# Homework Assignment Number Two Assigned: Thursday, September 9, 1999 Due: Thursday, September 23, 1999 BEGINNING OF CLASS.

(1) Find an application from your own experience or a classical problem in your own field of research that requires the use of a numerical method to solve for the root(s) of a single nonlinear algebraic equation. (This means I want polymer applications from the polymer scientists, mechanical engineering problems from the mechanical engineers, etc...

- (a) Describe the physical problem from which the equation arises.
- (b) Write the equation.
- (c) Solve for the root(s).
- (d) Explain the physical significance of the root(s).

(2) Equations of state are used to predict the phase behavior of liquids and gases. A pressure explicit equation of state gives the pressure, P, of a gas or liquid as a function of temperature, T, and molar volume, V. When fluid is at boiling point, T, for a given pressure, P, one can use the equation of state to obtain both the liquid molar volume and the vapor molar volume.

Historically, people have used cubic polynomials as equations of state. The Peng-Robinson equation of state is a cubic polynomial in molar volume.

 $P \cdot V^{3} + (bP - RT) \cdot V^{2} - (3b^{2}P + 2bRT - a) \cdot V + (b^{3}P + RTb^{2} - ab) = 0$ 

Since this equation is a cubic polynomial, it yields three roots. When the fluid is a region of T-P space where the liquid and vapor can coexist, the three roots are real. The largest molar volume is the vapor molar volume. The smallest molar volume is the liquid molar volume and the intermediate value is not physically meaningful. When the fluid is in a region of T-P space where only one phase can exist, the Peng-Robinson equation of state yields one real root (the molar volume) and two imaginary roots (without physical significance).

The Peng-Robinson equation of state is a pressure-explicit equation of state because it can also be written as

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

In either equation, we have the gas constant, R = 8.314 J/mol/K, and the Peng-Robinson

functions 
$$a(T) = 0.45724 \frac{R^2 T_c^2}{P_c} \alpha(T)$$
,  $b = 0.07780 \frac{RT_c}{P_c}$ ,  
 $\alpha(T) = \left[1 + \kappa \left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2$  where, for the oxygen molecule  $\kappa = 0.4069$ , the critical

temperature,  $T_c = 154.6$  K, and the critical pressure,  $P_c = 5.046 \cdot 10^6$  Pa. (The critical temperature is the temperature above which there can be only vapor.)

(a) Find all the real roots at T = 298 K and P = 101325 Pa. This temperature is above the critical temperature.

(b) Find all the real roots at T = 98 K and P = 101325 Pa. This temperature is below the critical temperature.

# HINTS for problem (2):

(To find the root that corresponds to the molar volume of the vapor phase: my suggestion is to use the molar volume from the ideal gas law PV = RT as an initial guess.)

(To find the root that corresponds to the molar volume of the liquid phase, my suggestion is to use something perhaps ten percent larger than b, the minimum molar volume.)

(To find the root between them, use an intermediate value.)

Make sure that the tolerance of your program is set high so that your convergence criteria is tight enough to find the molar volume to 2 or 3 significant figures.

### Solution:

I used the rootfinder.m MATLAB code (as it appears on the website) to find the solutions.

```
(a) Find all the real roots at T = 298 K and P = 101325 Pa
rootfinder(0.02,0.0001,0.03)
ans = 0.0244
(b) Find all the real roots at T = 98 K and P = 101325 Pa.
rootfinder(0.0002,0.00001,0.01)
ans = 2.584e-005
rootfinder(0.0002,0.00001,0.01)
ans = 1.5351e-004
rootfinder(0.008,0.00001,0.01)
ans = 0.0078
```

### Problem 3.

Consider a batch reactor (no flow in and no flow out) run at isothermal (constant temperature) conditions with the following reactions:

```
\begin{array}{l} A \leftrightarrow 2B + C \\ A + C \leftrightarrow D \\ 2B \leftrightarrow D + A \end{array}
```

The rates of reaction are:

$$\begin{aligned} & k_1 = 0.0001 \frac{1}{s}, \ k_{-1} = 0.1 \frac{\ell^2}{s \cdot \text{mol}^2}, \ k_2 = 0.1 \frac{\ell}{s \cdot \text{mol}}, \ k_{-2} = 0.002 \frac{1}{s}, \ k_3 = 0.5 \frac{\ell}{s \cdot \text{mol}}, \\ & k_{-3} = 0.7 \frac{\ell}{s \cdot \text{mol}} \end{aligned}$$

