10.34 – Fall 2006
Homework #2
Due Date: Wednesday, Sept. 20th, 2006 – 9 AM

Problem 1: Linear Regression

Complete problem 1.B.2 in Beers' textbook (page 82). Submit a graph with the rate data and fitted expression on the same plot, along with the values of the parameters determined by the linear regression.

Problem 2: Fitting heat capacity data sets using various functional forms

Part A:

Complete problem 1.A.3 in Beers' textbook.

Part B:

Apply your function `calc_poly_coeff.m` to interpolate between the following data for the heat capacity (C_V [=] cal/mole-K) of CO_2 using the following polynomial form:

$$C_V(T) = a_0 + a_1 T + a_2 T^2 + a_3 T^3$$

Temp (K)	300	600	900	1200
C_V	6.91	9.32	10.68	11.48

i.e. write a function `Cv = Cv_CO2_poly(T,T_data,Cv_data)` that takes in a vector of T values and returns estimates of the corresponding C_V(T) vector, given the data vectors for temperature and C_V. Note that in this special case, $N_{data} = N_{param}$, so the parameters are determined by solving a linear system (not regression).

These sorts of interpolations are needed for estimating the thermodynamic properties of gases. (In fact, often we need to extrapolate to predict the behavior of gases at very high T, where it is difficult or impossible to measure the properties directly.) Report the parameter values determined for the polynomial. Also report the condition number of the linear system matrix ($\underline{\underline{X}}$ *in*: $\underline{\underline{X}} \cdot \underline{a} = \underline{f}$, where $\underline{a}$ are the parameters).

Part C:

As T gets very high, it is known that molecular heat capacities are asymptote to values predicted by classical mechanics. For CO_2, the asymptotic value is $C_V = 6.5R$. Also, for CO_2, the heat capacity is expected to be a monotonically increasing function of T. Does your program `Cv_CO2_poly.m` give reasonable estimates? Does it give accurate extrapolations at high temperature?

Often a better extrapolation can be obtained using the Pade form:

$$C_V(T) = \frac{a_0 + a_1 T + C_V^{\infty} a_2 T^2}{1 + a_3 T + a_2 T^2}$$

Write a program `calc_Pade_coeff.m` that determines a_0, a_1, a_2, and a_3 and a program `Cv_CO2_Pade(T,T_data,Cv_data)` that estimates the C_V(T) of CO_2 using the Pade form. (Note that the Pade form can be posed as linear in the parameters, so a nonlinear solver is not needed) Report the parameter values determined for the Pade form. Compare the two interpolations graphically, and make some comments regarding the accuracy of their interpolations and extrapolations.

Part D:

Suppose that the problem is posed in a slightly different way, such that the variable is converted from T → T/1000. The polynomial would be:

$$C_V(\tau) = a_0 + a_1 \tau + a_2 \tau^2 + a_3 \tau^3 \qquad where: \ \tau \equiv \frac{T}{1000}$$

Using the previously written `calc_poly_coeff.m`, calculate the parameter values for this new scaled variable. Are these the expected values given the previous solution with the variable T? Calculate the condition number of the new linear system matrix. Typically a very large condition number implies the problem is near-singular and/or poorly scaled, which do you think is the problem in this case, and why?

Part E:

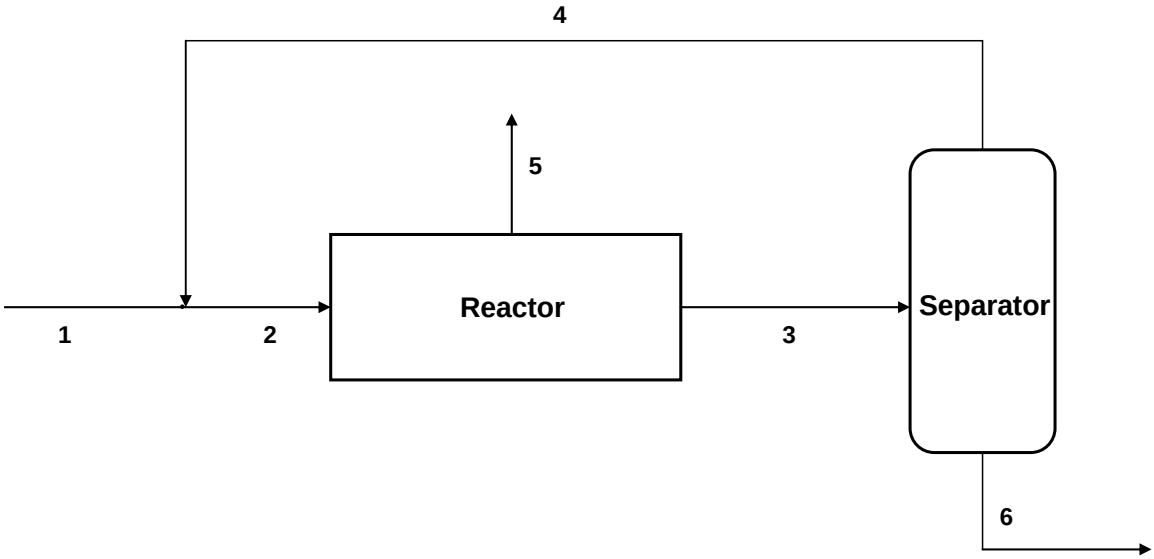
Suppose the C_V data for CO_2 were actually the following:

Temp (K)	300	600	900	2200
C_V	6.91	9.32	10.68	11.48

Compare the interpolation and extrapolation abilities for this set of C_V data by providing a plot comparing the polynomial and Pade forms. Comment on the results in this case.

