

Kinetics and Reactor Design HW1

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Due: February 16, 2023

1 Problem Statement

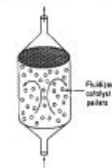
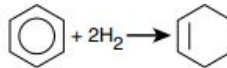
1.1 P4-5_A (c, d)

- (c) For the isothermal, isobaric, catalytic gas-phase oxidation



the feed enters a PBR at 6 atm and 260°C, and is a stoichiometric mixture of only oxygen and ethylene. Set up a stoichiometric table and then write $-r'_A$ as a function of partial pressures. Express the partial pressures and $-r'_A$ as a function of conversion for (1) a fluidized batch reactor and (2) a PBR. Finally, write $-r'_A$ solely as a function of the rate constant and conversion.

- (d) Set up a stoichiometric table for the isothermal, catalytic gas-phase reaction carried out in a fluidized CSTR.



Fluidized CSTR

The feed is stoichiometric and enters at 6 atm and 170°C. What catalyst weight is required to reach 80% conversion in a fluidized CSTR at 170°C and at 270°C? The rate constant is defined with respect to benzene and $v_0 = 50 \text{ dm}^3/\text{min}$.

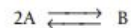
$$k_B = \frac{53 \text{ mol}}{\text{kgcat} \cdot \text{min} \cdot \text{atm}^3} \text{ at } 300 \text{ K with } E = 80 \text{ kJ/mol}$$

First write the rate law in terms of partial pressures and then express the rate law as a function of conversion. Assume $\Delta P = 0$.

Figure 1

1.2 P4-9_B

P4-9_B The elementary reversible reaction



is carried out isothermally in a flow reactor with no pressure drop and where pure A is fed at a concentration of 4.0 mol/dm^3 . If the equilibrium conversion is found to be 60%

- (a) What is the equilibrium constant, K_c , if the reaction occurs in the gas phase?
(b) What is the K_c if the reaction is a liquid-phase reaction?

Figure 2

1.3 P5-8_B

P5-8_B The elementary gas-phase reaction



takes place isobarically and isothermally in a PFR where 63.2% conversion is achieved. The feed is pure A. It is proposed to put a CSTR of equal volume upstream of the PFR. Based on the entering molar flow rate to A to the first reactor, what will be the intermediate from the CSTR, X_1 , and exit conversion from the PFR, X_2 , based on the feed to first reactor? The entering flow rates and all other variables remain the same as that for the single PFR. Source: Modified California Registration Exam Problem. (Ans.: $X_2 = 0.82$)



Figure 3

1.4 P5-10_B (b)

(b) The liquid-phase reaction



was carried out in a CSTR. For an entering concentration of 2 mol/dm³, the conversion was 40%. For the same reactor volume and entering conditions as the CSTR, the expected PFR conversion is 48.6%. However, the PFR conversion was, amazingly, 52.6% exactly. Brainstorm reasons for the disparity. Quantitatively show how these conversions came about (i.e., the expected conversion and the actual conversion). Part (b) is C-level difficulty.

Figure 4

1.5 P5-22_A

P5-22_A A very proprietary industrial-waste reaction, which we'll code as $A \rightarrow B + S$, is to be carried out in a 10-dm³ CSTR followed by a 10-dm³ PFR. The reaction is elementary, but A, which enters at a concentration of 0.001 mol/dm³ and a molar flow rate of 20 mol/min, has trouble decomposing. The specific reaction rate at 42°C (i.e., room temperature in the Mojave desert) is 0.0001 s⁻¹. However, we don't know the activation energy; therefore, we cannot carry out this reaction in the winter in Michigan.

Figure 5

2 Problem Solution

2.1 P4-5_A (c, d)

(c)

Species	Symbol	Initial	Change	Remaining
C ₂ H ₄	A	C_{A0}	$-C_{A0}X$	$C_{A0}(1-X)$
$\frac{1}{2}$ O ₂	B	$C_{A0}\theta_B$	$-C_{A0}X/2$	$C_{A0}(\theta_B - X/2)$
Ethylene Oxide	C	0	$C_{A0}X$	$C_{A0}X$

Since it's catalytic, it relies on pressures. $-r_A' = kp_A p_B^{1/2}$.

$$-r_A' = kp_A p_B^{1/2} \quad (1)$$

$$p_A = y_{A0}P = y_{A0}CRT = C_A RT \quad (2)$$

$$p_B = y_{B0}P = y_{B0}CRT = C_B RT \quad (3)$$

(1) Fluidized batch reactor implies V is constant. Thus $C_A = C_{A0}(1-X)$, $C_B = C_{A0}(\theta_B - \frac{b}{a}X)$. Stoichiometric feed, therefore $\theta_B = \frac{1}{2}$, $\frac{b}{a} = \frac{1}{2}$. $C_B = C_{A0}(\frac{1}{2} - \frac{1}{2}X)$. Thus, we can express $-r_A'$ as follows:

$$-r_A' = kp_A p_B^{1/2} \quad (4)$$

$$-r_A' = kC_A RT (C_B RT)^{0.5} \quad (5)$$

$$-r_A' = C_{A0}^{1.5} (RT)^{1.5} (1-X)^{1.5} / 2^{0.5} \quad (6)$$

(2) Packed bed reactor (flow).

