Homework 7

26 October 2006

Problem 1

There are a few ways to solve this problem, one could formulate it as a ODE or as a DAE (We are going to formulate the problem as a ODE). The governing equation in the problem are given below.

$$\frac{\pi}{4} D_p^2 v_p^2 = \frac{\pi}{4} [D(h)]^2 \left| \frac{dh}{dt} \right|^2 \tag{1}$$

$$\left[\frac{1}{2}\rho \left(\frac{dh}{dt} \right)^2 + p_{atm} + \rho g h \right] - \left[\frac{1}{2}\rho v_p^2 + p_{atm} + \rho g(-L_p) \right] = K_L \left(\frac{\pi}{4} D_p^2 v_p^2 \right) + f_D \left(\frac{L_p}{D_p} \right) \left(\frac{\pi}{4} D_p^2 v_p^2 \right) \tag{2}$$

where the friction factor f_D can be calculated as follows.

$$\begin{array}{ll} f_D = \frac{24}{Re} & Re < 2100 \\ \frac{1}{\sqrt{f_D}} = -2\log_{10}\left[\frac{(e/D_p)}{3.7} + \frac{2.51}{Re\sqrt{f_D}} \right] & Re > 4000 \end{array} \tag{3}$$

In this formulation we evaluate the value of v_p using equation (1) in terms of h and $\frac{dh}{dt}$. The friction factor can be calculated using v_p or in terms of h and $\frac{dh}{dt}$. Ofcourse none of this needs to be done analytically. Everything is coded as a matlab function. Using this friction factor and v_p, which are both functions of h and $\frac{dh}{dt}$, we can get one single equation which can be written as $g(h, \frac{dh}{dt}) = 0$. This equation can be solved to obtain a value of $\frac{dh}{dt}$ for any given value of h. The scheme outlined here can be used to solve the problem and calculate the height of the tank at any given point in time. We can stop the ode from integrating on after the height has reached 0, we use events function.To calculate the volume of the liquid in tank we use the equation
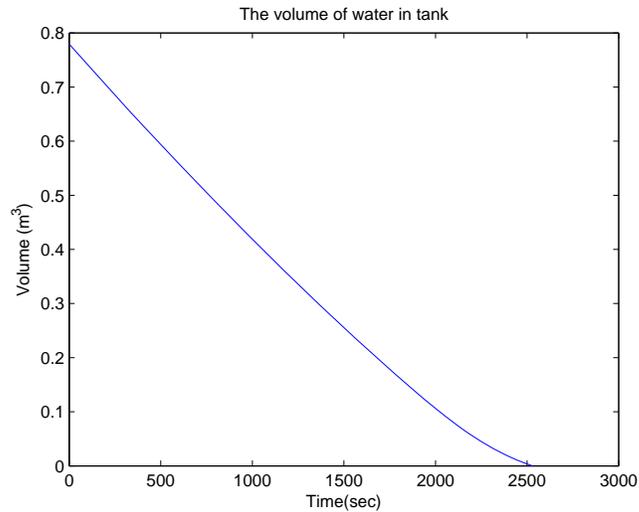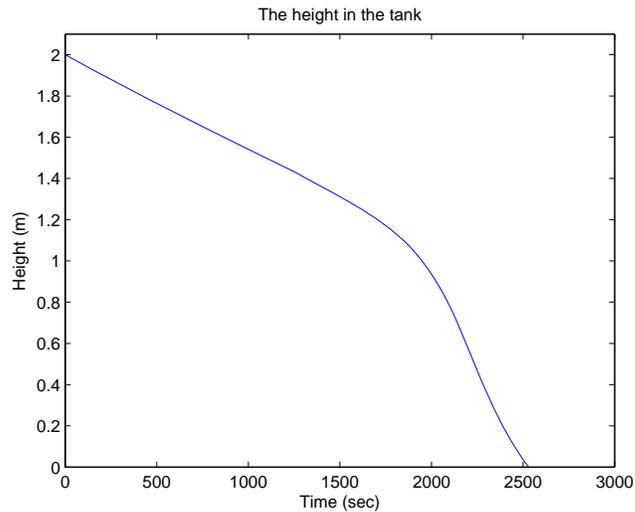
$$\frac{dV}{dh} = \frac{\pi [D(h)]^2}{4}$$

and integrate it. For the implimentation of this method see the function `problem1`. A sample run with the program is shown below

```
>> [t,h]=problem1;
```
The tank gets empty at time: 2529.8923 s

The height and volume of water in the tank are shown below.

