10.34 Numerical Methods Applied to Chemical Engineering Fall 2015

Homework #3: Systems of Nonlinear Equations and Optimization

Problem 1 (30 points)**.** A (homogeneous) azeotrope is a composition of a multicomponent mixture for which the vapor phase in equilibrium with a single liquid phase has the same composition as the liquid phase, i.e., for a C-component mixture:

$$\mathbf{y} = \mathbf{x}$$

where $\mathbf{y} \in \mathbb{R}^C$ and $\mathbf{x} \in \mathbb{R}^C$ are vectors of vapor and liquid phase mole fractions, respectively. Note that by this definition the pure component compositions are also azeotropes.

Mixtures of collections of components that can form azeotropes can be difficult to separate using distillation because the azeotropes can block separations that would be possible in an ideal mixture. The classical example of this is the water-ethanol azeotrope, which prevents pure ethanol being distilled from the results of a fermentation. When designing a separation process for a mixture of a collection of components that can form azeotropes, the first step is to identify all the azeotropes that can be formed, from which the blocked separations can then be determined and possibly circumvented by clever design.

This week's homework is about computing all the azeotropes occurring in mixtures of ethanol, methyl ethyl ketone and water at constant pressure $P = 1$ atm. Assuming a certain class of vapor-liquid equilibrium model, this amounts to finding all physically relevant solutions of the system of nonlinear equations:

$$\begin{aligned}
y_i &= x_i, \quad \forall i = 1, \ldots, C-1, \\
y_i &= \frac{\gamma_i(\mathbf{x}, T) P_i^{SAT}(T)}{P} x_i, \quad \forall i = 1, \ldots, C, \\
\sum_{i=1}^{C} x_i &= 1, \\
\sum_{i=1}^{C} y_i &= 1.
\end{aligned} \tag{VLE}$$

Note that this is a system of $2C + 1$ equations in the $2C + 1$ variables $(\mathbf{x}, \mathbf{y}, T)$ (i.e., at constant pressure there is a temperature associated with each azeotrope). For a solution to be physical it must also satisfy the inequalities:

$$\mathbf{x},\ \mathbf{y},\ T \geq \mathbf{0}.$$

Compute the activity coefficients $\gamma_i(\mathbf{x}, T)$ using the Wilson model:

$$\ln \gamma_i = 1 - \ln \left(\sum_j \Lambda_{ij} x_j \right) - \sum_j \frac{\Lambda_{ji} x_j}{\sum_k \Lambda_{jk} x_k},$$

$$\Lambda_{ij} = \frac{V_j^L}{V_i^L} \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT} \right).$$

Component	Molar Volume (mL/mol)	Interaction Energy Difference (cal/mol)		
i	V_i^L	$\lambda_{\mathrm{E}i} - \lambda_{\mathrm{EE}}$	$\lambda_{\mathrm{M}i} - \lambda_{\mathrm{MM}}$	$\lambda_{\mathrm{W}i} - \lambda_{\mathrm{WW}}$
E	56.68	0	-149.7978	926.2630
M	90.17	694.0825	0	1888.8509
W	18.07	393.1971	6811.3433	0

Table 1: Parameter values needed to compute binary parameters for the Wilson activity coefficient model.

Taking E, M and W as ethanol, methyl ethyl ketone and water, respectively, the necessary data are given in Table 1.

The pure component vapor pressures $P_i^{SAT}(T)$ should be calculated using the Antoine equation:

$$\log\left(\frac{P_i^{sat}}{\mathrm{torr}}\right) = A_i - \frac{B_i}{C_i + T(^o\mathrm{C})}, \tag{1}$$

with parameter values given in Table 2.

Component	Antoine Parameters		
i	A_i	B_i	C_i
E	8.11220	1592.864	226.184
M	7.06356	1261.339	221.969
W	8.07131	1730.630	233.426

Table 2: Antoine parameters for Equation (1).

