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Chemical Engineering Department

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(0905422) Chemical Reaction Engineering II — First Semester - 2019/2020

Quiz # 4 (Chapter 13)

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The following E(t) curve was obtained from a tracer test on a tubular reactor in which dispersion is believed to occur.

A second-order reaction $A \xrightarrow{k} B$ with $kC_{A0} = 0.1\ min^{-1}$ is to be carried out in this reactor. There is no dispersion occurring either upstream or downstream of the reactor, but there is dispersion inside the reactor.

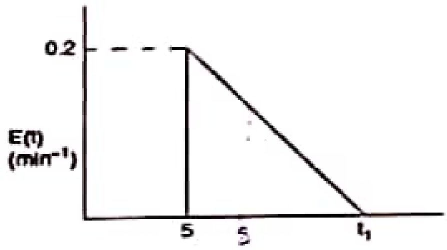
(a) What is the final time t_1 (in minutes) for the reactor?

(b) Find E(t).

(c) What is the mean residence time t_m?

(d) What is the fraction of the fluid that spends 8 minutes or longer?

(e) Find the conversion predicted by the segregation model.



[a] $\int_0^\infty E(t)\,dt = 1$ = Area under the curve

$\frac{1}{2} \times (t_1 - 5) \times 0.2 = 1$

$0.1\, t_1 - 0.5 = 1$

$t_1 = 15$ min

[b] slope $= \frac{-0.2}{15-5} = -0.02$

$(y - y_1) = \text{slope}\,(x - x_1)$

$(y - 0.2) = -0.02\,(x - 5)$

$y - 0.2 = -0.02x + 0.1$

$y = 0.3 - 0.02x$

$E(t) = 0.3 - 0.02t$ $5 < t < 15$

$E(t) = 0$ $0 < t < 5$

$E(t) = 0$ $t > 15$

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(0905422) Chemical Reaction Engineering II **In-Class Assessment # 13-2**

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The following data were obtained from a tracer test to a reactor.

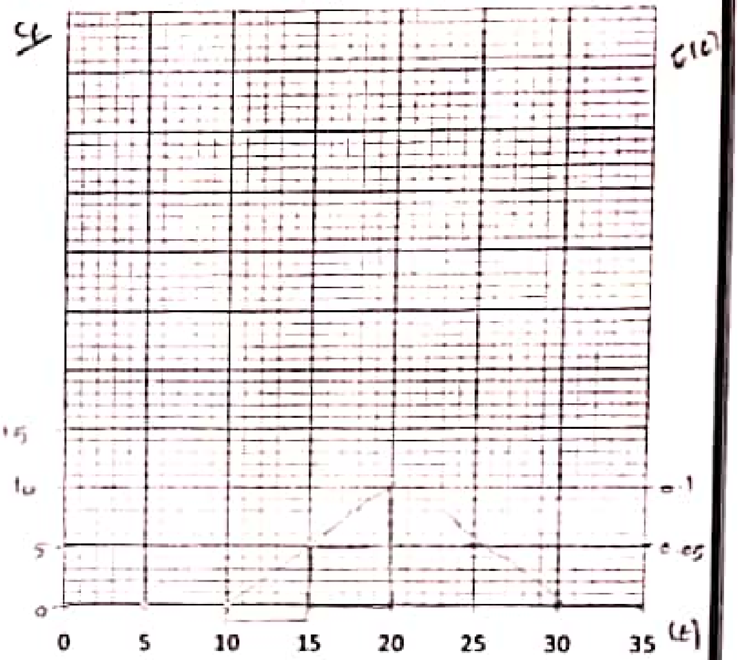
t(s)	0	5	10	15	20	25	30	35
C_t(mg/dm^3)	0	0	0	5	10	5	0	0
F(t)	0	0	0	0.125	0.500	0.875	1.00	1

