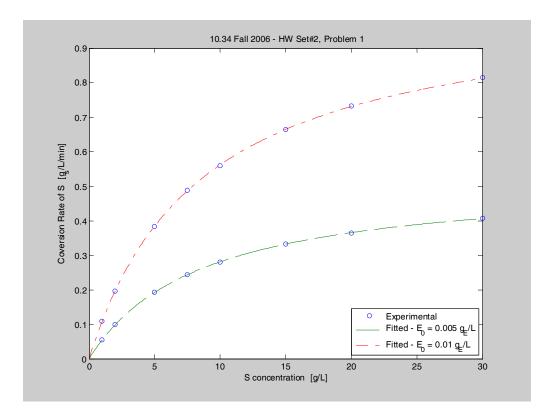**10.34 – Fall 2006**
HW Set #2
Solutions

Problem #1:

This was a straightforward linear regression problem that was well-outlined in the problem
statement in the textbook. The regression fits the data almost exactly. All of the rate data should
have been fit to only two parameters, as you would not expect the values of k_2 and K_m to change
if the initial enzyme concentration were to change.

```
k2  =  104.5041   g_S/min/g_E
Km  =  8.5924     g_S/L
```

Problem #2:

Part A:

This was a simple program writing exercise with no results needed for part A. A simple algorithm for this task would look like this if $N_{data} = N_{param}$:

```
function a_vec = calc_poly_coeff(x,f)

    for i=1:length(x)
        for j=1:length(x)
            X_mat(j,i) = x(j)^(i-1);
        end
    end

    a_vec = X_mat\f;
```

Part B:

The purpose of this part was to write a program that utilizes the result in part A that fit a set of Cv data. The best fit parameters for the 3rd order polynomial and the condition number of the polynomial system matrix are:

```
The condition number is:  1.568e+010

Polynomial coefficient values:
  a0 = 2.96   cal mole⁻¹ K⁻¹
  a1 = 0.016278   cal mole⁻¹ K⁻²
  a2 = -1.1278e-005   cal mole⁻¹ K⁻³
  a3 = 3.0247e-009   cal mole⁻¹ K⁻⁴
```

Part C:

This part was about comparing the results of the polynomial form and the Pade form, and determining which had more accurate interpolation/extrapolation abilities. Linearized form:

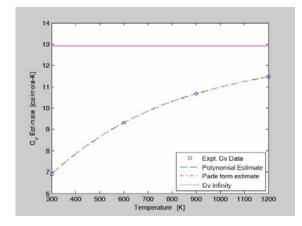$$C_V(T) = a_0 + T \cdot a_1 + \left[T^2 C_V^\infty - T^2 C_V(T) \right] \cdot a_2 - T \cdot C_V(T) \cdot a_3$$
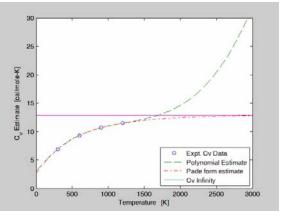
```
Pade coefficient values:
  a0 = 2.6799   cal mole⁻¹ K⁻¹
  a1 = 0.021745   cal mole⁻¹ K⁻²
  a2 = 1.3466e-006   K⁻²
  a3 = 0.0014574   K⁻¹
```


The first figure shows the interpolation ability of the two. Both will produce essentially the same quality of interpolation (although this will not always be the case... especially since polynomials

can often "snake" through the points instead of having a nice, monotonic increase as in the above case.).

However, when one looks to extrapolate the data to high temperatures, the results are wildly different. The polynomial case diverges quickly after the last data point and predicts an unphysical Cv value above ~1700 K. The Pade form proves to be well-behaved over range plotted, mainly due to the formulation of the equation such that the correct asymptote is reached at high temperatures (it can be readily seen that $C_v(T\rightarrow inf) = C_{v,inf}$.

