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Instructions: The exam is closed book and closed notes. 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. Gas-phase reaction in a PFR. 35 points.

I told you in class that I was required by law to ask an exam question of this type, so here goes. The following elementary, gas-phase reaction takes place in a PFR.

$$2A \longrightarrow B$$

The reactor is fed with a mixture of of reactant A and inert diluent I at feedrates N_{Af} and N_{If} at total molar concentration c_f. The feed conditions and rate constant are

$$c_f = 0.2\,\text{mol/L} \qquad N_{Af} = 2.0\,\text{mol/min} \qquad N_{If}/N_{Af} = 3 \qquad k = 20.0\,\text{L/mol}\cdot\text{min}$$

The pressure and temperature are constant in the PFR, and the gas may be assumed to behave as an ideal-gas mixture.

(a) Write a balance for the steady-state molar flow of A, N_A. Make sure that your right-hand side is a function of only N_A and known parameters. What is the initial condition for this differential equation?

(b) What reactor size is required to achieve 85 percent conversion?

(c) What happens to this reactor size if you

    1. Double the rate constant k?
    2. Double the feed flows N_{Af} and N_{If}, but keep feed concentration constant?
    3. Double the feed concentration, but keep the feed flows constant?

Solution.

(a) The steady-state PFR mass balances for the species are

$$\frac{d}{dV}N_A = R_A = -2r \qquad \frac{d}{dV}N_B = R_B = r \qquad \frac{d}{dV}N_I = R_I = 0 \qquad r = kc_A^2$$

    We obtain c_A from N_A by $c_A = N_A/Q$ and Q from $Q = c/N$ where $N = N_A + N_B + N_I$. The ideal-gas law gives $c = P/RT$, and since P and T are constant, $c = c_f$. Assembling these pieces gives

$$c_A = \frac{N_A}{N_A + N_B + N_I}c_f$$

Now we use the mass balances to eliminate N_B and N_I from this expression so that we have only one ODE to solve. From the mass balances

$$\dot{N}_A + 2\dot{N}_B = 0 \qquad N_B = (1/2)(2N_{Bf} + N_{Af} - N_A)$$
$$\dot{N}_I = 0 \qquad N_I = N_{If}$$

This gives for the total molar flow

$$N_A + N_B + N_I = (1/2)(N_{Af} + N_A) + N_{If}$$

Substituting into the mass balance for A gives

$$\frac{d}{dV}N_A = -8kc_f^2 \left(\frac{N_A}{N_A + (N_{Af} + 2N_{If})} \right)^2$$

Let $\alpha = N_{If}/N_{Af}$ and we have

$$\frac{d}{dV}N_A = -8kc_f^2 \left(\frac{N_A}{N_A + N_{Af}(1 + 2\alpha)} \right)^2$$
$$N_A(0) = N_{Af}$$

(b) It is convenient to let $N = N_A/N_{Af}$; then we separate and integrate this differential equation

$$\left(1 + (1 + 2\alpha)\frac{1}{N} \right)^2 dN = -8\frac{k}{N_{Af}}c_f^2 dV$$

$$\int_1^{1-x} \left(1 + 2(2 + \alpha)\frac{1}{N} + (1 + 2\alpha)^2 \frac{1}{N^2} \right) dN = -8\frac{k}{N_{Af}}c_f^2 \int_0^V dV$$

$$(1 - x - 1) + 2(1 + 2\alpha)\ln(1 - x) - (1 + 2\alpha)^2(\frac{1}{1 - x} - 1) = -8\frac{k}{N_{Af}}c_f^2 V$$

$$-x + 2(1 + 2\alpha)\ln(1 - x) - (1 + 2\alpha)^2\frac{x}{1 - x} = -8\frac{k}{N_{Af}}c_f^2 V$$

Rearranging the last expression gives

$$V = \frac{1}{8}\frac{N_{Af}}{kc_f^2} \left(x - 2(1 + 2\alpha)\ln(1 - x) + (1 + 2\alpha)^2\frac{x}{1 - x} \right)$$
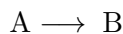
Putting in the parameter values gives

$$V = 95.3\,\text{L}$$

(c)   1. Reactor size is halved

      2. Reactor size is doubled

      3. Reactor size decreases by factor of four

$\square$

Exercise 2. PFR and CSTR sizing. 35 points.

Even for a simple stoichiometry like

$$A \longrightarrow B$$

depending on the mechanism, we derived a reaction rate expression in Chapter 5 as complex as

$$r = \frac{kc_A}{(1 + Kc_A)^2}$$

(a) What are the units of k and K? Draw a sketch of $r(c_A)$ as a function of c_A. Show what happens at both low c_A concentration and high c_A concentration.

(b) Draw a sketch of $1/r(c_A)$ as a function of c_A. Find the minimum of $1/r(c_A)$. Draw this point also on your sketch.