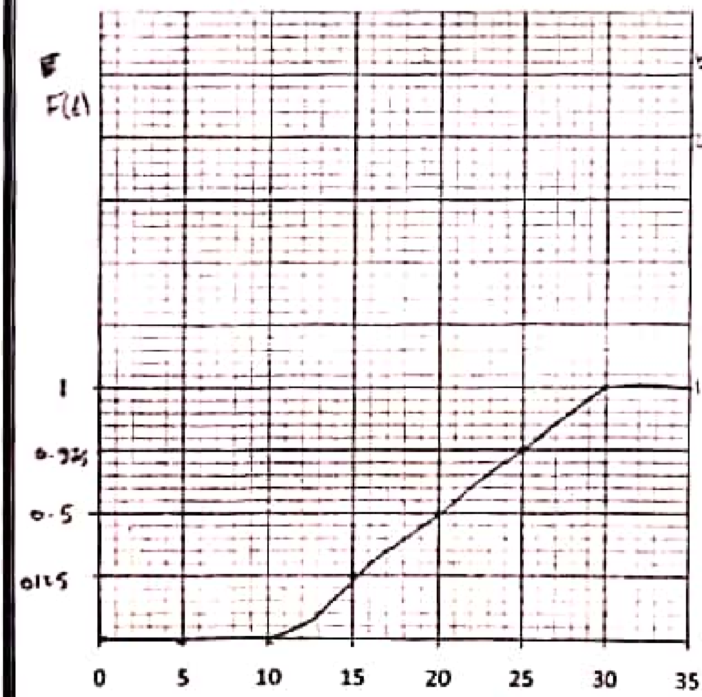
1) Plot $C_t(t)$.
2) Find $E(t)$. $= \frac{C(t)}{\int C(t)\,dt}$
3) Find the fraction of material that spends between 15 and 20 seconds in the reactor.
4) Find F(t) and, the fraction of material that spends 25 seconds or less in the reactor.
5) Evaluate mean residence time.
6) Evaluate the variance.

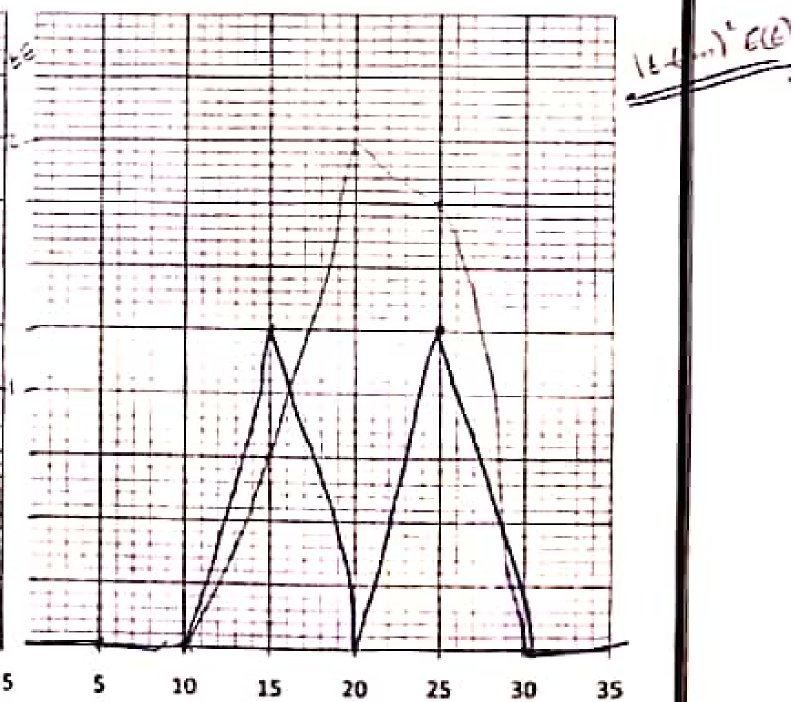
2) Area under the Curve = 1/2 × 20 × 10 = 100

3) $\int_{15}^{20} E(t)\,dt = 5 \times 0.05 + \frac{1}{2} \times 5 \times 0.05 = 0.375$

4) $F(t) = \int_0^t E(t)\,dt$







The CSTR

- Concentration $C(t) = C_0 e^{-t/\tau}$
- RTD Function $E(t) = \frac{e^{-t/\tau}}{\tau}$
- Cumulative Function $F(t) = 1 - e^{-t/\tau}$
- Space Time $\tau = \frac{V}{v_0}$

a. Perfect Operation (P)

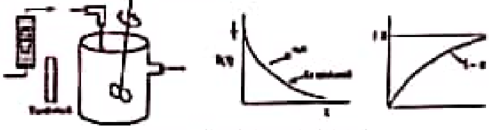


Figure 13-11 Perfect operation of a CSTR.

b. Bypassing (BP)

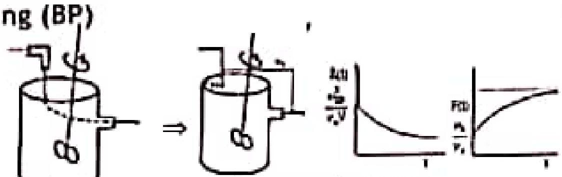


Figure 13-12 Ideal CSTR with bypass

- A volumetric flow rate, v_b, bypasses the reactor while a volumetric flow rate v_{SB} enters the system volume and $(v_0 = v_b + v_{SB})$.
- The reactor system volume V_s is the well-mixed portion of the reactor.
- $v_{SB} < v_0 \Rightarrow \tau_{SB} > \tau$ $E(t) = \frac{v_b}{v_0}\delta(t-0) + \frac{v_{SB}^2}{Vv_0} e^{-t/\tau_{SB}}$

c. Dead Volume (DV)