Part D:
This part is dealing with the same problem, but using a scale variable in the polynomial ($\tau = T/1000K$). The polynomial coefficients in this case are:

```
    The condition number is:   2.774e+002

    Polynomial coefficient values:
      a0 = 2.96   cal mole⁻¹ K⁻¹
      a1 = 16.2778   cal mole⁻¹ K⁻²
      a2 = -11.2778   cal mole⁻¹ K⁻³
      a3 = 3.0247   cal mole⁻¹ K⁻⁴
```

These coefficient values are exactly what you would expect, since they should all be scale (multiplied) by 10^{3n}, where "n" is the order of the T/1000 term.
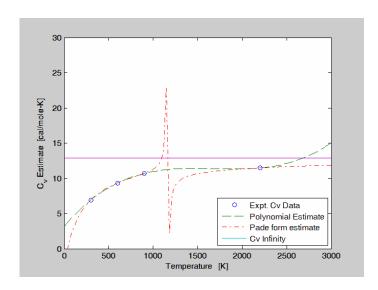
You will notice a sharp decrease in the condition number, when compared to the previous case... a decrease of 8 orders-of-magnitude. This implies that the problem was perfectly well-structured and has a unique solution, but the scaling is poor. This problem would be exacerbated even more if the polynomial was of higher order.

Part E:
In this case, neither of the forms fit very well (the polynomial is no longer monotonic), but the Pade is so bad that it has a singularity in the interpolation. The bad (and potentially dangerous) thing with a case like this is that the function still fits the data exactly but until you more fully examine the behavior of the equation, you cannot really know how good it is at estimating data.

```
(units are the same as above)
Polynomial coefficient values:
  a0 = 3.1614
  a1 = 0.015047
  a2 = -9.0398e-006
  a3 = 1.7814e-009


Pade coefficient values:
  a0 = -2.3819
  a1 = 0.06721
  a2 = -4.2846e-006
  a3 = 0.004127
```
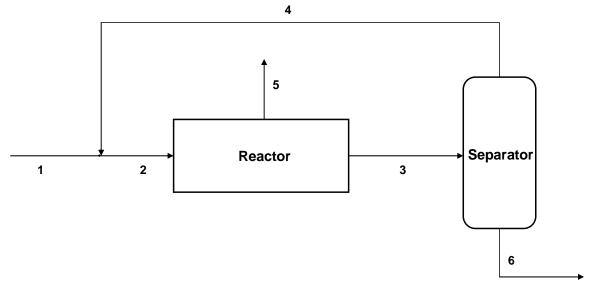
Problem #3:

Figure 1 Schematic Diagram of the Esterification Process.

The symbols:
W_i : water mass flow rate in stream i.
Ac_i: Acid mass flow rate in stream i.
Al_i: Alcohol mass flow rate in stream i.
E_i: Ester mass flow rate in stream i.
M_i: Total mass flow rate in stream i.
F_i: Total molar flow rate in stream i.

Known Quantities:
Ac_1, Al_1,
F_3, F_5, F_6
r_3: ratio of Ac_3/Al_3
r_4: ratio of Ac_4/Al_4

Unknown Quantities: (18 unknows)
W_1,
W_2, Ac_2, Al_2, E_2,
W_3, Ac_3, Al_3, E_3
W_4, Ac_4, Al_4, E_4
W_5, Al_5
W_6, E_6, Ac_6

Analysis of the System:
The total number of flow rates in the system is 20, the above 18 unknowns and Ac_1 and Al_1. We can draw 3 independent control volumes on the system to do the mass balance. The three control volumes are
  1. Balance over the junction of stream1, stream 2 and stream4. This balance gives us 4 equations, one for each species flow rate.
  2. The balance around reactor and this equation gives us 3 equations. We don't get 4 equations from this mass balance because there is a reaction happening in the reactor.

3. The balance around separator. This balance gives us 4 equations.

Thus there are in all 11 equations inherent in the system. To define the system completely we need another 9 constraints. In part 1 of the problem we are given 7 measurements and 2 other constraints (acid mass fraction is 10% of the recycle and separator puts 90% of the ester coming from stream 3 into stream 6. Thus we must be able to solve the system of equations.