The steady-state molar balances are:

accumulation = in - out + generation - consumption

So that, for example, we have for component A

$$\frac{dA}{dt} = 0 = 0 - 0 + k_{-1}B^2C + k_{-2}D + k_3B^2 - k_1A - k_2AC - k_{-3}AD$$

- (a) Write out the other three molar balances.
- (b) Only 3 of the 4 molar balances are linearly independent. Show this.
- (c) As your fourth equation, use the fact that mole fraction must sum to unity.

$$\mathbf{A} + \mathbf{B} + \mathbf{C} + \mathbf{D} = 1$$

Find the steady state composition of the batch reactor.

(d) Check that your answer to (c) is legitimate by using more than one initial guess to converge to the same solution.

# **Solution:**

$$\frac{dA}{dt} = 0 = 0 - 0 + k_{-1}B^{2}C + k_{-2}D + k_{3}B^{2} - k_{1}A - k_{2}AC - k_{-3}AD$$

$$\frac{dB}{dt} = 0 = 2(k_{1}A - k_{-1}B^{2}C - k_{3}B^{2} + k_{-3}AD)$$

$$\frac{dC}{dt} = 0 = k_{1}A - k_{-1}B^{2}C - k_{2}AC + k_{-2}D$$

$$\frac{dD}{dt} = 0 = k_{2}AC - k_{-2}D + k_{3}B^{2} - k_{-3}AD$$

(b) Show that these equations are linearly dependent.

Write these in matrix form as:

$$\frac{d}{dt}\begin{bmatrix} A\\ B\\ C\\ D\end{bmatrix} = \begin{bmatrix} -k_1 & k_{-1} & -k_2 & k_{-2} & k_3 & -k_{-3}\\ 2k_1 & -2k_{-1} & 0 & 0 & -2k_3 & 2k_{-3}\\ k_1 & -k_{-1} & -k_2 & k_{-2} & k_3 & -k_{-3}\\ 0 & 0 & k_2 & -k_{-2} & 0 & 0 \end{bmatrix} \begin{bmatrix} A\\ B^2C\\ AC\\ D\\ B^2\\ AD \end{bmatrix}$$

The rank of this matrix is three. Therefore only 3 equations are independent.

$$\frac{dD}{dt} = -2\frac{dA}{dt} - \frac{3}{2}\frac{dB}{dt} + \frac{dC}{dt}$$

(c) Using syseqn.m (as available on the Web) with syseqninput.m using:

```
function [f] = syseqninput(x0)
°
% batch reactor with 3 reactions
%
% A <--> 2B + C
% A + C <--> D
%
  2B <--> D + A
a = x0(1);
b = x0(2);
c = x0(3);
d = x0(4);
%
  rate constants (p=forward, n=backward)
°
2
kp1=0.0001;
kn1=0.1;
kp2=0.1;
kn2=0.002;
kp3=0.5;
kn3=0.7;
°
% molar balances
%
f(1) = -kp1*a + kn1*b^2*c - kp2*a*c + kn2*d + kp3*b^2 - kn3*a*d;
f(2) = kp1*a - kn1*b^2*c
                                            - kp3*b^2 + kn3*a*d;
f(3) = kp1*a - kn1*b^2*c - kp2*a*c + kn2*d + kp3*b^2 - kn3*a*d;
f(4) = a + b + c + d - 1;
```

» syseqn([0.25,0.25,0.25,0.25])
VARIABLE INPUT OUTPUT

2.5000000e-001 5.3489731e-001
2.5000000e-001 3.2171945e-001
3.2.5000000e-001 5.1679199e-003
4.2.5000000e-001 1.3821532e-001

So that the steady state concentrations are:

[A]		0.5349
В		0.3127
С	_	0.0052
D		0.1382

(d) Check that your answer to (c) is legitimate by using more than one initial guess to converge to the same solution.

