

Part I.

Problem 1. Packed-Bed Reactors. 25 pts.

A second order catalytic reaction



is carried out in an isothermal packed-bed reactor containing spherical catalyst pellets. The exit conversion is 85%. The reactant and product are gases. What happens to the required bed length to achieve 85% conversion if the feed pressure is doubled and the feed volumetric flowrate is held constant? You may assume that the flowrate is small enough that the pressure drop across the bed is unimportant. Consider the following two cases.

- (a) What is the new required bed length if the overall pellet reaction rate is controlled by the intrinsic reaction rate?

The material balance for component A in the fluid is

$$\frac{dN_A}{dV} = R_A$$

The production rate per volume of fluid is given by the production rate per volume of pellet times the bed density

$$R_A = (1 - \epsilon_B) \tilde{R}_{Ap}$$

Finally, the production rate per volume of pellet can be expressed as the rate at exterior conditions (assumed equal to fluid conditions, i.e. large mass transfer coefficient) times the pellet effectiveness factor

$$\frac{dN_A}{dV} = -(1 - \epsilon_B) \eta k c_A^2 \quad (1)$$

For this problem, we assume P and T are constant, and since the moles are conserved, $Q = Q_f$ is also constant and $c_A = N_A/Q$. The fluid mass balance is therefore

$$\frac{dN_A}{dV} = -k' \eta k N_A^2$$

in which $k' = k(1 - \epsilon_B)/Q_f^2$. For the reaction controlled case, $\eta = 1$, and solving the mass balance gives

$$\begin{aligned} \frac{N_A}{N_{Af}} &= \frac{1}{1 + k' N_{Af} V_R} \\ x_A &= \frac{k' N_{Af} V_R}{1 + k' N_{Af} V_R} \\ V_R &= \frac{1}{k' N_{Af}} \left(\frac{x_A}{1 - x_A} \right) \end{aligned}$$

Doubling P_f and keeping Q_f constant doubles N_{Af} . Therefore V_R is cut in half.

- (b) What is the new required bed length if the overall pellet reaction rate is controlled by the pellet diffusion rate?

For the diffusion controlled case, $\eta = 1/\Phi$. Substituting in the value of the Thiele modulus for a second-order reaction ($n = 2$) gives

$$\eta = \alpha c_A^{-1/2} \quad \alpha = \left(\frac{R}{3}\right)^{-1} \left[\frac{3}{2} \frac{k}{D_e}\right]^{-1/2}$$

Substituting this relation into Equation 1 produces

$$\frac{dN_A}{dV} = -\beta N_A^{3/2} \quad \beta = k(1 - \epsilon_B)\alpha/Q_f^{3/2}$$

Solving this mass balances produces

$$\begin{aligned} \frac{N_A}{N_{Af}} &= \frac{1}{(1 + \beta V_R \sqrt{N_{Af}}/2)^2} \\ x_A &= \frac{(1 + \beta V_R \sqrt{N_{Af}})^2 - 1}{(1 + \beta V_R \sqrt{N_{Af}})^2} \\ V_R &= \frac{1}{\beta \sqrt{N_{Af}}} \left(\sqrt{1/(1 - x_A)} - 1 \right) \end{aligned}$$

Doubling P_f and keeping Q_f constant doubles N_{Af} . Therefore V_R decrease by factor $1/\sqrt{2} = 0.707$.

You may assume the entire bed length is either in the intrinsic reaction rate or pellet diffusion rate limited regimes and that the external mass transfer resistance between the fluid and the solid catalyst is negligible.

Additional Data: The Thiele modulus is defined as:

$$\Phi = \frac{R}{3} \left[\frac{n+1}{2} \frac{k c_s^{n-1}}{D_e} \right]^{1/2}$$

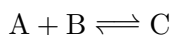
in which c_s is the outer pellet surface concentration and k is the intrinsic rate constant on a per volume of catalyst basis.

The effectiveness factor for positive order reactions in a sphere can be approximated by

$$\eta = \frac{1}{\Phi} \left[\frac{1}{\tanh 3\Phi} - \frac{1}{3\Phi} \right]$$

Problem 2. Surface reactions. 25 pts.

