

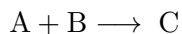
Figure 1: Run of Reactor 1 with changing residence time. Top: reactor residence time versus time. Bottom: reactor temperature versus time.

4. A, B, and C adsorb on surface sites S due to their large molecular sizes.
5. O<sub>2</sub> and H<sub>2</sub>O adsorb on surface sites S\* due to their small molecular sizes.

You have a measurement device that is calibrated to detect the total concentration of phenyl groups in the system, both in the gas phase and on the surface. What is the production rate of phenyl groups in the above mechanism in terms of gas-phase concentrations  $c_A$ ,  $c_C$ ,  $c_{O_2}$ ,  $c_{H_2O}$ , rate/equilibrium constants  $k_i$ ,  $k_{-i}$ ,  $K_i$ , and total metal sites  $c_m$  (for S) and  $c_{m^*}$  (for S\*)? No surface species concentration should appear in your final rate expression.

### Exercise 2. Deus ex machina. 50 points.

Your company is running a campaign of simple exothermic addition reactions in adiabatic, liquid-phase CSTRs



with a large excess of reactant B.

Your boss has asked you to troubleshoot some recent reactor operational problems that have arisen. “First of all,” he tells you, “the reactor operation does not appear to be reproducible. The operators complain that the steady-state reactor temperature and conversion of A vary shift-by-shift by large amounts even though the reactor operating parameters are held constant. None of the operators want to be assigned to this part of the plant because of the bad quality control caused by this reactor.”

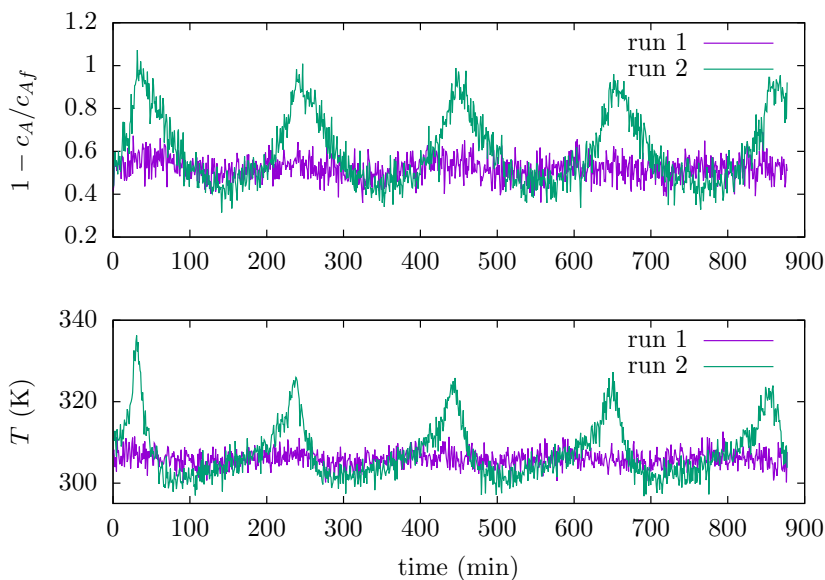


Figure 2: Two runs of Reactor 2 with approximately the same starting conditions. Top: scaled reactor A concentration (conversion) versus time. Bottom: reactor temperature versus time.

To get some quantitative idea of how much variation is occurring, you perform a long reactor run in which you vary the reactor residence time from 10 to 90 min, allowing the reactor to reach steady state after each change. You collect the reactor temperature measurements shown in Figure 1. Note that this older reactor does not have an online composition measurement. Your boss looks at these data and says, “Run the experiment again; something is wrong. How can the temperature be 305 K after  $t = 500$  min when the residence time is 40 min, and then almost 400 K after  $t = 1600$  min when the residence time is again 40 min?”

- Write down the mass and energy balances you would use to understand this reactor behavior. What is the minimum number of model parameters you need to estimate from data? Combine as many parameters as possible.
- Make a plot of steady-state  $T$  and  $x_A = 1 - c_A/c_{Af}$  (even though  $c_A$  wasn't measured) versus  $\tau$  for this reactor.
- How do you explain to your boss what is going on? Realize that, unlike you, he probably doesn't want to hear about a lot of math.

After your success on this project, word gets around, and you are called in to help with a different part of the plant. Your boss's boss tells you, “Look these reactors are all running simple addition reactions, but with this particular reaction chemistry, we see the following data for two consecutive start ups of the reactor. The residence time was about 70 min and we filled the reactor with half feed and half solvent and heated it to 308 K.” He shows you Figure 2; note

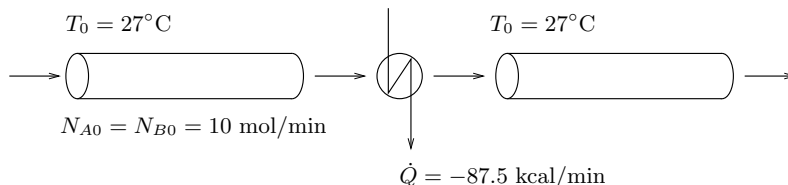


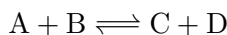
Figure 3: Tubular Reactors with Interstage Cooling.

that this newer reactor does have an online composition measurement. The big boss continues, “You’re a college hot-shot, how can the reactor operation change so drastically when we are basically trying to start it up the same way each time?” One of the other junior engineers at the meeting, who graduated from a different Big 10 school, helpfully replies, “That’s not unusual. Identical starting procedures often lead to quite different results. It’s called multiplicity of dynamic behavior. I had a class in it at Big Tech U.”

- (d) Do you agree with the concept of “multiplicity of dynamic behavior” as an explanation of Figure 2? Why or why not?
- (e) Using the same model form that you constructed for the previous problem, how can you explain that similar startup policies lead to different results in Figure 2?
- (f) Draw a sketch of  $1 - c_A/c_{Af}$  vs.  $T$  for runs 1 and 2 in a phase plane diagram, and explain the outcomes of runs 1 and 2 with your diagram.

### Exercise 3. Nonisothermal plug-flow reactor. 50 points.

The reaction



is carried out adiabatically in a series of tubular reactors with interstage cooling as shown in Figure 3. The feed is equimolar in A and B and enters each reactor at  $27^\circ\text{C}$ . The heat removed between the reactors is  $-87.5$  kcal/min.

- (a) What is the outlet temperature of the first reactor?
- (b) What is the conversion of A at the outlet of the first reactor?
- (c) Is the first reactor close to equilibrium at the exit?

State any assumptions that you make while solving the problem.

$$\text{Data: } \Delta H_R = -30 \text{ kcal/mol} \quad C_p = 25 \text{ cal/mol}\cdot\text{K} \quad K = 5.0 \times 10^5 \text{ at } 50^\circ\text{C}$$

$$N_{A0} = N_{B0} = 10 \text{ mol/min} \quad \dot{Q} = -87.5 \text{ kcal/min}$$