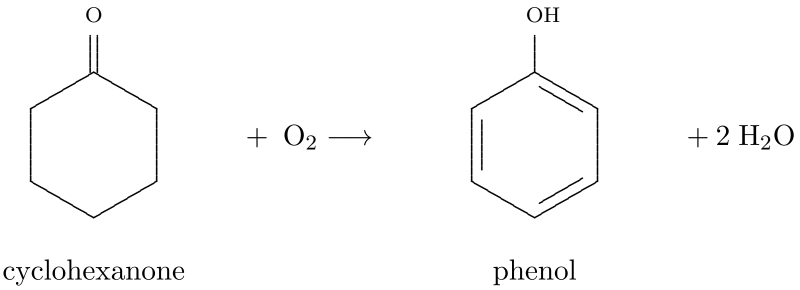
CBE 430 Exam 3 April 19, 2016

NAME: ____

Instructions: The exam is open book and notes. **Work Exercise 1 and either Exercise 2 or 3.** Write all answers on separate paper. Do not write any answers on the exam itself. Hand in your exam as well as your solution at the end. Make sure your name is on your solution and your exam.

Exercise 1. Catalytic reaction mechanism. 50 points.

You have been continuing studies on the following reaction and have noticed limitations in the previously given rate expression

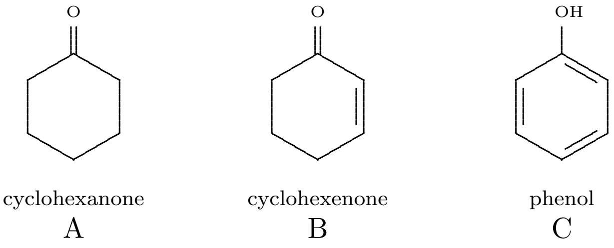


or

$$\mathrm{A} + \mathrm{O_2} \xrightarrow{k} \mathrm{C} + 2\mathrm{H_2O} \qquad r = k c_{\mathrm{A}} c_{\mathrm{O_2}}$$

Your chemist colleague does some experiments and comes up with the following mechanism consisting of six reactions involving two different types of catalyst sites S and S*

$$\begin{aligned}
\mathrm{A{\cdot}S} + \mathrm{O{\cdot}S^*} &\underset{k_{-1}}{\overset{k1}{\rightleftharpoons}} \mathrm{B{\cdot}S} + \mathrm{H_2O{\cdot}S^*}\\
\mathrm{B{\cdot}S} + \mathrm{O{\cdot}S^*} &\xrightarrow{k_2} \mathrm{C{\cdot}S} + \mathrm{H_2O{\cdot}S^*}\\
\mathrm{A} + \mathrm{S} &\overset{K_3}{\rightleftharpoons} \mathrm{A{\cdot}S}\\
\mathrm{O_2} + 2\mathrm{S^*} &\overset{K_4}{\rightleftharpoons} 2\,\mathrm{O{\cdot}S^*}\\
\mathrm{C} + \mathrm{S} &\overset{K_5}{\rightleftharpoons} \mathrm{C{\cdot}S}\\
\mathrm{H_2O} + \mathrm{S^*} &\overset{K_6}{\rightleftharpoons} \mathrm{H_2O{\cdot}S^*}
\end{aligned}$$



We make the following assumptions

1. Reaction 2 is irreversible.
2. All adsorption/desorption reactions are in equilibrium.
3. Species B·S is a highly-reactive intermediate and the QSSA can be used.

4. A, B, and C adsorb on surface sites S due to their large molecular sizes.
5. O_2 and H_2O 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}, $c_{\mathrm{O_2}}$, $c_{\mathrm{H_2O}}$, 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.