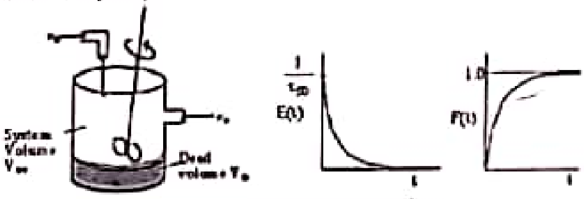
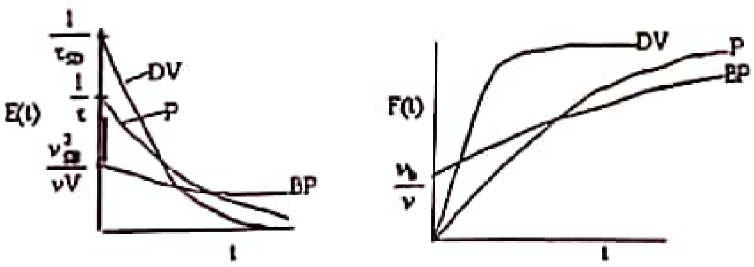


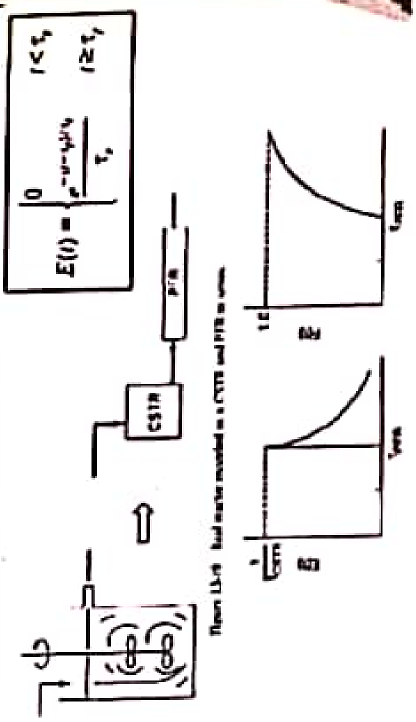
Figure 13-13 Ideal CSTR with dead volume

- The total volume, V, is the same as that for perfect operation, with $V = V_D + V_{SD}$.
- $V_{SD} < V \Rightarrow \tau_{SD} < \tau$

Summary



PFR/CSTR Series RTD



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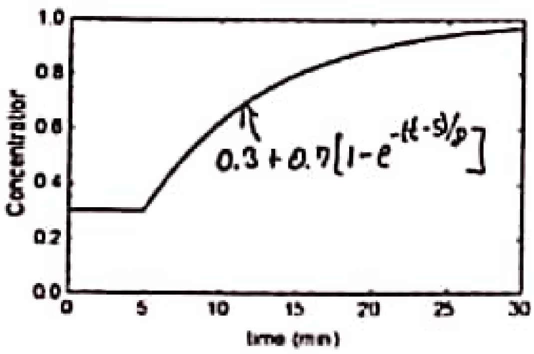
Model non-ideal CSTR

A non-ideal, continuous stirred tank reactor (CSTR) has the normalized response to a step function input of a tracer shown in the figure. The step input starts at t = 0.



a) Develop a 3-parameter model of this non-ideal reactor. The model can consist of ideal reactors, recycle, bypass, and hold-up,

b) Determine the values of the parameters for the model. The total reactor volume is 1.5 L and the inlet volumetric feedrate is 0.10 L/min.

c) Sketch the exit age distribution for the non-ideal reactor.

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P10-11 Cyclohexanol was passed over a catalyst to form water and cyclohexene:

Cyclohexanol → Water + Cyclohexene *dehydration*

The following data were obtained.

Run	Reaction Rate (mol/dm³·s) × 10⁵	Partial Pressure of Cyclohexanol (H)	Partial Pressure of Cyclohexene (E)	Partial Pressure of Steam (H_2O) (W)
1	3.3	1	1	1
2	1.05	5	1	1
3	0.565	10	1	1
4	1.826	2	5	1
5	1.49	2	10	1
6	1.36	3	0	5
7	1.08	3	0	10
8	0.862	1	10	10
9	0	0 (H reactant)	5	8
10	1.37	3	3	3

It is suspected that the reaction may involve a dual-site mechanism, but it is not known for certain. It is believed that the adsorption equilibrium constant for cyclohexanol is around 1 and is roughly one or two orders of magnitude greater than the adsorption equilibrium constants for the other compounds. Using these data:

(a) Suggest a rate law and mechanism consistent with the data given here.

