Project
due Thursday March 29

Two different chemical phases are in equilibrium when they are at the same temperature and pressure and when the net flux of each molecule type between phases is zero. For each component (i.e. molecule type) i, this condition of "zero net flux" is reached when its chemical potential has the same value in each phase j. For an ideal solution in equilibrium with an ideal vapor, these conditions reduce to Raoult's Law:

$$x_i P_i^{\mathrm{sat}} = y_i P \tag{1}$$

One independent equation results from equation 1 for each component. P is the total pressure, x_i and y_i are the mole fractions of component i in the liquid and vapor phases, respectively, and P_i^{sat} is the temperature-dependent vapor pressure of component i. The vapor pressure can be measured experimentally, and data are often analyzed (curve fitting!) to obtain parameters for the Antoine equation:

$$\log_{10} P_i^{\mathrm{sat}} = A_i - \frac{B_i}{T + C_i} \tag{2}$$

Often temperature T is in degrees C, and parameters are available from sources such as textbooks by Felder and Rousseau and by Elliott and Lira.

This problem will deal with the numerics of a phase equilibrium problem. In particular, you will need to use **matrix methods** to solve **coupled nonlinear equations** numerically in order to determine the amounts and compositions of phases in equilibrium with each other.

Initially, 5 mol of a model liquid fuel are added to a container that contains no vapor. Next, a piston is used to increase the container volume, creating a vapor space, and the system is heated until the pressure reaches 3 atm. The liquid initially contains isopentane (40 mol%), iso-octane (50 mol%), and n-decane (10 mol%). Some of each compound evaporates in order to create 2 L of vapor space. Assume the vapor can be described by the ideal gas law. The final temperature required for solving the problem is not known.

1. Write the governing equations, being clear about unknown variables. If you have more unknowns than equations, find additional equations that relate your unknowns and the given information.
2. Move all the terms in your equations to one side, creating functions f_1, f_2, etc. that equal zero. What is the physical meaning of the root(s) of these equations?

Earlier in the semester we discussed the **Newton-Raphson** method for finding roots. For a function of one variable, $f(x)$, the Newton-Raphson formula is $x_{i+1} = -f(x_i)/f'(x_i) + x_i$. The term $f'(x_i)$ is the derivative of f evaluated at $x = x_i$. With a good initial guess x_0, repeated iterations can converge to the root, at which $f(x_n) = 0$.

For multiple non-linear equations that are solved simultaneously, the Newton-Raphson formula is

$$\mathbf{Z}\,\mathbf{x}_{i+1} = -\mathbf{f} + \mathbf{Z}\,\mathbf{x}_i \tag{3}$$

where $\mathbf{f} = \begin{pmatrix} f_1 \\ f_2 \\ \vdots \end{pmatrix}$ is the vector of functions, each evaluated at the current point $\mathbf{x}_i$. $\mathbf{x}$ is a vector of the unknown variables. $\mathbf{Z}$ is a matrix of partial derivatives, e.g.

$$\mathbf{Z} \equiv \begin{pmatrix} \frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} & \cdots \\ \frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2} & \\ \vdots & & \ddots \end{pmatrix} \tag{4}$$

$\mathbf{Z}$ contains derivatives of the functions f_1, f_2, etc. with respect to the variables x_1, x_2, etc. The dimensions of square matrix $\mathbf{Z}$ equal the number of unknowns and functions.

(c) Set up the matrix equations to be solved (e.g. equation 3) for the next estimate of the unknown variables, given a current estimate $\mathbf{x}_0$ and your functions $\mathbf{f}$ from part (a).

(d) Choose initial guesses for your unknowns. Justify this choice. Next evaluate the function $\mathbf{f}$, the matrix $\mathbf{Z}$, and the overall right-hand side of equation 3. Finally, solve for the new unknowns using LU decomposition. (Remember, you can calculate both L and U via Gaussian elimination.) Using a computer to calculate L and U is fine.

(e) Write a MATLAB program that can iterate your form of equation 3 (from parts b and c) to convergence in order to solve for the unknown moles and temperature that are consistent with the given information. How much of each compound is in the liquid and vapor after the final conditions are reached? What are the mole fractions in each phase? What are the values of each function f_i at these points?

Hints:

- It will be useful to formulate the mole fractions x_i and y_i using material balances, i.e.

  moles i remaining in liquid = (initial moles of i) - (moles i that evaporated)

- The mole fractions you calculate this way must be between 0 and 1.

Show your work (a computer printout is fine) of how you reach this solution. Also include a (typed) write-up that describes your choice of unknowns, your initial estimates, and the physical meaning of your final answers. Comment (using a graph) on the convergence of your functions to the final answer, i.e. how do the function values change with each iteration? You will also need to submit your Matlab program (hardcopy and by email).