Homework Assignment Number Eleven

This homework set requires solution of nonlinear algebraic equations. You are welcome to use a prewritten program available on the course website. It is also perfectly acceptable to write your own nonlinear algebraic equation solving routines.

Read these instructions carefully.

If you want to use the prewritten MATLAB nonlinear algebraic equation solver:

(1) Download from the website MATLAB routines page "eqns.zip".
(2) Create a directory in your personal space called something like che301/eqns.
(3) Unzip the file "eqns.zip" using WinZip. Extract all the files inside to the directory you have just created.
(4) Start MATLAB
(5) move to the directory you have created (e.g., `cd z:\keffer\che301\eqns`)
(6) Make sure that you extracted the files properly by looking at the directory contents (e.g., `dir`)
(7) type `help rootfinder` and `help syseqn` to view the instructions
(8) You are ready to begin.

Notes:

(a) For all these problems you can use the code, rootfinder.m if the problem has only one equation or syseqn.m if the problem has more than one equation.
(b) You can view rootfinder.m or syseqn.m using the *.m file editor in MATLAB.
(c) You do not need to alter rootfinder.m or syseqn.m but you should look at them.
(d) type `help rootfinder` for instructions on how to use rootfinder.m
(e) type `help syseqn` for instructions on how to use syseqn.m

Follow these steps to do the homework:

(1) Go to http://clausius.engr.utk.edu/che301/webhw/choose_action.html
and print out a version of the homework. This will require your student id and assign you a unique homework set.
(2) Work the homework problems as you usually would.
(3) When you are finished and you have the answers, submit them back to
http://clausius.engr.utk.edu/che301/webhw/choose_action.html

Notes:

(a) The numbers in your homework will be different than everyone else's homework.
(b) No work will be turned into class. All work must be turned into the webpage by the deadline.
(c) The grading scale for this assignment is 1 point for each correct answer and 0 points for each incorrect answer.
(d) If you experience technical difficulties with this site, please email the instructor.
(e) You can only submit your solutions once so make sure you have all the problems done before you submit your work. Warning: On Microsoft Internet Explorer, hitting the "enter" key is equivalent to hitting the "submit" button. So don't hit "enter" until you are done. On Netscape, this is not a problem.

All information below this point is background information for problems 6 & 7.

Chemical Equilibria Synopsis

Chemical engineering problems frequently give rise to single and systems of nonlinear algebraic equations. For example, determining the chemical equilibrium of a set of reactions results in a system of non-linear equations. If we put a mixture of gases or liquids in a batch reactor and wait an infinitely long time, all reactions will proceed to thermodynamic equilibrium. The composition and temperature of the final equilibrium depend upon the initial composition and temperature as well as on the nature of the species involved.

A. Isothermal case

For an isothermal, homogeneous, single-phase system with n_r reactions at a given temperature, we have n_r unknowns, (n_r extents of reaction, $\{X_i\}$). The composition of the exit stream, $\{x_{E,j}\}$ can be determined from the extents of the reaction, so we don't consider the compositions unknown variables. So we have n_r unknowns and we need n_r equations.

The n_r equations are i = 1 to n_r reaction equilibria constraints involving j =1 to n_c components:

$$f_i(\{X_i\},T) = 0 = Ka_i(T) - \prod_{j=1}^{nc} x_j^{\nu_{i,j}} P^{\nu_{i,j}} \quad \text{for i = 1 to } n_r$$

where $\nu_{i,j}$ is the stoichiometric coefficient of the jth component in the ith reaction.

If we guess the extent of reactions then we can solve for the extents of reactions, using a standard iterative solution technique. Then we can compute the mole fractions of the exit stream, $x_{E,j}$ for j = 1 to nc by:

$$x_{E,j} = \frac{\text{moles\_in}_j + \sum_{i=1}^{nr} \nu_{i,j} X_i}{\sum_{k=1}^{nc} \left(\text{moles\_in}_k + \sum_{i=1}^{nr} \nu_{i,k} X_i \right)}$$

Again, since the mole fractions are totally determined by the extent of the reaction, we don't need to consider these independent variables.

This problem is easy if someone gives us the equilibrium coefficients but, of course, no one is going to give us the equilibrium coefficients because we are engineers, all forlorn and alone, who have to calculate such things for ourselves. Fortunately, we know how to calculate equilibrium coefficients from physical chemistry.