Solution. We have for the adsorption reactions at equilibrium

$$c_{\mathrm{AS}} = K_3 c_A c_v \qquad c_{\mathrm{CS}} = K_5 c_C c_v$$
$$c_{\mathrm{OS^*}} = \sqrt{K_4 c_{\mathrm{O_2}}}\, c_{v^*} \qquad c_{\mathrm{H_2OS^*}} = K_6 c_{\mathrm{H_2O}} c_{v^*}$$

The QSSA assumption on species B·S gives

$$R_{\mathrm{BS}} = 0 = k_1 c_{\mathrm{AS}} c_{\mathrm{OS^*}} - k_{-1} c_{\mathrm{BS}} c_{\mathrm{H_20S^*}} - k_2 c_{\mathrm{BS}} c_{\mathrm{OS^*}}$$
$$c_{\mathrm{BS}} = \frac{k_1 c_{\mathrm{AS}} c_{\mathrm{OS^*}}}{k_{-1} c_{\mathrm{H_2OS^*}} + k_2 c_{\mathrm{OS^*}}}$$

The site balance for site type S gives

$$c_{m^*} = c_{v^*} + c_{\mathrm{OS^*}} + c_{\mathrm{H_2OS^*}}$$
$$c_{m^*} = c_{v^*} + \sqrt{K_4 c_{\mathrm{O_2}}}\, c_{v^*} + K_6 c_{\mathrm{H_2O}} c_{v^*}$$
$$c_{m^*} = c_{v^*}\big(1 + \sqrt{K_4 c_{\mathrm{O_2}}} + K_6 c_{\mathrm{H_2O}}\big)$$
$$c_{v^*} = \frac{c_{m^*}}{1 + \sqrt{K_4 c_{\mathrm{O_2}}} + K_6 c_{\mathrm{H_2O}}}$$

The site balance for site type S^*, and assuming B·S is a QSS species gives

$$c_m = c_v + c_{\mathrm{AS}} + c_{\mathrm{BS}} + c_{\mathrm{CS}}$$
$$c_m \approx c_v + K_3 c_A c_v + K_5 c_C c_v$$
$$c_m = c_v\big(1 + K_3 c_A + K_5 c_C\big)$$
$$c_v = \frac{c_m}{1 + K_3 c_A + K_5 c_C}$$

Phenyl groups are produced only in the second reaction. The fifth reaction is simply transferring them from one phase to another. Therefore production rate of phenyl is the rate r_2, which is given by

$$r_2 = k_2 c_{\mathrm{BS}} c_{\mathrm{OS^*}}$$
$$r_2 = \frac{k_2 k_1 c_{\mathrm{AS}} c_{\mathrm{OS^*}}^2}{k_{-1} c_{\mathrm{H_2OS^*}} + k_2 c_{\mathrm{OS^*}}}$$
$$r_2 = \frac{k_2 k_1 K_3 c_{\mathrm{A}} K_4 c_{\mathrm{O_2}}}{k_{-1} K_6 c_{\mathrm{H_2O}} + k_2 \sqrt{K_4 c_{\mathrm{O_2}}}} \frac{c_v c_{v^*}^2}{c_{v^*}}$$
$$r_2 = \left(\frac{k_2 k_1 K_3 K_4 c_{\mathrm{A}} c_{\mathrm{O_2}}}{k_{-1} K_6 c_{\mathrm{H_2O}} + k_2 \sqrt{K_4 c_{\mathrm{O_2}}}}\right)\left(\frac{c_m}{1 + K_3 c_A + K_5 c_C}\right)\left(\frac{c_{m^*}}{1 + \sqrt{K_4 c_{\mathrm{O_2}}} + K_6 c_{\mathrm{H_2O}}}\right)$$

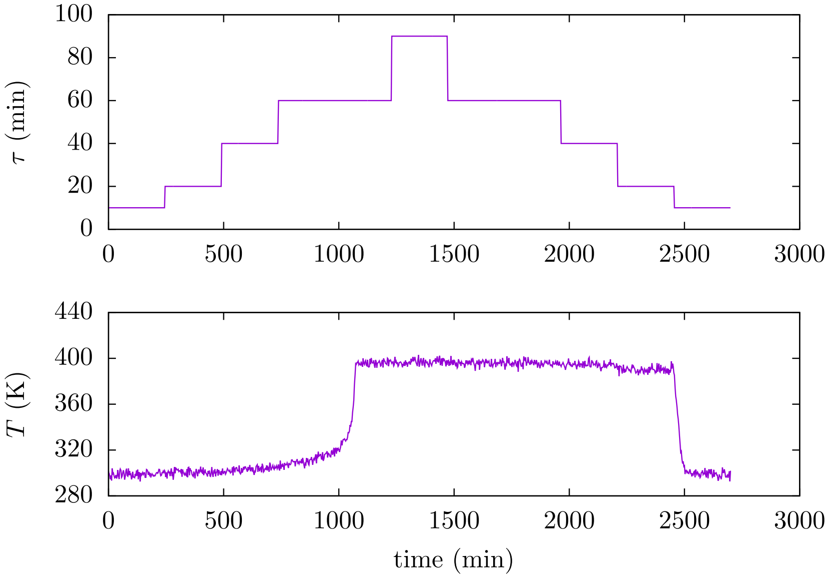


Figure 1: Run of Reactor 1 with changing residence time. Top: reactor residence time versus time. Bottom: reactor temperature versus time.