Species	Symbol	Initial	Change	Remaining
C ₂ H ₄	A	F _{A0}	-F _{A0} X	F _{A0} (1-X)
$\frac{1}{2}$ O ₂	B	F _{A0} θ_B	-F _{A0} X/2	F _{A0} (θ_B -X/2)
Ethylene Oxide	C	0	F _{A0} X	F _{A0} X

Once again θ_B is 1/2. Here the volume changes, so we must figure out the y_{A0} and ϵ terms. $y_{A0} = \frac{F_{A0}}{F_{T0}} = \frac{2}{3} (A + B/2)$. $\epsilon = y_{A0}\delta = \frac{2}{3} (1 - \frac{1}{2} - 1) = -\frac{1}{3}$. $C_{A0} = y_{A0}C_{T0} = y_{A0}\frac{P}{RT}$.

$$C_A = \frac{F_A}{\nu} = \frac{F_{A0}(1-X)}{\nu(1+\epsilon X)} \quad (7)$$

$$C_B = \frac{F_B}{\nu} = \frac{F_{A0}(\theta_B - X/2)}{\nu(1+\epsilon X)} \quad (8)$$

$$-r_A' = kC_A C_B^{0.5} (RT)^{1.5} \text{ Assuming elementary rxn} \quad (9)$$

Plugging in the numbers (as we have both temperature and pressure given) we can express $-r_A'$ more concisely.

$$-r_A' = k \left(\frac{.092(1-X)}{1-.33X} \right) \left(\frac{.046(1-X)}{1-.33X} \right)^{0.5} (RT)^{1.5} \quad (10)$$

(d) Given: Isothermal and isobaric PBR.

Species	Symbol	Initial	Change	Remaining
C ₆ H ₆	A	F _{A0}	-F _{A0} X	F _{A0} (1-X)
2H ₂	B	F _{A0} θ_B	-2F _{A0} X	F _{A0} (θ_B -2X)
C ₆ H ₁₀	C	0	F _{A0} X	F _{A0} X

$\theta_B = \frac{F_{A0}}{F_{B0}} = 2$. Functionally, we can start solving this problem the exact same way we solved (2) in (c), albeit with different numbers for δ, ϵ , and temperature.

$$C_A = \frac{F_A}{\nu} = \frac{F_{A0}(1-X)}{\nu(1+\epsilon X)} \quad (11)$$

$$C_B = \frac{F_B}{\nu} = \frac{F_{A0}(\theta_B - X/2)}{\nu(1+\epsilon X)} \quad (12)$$

$$C_{A0} = y_{A0}C_{T0} = y_{A0}\frac{P}{RT} \quad (13)$$

$$C_A = C_{A0} \left(\frac{(1-X)}{1-.66X} \right) \quad (14)$$

$$C_B = 2C_{A0} \left(\frac{(1-X)}{1-.66X} \right) \quad (15)$$

$$-r'_A = kC_A C_B^2 = 4kC_{A0}^3 \left(\frac{(1-X)}{1-.66X} \right) \left(\frac{(1-X)}{1-.66X} \right)^2 (RT)^3 \quad (16)$$

For a fluidized CSTR, $W = \frac{F_{A0}X}{-r'_A}$. Plugging in (16) and using $\frac{F_{A0}}{C_{A0}} = \nu_0$:

$$W = \frac{F_{A0}X}{4kC_{A0}^3 \left(\frac{(1-X)}{1-.66X} \right) \left(\frac{(1-X)}{1-.66X} \right)^2 (RT)^3} = \frac{\nu_0 X}{4kC_{A0}^2 \left(\frac{(1-X)}{1-.66X} \right) \left(\frac{(1-X)}{1-.66X} \right)^2 (RT)^3} \quad (17)$$

We are given k at 300K to be 53 mol per kgcat per minute per atmosphere cubed. E is 80 kJ per mol. We need to recalculate for k at 170C and 270C, or 443K and 543K respectively, using:

$$k_{new} = k e^{\frac{E}{R} \left(\frac{1}{T_{old}} - \frac{1}{T_{new}} \right)} \quad (18)$$

This yields $k_{443} = 1.66 \times 10^6 \frac{\text{mol}}{\text{kgcat} \times \text{min} \times \text{atm}^3}$ and $k_{543} = 9.08 \times 10^7 \frac{\text{mol}}{\text{kgcat} \times \text{min} \times \text{atm}^3}$. To evaluate W at $X = 0.8$, we plug in the respective k, X, and T values to solve. $\nu_0 = 50 \text{ dm}^3/\text{min}$. $W_{443} = 5.25 \times 10^{-7} \text{ kgcat}$ and $W_{543} = 5.22 \times 10^{-9} \text{ kgcat}$.