(b) Determine the constants needed for the rate law.

$K_H \approx 1$

$K_E \approx 0.1 - 0.01$

$K_W \approx 0.1 - 0.01$

Run 1, 2, 3 $P_E = P_W = 1$ constant

$-r_H \propto \frac{P_H}{(P_H)^2}$ — reactant

$$-r_H = \frac{k P_H}{(1 + K_H P_H + K_E P_E + K_W P_W)^2}$$

Run 4, 5 $P_H = 2$, $P_W = 1$ const

$-r_H \propto \frac{1}{P_E}$ K_E $K_E \approx 0.01$

→ $H + S \rightleftharpoons H \cdot S$

→ $H \cdot S + S \rightarrow E \cdot S + W \cdot S$

→ $E \cdot S \rightleftharpoons E + S$

$W \cdot S \rightleftharpoons W + S$

Run 6, 7 ($P_H = 3$, $P_E = 0$)

$-r_H \propto \frac{1}{P_W}$ E $K_W \approx 0.1$

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(0905422) Chemical Reaction Engineering II **In-Class Assessment # 10-3**

Partner (1) Name: ____________________ **Partner (2) Name:** ____________________

Partner (1) ID # ____________________ **Partner (2) ID #** ____________________

For the reaction:

$$2CO + O_2 \underset{cat}{\rightleftarrows} 2CO_2$$

The following data were obtained for the oxidation of CO over a catalyst. All rates are initial rates

	$-r'_{CO}$ $(mol/dm^3 \cdot s)$	C_{CO} (mol/dm^3)	C_{O_2} (mol/dm^3)
1	0.02	0.01	1
2	0.035	0.01	3
3	0.049	0.01	6
4	0.06	0.01	9
5	0.196	0.1	1
6	0.384	0.2	1
7	0.902	0.5	1
8	1.653	1	1
9	4.44	5	1
10	5.00	10	1
11	4.44	20	1
12	2.77	50	1

run 2/1 : 0.035/0.02 = 1.75 / 3/1 = 3

run 3/1 : 0.049/0.02 = 2.5 / 6/1 = 6

run 4/1 : 0.06/0.02 = 3 / 9/1 = 9

rate ∝ $P_{O_2}^{1/2}$

reversible

The initial rate was found to be independent of CO_2. → No P_{CO_2} in the rate law ← irreversible, No desorption

a) Suggest a rate law consistent with the data

b) Suggest mechanisms consistent with the rate law

run (1, 2, 3, 4) $C_{CO} = 0.01$ constant

$-r'_{CO} \propto \dfrac{C_{O_2}^{1/2}}{(1 + C_{O_2}K_{O_2} + \dots)}$

$-r'_{CO} = \dfrac{k (P_{CO} P_{O_2})^{1/2}}{(1 + K_{CO} C_{CO})^2}$

ف تأثير الالتصاق

run (5 - 12) $C_{O_2} = 1$ constant

Low P_{CO} → $-r'_{CO} \propto P_{CO}$

Run 6/5 : 0.384/0.196 ≈ 2 0.2/0.1 = 2

Linear

⇒ b) $CO + S \rightleftarrows CO \cdot S$

$CO \cdot S + \frac{1}{2} O_2 + S \rightarrow CO_2 + 2S$

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(0905422) Chemical Reaction Engineering II — In-Class Assessment #10-5

Partner (1) Name: ______________ Partner (2) Name: ______________

Partner (1) ID #: ______________ Partner (2) ID #: ______________

P10-13

Vanadium oxides are of interest for various sensor applications, owing to the sharp metal–insulator transitions they undergo as a function of temperature, pressure, or stress. Vanadium triisopropoxide (VTIPO) was used to grow vanadium oxide films by *chemical vapor deposition* [*J. Electrochem. Soc.*, *136*, 897 (1989)]. The deposition rate as a function of VTIPO pressure for two different temperatures follows:

T = 120°C:

Growth Rate (μm/h)	0.004	0.015	0.025	0.04	0.068	0.08	0.095	0.1
VTIPO Pressure (torr)	0.1	0.2	0.3	0.5	0.8	1.0	1.5	2.0

T = 200°C:

Growth Rate (μm/h)	0.028	0.45	1.8	2.8	7.2
VTIPO Pressure (torr)	0.05	0.2	0.4	0.5	0.8

In light of the material presented in this chapter, analyze the data and describe your results. Specify where additional data should be taken.