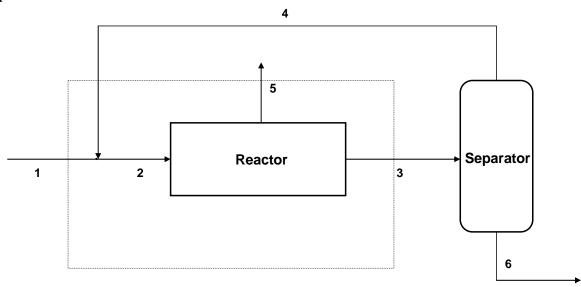## Equation1

Total molar Flow rate of 3:
$E_3/190 + Ac_3/190 + Al_3/32 + W_3/18 = F_3$

Equation2

Total molar Flow rate of 5:
$W_5/18 + Al_5/32 = F_5$

Equation 3-6

Species Balance due to Stoichiometry of Reaction:
$Ac_4/176 + Ac_1/176 - Ac_3/176 = E_3/190 – E_4/190$ (moles of ester formed equals the
moles of acid lost)

Rearranging the terms,
$E_3/190 – E_4/190 + Ac_3/176 - Ac_4/176 = Ac_1/176$

$E_3/190 – E_4/190 = W_3/18 + W_5/18 - W_1/18 - W_4/18$ (moles of ester
formed equals the moles of water formed)

Rearranging the therms,
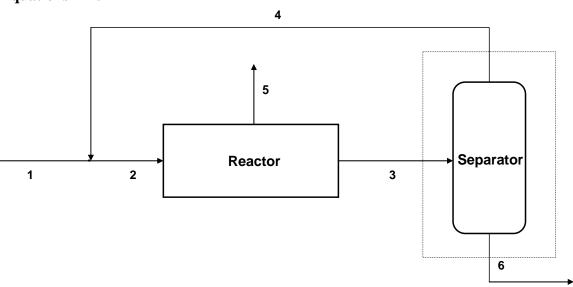$E_3/190 – E_4/190 – W_3/18 – W_5/18 + W_4/18 + W_1/18 = 0$

E3/190 – E4/190 =   Al1/32 + Al4/32 – Al3/32 – Al5/32 (moles of ester

formed equals the moles of alcohol consumed)

Rearranging the therms,

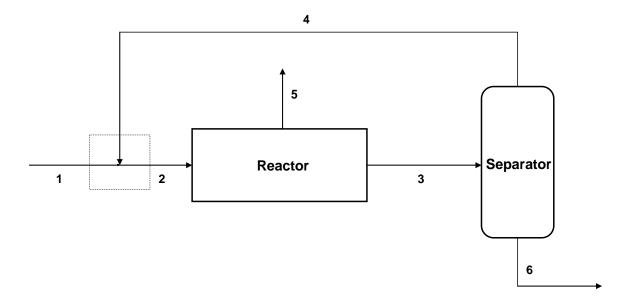E3/190 – E4/190 + Al3/32 + Al5/32 - Al4/32 = Al1/32

Equations 7-10

Since no reactions take place in separator we can do species balance across it.

Species Mass Balance:

W3 + Al3 + Ac3 + E3 - W6 – E6 – Ac6 – E4 – Ac4 – Al4 – W4 = 0

Ac3 - Ac4 - Ac6 = 0 (Acid Mass Balance)

E3 - E4 - E6 = 0   (Ester Mass Balance)

Al3 - Al4=0   (Alcohol Mass Balance)

Equations 11-14

Since no reactions take place in separator we can do species balance across it.

Species Mass Balance:
W2 + Al2 + Ac2 + E2 – W4 – Al4 – Ac4 – E4 – W1 = Al1 + Ac1
Al2 – Al4 = Al1
Ac2 – Ac4 = Ac1
W2 – W4 – W1 = 0

Equation 15

Total Molar Flow rate of 6:
W6/18 + E6/190 + Ac6/176 = F6

Equation 16

Ac4 = 0.1(Ac4 + Al4 + E4 + W4)

Rearranging the terms:
0.9 Ac4 – 0.1 Al4 – 0.1 E4 – 0.1 W4 = 0

Equation 17

Ac4 – r4 * Al4 = 0

Equation 18

Ac3 – r3 * Al3 = 0

The above set of equations give us 18 unknowns for 18 equations. If this problem is well posed then it should be solvable.