2.2 P4-9_B

Isothermal and isobaric flow reactor. (a) Gas phase. $C_{A0} = 4 \text{ mol/dm}^3$. $P_{A0} = C_{A0}RT$. $X_e = 0.6$. $K_C = \frac{C_B}{C_A^2}$. $C_A = P_A/RT$ and $C_B = P_B/RT$. $\epsilon = y_{A0}\delta = 1 \times (1 - 2) = -1$.

$$P_A = P_{A0} \frac{1 - X_e}{1 + \epsilon X_e} \quad (19)$$

$$P_B = P_{A0} \frac{X_e}{2 \times (1 + \epsilon X_e)} \quad (20)$$

$$P_A = P_{A0} \frac{.4}{.4} \quad (21)$$

$$P_B = P_{A0} \frac{.6}{.8} \quad (22)$$

$$C_A = 4 \frac{\text{mol}}{\text{dm}^3} \quad (23)$$

$$C_B = 3 \frac{\text{mol}}{\text{dm}^3} \quad (24)$$

$$K_C = \frac{3}{4^2} = 0.1875 \frac{\text{dm}^3}{\text{mol}} \quad (25)$$

(b) Liquid phase. Similar setup as in gas, but no epsilon term. So $C_A = C_{A0}(1 - X_e)$ and $C_B = C_{A0}(X_e)/2$. K_C is the same, $\frac{C_B}{C_A^2}$. $C_A = 4 \times 0.4 \frac{\text{mol}}{\text{dm}^3} = 1.6 \frac{\text{mol}}{\text{dm}^3}$, $C_B = 4 \times 0.6/2 \frac{\text{mol}}{\text{dm}^3} = 1.2 \frac{\text{mol}}{\text{dm}^3}$. $K_C = \frac{1.2}{1.6^2} = 0.469 \frac{\text{dm}^3}{\text{mol}}$.

2.3 P5-8_B

Elementary gas phase reaction, isobaric and isothermal in a PFR. $X = 0.632$. Feed is pure A. Proposed to put CSTR of equal volume upstream of the PFR. Conversion X_1 from CSTR and X_2 from PFR? Mole balance for original situation: $\frac{dX}{dV} = -r_A$. $-r_A = kC_A$. $C_A = C_{A0}(1 - X)$. $\frac{dX}{dV} = \frac{kC_{A0}}{F_{A0}}(1 - X) = \frac{k}{\nu_0}(1 - X)$. $\frac{dX}{1 - X} = \frac{k}{\nu_0}dV$, $\ln \frac{1}{1 - X} = k\tau = 1$. If an equal volume CSTR was there instead, $V = \frac{F_{A0}X}{kC_{A0}(1 - X)} = \frac{\nu_0 X}{k(1 - X)}$, so $k\tau = \frac{X}{1 - X} = 1$, therefore X_1 is 0.5. For the PFR now downstream from the CSTR, $k\tau = 1 = \int_{X_1}^{X_2} \frac{dX}{1 - X}$. We know X_1 is 0.5, therefore $1 = \ln \frac{1}{1 - X_2} - \ln \frac{1}{0.5}$. Solving for X_2 yields 0.816 (exponentiation of $\ln \frac{1}{1 - X_2}$, then algebraic manipulation).

2.4 P5-10_B (b)

Liquid phase reaction in CSTR. $C_{A0} = 2 \text{ mol/dm}^3$. $X = 0.4$. Expected PFR conversion of $X = 0.486$ if it was the same volume as CSTR. Actual conversion of 0.526. Why could the disparity occur? If the expected conversion rate was 0.486, then we need to look at typical assumptions made for reactions. Commonly, a reaction is assumed to be elementary ($-r_A = kC_{A0}(1 - X)$), so the PFR setup will be $k\tau = \int_0^X \frac{dX}{1 - X}$. Solving this yields the

expected value of 0.486 as X. So the reaction might be non-elementary. Testing second order:

$$-r_A = kC_{A0}^2(1 - X)^2 \quad (26)$$

$$k\tau = \frac{1}{C_{A0}} \int_0^X \frac{dX}{(1 - X)^2} \quad (27)$$

$$X = \frac{1}{1 + \tau k C_{A0}} = 0.526 \quad (28)$$

Therefore the reaction was second order, not elementary.

2.5 P5-22_A

Okay :)