The height in the tank

The volume of water in tank

10.34 – Fall 2006

Homework #7 - Solutions

Problem 2 – CSTR Optimization (Beers' text 5.B.4)

In this problem, we wished to find the optimal operating condition for a CSTR in order to produce the maximum amount of [C]. We were given a reaction mechanism and the necessary rate constants, and we asked to vary the initial concentrations of A and B, the reactor temperature between 298 K and 335 K, and the reactor volume from 10 L to 10000 L.

The solution procedure involves using a constrained optimization program (fmincon in Matlab) to solve the problem. The other potential difficulty in the problem is that the we do not have an explicit cost function, but must solve for the steady-state concentrations in the CSTR. This can be done using fsolve to solve the nonlinear equations, or using an ODE solver to integrate to a long time so that the reactor is at a steady state. The general reactor equations are:

$$\frac{d[X]}{dt} = \sum_{n\ reactions} v_{X,n} R_n + \frac{V_{flow}}{V_{rxtr}}\left([X]_{in} - [X]\right) \qquad where: R_n = k_n[A][B]$$

In the above expression, $v_{X,n}$ is the stoichiometric coefficient of species X in reaction n, R_n is the rate of reaction n. At steady-state, the time derivative will be equal to zero, yielding a set of nonlinear equations.

One notable problem encountered in this problem was that fmincon would not vary the reactor volume variable when trying to perform the optimization. This problem could be remedied in several ways. Perhaps the best way was to scale this variable, one possibility was to make the optimization variable LN(V_rxtr). What this does is to effectively make the variable smaller, and a unit change in the scaled variable will make a much larger change in the cost function that a unit change in the unscaled variable. Another way to improve the optimizer performance when using unscaled variables was to increase the tolerances (TolFun, TolX, and TolCon). Making these small helped to gain a true solution for a wide range of initial guesses. Matlab codes that solve the problem using scaling and an ODE solver, and well as solving the unscaled problem using an ODE solver and fsolve are included.
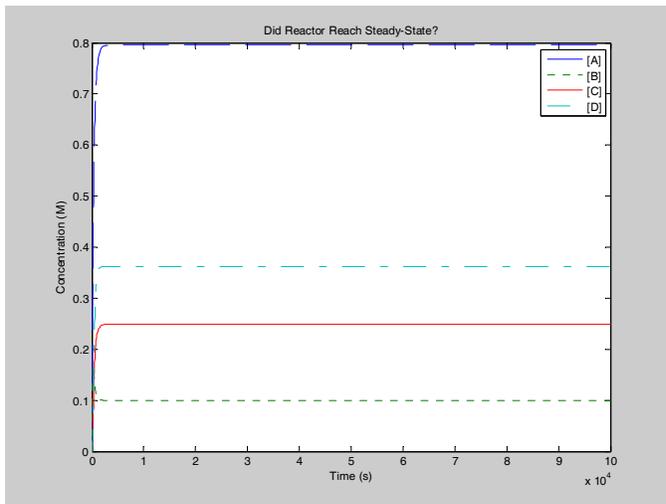
The optimal reactor operating conditions are:

```
Inlet [A] = 1.3515 M
Inlet [B] = 0.64845 M
Reactor Temperature = 298 K
Reactor Volume = 478.896 L

Outlet [C] = 0.24913 M
```