We can write this problem in matrix notation as
Ax = b, where

$$A = \begin{bmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1/190 & 1/18 & 1/176 & 1/32 & 0 & 0 & 0 & 0 \\
0 & 1/32 & 1/18 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -1/190 & 0 & -1/176 & 0 & 1/190 & 0 & 1/176 & 0 & 0 & 0 & 0 & 0 \\
1/18 & 0 & -1/18 & 0 & 0 & 0 & -1/190 & 1/18 & 0 & 0 & 1/190 & -1/18 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1/32 & 0 & 0 & 0 & 0 & -1/190 & 0 & 0 & -1/32 & 1/190 & 0 & 0 & 1/32 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -1 & -1 & -1 & -1 & -1 & -1 & -1 & 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & -1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -1 & 0 & 0 & -1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & -0.1 & -0.1 & 0.9 & -0.1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1/190 & 1/18 & 1/176 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -r3 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -r4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & -0.9 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-1 & 0 & 0 & 0 & 0 & 0 & -1 & -1 & -1 & -1 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
-1 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0
\end{bmatrix}, b = \begin{bmatrix}
F3 \\ F5 \\ Ac1/176 \\ 0 \\ Al1/32 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ F6 \\ 0 \\ 0 \\ 0 \\ Ac1 + Al1 \\ Al1 \\ Ac1 \\ 0
\end{bmatrix}$$

The rank of matrix A is 18 and so the problem is well posed and has a unique solution.

The condition number of matrix A is 1.0708e+003. From the class notes we know that

$$\frac{\|\delta x\|}{\|x\|} \le \|A\|\|A^{-1}\|\left(\frac{\|\delta b\|}{\|b\|} + \frac{\|\delta A\|}{\|A\|}\right)$$

$$\|A\|\|A^{-1}\| \approx 10^3$$

Using this test we obtain that value of $\frac{\|\delta x\|}{\|x\|} \approx 1$. In the worst case scenario the numbers that we obtain for x have no meaning. This has nothing to do with machine precision and is only the property of the system of equations.

The program is written in file pset1problem3

The sample input and output for the program is given below.

```
>> input1 = [50.04 10.04 1.204 0.2124 0.6624 1.934 0.1574];
>> ouput1 = Problem3(input1);
Flow rate of water in recycle stream (W4) =2.0445 Kg/mol
Flow rate of Ester in recycle stream (E4) =3.2791 Kg/mol
Flow rate of Acid in recycle stream (W4) =2.0114 Kg/mol
Flow rate of Alcohol in recycle stream (Al4) =12.7786 Kg/mol
>>
```
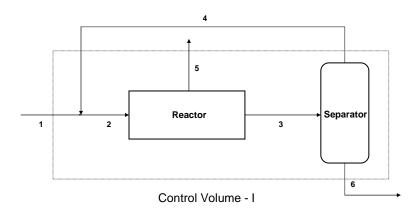
The output1 is a vector of size 18 and contains the flow rates of all the components in all the streams.

Part 2:

In this problem again we have 11 inherent equations due to system configuration and 20 unkowns. Here we are given 8 measured quantities and another constraint, namely acid flow rate is 10% on the total mass flow rate in the recycle stream. Thus at first look it seems that the system should be solvable. But let us analyze it more closely by taking the control volume shown below.

Control Volume - I

Ester is coming out only in stream 6 with a known flowrate E6. This ester is being formed in the reactor. Also the Acid is going into the system with a known flow rate Ac1 and is coming out with a known flow rate Ac6. The difference between the inflow rate and the outflow rate of acid is the amount of acid that is getting reacted in the reactor. Thus due to the stoichiometry of the reaction taking place in the system we realize.

E6/190 = (Ac1 – Ac6)/176

Thus some of the specified quantities are related by an inherent constraint of the system, which implies that there are really only 5 independent quantities that are specified. Further analysis will show that specifying the input and output flow rate of alcohol is also redundant. Thus on formulation of the problem the overall system will be rank deficient by 2. Thus the system of equation will not have a unique solution if at all it has a solution.

Problem #4:

Modeling equations:
There are two equations that one needs to solve the problem: an energy balance and an extent of reaction equation. You could also formulate the problem using the atom conservation or explicit equations for each specie and the extent of reaction, but this would lead to more equations, which can make non-linear problems more difficult to solve… less variables is better. The fact that the reaction is equimolar and the heat capacities of the products and reactants are equal simplifies the problems.