There appear to be at least two solutions to this system of nonlinear algebraic equations.

	solution	initial guesses
root #1 (initial guesses with large A or B lead to this root)	$\begin{bmatrix} A \\ B \\ C \\ D \end{bmatrix} = \begin{bmatrix} 0.5349 \\ 0.3127 \\ 0.0052 \\ 0.1382 \end{bmatrix}$	$\begin{bmatrix} 0.25, 0.25, 0.25, 0.25 \end{bmatrix}$ $\begin{bmatrix} 0.4, 0.3, 0.2, 0.1 \end{bmatrix}$ $\begin{bmatrix} 0.1, 0.7, 0.1, 0.1 \end{bmatrix}$ $\begin{bmatrix} 0.7, 0.1, 0.1, 0.1 \end{bmatrix}$
root #2 (initial guesses with large C or D lead to this root)	$\begin{bmatrix} A \\ B \\ C \\ D \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix}$	$\begin{bmatrix} 0.1, 0.1, 0.7, 0.1 \\ [0.1, 0.2, 0.3, 0.4 ] \\ [0.1, 0.1, 0.1, 0.7 ] \\ [0.2, 0.2, 0.2, 0.4 ] \\ [0.3, 0.1, 0.1, 0.5 ] \end{bmatrix}$

#### Problem 4-5.

Determining the chemical equilibrium of a set of reactions results in a system of non-linear equations. 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). For an <u>isothermal</u>, 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,  $\{x_{E,i}\}$  can be determined from the extents of the reaction.

The working equations are i = 1 to  $\mathbf{n}_{r}$  reaction equilibria constraints involving j = 1 to  $\mathbf{n}_{c}$  components:

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

where  $V_{i,j}$  is the stoichiometric coefficient of the jth component in the ith reaction, and (for the adiabatic case) one energy balance:

$$f_{n+1}({X_i}, T) = 0 = energy_{in} - energy_{out} + energy_{rxn}$$

If we guess the extent of reactions and (for the adiabatic case) the temperature, then we can solve for the extents of reactions and for the temperature. Then we can compute the mole fractions of the exit stream,  $X_{E,j}$  for j = 1 to nc by:

$$x_{E,j} = \frac{\text{moles}_{i=1} \text{in}_{j} + \sum_{i=1}^{nr} \nu_{i,j} X_{i}}{\sum_{k=1}^{nc} \left(\text{moles}_{i=1} \text{in}_{k} + \sum_{i=1}^{nr} \nu_{i,k} X_{i}\right)}$$

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

The energy balance has the form:

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

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

$$\mathsf{Ka}_{\mathsf{i}}(\mathsf{T}) = \mathsf{Ka}_{\mathsf{i}}(\mathsf{T}_{\mathsf{ref}}) \cdot \exp\!\left(\int_{\mathsf{T}_{\mathsf{ref}}}^{\mathsf{T}} \frac{\Delta\mathsf{H}_{\mathsf{r},\mathsf{i}}(\mathsf{T})}{\mathsf{R}\mathsf{T}^2} \mathsf{d}\mathsf{T}\right)$$

where

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

and where

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

and where

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

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", 2<sup>nd</sup> Ed., Stanley I. Sandler, Wiley, 1989.

You can use the syseqn.m matlab file to solve for the extent of reactions and for the adiabatic temperature.

From the MATLAB Library on the website, download one of the sample syseqninput.m files which sets up the system of equations for Problem 1 below. You will be required to change the syseqninput.m for the various problems given below.

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.

### Problem 4.

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

 $\frac{1}{2}$  N<sub>2</sub> + 3/2 H<sub>2</sub>  $\leftarrow \rightarrow$  NH<sub>3</sub>

at a pressure of 1 atmosphere when the system is run under adiabatic conditions. After the extent of reaction is found, determine the composition of the exit stream.

A. Physical constants:

```
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];

**B.** Problem Specifications

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

### Solution:

Using syseqn.m (as available on the Web) with syseqninput.m containing the chemical equilibria example on the webpage (syseqninput\_chemeq\_nh3.m).

First we need to get a reasonable initial guess. We have two unknowns: the extent of reaction and the adiabatic temperature. The extent of reaction is bounded between 0 moles and 1 mole, so we choose an initial value of 0.5 moles. The adiabatic temperature is unknown, so we guess 500 K.