1. Write functions `antoine_eq` and `wilson_activity` that calculate $P_i^{sat}(T)$ and $\gamma_i(\mathbf{x}, T)$, respectively, for all three components (E, M and W). The function `antoine_eq` takes T as an input and returns a vector of vapor pressure values that are calculated based on the Antoine's equation. Test that your `antoine_eq` function is working correctly by checking these values: at $T = 100^o$C, ${P_E}^{sat}$=1694 torr, ${P_M}^{sat}$=1400 torr, and ${P_W}^{sat}$=760 torr.

   Similarly, `wilson_activity` function takes a vector of compositions ($\mathbf{x}$) and a temperature value T as inputs and returns a vector of acitivty coefficients that are calculated based on the Wilson model. Test that your `wilson_activity` function are working correctly by checking these values: at $T = 70^o$C (343.15 K), $x_E = 0.25$, $x_M = 0.5$ and $x_W = 0.25$, $\gamma_E = 1.2428$, $\gamma_M = 1.3085$ and $\gamma_W = 2.7456$.

2. Use the equations $\mathbf{y} = \mathbf{x}$ to eliminate $\mathbf{y}$ and derive a system of $C + 1$ equations just in $(\mathbf{x}, T)$ of the form:

   $$\mathbf{f}(\mathbf{x}, T) = \mathbf{0}.$$

   Write a function called `function_evaluator_wilson` for your equations $\mathbf{f}(\mathbf{x}, T) = \mathbf{0}$. This is a function that takes as input a vector $\mathbf{z} = (\mathbf{x}, T)$ and returns a vector of the values of the functions $\mathbf{f}$ defining your system of equations at $\mathbf{z}$. Test that your function is functioning correctly by applying it to the pure component compositions.

3. Write a MATLAB$^{\text{È}}$script that uses the built-in routine `fsolve` to solve the equation $\mathbf{f}(\exp(\hat{\mathbf{x}}), \exp(\hat{T})) = 0$ for $\hat{\mathbf{x}}$ and $\hat{T}$, where the composition and temperature are defined in terms of the auxiliary "hat" variables as $\mathbf{x} = \exp(\hat{\mathbf{x}})$ and $T = \exp(\hat{T})$. This change of variables is recommended because it ensures that $\mathbf{x}$ and T are positive throughout the solution process. However, with

this change, some approximation of the pure component solutions is required. Why? Use your script to solve for the azeotropes in ethanol, methyl ethyl ketone and water mixtures at 1 atm by providing `fsolve` with a selection of different initial guesses. Report values for any numerical tolerances used. Prepare a table displaying information on the initial guesses used and the corresponding number of iterations and solutions found.

HINT: There should be a total of 7 azeotropes: 3 pure compoments, 3 binary mixtures, and 1 ternary mixture.

4. As an alternative to randomly selecting initial guesses, replace Equation (VLE) with the following physically-inspired homotopy

$$y_i = ((1-\lambda) + \lambda\gamma_i(\mathbf{x}, T))\,\frac{P_i^{SAT}(T)}{P}x_i, \quad \forall i = 1, \ldots, C,$$

where the vapor-liquid equilibrium model is Raoult's law when $\lambda = 0$ and the Wilson model when $\lambda = 1$. Implement in MATLAB a basic continuation method with this homotopy by copying and modifying the code you had previously written. Explain the steps you took to do this. Plot $T(^o\text{C})$ versus $0 \leq \lambda \leq 1$. for all three pure compoments to make sure that your code can track the solution branches corresponding to the three pure component compositions from $\lambda = 0$ to $\lambda = 1$.