As given in the problem, the rate expression is:

$$rate(T, P_i) = A \exp\left(\frac{-E_A}{RT}\right) \cdot \left[\frac{P_{CO} P_{H_2O} - P_{CO_2} P_{H_2} \exp\left(\Delta G_{Rxn}/RT\right)}{1 + P_{CO}/0.2 \ atm}\right]$$

The energy balance is as follows. The term n/t is the number of moles in the reactor divided by the residence time, which also equals the flow rate into the system. This could get much more complicated if heat capacities vary

Heat Generated by Rxn = Energy to Heat Inlet to Reactor Temp + Heat Loss

$$-\Delta H_{Rxn} \cdot rate(z, T_{Rxtr}) = \frac{n_{Rxtr}}{t_{res}} C_{P,mixture} \cdot (T_{Rxtr} - T_{In}) + h \cdot (T_{Rxtr} - 300K)$$

The other equation keeps track of the reaction extent, and says the number of moles of CO consumed in the reactor (z) is equal to product of the rate and residence time:
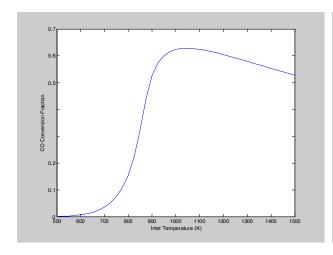
$$z = t_{res} \cdot rate(z, T_{Rxtr})$$

We want to reduce the rate equation to be only a function of T and the progress variable, z, so we have 2 equations. A balance could be written out in terms of each species/atom, but this case is simple enough to simplify without that. The equations we need are:
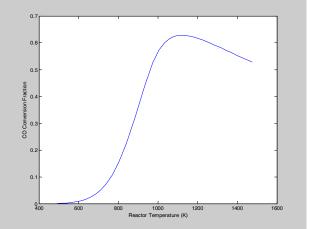
$$P_i = P_{i,Inlet} + v_i \left(z \cdot \frac{RT_{Rxtr}}{V_{Rxtr}}\right) \qquad where: \ v_i = \text{stoichiometric coefficient}$$

Now the two balances now have $rate(z, T_{Rxtr})$ and can be solved for these variables.

```
Results for Inlet Temperature = 700 K
Reactor Temperature = 684.876 K
Outlet Mole Fraction of CO = 0.19297
Outlet Mole Fraction of H2O = 0.79297
Outlet Mole Fraction of CO2 = 0.0070318
Outlet Mole Fraction of H2 = 0.0070318

Operating Condition to Achieve Maximum CO conversion
Inlet Temperature = 1050 K
Reactor Temperature = 1124.4341 K
Maximum Conversion of CO = 62.8301 %
```
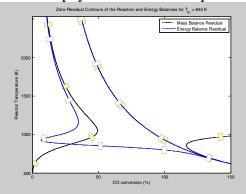
The graphical representation of the maximum CO conversion is shown below in the plots with inlet temperature and reactor temperature.
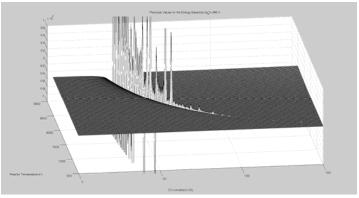
An example of the graphic "solution" at $T_{in} = 845$ K:
The solution would be where the zero contours of the two equations intersect each other. Graphically, it also looks like there is a line of infinite solutions sloping from the top-left to bottom-right, but this is not true. In actuality, this is an asymptote caused by $(1 + P_{CO}/0.2) \to 0$, as can be seen in the 3-D residual plot (yes, P_{CO} becomes negative because the solver does not know the physical limits of the problem).

Solving nonlinear problems is typically a problematic process because it is difficult to determine a priori how many solutions there are to a particular problem, if a problem has a physical solution, or what initial guess will yield the desired solution. This problem is particularly problematic because of the singularity that occurs in the rate expression. Since the solver does not know the physical range of the parameters, it may decide to "jump" the singularity into non-physical space and is then unable to return to the correct solution. Choosing an accurate initial guess is the best way to ensure that you get good convergence, and tweaking solver parameters can also help (though it is not always clear exactly what you are tweaking). These sort of nonlinearities make nonlinear solvers unstable and unreliable, especially in much more complex problems with many more variables. Other techniques to solve nonlinear equations include optimization techniques, which may allow for constraints that help the solver stay out of trouble.