The following plots are for diagnostic reason only, and were not required for the homework:
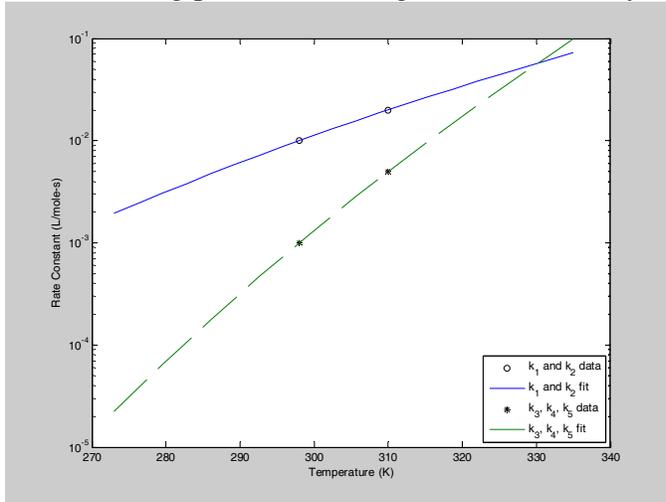
This plot simply serves to show that the fitted value of A and E_A for the rate constant are correct and fit the data

In the cases where an ODE solver is used to estimate the SS condition of the reactor, it is useful to run the time-dependence to convince yourself that you integrating to a large enough time to ensure that a SS is achieved. This is not a guarantee that all parameters sets encountered during the optimization yield a SS at this length of time.
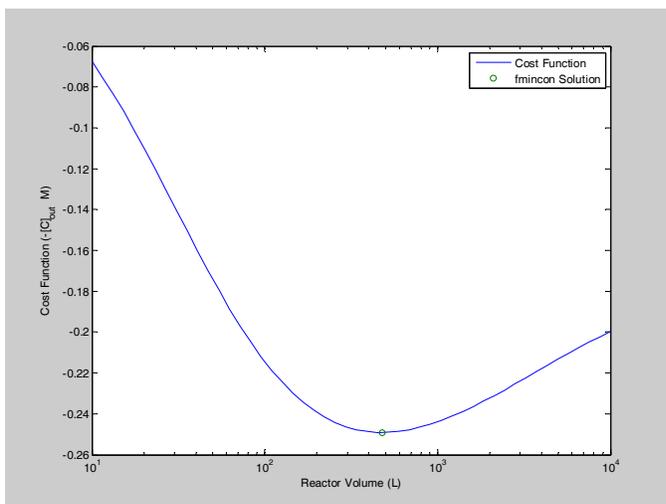
Since the reactor volume was giving us problems, it is useful to see how the cost function varies with V_rxtr at the "optimal" solution returned by fmincon. In this case, you can see that the fmincon solution appears to be correct. If the volume was not adjusted to its optimum value by fmincon, the open circle would not be at the minimum of the cost function.

Problem 3 – Chemical Equilibria

This problem with chemical equilibria in a system where the reactions are not known, and the assumption is that there are enough reactions that connect the species that there are no stoichiometric constraints imposed by reactions. This could also be considered the "absolute" equilibrium condition of the system for a given initial condition (meaning that this will be the absolute lowest Gibbs free energy obtainable for the given conditions).

The cost function was set up in the problem for you, and essentially was minimizing the total Gibbs free energy of the system.

$$G_{total} = \sum_{species} n_i \left(G_i^o + RT \ln \left(\frac{n_i}{\sum n_i} \right) \right)$$

What you end up with is an optimization problem based on the number of moles each species. The constraints on the system are two-fold. The first is obvious and is that all species must have a number of moles that is greater than zero (in this problem, the lower bound actually needs to be set to a number greater than zero, if not, the natural log term will cause problems). The other constraint is based on the atom balances, saying that the total moles of H, C, and O initially in the system must be equal to the number of moles of H, C, and O at equilibrium. This type of constraint can be written as follows:

$$A_{jk} \cdot \underline{n_{eq}} = A_{jk} \cdot \underline{n_0}$$

where the elements of A_{jk} are number of j atoms in species k. We can then use fmincon to solve this optimization problem.

