

SOLUTIONS MANUAL

Wastewater Engineering: Treatment and Resource Recovery Fifth Edition

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PREFACE

This Solutions Manual for the Fifth Edition of *Wastewater Engineering* is designed to make the text more useful for both undergraduate and graduate teaching. Each problem has been worked out in detail, and where necessary additional material in the form of *Instructors Notes* is provided (as shown in boxes). The additional material is furnished either for further guidance to the instructor for grading homework problems or to make corrections to the Problem Statement as written in the First Printing of the text. Where corrections to the Problem Statement are made, these corrections have been incorporated into the Second Printing of the text.

For many of the problems in the text, alternative parameters are provided and the values are noted “to be selected by instructor”. The alternative parameters are provided to extend the usefulness of the problems in future assignments. In most cases, a solution has been worked in detail for only one set of values. When alternative values are assigned by the instructor for which an answer has not been provided, the same computational procedure applies as used in the worked solution.

Because of the magnitude of the fifth edition, a number of persons contributed to the preparation of this solutions manual; their assistance is acknowledged gratefully. The contributors are listed alphabetically on the title page. Although this manual has been reviewed carefully, the authors will be appreciative if any errors that have been found are brought to our attention. Other comments that will be helpful in improving the usability of the problems or the manual will also be appreciated.

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INTRODUCTION TO WASTEWATER TREATMENT

PROBLEM 1-1

Instructors Note: The first six problems are designed to illustrate the application of the mass balance principle using examples from hydraulics with which the students should be familiar.

Problem Statement - See text, page 53

Solution

1. Write a materials balance on the water in the tank

Accumulation = inflow – outflow + generation

$$\frac{dV}{dt} = \frac{dh}{dt} A = Q_{in} - Q_{out} + 0$$

2. Substitute given values for variable items and solve for h

$$\frac{dh}{dt} A = 0.2 \text{ m}^3 / \text{s} - 0.2 \left(1 - \cos \frac{\pi t}{43,200} \right) \text{ m}^3 / \text{s}$$

$$A = 1000 \text{ m}^2$$

3. $dh = 2 \times 10^{-4} \left(\cos \frac{\pi t}{43,200} \right) dt$

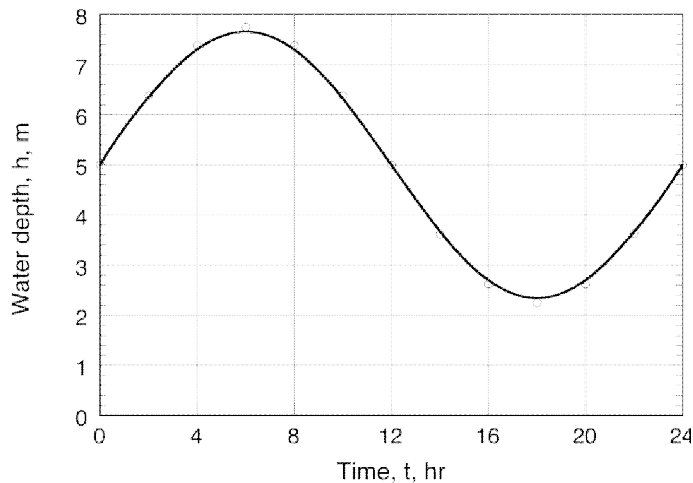
Integrating the above expression yields:

$$h - h_o = \left[\frac{(43,200) (2 \times 10^{-4})}{\pi} \right] \left(\sin \frac{\pi t}{43,200} \right)$$

4. Determine h as a function of time for a 24 hour cycle

t, hr	t, s	h, m	t, hr	t, s	h, m
0	0	5.00	14	50,400	3.62
2	7200	6.38	16	57,600	2.62
4	14,400	7.38	18	64,800	2.25
6	21,600	7.75	20	72,000	2.62
8	28,800	7.38	22	79,200	3.62
10	36,000	6.38	24	84,400	5.00
12	43,200	5.00			

5. Plot the water depth versus time



PROBLEM 1-2

Instructors Note: The first six problems are designed to illustrate the application of the mass balance principle using examples from hydraulics with which the students should be familiar.

Problem Statement - See text, page 53

Solution

1. Write a materials balance on the water in the tank

$$\text{Accumulation} = \text{inflow} - \text{outflow} + \text{generation}$$

$$\frac{dV}{dt} = \frac{dh}{dt} A = Q_{in} - Q_{out} + 0$$

2. Substitute given values for variable items and solve for h

$$\frac{dh}{dt}A = 0.33 \text{ m}^3 / \text{s} - 0.2 \left(1 - \cos \frac{\pi t}{43,200} \right) \text{ m}^3 / \text{s}$$

$$\frac{dh}{dt}A = 0.13 \text{ m}^3 / \text{s} + 0.2 \left(\cos \frac{\pi t}{43,200} \right) \text{ m}^3 / \text{s}$$

$$A = 1600 \text{ m}^2$$

$$\frac{dh}{dt}(1600) = 0.13 \text{ m}^3 / \text{s} + 0.2 \left(\cos \frac{\pi t}{43,200} \right) \text{ m}^3 / \text{s}$$