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Exercise 2. Deus ex machina. 50 points.

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

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

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."

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?"

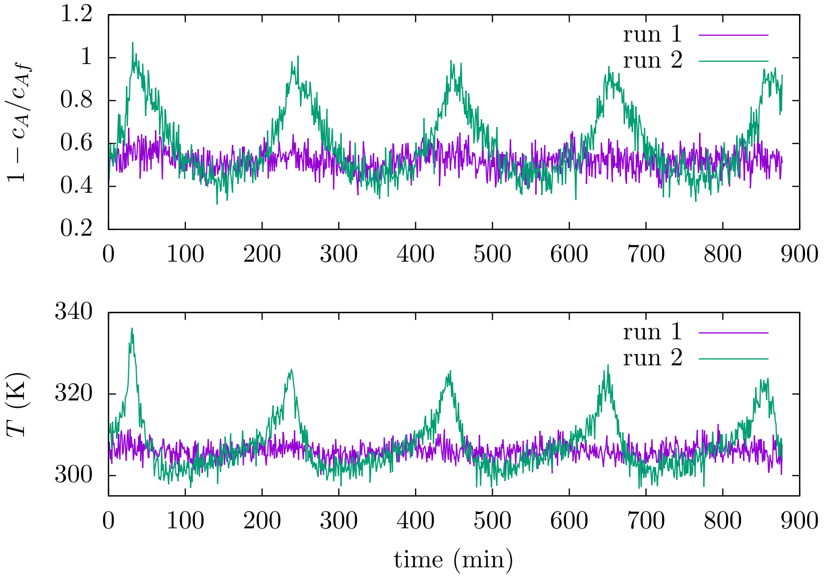

Figure 2: Two runs of Reactor 2 with approximately the same starting conditions. Top: scaled reactor A concentration (conversion) versus time. Bottom: reactor temperature versus time.

(a) Write down the mass and energy balances would you 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.

(b) Make a plot of steady-state T and $x_A = 1 - c_A/c_{Af}$ (even though c_A wasn't measured) versus τ for this reactor.

(c) 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 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 polices 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.

Solution.

(a) Given the large excess of reactant B, it makes sense to absorb its concentration into the rate constant and assume first-order, irreversible kinetics, so an appropriate starting point is

$$\frac{dc_A}{dt} = \frac{c_{Af} - c_A}{\tau} - k_0 e^{-E/T} c_A \tag{1}$$

$$\frac{dT}{dt} = \frac{T_f - T}{\tau} - \frac{\Delta H_R}{C_{Ps}} k_0 e^{-E/T} c_A \tag{2}$$

We have six parameters:

$$c_{Af} \quad T_f \quad \tau \quad k_0 \quad E \quad \Delta H_R/C_{Ps}$$

(b) The steady-state solution for the parameter values that generated the data are given in Figure 3.

(c) Since the mass and energy balances are nonlinear, the data shown can be explained by a simple steady-state multiplicity. As shown in Figure 3 there is an ignition point at about $\tau = 50$ min, which is shown in the operating run at about $t = 1000$ min. Then there is an extinction point at $\tau = 15$ min, which is shown at $t = 2500$ min.

(d) There is no such thing as multiplicity of *dynamic* behavior. The solution to initial value problems is generally unique for the right-hand sides like those given in our mass and energy balances (Lipschitz continuous functions).

(e) The model can also produce sustained oscillations or limit cycles. Some initial conditions are attracted to the limit cycle. Nearby initial conditions may be attracted to a steady state instead. That would explain the run-to-run differences shown in the operating data.