The reactions equilibrium constants, $Ka_i(X,T)$, have the form

$$Ka_i(T) = Ka_i(T_{ref}) \cdot \exp\left(\int_{T_{ref}}^{T} \frac{\Delta H_{r,i}(T)}{RT^2} dT \right)$$

where the reaction equilibrium coefficint at the reference temperature can be determined by

$$Ka_i(T_{ref}) = \exp\left(-\frac{\Delta G_{r,i}(T_{ref})}{RT} \right)$$

and where the heat of reaction at any arbitrary temperature is given by

$$\Delta H_{r,i}(T) = \Delta H_{r,i}(T_{ref}) + \int_{T_{ref}}^{T} C_{p.i}(T)dT$$

and where the heat of reaction and free energy of reaction are calculable from only the heats and free energies of formation and the stoichiometry of the reactions.

$$\Delta H_{r,i}(T_{ref}) = \sum_{j=1}^{n_c} \nu_{i,j} H_{f,j}$$

$$\Delta G_{r,i}(T_{ref}) = \sum_{j=1}^{n_c} \nu_{i,j} G_{f,j}$$

The only physical data required to solve this system of equations includes: the free energy of formation for each component, $G_{f,j}$,and the enthalpy of formation for each component, $H_{f,j}$, at the reference temperature, which are widely available in a source like the CRC handbook of chemistry and physics.

We also need the heat capacities as a function of temperature, $C_{p,j}(T)$, for each component in order to obtain the heat of reaction at any arbitrary temperature. For this problem we assume:

$$C_{p,j}(T) = a_j + b_j T + c_j T^2 + d_j T^3$$

The free energy and heats of formation and the constants in the heat capacity function can be found in reference books. For these problems, I took the values from the appendices of "Chemical and Engineering Thermodynamics", 2nd Ed., Stanley I. Sandler, Wiley, 1989.

You can use the syseqn.m matlab file to solve for the extent of reactions. From the MATLAB Library on the website, download one of the sample syseqninput.m files which does a similar chemical equilibria problem. You can alter that one to suit your needs.

All these codes can be solved with the syseqn.m solver and the equations of syseqninput.m. The trick will be in exploring different combinations of initial conditions so as to be to locate the solution.

B. Adiabatic case

For an <u>adiabatic</u>, homogeneous, gas-phase system with n_r reactions, we have n_r +1 unknowns, (n_r extents of reaction, $\{X_i\}$, and the adiabatic temperature, T). The composition of the exit stream, $\{x_{E,j}\}$ can be determined from the extents of the reaction and again are not considered unknowns.

The working equations are i = 1 to n_r reaction equilibria constraints involving j =1 to n_c components:

$$f_i(\{X_i\}, T) = 0 = Ka_i(T) - \prod_{j=1}^{nc} x_j^{\nu_{i,j}} P^{\nu_{i,j}} \quad \text{for i = 1 to } n_r$$

where $\nu_{i,j}$ is the stoichiometric coefficient of the jth component in the ith reaction,

and one energy balance:

$$f_{n+1}(\{X_i\},T) = 0 = \text{energy}_{in} - \text{energy}_{out} + \text{energy}_{rxn}$$

The energy balance has the form:

$$f_{n+1}(\{X_i\},T) = 0 = \sum_{j=1}^{nc}\left(F \cdot x_{F,j}\int_{T_{ref}}^{T_{in}} C_{p,j}(T)dT\right) - \sum_{j=1}^{nc}\left(E \cdot x_{E,j}\int_{T_{ref}}^{T_{out}} C_{p,j}(T)dT\right) - \sum_{i=1}^{nr}\Delta H_r(T_{out})X_i$$

We already know all of the terms and functions in the energy balance from the isothermal case. So we can proceed to solve this system of highly nonlinear algebraic equations for the n_r +1 unknowns. Once we have these unknowns, we can obtain the mole fractions of the exit stream and we are done.

C. An example

Determine the extent of reaction and the adiabatic temperature for the reaction:

½ N_2 + 3/2 H_2 ←→ NH_3

at a pressure of P atmospheres when the system is run under adiabatic conditions.

Heats of formation (Kcal/mol)

```
%     nitrogen hydrogen ammonia
Hf = [0;       0;          -10.960];
```

Free energies of formation (Kcal/mol)

```
%     nitrogen hydrogen ammonia
Gf = [0.0;     0.0;        -3.903];
```

Heat capacity constants (a in first row , b in second row, c in third row, d in fourth row)

```
%           nitrogen hydrogen    ammonia
Cpcon =  [6.903      6.952       6.5846
            -0.03753 -0.04576    0.61251
            0.1930      0.09563        0.23663
            -0.6861     -0.2079        -1.5981];
```

Problem Specifications

initial moles of nitrogen = 0.5 mole
initial moles of hydrogen = 1.5 mole
initial temperature of nitrogen = 298.1 K
initial temperature of hydrogen = 298.1 K