5. Along the pure component branches, your homotopy method will encounter bifurcations signaled by a change in the sign of the determinant of the Jacobian of $\mathbf{f}(\mathbf{x}, T)$. In fact, it can be shown that any binary azeotropes occur on solution branches that bifurcate off the pure component branches at some $0 < \lambda < 1$. Similarly, any ternary azeotropes occur on solution branches that bifurcate off the binary azeotrope branches at some $0 < \lambda < 1$. Copy and then modify your homotopy method to detect these bifurcations. At (or just before) a bifurcation point, your code should pick up a new branch of the solution by perturbing your initial guesses in a direction indicated by vectors in (or near) the null space of the Jacobian. Use your code to locate systematically all azeotropes in ethanol, methyl ethyl ketone and water mixtures at 1 atm. Prepare a table with the composition and temperatures of all the azeotropes. Prepare a bifurcation diagram plotting the temperature of all solution branches versus $0 \leq \lambda \leq 1$.

Problem 2 (20 points)**.** In this problem you will optimize the design of a chemical reactor using MATLAB's built-in constrained optimization tools. We have a CSTR (continuous stirred tank reactor) which produces species C from reactants A and B using the following reaction network. Note that in this problem the reaction rate coefficients are given as functions of temperature.

$$\begin{aligned}
A + B &\rightarrow C + D & r_1 &= k_1(T)C_AC_B \\
C + B &\rightarrow S_1 + D & r_2 &= k_2(T)C_CC_B \\
A + D &\rightarrow S_2 & r_3 &= k_3(T)C_AC_D \\
A + B &\rightarrow S_3 & r_4 &= k_4(T)C_AC_B \\
C + B &\rightarrow S_4 & r_5 &= k_5(T)C_CC_B
\end{aligned}$$

We provide to the CSTR an input stream with a volumetric flow rate of $Q = 10$ L/s containing species A and B in a solvent. To provide better temperature control, the total concentration of A and B is kept minimal:

$$C_{A_{in}} + C_{B_{in}} = 0.1\frac{\text{mol}}{\text{L}}\ .$$

Rate data has been collected and an Arrhenius dependence of the rate on temperature can be assumed for all $k_j(T)$.

$$k_1(298K) = 0.01 \frac{\text{L}}{\text{mol} \cdot \text{s}} \qquad k_1(310K) = 0.02 \frac{\text{L}}{\text{mol} \cdot \text{s}}$$

$$k_2(T) = k_1(T)$$

$$k_3(298K) = 0.001 \frac{\text{L}}{\text{mol} \cdot \text{s}} \qquad k_3(310K) = 0.005 \frac{\text{L}}{\text{mol} \cdot \text{s}}$$

$$k_4(298K) = 0.001 \frac{\text{L}}{\text{mol} \cdot \text{s}} \qquad k_4(310K) = 0.005 \frac{\text{L}}{\text{mol} \cdot \text{s}}$$

$$k_5(T) = k_4(T)$$

We design the reactor to operate isothermally so as to maximize the concentration of our desired product C in the output stream. We have three design variables: the ratio of reactant inlet concentrations $\alpha \equiv C_{A_{in}}/C_{B_{in}}$, and the volume of the reactor which is restricted to the range $100 \leq V \leq 10,000$ L, and the operating temperature $298 \leq T \leq 335$ K.

1. Report the constants for all rate laws based upon the data provided.
2. Write a MATLAB function that computes the steady-state concentrations of A,B,C and D. Ensure your code returns stable steady state values. Describe how you calculate steady-state concentrations for this system and how you confirm such results are stable steady states.
3. Using your MATLAB function for the steady-state concentrations in the system utilize `fmincon` in MATLAB to optimize the design of the reactor to maximize the concentration of C. Describe the optimal design point, your objective function, and the implementation of the constraints in your report. Do you need to add additional constraints to keep the system physically meaningful? Use a value of 10^{-10} for the function and x value tolerances (see `optimoptions` for syntax).
4. We may choose to design to maximize the yield of C instead. In this case we have a different objective function. Report your objective function under this scenario and use `fmincon` in MATLAB to optimize the design of the reactor. Describe the optimal design point, and if it differs from the previous optimal design point describe how and why. If you needed to add any constraints describe them and why they were added.
5. Produce a contour plot indicating the position and objective value of each design point. Make your plots at constant T, with the objective on the z axis and α and V as the x and y axes.

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