(f) Removing the measurement noise, the phase plane for the value of $\tau = 73.1$ min is shown in Figure 4. Note that run 1 is in the region of attraction of the stable steady state. But run 2 is in the region of attraction of the stable limit cycle; this explains their different transient behaviors. It may appear that "identical" starting conditions lead to quite different solutions, but that is not what is really happening. You just happen to be starting the reactor close to the boundary.

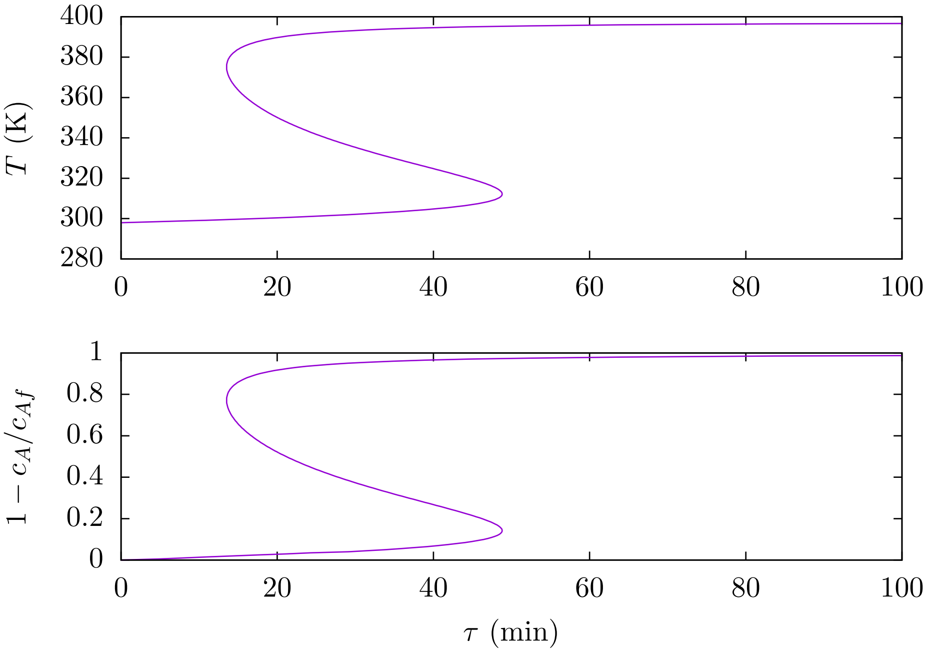

Figure 3: Steady-state solution versus reactor residence time. Note that there are three steady states for residence time in the interval $15 \leq \tau \leq 50$.

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

The reaction

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

is carried out adiabatically in a series of tubular reactors with interstage cooling as shown in Figure 5. The feed is equimolar in A and B and enters each reactor at 27°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.