(c) Assume we run this reaction in liquid phase in a CSTR and also in a PFR.

To achieve a conversion of A of 50 percent, and with the following parameter values, which reactor has more volume, the CSTR or the PFR?

$$c_{Af} = 1.4 \, \text{mol/L} \qquad K = 2.0 \, \text{L/mol}$$

Justify your answer. You might find your sketch of $1/r(c_A)$ in the previous part useful.

(d) To achieve the same 50 percent conversion of A and with the following parameter values, which reactor has more volume, the CSTR or the PFR?

$$c_{Af} = 0.6 \, \text{mol/L} \qquad K = 1.0 \, \text{L/mol}$$

Justify your answer. You might find your sketch of $1/r(c_A)$ in the previous part useful.

Solution.

(a) The units of k are inverse time.

The units of K are inverse concentration.

The function $r(c_A)$ is approximately kc_A at small c_A concentration (increasing) and $(k/K)(1/c_A)$ at large c_A concentration (decreasing).

(b) Now we have that inverse rate is decreasing at small concentration and increasing at large concentration

$$\frac{1}{r(c_A)} = \frac{1}{kc_A} + 2(K/k) + \frac{K^2}{k}c_A$$
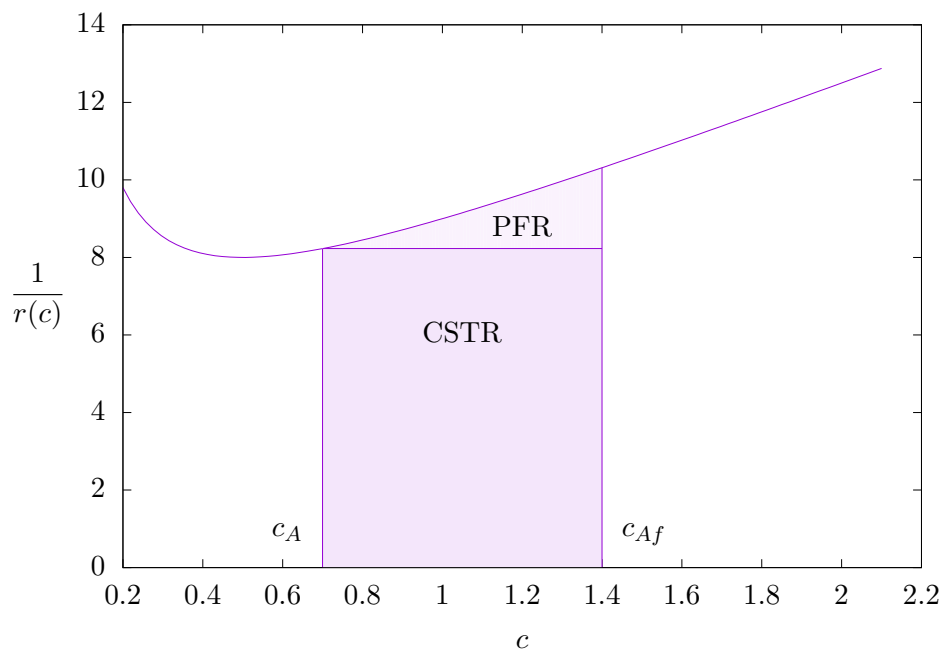
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Figure 1: Sizes of CSTR and PFR for the inhibition side of the maximum rate.

Taking the derivative, setting to zero and solving gives

$$\frac{d}{dc_A}\frac{1}{r(c_A)} = -\frac{1}{kc_A^2} + \frac{K^2}{k} = 0$$
$$c_A^0 = 1/K$$

(c) In this case, $c_{Af} = 1.4$, $c_A = 0.7$, and both are greater than $c_A^0 = 1/2$. From the sketch shown in Figure 1, when c_{Af} and c_A are to the right of c_A^0, the inverse reaction rate is increasing with c_A. In such cases, the CSTR is smaller than the PFR.

(d) In this case, $c_{Af} = 0.6$ and $c_A = 0.3$, and both are less than $c_A^0 = 1$. From Figure 2, when c_{Af} and c_A are to the left of c_{A0}, the inverse reaction rate is decreasing with c_A. In such cases the PFR is smaller than the CSTR.

□

Exercise 3. Rate expression from mechanism. 30 points.