```
» syseqn(3,[0.5,500])
Attempting solution with modified multivariate Newton-Raphson Method
xE = 1.666667e-001 5.000000e-001 3.333333e-001
xE = 1.688742e-001 5.066225e-001 3.245033e-001
...
xE = 2.214652e-001 6.643956e-001 1.141393e-001
xE = 2.214652e-001 6.643956e-001 1.141393e-001
VARIABLE INPUT OUTPUT
1 5.0000000e-001 2.0489227e-001
2 5.0000000e+002 4.8556955e+002
```

The extent of reaction is 0.205 moles, the temperature is 486 K, the composition of the exit stream is 0.221  $N_2$ , 0.664  $H_2$ , and 0.114  $NH_3$ .

### Problem 5.

Consider the steam-carbon system of reactions:

 $C_{(s)} + 2H_2O \leftrightarrow O_2 + 2H_2$   $C_{(s)} + H_2O \leftrightarrow O + H_2$  $C_{(s)} + 2H_2 \leftrightarrow O + H_2$ 

at a pressure of 1 atmosphere when the system is run under isothermal conditions where T = 900K. Because the solid carbon is not in the gas phase, we can ignore it completely. (A component in the solid phase which does not have any presence in the gas phase, does not affect the gas-phase equilibria. Also, we assume negligible heat capacity for the solid carbon.)

A. Physical constants:

Heats of formation (Kcal/mol) CH4 CO CO2 Н2О Н2 Hf = [-17.889; -26.416; -94.052; -57.7979; 0.0]; Free energies of formation (Kcal/mol) CO2 Н2 CH4 CO H20 Gf = [-12.140; -32.808; -94.260; -54.6351; 0.0]; Heat capacity constants (a in first row, b in second row, c in third row, d in fourth row) CH4 CO CO2 H20 H2

Cpcon	= [4.750	6.726	5.316 7	7.700 6	.952	
	1.200	0.04001	1.4285	0.04	594 -0.	.04576
	0.3030	0.1283	-0.8	362 0	.2521	0.09563
	-2.630	-0.5307	1.784	-0.8587	-0.207	79];

**B.** Problem Specifications

inlet moles of steam = 1.0 mole inlet temperature of steam = 900 K

(a) Determine the extent of reaction at 900 K. Determine the exit stream compositions.

(b) Repeat problem part (a) where the inlet temperature of steam = 1000K and the reactor is adiabatic with pressure = 1 atm. In addition to the extent of reaction and the composition of the exit stream, also find the adiabatic temperature of the reactor.

(NOTE: A sample syseqninput.m file, syseqninput\_chemeq\_NH3.m, is given on the website in the AE505.zip package of MATLAB subroutines. You can copy this file to syseqninput.m to use as the input file for syseqn.m).

#### Solution:

Using syseqn.m (as available on the Web) with a modified version of the syseqninput.m containing the chemical equilibria example on the webpage (syseqninput\_chemeq\_nh3.m).

The modifications included changing:

```
nr = 3;
nc = 5;
ng = 5;
adiabatic = 0;
Tiso = 900;
and the stoichiometric matrix, the Hf, Gf, and Cp matrices.
```

(a) Determine the extent of reaction at 900 K. Determine the exit stream compositions.

First we must pick some decent initial guesses. We have three reactions, so we need three initial guesses. Since we initially have one mole of steam, and we know that rxn 1 consumes 2 moles of steam and rxn 2 consumes 1 mole of steam, the extents of reaction for rxns 1 and 2 are bounded by:

0 < x(1) < 0.5

0 < x(2) < 1.0

but since both are using the same steam,

0 < 2x(1) + x(2) < 1.0

For the third reaction we are using hydrogen generated from reactions 1 and 2. We know that the amount of hydrogen we use in reaction 3 must be less than the amount produced in 1 and 2 so: 0 < 2x(3) < 2x(1) + x(2) or 0 < x(3) < x(1) + 0.5\*x(2)

So, as a first initial guess we can pick x(1) in the middle of its range.

If we pick x(2) in the middle of its range, 0 < x(2) < 1.0 - 2x(1), then  $x(2) = 0.5^*(1.0 - 2^*x(1)) = 0.25$ If we pick x(3) in the middle of its range,  $0 < x(3) < x(1) + 0.5^*x(2)$ , then  $x(3) = 0.5^*(x(1) + 0.5^*x(2)) = 0.1875$ This is a consistent set of initial conditions.

First initial guess: » syseqn(1,[0.25,0.25,0.1875]) Attempting solution with MATLABs fsolve function xE = 1.428571e-001 1.904762e-001 1.904762e-001 1.904762e-001 2.857143e-001 xE = 1.428571e-0011.904762e-001 1.904763e-001 1.904760e-001 2.857144e-001 xE = 1.428571e-0011.904763e-001 1.904762e-001 1.904761e-001 2.857144e-001 xE = 3.912812e-001 -6.627762e-001 1.106129e+000 -6.015531e-001 7.669192e-001 xE = 3.912812e-001 - 6.627762e-0011.106129e+000 -6.015531e-001 7.669192e-001 FINAL MOLE FRACTIONS: CH4 CO CO<sub>2</sub> H<sub>2</sub>O H2 1.106129e+000 -6.015531e-001 7.669192e-001 xE = 3.912812e-001 - 6.627763e-001VARIABLE INPUT OUTPUT 1 2.500000e-001 1.1668906e+000 2 2.500000e-001 -6.9918377e-001 3 1.8750000e-001 4.1277500e-001

We have found a root to the system of equations. However, we see that it yields negative mole fractions, so the root, while a legitimate mathematical root, is not a physically reasonable root. So, we need to pick a different set of initial conditions.

Second initial guess:

Examining the solution above, we see that we have negative amounts of CO and H20. Therefore, we need to start with initial conditions that give more CO and H2O. Namely, increase x(2) and decrease x(1). So, if we pick a lower x(1), x(1) = 0.20Using 0 < x(2) < 1.0 - 2x(1), if we again pick x(2) in the middle of its range, x(2) = 0.3Using 0 < x(3) < x(1) + 0.5\*x(2), we pick x(3) in the middle of its range, x(3) = 0.175This is a consistent set of initial conditions.

» syseqn(1,[0.20,0.30,0.25]) Attempting solution with MATLABs fsolve function xE = 1.320755e-001 2.264151e-001 1.509434e-001 2.264151e-001 2.641509e-001

FINAL MOLE FRACTIONS:

 CH4
 CO
 CO2
 H2O
 H2

 xE = 3.912812e-001
 -6.627763e-001
 1.106129e+000
 -6.015531e-001
 7.669192e-001

 VARIABLE
 INPUT
 OUTPUT
 1
 2.0000000e-001
 1.1668906e+000
 2
 3.0000000e-001
 -6.9918377e-001
 3
 1.7500000e-001
 4.1277500e-001

We have found the same unphysical root to the system of equations. So, we need to pick a different set of initial conditions.

Third initial guess:

Now we are just searching for a good guess in three dimensional space. We still have negative values of CO and H2O so let's decrease x(1) even more.

So, if we pick a lower x(1), x(1) = 0.10

Using 0 < x(2) < 1.0 - 2x(1), if we again pick x(2) in the middle of its range, x(2) = 0.4Using 0 < x(3) < x(1) + 0.5\*x(2), we pick x(3) in the middle of its range, x(3) = 0.15This is a consistent set of initial conditions.

Third initial guess. » syseqn(1,[0.15,0.4,0.15]) xE = 1.111111e-001 2.962963e-001 7.407407e-002 2.962963e-001 2.222222e-001 ... FINAL MOLE FRACTIONS: CH4 CO CO<sub>2</sub> H2O H2 xE = 3.912812e-001 -6.627763e-001 1.106129e+000 -6.015531e-001 7.669192e-001 VARIABLE INPUT OUTPUT 1 1.000000e-001 1.1668906e+000 2 4.000000e-001 -6.9918377e-001 3 1.500000e-001 4.1277500e-001

This root is still no good. It gives us the same root as our first initial guess.

Fourth initial guess. Decreasing x(1) didn't help. Let's try increasing x(1). So, if we pick a lower x(1), x(1) = 0.30 Using 0 < x(2) < 1.0 - 2x(1), if we again pick x(2) in the middle of its range, x(2) = 0.2 Using 0 < x(3) < x(1) + 0.5\*x(2), we pick x(3) in the middle of its range, x(3) = 0.2 This is a consistent set of initial conditions.

» syse	eqn(1,[0.3,0.2,0.2]	))			
FINA	L MOLE FRACT	'IONS:			
	CH4	CO	CO2	H2O	H2
xE =	1.538462e-001	1.538462e-001	2.307692e-001	1.538462e-001	3.076923e-001
xE =	1.538461e-001	1.538461e-001	2.307693e-001	1.538459e-001	3.076925e-001
xE =	1.538461e-001	1.538462e-001	2.307692e-001	1.538460e-001	3.076924e-001
xE =	9.583105e-002	2.518260e-001	1.596883e-001	1.131140e-001	3.795406e-001
xE =	9.583105e-002	2.518261e-001	1.596883e-001	1.131140e-001	3.795406e-001
FINA	L MOLE FRACT	'IONS:			
	CH4	CO	CO2	H2O	H2
xE =	9.583106e-002	2.518260e-001	1.596883e-001	1.131140e-001	3.795406e-001
VAR	ABLE INPUT	OUTPUT			
1	3.000000e-001	2.3335443e-001			
2	2.000000e-001	3.6799636e-001			
3	2.000000e-001	1.4003904e-001			

Here we find that all of the mole fractions are positive and bounded by 0 and 1. Thus they are physically reasonable.

Therefore, we have the root. The equilibrium mole fractions are given above. The extent of reaction 1 is 0.233 moles, the extent of reaction 2 is 0.368 moles, and the extent of reaction 3 is 0.140 moles.

(b) Repeat problem three part (a) where the inlet temperature of steam = 1000K and the reactor is adiabatic with pressure = 1 atm. In addition to the extent of reaction and the composition of the exit stream, also find the adiabatic temperature of the reactor.

In terms of modifying the input equations, all that needs to be changed in system part (a) is to make the variable adiabatic = 1, and the input temperature of steam = 1000 K. Changing these two lines is all that is required.

Now we need a good initial guess.

Let's use the converged solution from part(a) as our initial guess. Our vector of initial guesses is now four elements long because we do not know the 3 extents of reaction or the adiabatic temperature.