Consider the overall reaction:



A possible catalyst material contains two different types of reactive sites, X and Y. Both A and B adsorb on X and Y, but the reaction proceeds only if A adsorbs on X and B on Y. This reaction is described by the following mechanism:



- (a) What is the production rate of C if Reaction 5 is irreversible and Reactions 1–4 reach equilibrium? Hint: you can assume you know the monolayer coverage amounts of both the X and Y available sites, \bar{c}_{mX} , \bar{c}_{mY} .

If Reactions 1–4 are at equilibrium, we have

$$\bar{c}_{AX} = K_1 c_A \bar{c}_X \quad \bar{c}_{AY} = K_2 c_A \bar{c}_Y \quad \bar{c}_{BX} = K_3 c_B \bar{c}_X \quad \bar{c}_{BY} = K_4 c_B \bar{c}_Y \quad (7)$$

Site balances for both X and Y sites give

$$\bar{c}_{mX} = \bar{c}_{AX} + \bar{c}_{BX} + \bar{c}_X \quad \bar{c}_{mY} = \bar{c}_{AY} + \bar{c}_{BY} + \bar{c}_Y \quad (8)$$

Substituting Equations 7 into Equations 8 and solving for the vacant sites of type X and Y gives

$$\bar{c}_X = \frac{\bar{c}_{mX}}{1 + K_1 c_A + K_3 c_B} \quad \bar{c}_Y = \frac{\bar{c}_{mY}}{1 + K_2 c_A + K_4 c_B} \quad (9)$$

The production rate of C is then given by

$$R_C = r_5 = k_5 \bar{c}_{AX} \bar{c}_{BY}$$

Substituting Equations 7 and 8 into this relation gives

$$R_C = k_5 \left[\frac{K_1 c_A \bar{c}_{mX}}{1 + K_1 c_A + K_3 c_B} \right] \left[\frac{K_4 c_B \bar{c}_{mY}}{1 + K_2 c_A + K_4 c_B} \right]$$

- (b) If the equilibrium constants for Reactions 1–4 are of the same order of magnitude, what happens to the production rate of C if very large or very small ratios of A to B are feed to the reactor? Why?

From Equation 2a

$$c_A \gg c_B \quad R_C = k_5 \bar{c}_{mX} \frac{K_4 c_B \bar{c}_{mY}}{K_2 c_A} \quad \text{Inverse order in A, first order in B}$$

$$c_B \gg c_A \quad R_C = k_5 \bar{c}_{mY} \frac{K_1 c_A \bar{c}_{mX}}{K_3 c_B} \quad \text{Inverse order in B, first order in A}$$

- (c) Two sets of experiments were performed to determine kinetic information for the overall reaction. These experiments were performed under the conditions that $K_1 c_A$, $K_2 c_A$, $K_3 c_B$, and $K_4 c_B \ll 1$. The effective rate constant for the production of C, k_{eff} was measured at various temperatures and the plots in Figure 1 were developed. Does this catalyst material promote or inhibit the production rate? Why do you think so?

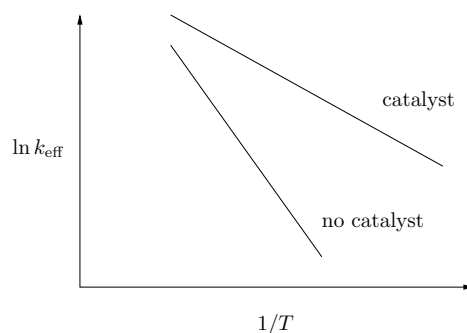


Figure 1: Effective rate constant versus inverse temperature.

The catalyst promotes the reaction. The activation energy of the rate process is smaller with the catalyst. The catalyst has therefore reduced the barrier height for reaction leading to promoting the reaction.

Part II.

Problem 3. Pulse response of a mixing model. 20 pts.

Consider the mixing model depicted below. Suppose that a tracer is injected with the A feed stream with concentration profile given in Figure 2. You may assume that there is no tracer in the reactor up to time $t = 0$. The reactor parameters are given below. Plot the dynamic response of the effluent tracer concentration for $0 \leq t \leq 50$ minutes.

