10.34 **Numerical Methods Applied to Chemical Engineering** **Fall 2015**

Homework #8: Models and Data

Problem 1. (10 points)

You are trying to build a precise model for a simple steady-state reactor-separator-recycle system (see Fig. 1).

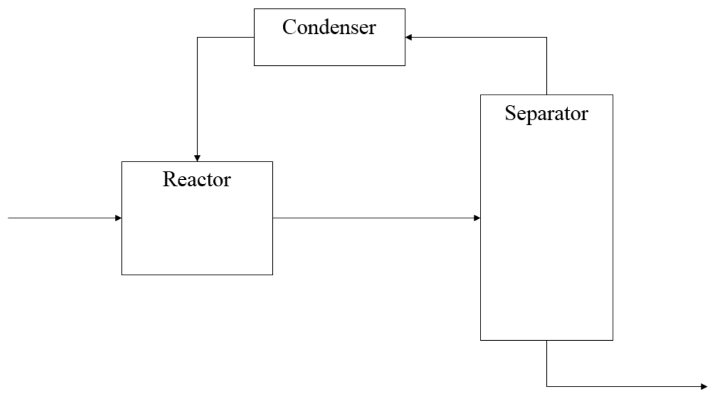

Figure 1: Flow diagram for the process.

The reactor is full of liquid and has strong mixing; in the reactor the reaction

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C}$$

is occuring. C is the desired product. The reaction rate is negligible outside of the reactor. The output of the reactor rapidly flows to a flash separator, where some of it evaporates. The liquid phase in the flash unit, which is predominantly C, flows to the output. The gas phase stream coming out of the flash separator is condensed and recycled to the reactor.

The proposed MODEL for this system:

1. Assume the concentrations are uniform throughout the reactor, the composition of the flow to the flash separator has the same as the composition in the reactor, and the reaction follows elementary step kinetics:

   $$r = k_f[A][B] - k_r[C]$$

   In other words, (mol/s of A flowing out of the reactor) = (mol/s of A in the input stream) + (mol/s of A in the recycle stream) - rV_r. V_r is the reactor volume.

2. Assume the liquid phase in the separator is well-mixed, and its composition is the same as the composition of the output stream.

3. Assume the gas phase in the separator is well-mixed, and its composition is the same as the composition of the recycle stream (note: it starts as gas phase, but after the condenser the recycle stream is liquid-phase).

4. Assume the composition of the gas phase in the separator is given by a simple ideal-solution extrapolation:

$$y_A = [(P_A - H_A)x_A^2 + H_A x_A]/P_{total}$$
$$y_B = [(P_B - H_B)x_B^2 + H_B x_B]/P_{total}$$
$$y_C = [(P_C - H_C)x_C^2 + H_C x_C]/P_{total}$$

where y_A, y_B, and y_C are the mole fractions of A, B, and C, in the gas phase and x_A, x_B, and x_C are the mole fractions in the liquid phase. P_A, P_B, P_C are the well-known vapor pressures of pure A, B, or C. H_A, H_B, and H_C are estimates of the Henry's law constants and

$$P_{total} = [(P_A - H_A)x_A^2 + H_A x_A] + [(P_B - H_B)x_B^2 + H_B x_B] + [(P_C - H_C)x_C^2 + H_C x_C]$$

5. Assume molar volume of liquid has ideal behavior:

(Total Volume of Liquid)/(total moles of liquid) $= x_A V_A + x_B V_B + x_C V_C$

Parameters that are well known (treat as exact):

Molecular weight of A = 102.34 g/mol	Density of A (liquid phase) = 0.7995 kg/L
Molecular weight of B = 124.08 g/mol	Density of B (liquid phase) = 1.241 kg/L
Molecular weight of C = 226.42 g/mol	Density of C (liquid phase) = 1.132 kg/L
$P_A = 0.52\ bar$	$V_r = 1.53\ L$
$P_B = 0.34\ bar$	Input of A = 1.23 mol/s
$P_C = 0.012\ bar$	Input of C = 0 mol/s

Estimates of parameters which are questional (you may want to adjust these to improve the fit):

$k_f = 0.42\ L/(mol - s)$ (very rough)
$k_r = 0.042\ s^{-1}$ (rough)
$H_C = 0.0142\ bar$ (rough)
$H_A = 0.942\ bar$ (should be pretty accurate)
$H_B = 0.542\ bar$ (should be pretty accurate)

Data:

Sensors have been installed which measure the recycle rate, the feed rate of B, the composition of the output stream, the mole fraction of A in the recycle and intermediate streams, and the mole fraction of B in the recycle stream. Three different experiments were performed, each time adjusting the recycle rate and the input of B. Each experiment was repeated several times, see the data set (Excel sheet).

Questions:

1. Look at the data and make some comments. Is there anything unexpected? Do the data satisfy the expected mass/element conservation laws?

2. What are the best-fit values of the parameters using the weighted-χ^2 fit? We suggest you might first try to fit the most uncertain parameter(s), and then add in the others. The best-fit parameters you find may not be physical: see Question 3.

3. For this best-fit you found, does it appear that the model and the data are consistent? Use a quantitative consistency test.

4. What are the uncertainties in the parameters? Are the uncertainties correlated? You should start by considering the sensitivity of χ^2 to each of the parameters (use the normalized sensitivities d(ln χ^2)/d(ln param) so that your results do not depend on the units of the parameters). Which of the parameters could be significantly refined (relative to the prior estimates) using this experimental data, and which cannot?

5. 5) Try using a quadratic approximation to 2 at your best-fit parameter values, and plot how χ^2 depends on k_f and k_r. Based on this, compute the 95% confidence intervals for k_f and k_r separately, and taken together. Try replotting this using logarithmic axes, i.e. plot χ^2 versus $\ln(k_f)$ and $\ln(k_r)$. Would there be any advantage in using $K_{eq} = k_f/k_r$ as one of the fitting variables? Explain.

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