```
» syseqn(1,[2.3335443e-001,3.6799636e-001,1.4003904e-001,900])
```

Attem	pting solution with	th MATLABs fsol	ve function		
xE =	9.583105e-002	2.518260e-001	1.596883e-001	1.131140e-001	3.795406e-001
xE =	9.583104e-002	2.518260e-001	1.596884e-001	1.131138e-001	3.795407e-001
xE =	9.583104e-002	2.518261e-001	1.596883e-001	1.131139e-001	3.795407e-001
xE =	2.248999e-001	5.122482e-003	2.688459e-001	4.081172e-001	9.301446e-002
xE =	2.248999e-001	5.122473e-003	2.688459e-001	4.081173e-001	9.301444e-002
EIN A	IMOLEEDACT	IONS			
I'IINA.	L MOLL FRACT	IONS.			
I'IINA.	CH4	CO	CO2	H2O	H2
xE =	CH4 2.248999e-001	CO 5.122473e-003	CO2 2.688459e-001	H2O 4.081173e-001	H2 9.301445e-002
xE = VARI	CH4 2.248999e-001 ABLE INPUT	CO 5.122473e-003 OUTPUT	CO2 2.688459e-001	H2O 4.081173e-001	H2 9.301445e-002
xE = VARI 1	CH4 2.248999e-001 ABLE INPUT 2.3335443e-001	CO 5.122473e-003 OUTPUT 2.8271846e-001	CO2 2.688459e-001	H2O 4.081173e-001	H2 9.301445e-002
xE = VARI $1$ $2$	CH4 2.248999e-001 ABLE INPUT 2.3335443e-001 3.6799636e-001	CO 5.122473e-003 OUTPUT 2.8271846e-001 5.3867945e-003	CO2 2.688459e-001	H2O 4.081173e-001	H2 9.301445e-002
xE = VARI $1$ $2$ $3$	CH4 2.248999e-001 ABLE INPUT 2.3335443e-001 3.6799636e-001 1.4003904e-001	CO 5.122473e-003 OUTPUT 2.8271846e-001 5.3867945e-003 2.3650484e-001	CO2 2.688459e-001	H2O 4.081173e-001	H2 9.301445e-002

Lucky us! Oh, happy day! The mole fractions are all positive. They sum to one, and they are bounded by 0 and 1. The solution at 900 K was good enough to direct us to the solution at the adiabatic temperature of 668.8 K, where the extent of reaction 1 is 0.283 moles, the extent of reaction 2 is 0.005 moles, and the extent of reaction 3 is 0.237 moles.

As a sidenote, attempting to solve using multivariate Newton-Raphson yields the same result from the same initial guess.

The amount of time required is as follows:

Attempting solution with MATLABs folve function method = 1 elapsed time = 38.14 cpu time = 38.17

Attempting solution with modified multivariate Newton-Raphson Method method = 3 elapsed time = 14.71 cpu time = 14.72

Attempting solution with Nelder and Meads Downhill Simplex Method DID NOT CONVERGE.

Attempting solution with Polak and Ribieres Conjugate Gradient Method (with numerical derivatives)

## DID NOT CONVERGE.

The conclusion: multivariate Newton-Raphson Method rules!!!