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(0905422) Chemical Reaction Engineering II — **In-Class Assessment # 10-1**

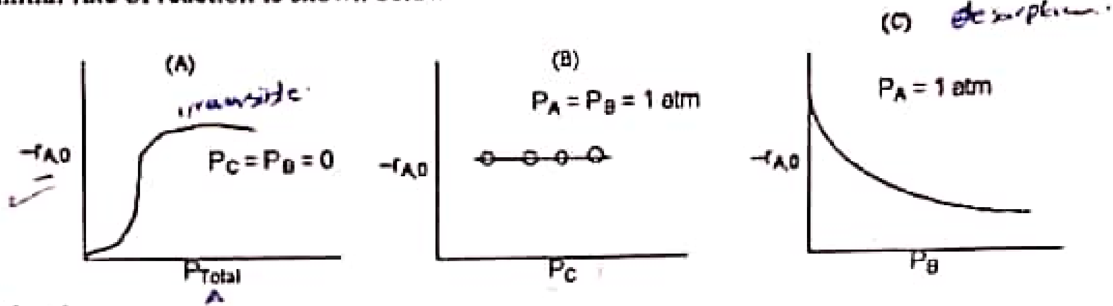
Partner (1) Name: ____________________ **Partner (2) Name:** ____________________

Partner (1) ID # ____________________ **Partner (2) ID #** ____________________

For the reaction:

$$A \rightleftarrows B + C$$

The initial rate of reaction is shown below



Question 1

1. The reaction is irreversible.
2. Species B is on the surface.
3. Species C is on the surface.

Choose the true one of the following:

A. 1 and 2 are true.
B. 1 and 2 are false.
C. 1 and 3 are false.
D. 2 and 3 are false.
E. 2 and 3 are true.

Question 2:
The rate law is

(A)
$$-r_A = \frac{kP_A}{1 + K_AP_A + K_BP_B}$$

(B)
$$-r_A = \frac{kP_A^2}{(1 + K_AP_A + K_CP_C)^2}$$

(C)
$$-r_A = \frac{kP_A}{(1 + K_AP_A + K_BP_B)^2}$$

(D)
$$-r_A = \frac{kP_A}{1 + K_AP_A + K_CP_C}$$

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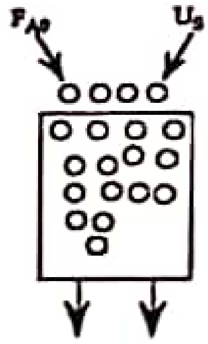
(0905422) Chemical Reaction Engineering II	In-Class Assessment # 10-6
Partner (1) Name: ______________________	ID # ______________________
Partner (2) Name: ______________________	ID # ______________________

The elementary gas phase irreversible reaction $2A \rightarrow 2B$ is carried out isothermally in a moving bed reactor in which there is significant pressure drop. Pure A enters the reactor at a concentration of 0.1 mol/dm³ and a flow rate of 2 mol/min. The entering pressure is 10 atm and the pressure at the exit is 4.472 atm. The catalyst decay is by poisoning and of zero order. The catalyst loading rate is 10 kg/min and the catalyst bed contains 40 kg of catalyst.



Additional information: Specific reaction rate k = 20.0 dm⁶/(mol-kg cat-min)
Catalyst decay constant k_d = 0.25/min

For catalyst decay by poisoning:

$$-\frac{da}{dt} = k_d a^n$$

For isothermal gas-phase reaction with ε = 0,

$$y = \frac{P}{P_o} = (1 - \alpha W)^{1/2}$$

For moving-bed reactor:

$$t = \frac{W}{U_s} \qquad \frac{dX}{dW} = \frac{a[-r_A'(t=0)]}{F_{A0}}$$

(Loading rate → U_s)

(a) Show that the pressure drop parameter α = 0.02 kg⁻¹.