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

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

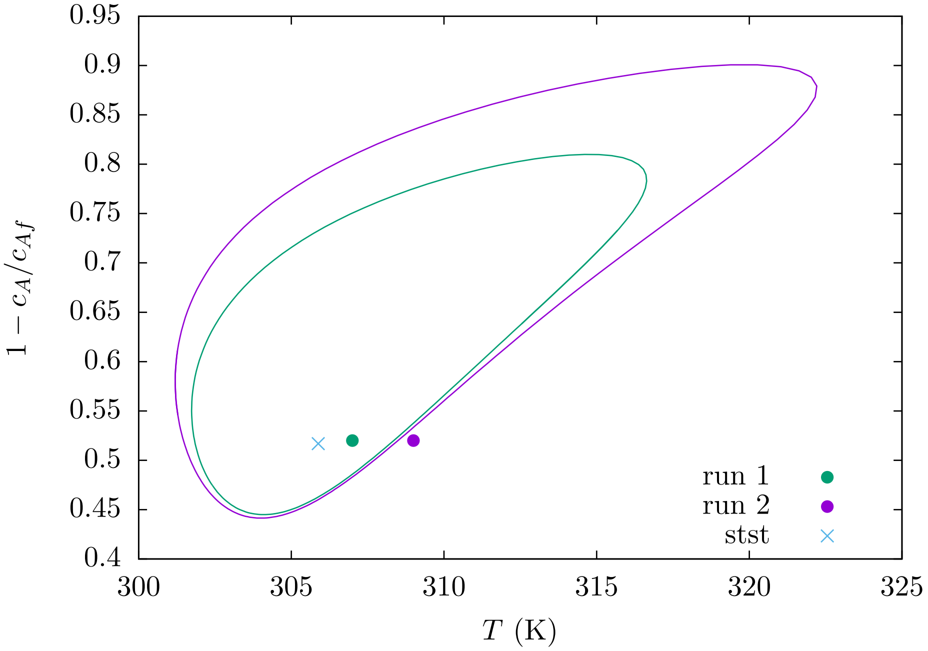

Figure 4: The x_A, T phase plane. The outer limit cycle is stable; the inner limit cycle is unstable; the steady state is also stable. Initial conditions inside the unstable limit cycle (run 1) are attracted to the stable steady state. Initial conditions outside the unstable limit cycle (run 2) are attracted to the stable limit cycle.

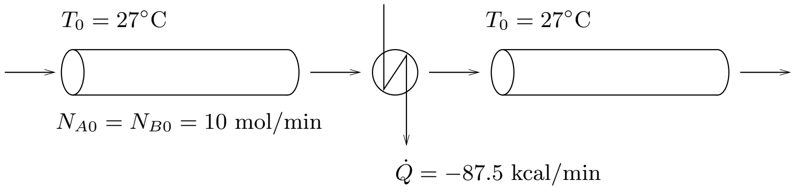

Figure 5: Tubular Reactors with Interstage Cooling.

Solution.

(a) Given the heat removed, we can find the temperature of the stream entering the heat exchanger

$$\begin{aligned}
\Delta T &= \frac{\dot{Q}}{N_T C_P} = \frac{-87.5 \times 10^3}{(20)(25)} = -175^\circ\text{C} \\
\Delta T &= T_0 - T_1 \\
T_1 &= 27 + 175^\circ\text{C} = 202^\circ\text{C}
\end{aligned}$$

(b) From the first reactor outlet temperature we can find the molar outflow because the reactor is adiabatic. We have

$$\begin{aligned}
\frac{dN_A}{dV} &= -r \\
N_T C_P \frac{dT}{dV} &= -\Delta H_R r
\end{aligned}$$

Equating these allows us to deduce

$$\begin{aligned}
N_T C_P dT &= \Delta H_R dN_A \\
N_{A1} - N_{A0} &= \frac{N_T C_P}{\Delta H_R}(T_1 - T_0) \\
N_{A1} - N_{A0} &= \frac{(20)(25)}{-30 \times 10^3}(175) = -2.92 \text{ mol/min}
\end{aligned}$$

From this change in N_A we find the conversion for the first tubular reactor

$$x_{A1} = \frac{N_{A0} - N_{A1}}{N_{A0}} = 0.292$$

(c) If we assume an ideal solution, we have

$$K = \frac{a_C a_D}{a_A a_B} = \frac{c_C c_D}{c_A c_B} = \frac{N_C N_D}{N_A N_B}$$

From the stoichiometry and feed condition, we know

$$N_B = N_A \qquad N_C = N_D = N_{A0} - N_A$$

So we have

$$K = \frac{N_C N_D}{N_A N_B} = \frac{(N_{A0} - N_A)^2}{N_A^2}$$

Let $x = N_{A0}/N_A$ and we have

$$K = (x-1)^2 \qquad x^2 - 2x + (1-K) = 0$$

The solution is

$$x = 1 + \sqrt{K} \qquad x_A = 1 - 1/x = \frac{\sqrt{K}}{1+\sqrt{K}}$$

If we use the van 't Hoff equation to evaluate the equilibrium constant, which assumes ΔH_R is independent of temperature, we have

$$\begin{aligned}
\ln(K_2/K_1) &= \frac{-\Delta H_R}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \\
\ln(K_2/K_1) &= \frac{30 \times 10^3}{1.987}\left(\frac{1}{202+273} - \frac{1}{50+273}\right) \\
\ln(K_2/K_1) &= -14.96 \\
K_2 &= K_1 e^{-14.96} = 5 \times 10^5 e^{-14.96} = 0.16
\end{aligned}$$

Substituting this value into the conversion equation gives

$$x_{A1,\text{eq}} = \frac{\sqrt{0.16}}{1+\sqrt{0.16}} = 0.29$$

So, yes, the first tubular reactor is near equilibrium by the exit.

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