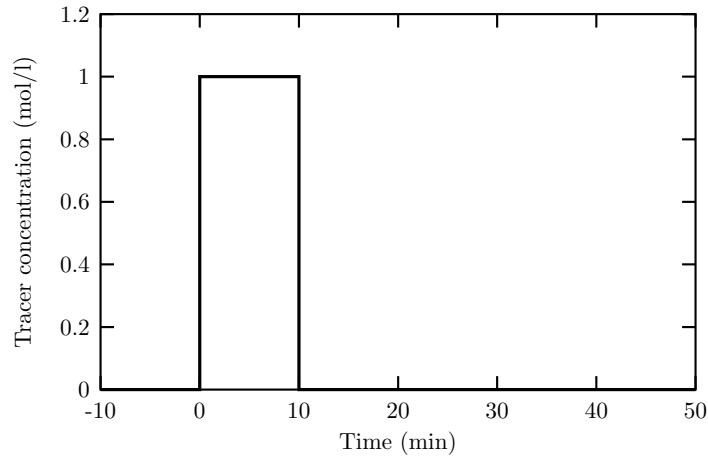
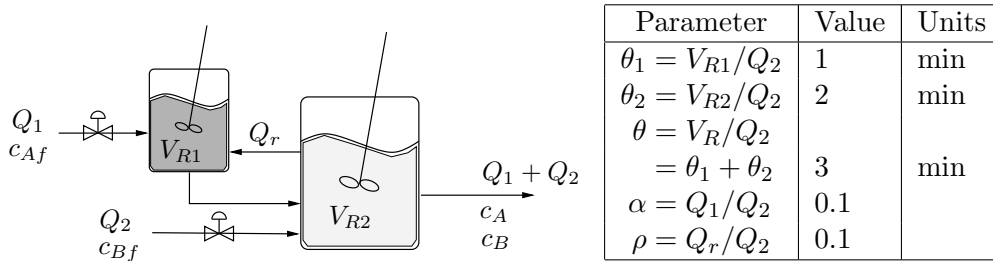


Figure 2: Tracer concentration profile

Assuming constant volume and density, the material balances for the tracer are:

$$\frac{dc_{T1}}{dt} = \frac{1}{\tau_1} (\alpha c_{Tf} - (\alpha + \rho)c_{T1} + \rho c_{A2}) \quad (10)$$

$$\frac{dc_{T2}}{dt} = \frac{1}{\tau_2} ((\alpha + \rho)c_{T1} - \rho c_{T2} - (1 + \alpha)c_{T2}) \quad (11)$$

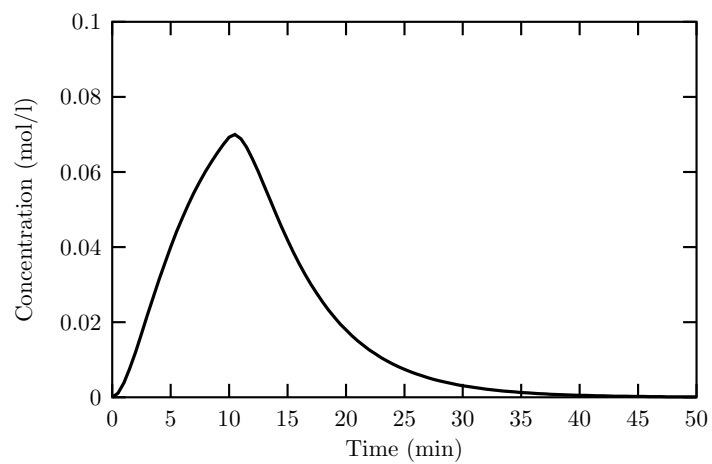
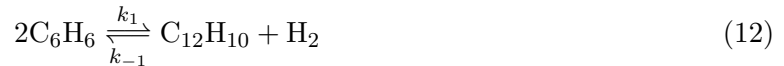


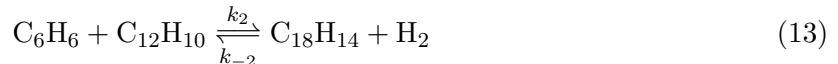
Figure 3: Tracer concentration profile for the effluent stream

Problem 4. Benzene pyrolysis for different reactor configurations. 30 pts.