Problem 3: Solving Linear Systems for "Real" System Problems

Consider the reactor-separator esterification system discussed in class:



Contrary to the idealized assumptions made in class, the separators are not perfect. The product stream 6 is actually a mixture of ester, acid, and acid. The steam stream 5 is actually a mixture of H_2O and alcohol. There is some ester in the recycle stream. The input stream is a mix of H_2O, alcohol and acid.

The molecular weight of the alcohol is 32 g/mole. The molecular weight of the acid is 176 g/mol. The reaction is acid + alcohol = H_2O + ester. The symbols used for this problem are explained below.

The symbols:
Wi : water mass flow rate in stream i.
Aci: Acid mass flow rate in stream i.
Ali: Alcohol mass flow rate in stream i.
Ei: Ester mass flow rate in stream i.
Mi: Total mass flow rate in stream i.
Fi: Total molar flow rate in stream i.

The measurements available to you are:

1) The mass flow rates of Alcohol and Acid in the input stream. (Ac1, Al1)
2) The total molar flow rate of stream 3, stream 5 and stream 6. (F3, F5, F6)
3) Performing an IR spectroscopy gives the ratio of Acid and Alcohol in stream 4 and stream 3. (r3, r4)

All the measurements are good to 3 significant figures.

To ensure material compatibility, the system is always adjusted to maintain the concentration of acid in the recycle stream at 10.00 mass%. Also the separator extracts 90% of ester from stream 3 into stream 6.

Write a Matlab function which takes as its input a vector containing the 7 measured numbers (in order Ac1, Al1, F3, F5, F6, r3, r4) and constructs and solves the linear system of equations to compute the composition of all the streams.

1. Use your function to compute the composition of the recycle stream for the following cases:
   a) Ac1 = 50.0 Kg/sec, Al1 = 10.0 Kg/sec, F3 = 1.20 Kmol/sec, F5 = 0.212 Kmol/sec, F6 = 0.662 Kmol/sec, r3 = 1.93 and r4 = 0.157.

   Is there a unique solution to the problem?

   Also estimate the uncertainty in your answers due to the conditioning of the system of equations and the uncertainty in the measurements.

2. Now instead of the above measurements suppose someone made measurements of Mass flow rate of all the components in stream 1 and stream 6 (Ac1, Al1, W1, E6, Ac6, W6). The total mass flow rate of the recycle stream is provided (M4). The total molar flow rate of stream 5 is given F5.

   To ensure material compatibility, the system is always adjusted to maintain the concentration of acid in the recycle stream at 10.00 mass%.

   For these given inputs form the system of equations to solve for the composition of all the streams. Is there a unique solution to the problem? If so calculate the flow rates in the recycle stream for these sets of inputs. If not, why not?

   a) Ac1 = 50.0 Kg/sec, Al1 = 10.0 Kg/sec, W1 = 5.00 Kg/sec, E6 = 29.7 Kg/mol, W6 = 6.81 Kg/mol, Ac6 = 22.5 Kg/sec, M4 = 20 Kg/sec and F5 = 0.212 Kmol/sec.

Problem 4: Non-linear Reactor Design Problem

Hydrogen is often produced from syngas (mixture of CO & H_2) by the water gas shift reaction:

$$CO + H_2O \Leftrightarrow H_2 + CO_2$$

in a catalytic reactor that can be modeled as a constant pressure, constant volume CSTR. The rate of the reaction in this reactor is given by this expression:

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

At the reactor temperature,

$A = 32\ \frac{mole}{s\cdot atm^2}$

$E_A = 53000\ \frac{J}{mole}$

$\Delta H_{Rxn} = -41000\ \frac{J}{mole}$

$\Delta S_{Rxn} = -42\ \frac{J}{mole\cdot K}$

The residence time in the 5 liter reactor is 1.5 seconds. The reactor loses heat to the environment at rate:

$$Q = h(T - 300) \qquad T\ in\ Kelvin,\ where:\quad h = 1.2\ \frac{Watts}{K}$$

When doing the energy balance, you will need to consider the energy required to raise the temperature of the inlet to the reactor temperature. For this purpose, estimate the heat capacity of the gaseous mixture using ideal-mixing:

$$C_{P,mixture}(T) = \sum_{species} x_i \cdot C_{P,i}(T)$$

and set the heat capacities of CO and H_2 to $C_P = 3.5R$ and H_2O and CO_2 to $C_P = 4R$. Later we'll discuss how to handle the fact that C_P is actually a function of T.

Write a Matlab function that takes as input the system pressure (in *atm*), the inlet gas temperature, and the mole fractions of the four gases in the inlet, and returns as output the reactor temperature and the product stream composition (use `fsolve` in your program):

```
[xout,Treactor] = WaterGasShift(P,Tinlet,xinlet)
```

Test your function for the case: P = 10 atm, T_{inlet} = 700 K, $x_{inlet,\ H2O}$ = 0.8, $x_{inlet,\ CO}$ = 0.2. Report the outlet mole fractions and the reactor temperature.

Additionally, if you were designing this reactor for industrial use, you would be interested to know what operating conditions produced the most hydrogen. You believe that your CrMoV-Steel vessel (and catalyst) can withstand inlet temperatures of up to 1500 K, which represents the physically-realizable operating conditions of the reactor.

Using your function, determine the CO conversion as a function of T_{inlet} (use a vector of T's from 500 K → 1500 K in 25 K increments). Plot the CO conversion vs. T_{inlet} and state maximum conversion and the corresponding T_{inlet} and $T_{reactor}$ values. Explain the low temperature and high temperature behaviors seen in the plot. The pressure and inlet stream are the same as before.

Comment on the stability of nonlinear problems/solvers and on the importance of the initial guess. In your write-up for this problem, be sure to give the equations you solved and how you arrived at them.