Part A:
Consider a constant T and P equilibrium reactor, with T = 1000 K and P = 1 atm. The initial charge of reactants is: 2 moles CH_4, 3 moles H_2O, 0.5 moles CO, and 1 mole of H_2. Give the number of moles of each species at equilibrium, as well as the corresponding mole fraction.

```
Total moles initially:  6.5
Initial Volume (L):   533.39

Total moles at equilibrium:  10.0216
Final Volume (L):  822.3757

CH4:   mole fraction: 0.02387,    number of moles: 0.23918
H2O:   mole fraction: 0.08495,    number of moles: 0.85129
CO:    mole fraction: 0.19015,    number of moles: 1.90558
CO2:   mole fraction: 0.03545,    number of moles: 0.35524
H2:    mole fraction: 0.66397,    number of moles: 6.65402
HOOH:  mole fraction: 0.00163,    number of moles: 0.01632
HO2:   mole fraction: 9.98e-014,  number of moles: 1.00e-012
```

Part B:
The species HO_2 is a radical species and would typically be found in very small quantities. What would be the approximate number of moles at equilibrium for HO_2 estimated using the concentrations of the major species? Does the value found using the minimization make sense, explain?

The idea of this part was to show that you cannot always trust the numerical estimates when you have many orders of magnitudes between variables. If you played with the tolerances in fmincon, you may have found that the number of moles of HO_2 found using fmincon typically be at the lower bound set for the solver, even if it is set at 1e-14.

However, there is a manual technique that can be used to estimate the concentration of a minor species in equilibrium with other major species. The inherent assumption is that the major species' concentrations are constant and unaffected by changes in the minor species concentration. First, you have to think of an arbitrary reaction that relates the major species the minor species. This reaction can be anything you want and does not have to be physical in any way. Two such reactions for this system could be:

$$4H_2O \rightleftharpoons 3H_2 + 2HO_2 \qquad or \qquad 2HOOH \rightleftharpoons H_2 + 2HO_2$$
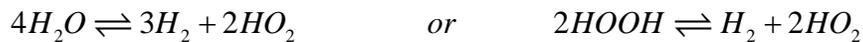
Then you can write an equilibrium expression for this reaction in terms of the Gibbs free energies of the species:

$$K_A = \exp\left(\frac{-\Delta G_{reaction}}{RT}\right) \qquad and \qquad K_A = \prod\left(\frac{\hat{\phi}_i y_i P}{P^0}\right)^{\nu_i}$$

If you assume that the system behave ideally, then phi = 1 and the following holds:

$$K_A = \prod\left(\frac{y_i P}{P^0}\right)^{\nu_i} = \left(\frac{P}{P^0}\right)^{\Delta n_{reaction}} \prod(y_i)^{\nu_i} \quad \xrightarrow{const. \ P} \quad K_A = \prod(y_i)^{\nu_i}$$

or

$$\exp\left(\frac{-\Delta G_{reaction}}{RT}\right) = \prod(y_i)^{\nu_i}$$

We will take the 2nd reaction listed above: $2HOOH \Leftrightarrow H_2 + 2HO_2$. The delta G of reaction for this can be calculated to be 284120 J/mole.

$$\exp\left(\frac{-284120}{8.314 \times 1000}\right) = \frac{y_{H_2} y_{HO_2}^2}{y_{HOOH}^2} \quad \Rightarrow \quad y_{HO_2} = \sqrt{\frac{y_{HOOH}^2}{y_{H_2}} \cdot 1.4406 \times 10^{-15}} = 7.593 \times 10^{-11}$$

The approximate number of moles should be 7.61×10^{-10}. This shows that the value calculated by fmincon is incorrect, and even inconsistent with the given data. For numerical reason, this very small number cannot be calculated accurately, and changes depending on the tolerances given.