A proposed mechanism for catalytic CO oxidation
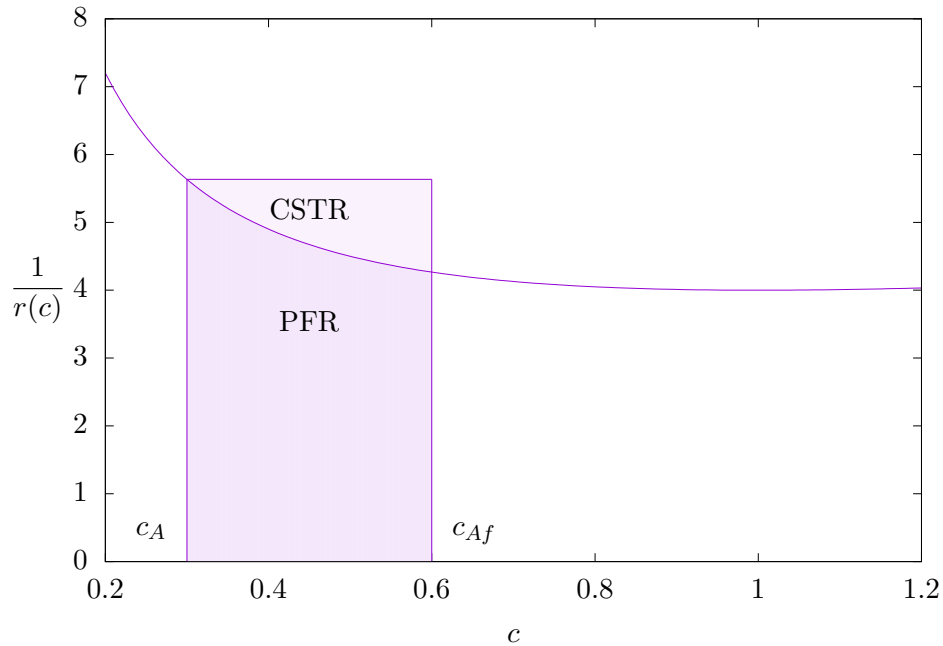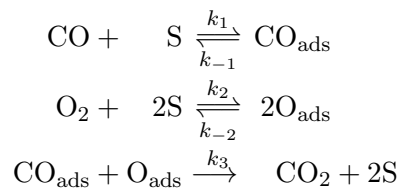
$$2CO + O_2 \longrightarrow 2CO_2$$
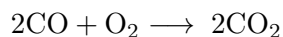
Figure 2: Sizes of CSTR and PFR for the increasing reaction rate (decreasing inverse rate) side of the maximum rate.

consists of the following steps: associative adsorption of CO, dissociative adsorption of O_2, and the bimolecular surface reaction

$$CO + \quad S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CO_{ads}$$

$$O_2 + \quad 2S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2O_{ads}$$

$$CO_{ads} + O_{ads} \overset{k_3}{\longrightarrow} \quad CO_2 + 2S$$

Assume the O_2 and CO adsorption steps are at equilibrium and the surface reaction step is slow and irreversible.

(a) Find the surface concentrations $\bar{c}_{CO}$ and $\bar{c}_{O}$ as a function of the gas-phase concentrations.

(b) Given these surface concentrations find the production rate of CO_2 in terms of gas-phase concentrations.

(c) Make a log-log plot of the production rate of CO_2 versus gas-phase CO concentration at constant gas-phase O_2 concentration. What are the slopes of the production rate at high and low CO concentrations?

Solution.

(a) At equilibrium the net rates of the two reactions are zero (adsorption rate equals desorption rate)

$$r_1 = 0 = k_1 c_{CO} \bar{c}_v - k_{-1} \bar{c}_{CO}$$
$$r_2 = 0 = k_2 c_{O_2} \bar{c}_v^2 - k_{-2} \bar{c}_O^2$$

Solving for the surface coverages in terms of the concentration of vacant sites gives

$$\bar{c}_{CO} = K_1 c_{CO} \bar{c}_v$$
$$\bar{c}_O = \sqrt{K_2 c_{O_2}} \bar{c}_v$$

The remaining unknown is $\bar{c}_v$, which can be found using the site balance

$$\bar{c}_m = \bar{c}_v + \bar{c}_{CO} + \bar{c}_O$$

Combining these gives

$$\bar{c}_v = \frac{\bar{c}_m}{1 + K_1 c_{CO} + \sqrt{K_2 c_{O_2}}}$$

and

$$\bar{c}_{CO} = \frac{\bar{c}_m K_1 c_{CO}}{1 + K_1 c_{CO} + \sqrt{K_2 c_{O_2}}}$$
$$\bar{c}_O = \frac{\bar{c}_m \sqrt{K_2 c_{O_2}}}{1 + K_1 c_{CO} + \sqrt{K_2 c_{O_2}}}$$

(b) The production rate of CO_2 is given by

$$R_{CO_2} = k_3 \bar{c}_{CO} \bar{c}_O$$

Substituting the surface concentrations gives the rate of CO_2 production

$$R_{CO_2} = \frac{k_3 \bar{c}_m^2 K_1 c_{CO} \sqrt{K_2 c_{O_2}}}{\left(1 + K_1 c_{CO} + \sqrt{K_2 c_{O_2}}\right)^2}$$

(c) The log-log plot of R_{CO_2} versus c_{CO} has a slope of $+1$ at low c_A and -1 at high c_A.

$\square$