4$$

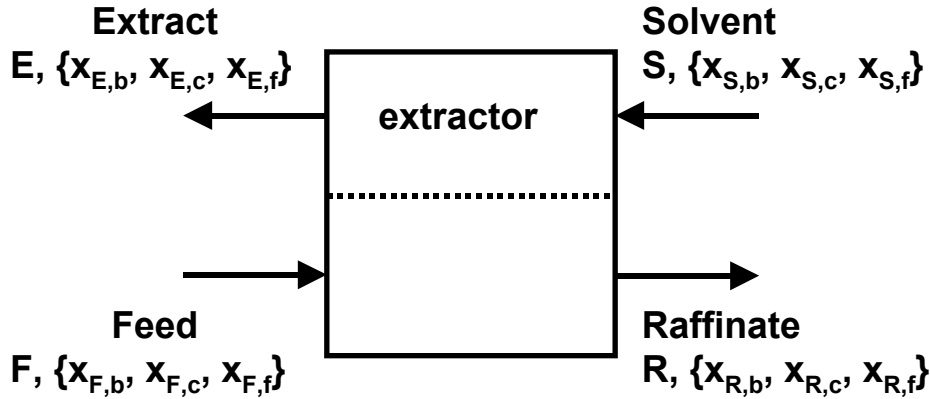
$$f_2 = x_1^3 - 4x_2^3$$

$$f_3 = x_3 - \sin x_3$$

Problem 4.

This problem requires steady state mass balances on a single-stage liquid-liquid extractor.

Consider an extractor:



In this system, a solvent stream, S, removes an impurity, b=benzene, from a feed stream, F. Exiting the extractor are two streams, the raffinate stream, R, which is the cleaned-up feed stream, and the extract stream, E, which now contains the impurity. This unit uses a recycled furfural stream as the solvent to extract benzene from a cyclohexane product stream. F, E, S and R are feed rates with units of moles per hour. The x variables are mole fractions. The mole fractions have two indices. The first uppercase letter indicates the stream and the second lowercase letter indicates the component. The data you are given is as follows.

$$\begin{array}{cccc}
 F = 100 \text{ mol/hr} & S = 150 \text{ mol/hr} & R = ? \text{ mol/hr} & E = ? \text{ mol/hr} \\
 x_{F,b} = 0.1 & x_{S,b} = 0.0010 & x_{R,b} = ? & x_{E,b} = ? \\
 x_{F,c} = 0.9 & x_{S,c} = 0.0001 & x_{R,c} = ? & x_{E,c} = ? \\
 x_{F,f} = 0.0 & x_{S,f} = 0.9989 & x_{R,f} = ? & x_{E,f} = ?
 \end{array}$$

The equilibrium constants are: $K_b = \frac{x_{E,b}}{x_{R,b}} = 25.0$, $K_c = \frac{x_{E,c}}{x_{R,c}} = 0.04$ and $K_f = \frac{x_{E,f}}{x_{R,f}} = 50.0$.

You have eight unknowns, the flowrates of the raffinate and extract and the compositions of the raffinate stream and the composition of the extract stream.

- (a) Write a set of eight independent algebraic equations describing this system.
- (b) Is the set of equations linear or non-linear?
- (c) Solve for the 8 unknowns. Clearly identify each variable.

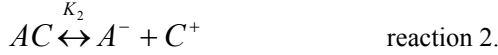
For those unfamiliar with liquid-liquid extractors, the relative steady state mass balance has the form

$$\text{traditional mole balance:} \quad \textit{accumulation} = \textit{in} - \textit{out} + \textit{generation} - \textit{consumption}$$

In this system, since it is at steady state, there is no accumulation term. There is no chemical reaction so the generation and consumption terms are zero. Each component has two inputs and two outputs. Furthermore, the sum of the mole fractions in each stream must be zero.

Problem 5.

Consider a system with two anions, A and B, and two cations, C and H. The following reactions are possible



There are a total of eight species: $AH, AC, BH, BC, A^-, B^-, H^+$ and C^+ . Potentially the composition of each of these eight species is unknown. In general, if we have eight unknowns, then we need eight equations to solve for a unique solution. Four of the equations come from thermodynamic equilibrium coefficients. Equilibrium coefficients govern the distribution of each of these reactions. Presumably the equilibrium coefficients are given.

$$K_1 = \frac{[A^-][H^+]}{[AH]} \quad \text{or} \quad [AH] = \frac{[A^-][H^+]}{K_1} \quad \text{equation 1.}$$

$$K_2 = \frac{[A^-][C^+]}{[AC]} \quad \text{or} \quad [AC] = \frac{[A^-][C^+]}{K_2} \quad \text{equation 2.}$$

$$K_3 = \frac{[B^-][H^+]}{[BH]} \quad \text{or} \quad [BH] = \frac{[B^-][H^+]}{K_3} \quad \text{equation 3.}$$

$$K_4 = \frac{[B^-][C^+]}{[BC]} \quad \text{or} \quad [BC] = \frac{[B^-][C^+]}{K_4} \quad \text{equation 4.}$$

Four more reactions come from molar balances on A, B, C and H .

$$[A_{Tot}] = [AH] + [AC] + [A^-] \quad \text{equation 5.}$$

$$[B_{Tot}] = [BH] + [BC] + [B^-] \quad \text{equation 6.}$$

$$[C_{Tot}] = [AC] + [BC] + [C^+] \quad \text{equation 7.}$$

$$[H_{Tot}] = [AH] + [BH] + [H^+] \quad \text{equation 8.}$$

Presumably the total amounts of each component added to the solution are given. Often the pH of the solution is given, which effectively provides the value of $[H^+]$, in which case we have one less unknown and equation 8 is redundant.

You could choose to solve this as 8 (or 7) equations with 8 (or 7) unknowns. Since the relationships in the equilibrium coefficients are so simple, one can alternatively eliminate some of the ions (AH, AC, BH and BC) from the molar balances. This leaves just four equations (the molar balances) (three if the pH is given) and four unknowns (A^-, B^-, C^+ and H^+), (three if the pH is given).

Assume the pH is given. Solve for the concentration of the other seven ions as a function of pH from 1 to 7 for the following parameter values. Both the equilibrium coefficients and the concentrations have units of $\frac{mol}{\ell}$.

$$K_1 = 10^{-1}, K_2 = 10^{-2}, K_3 = 10^{-3} \text{ and } K_4 = 10^{-4}, [A_{Tot}] = 1.0 \cdot 10^{-3}, [B_{Tot}] = 2.0 \cdot 10^{-5}, \text{ and } [C_{Tot}] = 0.5 \cdot 10^{-3}.$$