Hougen and Watson analyzed the rate data for the pyrolysis of benzene by the following two reactions. Diphenyl is produced by the dehydrogenation of benzene,



Triphenyl is formed by the secondary reaction,



The reactions are assumed to be elementary so that the rate expressions are

$$r_1 = k_1 \left(c_B^2 - \frac{c_D c_H}{K_1} \right) \quad r_2 = k_2 \left(c_B c_D - \frac{c_T c_H}{K_2} \right) \quad (14)$$

in which the subscripts, B, D, T and H represent benzene, diphenyl, triphenyl and hydrogen, respectively. We would like to isothermally react benzene at 1033 K and 1.0 atm. The rate and equilibrium constants at $T = 1033$ K and $P = 1.0$ atm are given in Hougen and Watson,

$$\begin{aligned} k_1 &= 7 \times 10^5 \text{ L/mol} \cdot \text{hr} & K_1 &= 0.31 \\ k_2 &= 4 \times 10^5 \text{ L/mol} \cdot \text{hr} & K_2 &= 0.48 \end{aligned}$$

The feed stream is 60 kmol/hr of pure benzene. The value of the gas constant is $R = 82.06 \text{ atm} \cdot \text{cm}^3/\text{mol} \cdot \text{K}$.

- (a) Write down the steady-state material balances for a PFR. Calculate the overall conversion of benzene for an 800 liter PFR.

Assume ideal gas (low pressure, high temperature) and negligible pressure drop across the reactor. First define the species list, A , and the stoichiometric matrix, ν :

$$A = [\text{B} \quad \text{D} \quad \text{T} \quad \text{H}]^T \quad (15)$$

$$\nu = \begin{bmatrix} -2 & 1 & 0 & 1 \\ -1 & -1 & 1 & 1 \end{bmatrix} \quad (16)$$

Defining the molar flow rates N in the same order as the species list, the steady-state material balances for a PFR are:

$$\frac{dN}{dV} = \nu^T r \quad (17)$$

$$r = \begin{bmatrix} k_1 \left(c_B^2 - \frac{c_D c_H}{K_1} \right) \\ k_2 \left(c_B c_D - \frac{c_T c_H}{K_2} \right) \end{bmatrix} \quad (18)$$

$$c_j = \frac{P}{RT} \frac{N_j}{\sum_k N_k} \quad (19)$$

Solving for the effluent of the PFR yields:

$$N_{\text{PFR}} = \begin{bmatrix} 26.553 \\ 11.709 \\ 18.395 \\ 3.343 \end{bmatrix} \frac{\text{kmol}}{\text{hr}} \quad (20)$$

The overall conversion for this reactor configuration is:

$$X = \frac{60 - 26.55}{60} = 0.557 \quad (21)$$

- (b) Write down the steady-state material balances for a CSTR. Calculate the overall conversion of benzene for an 800 liter CSTR.

Same assumptions and notation as in 4a. The CSTR steady-state material balances are:

$$\frac{dN}{dt} = 0 = N_f - N + \nu^T r V_R \quad (22)$$

$$r = \begin{bmatrix} k_1 \left(c_B^2 - \frac{c_D c_H}{K_1} \right) \\ k_2 \left(c_B c_D - \frac{c_T c_H}{K_2} \right) \end{bmatrix} \quad (23)$$

$$c_j = \frac{P}{RT} \frac{N_j}{\sum_k N_k} \quad (24)$$

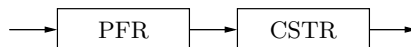
Solving for the effluent of the CSTR yields:

$$N_{\text{CSTR}} = \begin{bmatrix} 32.37 \\ 9.65 \\ 15.21 \\ 2.78 \end{bmatrix} \frac{\text{kmol}}{\text{hr}} \quad (25)$$

The overall conversion for this reactor configuration is:

$$X = \frac{60 - 32.37}{60} = 0.461 \quad (26)$$

- (c) Calculate the overall conversion of benzene for the configuration given below. The volume of each reactor is 400 L.



The feed to the CSTR is the effluent of the PFR. Solving for the effluent of the PFR yields:

$$N_{\text{PFR}} = \begin{bmatrix} 30.07 \\ 12.17 \\ 15.90 \\ 1.86 \end{bmatrix} \frac{\text{kmol}}{\text{hr}} \quad (27)$$

The effluent of the CSTR is then:

$$N_{\text{CSTR}} = \begin{bmatrix} 27.29 \\ 11.68 \\ 17.91 \\ 3.12 \end{bmatrix} \frac{\text{kmol}}{\text{hr}} \quad (28)$$

The overall conversion for this reactor configuration is:

$$X = \frac{60 - 27.29}{60} = 0.545 \quad (29)$$