(b) What is the conversion at the exit of the reactor?

gas - phase

Elementary → $-r_A = kC_A^2$

$\frac{T}{T_o} = 1$ $\quad \frac{P}{P_o} \neq 1$ $\quad y_{A0} = 1$ $\quad C_{A0} = 0.1$ mol/dm³

$F_{A0} = 2$ mol/min $\quad P_o = 10$ atm $\quad P = 4.472$ atm

Decay ⇒ n = zero $\quad$ Catalyst Loading rate = 10 kg/min

ε = zero $\quad$ W = 40 kg

(a) ⇒ $\frac{P}{P_o} = (1 - \alpha W)^{1/2}$

$\frac{4.472}{10} = (1 - \alpha 40)^{1/2}$

$\alpha = 0.02\ kg^{-1}$

(b) → $\frac{dX}{dW} = \frac{a(-r_A'(t=0))}{F_{A0}}$

→ $-r_A = kC_A^2$

→ $\frac{da}{dt} = k_d a^{zero}$

$a = -k_d t + 1$ → $a = 1 - k_d \frac{W}{U_s}$

→ $C_A = \frac{C_{A0}(1-X)}{1+\varepsilon X}\frac{T_o}{T}\frac{P}{P_o} = C_{A0}(1-X)(1-\alpha W)^{1/2}$

→ Combine
$\frac{dX}{dW} = \frac{(1 - k_d \frac{W}{U_s}) k C_{A0}^2 (1-X)^2 (1-\alpha W)}{F_{A0}}$

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(0905422) Chemical Reaction Engineering II	In-Class Assessment # 7-3
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Partner (1) ID No.: ________________	Partner (2) ID No.: ________________

P7-11

Beef catalase has been used to accelerate the decomposition of hydrogen peroxide to yield water and oxygen. The concentration of hydrogen peroxide is given as a function of time for a reaction mixture with a pH of 6.76 maintained at 30°C. $H_2O_2 \xrightarrow{E} H_2 + O_2$

t (min)	0	10	20	50	100
$C_{H_2O_2}$(mol/L)	0.02	0.01775	0.0158	0.0106	0.005

(a) Determine the Michaelis-Menten parameters V_{max} and K_M.
(b) If the total enzyme concentration is tripled, what will the substrate concentration be after 20 minutes?

$-r_s = \frac{V_{max} C_s}{K_M + C_s}$

Constant volume batch reactor

$-\frac{dC_s}{dt} = r_s$

$\frac{dC_s}{dt} = \frac{V_{max} C_s}{K_M + C_s}$

$\int_{C_{s0}}^{C_s} \left(\frac{K_M}{V_{max} C_s} + \frac{1}{V_{max}} \right) dC_s = \int_0^t dt$

x	2.25×10⁻⁴	2.11×10⁻⁴	1.55×10⁻⁴	1.5×10⁻⁴
y	-0.0119	-0.0118	-0.0117	-0.0138

$\frac{K_M}{V_{max}} \ln \frac{C_s}{C_{s0}} + \frac{1}{V_{max}} (C_s - C_{s0}) = t$

From table, at t=0

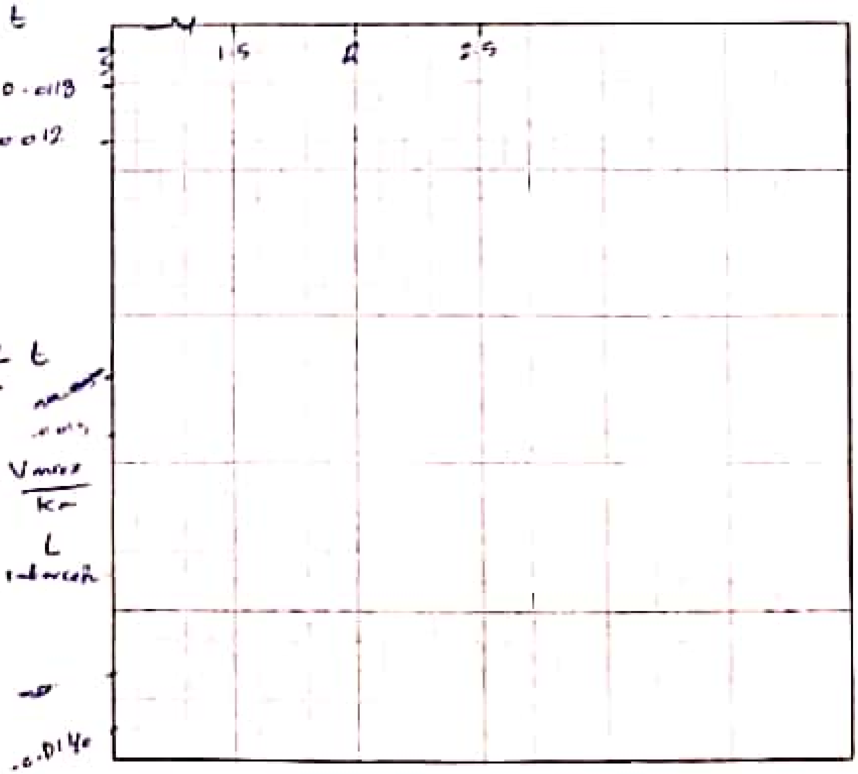
$C_{s0} = 0.02$ mol/L

$y = ax + b$

$\ln \frac{C_s}{C_{s0}} + \frac{1}{K_m} (C_s - C_{s0}) = \frac{V_{max}}{K_m} t$

$\frac{1}{t} \ln \frac{C_s}{C_{s0}} = \frac{1}{K_m} \frac{(C_{s0} - C_s)}{t} + \frac{V_{max}}{K_m}$

y, slope, x, intercept



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(0905422) Chemical Reaction Engineering II — In-Class Assessment # 2 (Chapter 7)

Partner (1) Name: ____________ Partner (2) Name: ____________

Identity (1) #: ____________ Identity (2) #: ____________

P7-6 Ozone is a reactive gas that has been associated with respiratory illness and decreased lung function. The following reactions are involved in ozone formation

$$NO_2 + h\nu \xrightarrow{k_1} NO + O \qquad -r_{NO_2} = k_1[NO_2]$$
$$O_2 + O + M \xrightarrow{k_2} O_3 + M \qquad -r_{O_2} = k_2[O_2][O][M]$$
$$O_3 + NO \xrightarrow{k_3} NO_2 + O_2 \qquad -r_{O_3} = k_3[O_3][NO]$$

NO_2 is primarily generated by combustion in the automobile engine.

(a) Show that the steady-state concentration of ozone is directly proportional to NO_2 and inversely proportional to NO.

(b) In the absence of NO and NO_2, the rate law for ozone decomposition is

$$-r_{O_3} = \frac{k[O_3]^2[M]}{[O_2][M] + k'[O_3]}$$

Suggest a mechanism.

$M + O_3 \rightleftharpoons O + O_2 + M$

$O_2 + M + O$

$O_3 + O \rightarrow 2O_2$

(a)

at steady state: $\sum r_{O_3} = 0$

$[O_3] = ??$

$\sum r_{O_3} = k_2[O_2][O][M] - k_3[O_3][NO] = 0$

$[O_3] = \dfrac{k_2[O_2][O][M]}{k_3[NO]} \longrightarrow (1)$

$\sum r_O = 0 = k_1[NO_2] - k_2[O_2][O][M]$

$[O] = \dfrac{k_1[NO_2]}{k_2[O_2][M]} \longrightarrow (2)$

subs in (1)

$[O_3] = \dfrac{k_1[NO_2]}{k_3[NO]}$

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(0905422) Chemical Reaction Engineering II	In-Class Assessment # 1 (Chapter 7)
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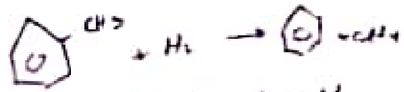
Identity (1) #: ______________	Identity (2) #: ______________

A process for the hydrodealkylation of toluene to produce benzene and methane has been developed. The hydrodealkylation occurs in the gas phase at high temperature and involves free radical. The free radical mechanism is believed to proceed by the sequence

Initiation: $H_2 \xrightarrow{k_1} 2H\bullet$

Propagation:
$$\begin{cases} H\bullet + C_6H_5CH_3 \xrightarrow{k_2} C_6H_5\bullet + CH_4 \\ C_6H_5\bullet + H_2 \xrightarrow{k_3} H\bullet + C_6H_6 \end{cases}$$

Termination: $2H\bullet \xrightarrow{k_4} H_2$



T + H → B + M

The specific reaction rates k_1 and k_4 are defined w.r.t. H_2.

Derive the reaction rate law for the rate of formation of benzene based on this mechanism.

Hint: the reaction is 1/2 order in H_2 and 1st order in toluene.

$r_{A,B} = k_3 C_{C_6H_5\bullet} C_{H_2}$

$r_B = k_3 \frac{k_2}{k_3}\sqrt{\frac{k_1}{k_4}} \frac{C_T C_{H_2}^{1/2}}{C_{H_2}} C_{H_2}$

$\boxed{r_B = k\, C_T\, C_{H_2}^{1/2}}$

$\Sigma r_{C_6H_5\bullet} = 0$

$k_2 C_{H\bullet} C_A - k_3 C_{C_6H_5\bullet} C_{H_2} = 0 \rightarrow (1)$

$\Sigma r_{H\bullet} = 0$

$2k_1 C_{H_2} - k_2 C_{H\bullet} C_A + k_3 C_{C_6H_5\bullet} C_{H_2} - 2k_4 C_{H\bullet}^2 = 0 \rightarrow (2)$

initiation, termination

$1 + 2$

$0 = 2k_1 C_{H_2} - 2k_4 C_{H\bullet}^2$

$C_{H\bullet} = \sqrt{\frac{k_1}{k_4}} C_{H_2}^{1/2}$

Sub in 1

$k_2 \sqrt{\frac{k_1}{k_4}} C_{H_2}^{1/2} C_A - k_3 C_{C_6H_5\bullet} C_{H_2} = 0$

$C_{C_6H_5\bullet} = \frac{k_2}{k_3}\sqrt{\frac{k_1}{k_4}} \frac{C_A C_{H_2}^{1/2}}{C_{H_2}}$

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(0905422) Chemical Reaction Engineering II | In-Class Assessment # 1 (Chapter 7)

Partner (1) Name: ____________ Partner (2) Name: ____________

Identity (1) #: ____________ Identity (2) #: ____________

P7-4

The pyrolysis of acetaldehyde is believed to take place according to the following sequence:

$$CH_3CHO \xrightarrow{k_1} CH_3^{\cdot} + CHO^{\cdot}$$

$$CH_3^{\cdot} + CH_3CHO \xrightarrow{k_2} CH_3^{\cdot} + CO + CH_4$$

$$CHO^{\cdot} + CH_3CHO \xrightarrow{k_3} CH_3^{\cdot} + 2CO + H_2$$

$$2CH_3^{\cdot} \xrightarrow{k_4} C_2H_6$$

(a) Derive the rate expression for the rate of disappearance of acetaldehyde $-r_A$.

(b) Under what conditions does it reduce to the following equation:

$$-r_{CH_3CHO} = kC_{CH_3CHO}^{3/2}$$

For the previous problem:

1- What are the new terms to you?

$CHO^{\cdot}$, $CH_3^{\cdot}$ radicals

2- What information you need to know to be able to solve this problem?

type of rxn, Limiting step

3- What do you need to learn to be able to solve this problem?

$\sum r_{CH_3^{\cdot}} = k_1 C_A - k_2 C_A C_{CH_3^{\cdot}} + k_3 C_A C_{CHO^{\cdot}} - 2k_4 C_{CH_3^{\cdot}}^2 = 0 \rightarrow (2)$

$k_1 C_A + k_3 C_A C_{CHO^{\cdot}} + 2 k_4 C_{CH_3^{\cdot}}^2 = 0$

$\sum r_{CHO^{\cdot}} = k_1 C_A - k_3 C_A C_{CHO^{\cdot}} = 0 \rightarrow (3)$

$C_{CHO^{\cdot}} = \frac{k_1}{k_3}$

$-r_A = k_1 C_A + k_2 C_A C_{CH_3^{\cdot}} + k_3 C_A C_{CHO} \rightarrow (1)$

(c) $t_m = \int_0^\infty t\, E(t)\, dt$

$= \int_0^5 t\,(0)\, dt + \int_5^{15} t\,(0.3 - 0.02t)\, dt$

$= 0 + \frac{0.3t^2}{2} - \frac{0.02t^3}{3} \Big|_5^{15}$

$= 11.25 - 2.91$

$= 8.34$ min

(d) $\int F(t) = \int_8^\infty E(t)\, dt$

$= \frac{1}{2}(15-8) * E(8)$

$= 0.5(7) * 0.14 = 0.196$

(e) $\bar{X} = \int_0^\infty x(t)\, E(t)\, dt$

$= \int_0^5 x(t)\, E(t)\, dt + \int_5^{15} x(t)\, E(t)\, dt$

$= 0 + \int_5^{15} \left(\frac{0.1t}{1+0.1t}\right)(0.3 - 0.02t)\, dt$

$= 0.445$

For ~~batch~~ tubular reactor

$\Rightarrow \frac{dx}{dt} = \frac{-r_A}{C_{A0}} = \frac{kC_{A0}^2(1-x)^2}{C_{A0}}$

$\int_0^x \frac{dx}{(1-x)^2} = \int_0^\tau kC_{A0}\, d\tau$

$\frac{x}{1-x} = kC_{A0}\tau$

$x = kC_{A0}\tau - kC_{A0}\tau x$

$x = \frac{kC_{A0}\tau}{1+kC_{A0}\tau}$

=

For batch reactor

$\frac{dx}{dt} = \frac{-r_A}{C_{A0}} = \frac{kC_{A0}^2(1-x)^2}{C_{A0}}$

$\int \frac{dx}{(1-x)^2} = \int kC_{A0}\, dt$

$\frac{x}{1-x} = kC_{A0}t$

$x = \frac{kC_{A0}t}{1+kC_{A0}t}$