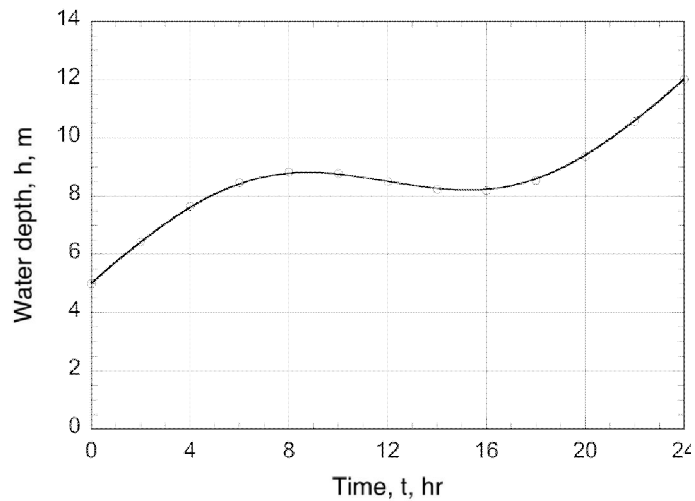
3. Integrating the above expression yields:

$$h - h_0 = \frac{(0.13 \text{ m}^3 / \text{s})t}{1600} + \frac{(0.2)(43,200)}{\pi 1600} \left(\sin \frac{\pi t}{43,200} \right) \text{ m}^3 / \text{s}$$

Determine h as a function of time for a 24 hour cycle

t, hr	t, s	h, m	t, hr	t, s	h, m
0	0	5.00	14	50,400	8.24
2	7200	6.44	16	57,600	8.19
4	14,400	7.66	18	64,800	8.55
6	21,600	8.47	20	72,000	9.36
8	28,800	8.83	22	79,200	10.58
10	36,000	8.78	24	84,400	12.02
12	43,200	8.51			

4. Plot the water depth versus time



PROBLEM 1-3

Instructors Note: The first six problems are designed to illustrate the application of the mass balance principle using examples from hydraulics with which the students should be familiar.

Problem Statement - See text, page 53

Solution

1. Write a materials balance on the water in the tank

Accumulation = inflow – outflow + generation

$$\frac{dV}{dt} = \frac{dh}{dt} A = Q_{in} - Q_{out} + 0$$

2. Substitute given values for variable items and solve for h

$$\frac{dh}{dt} A = 0.3 \left(1 + \cos \frac{\pi t}{43,200} \right) \text{ m}^3 / \text{s} - 0.3 \text{ m}^3 / \text{s}$$

$$A = 1000 \text{ m}^2$$

$$dh = 3 \times 10^{-4} \left(\cos \frac{\pi t}{43,200} \right) dt$$

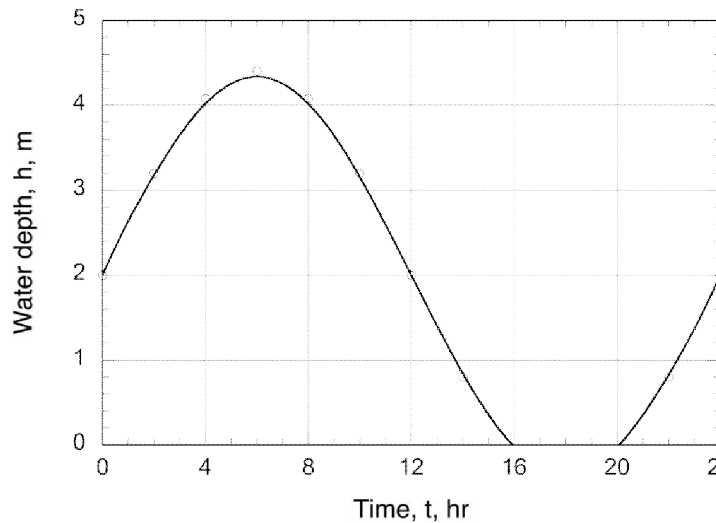
3. Integrating the above expression yields:

$$h - h_0 = \left[\frac{(43,200) (3 \times 10^{-4})}{\pi} \right] \left(\sin \frac{\pi t}{43,200} \right)$$

1. Determine h as a function of time for a 24 hour cycle

t, hr	t, s	h, m	t, hr	t, s	h, m
0	0	5.00	14	50,400	2.94
2	7200	7.06	16	57,600	1.43
4	14,400	8.57	18	64,800	0.87
6	21,600	9.13	20	72,000	1.43
8	28,800	8.57	22	79,200	2.94
10	36,000	7.06	24	84,400	5.00
12	43,200	5.00			

5. Plot the water depth versus time



PROBLEM 1-4

Instructors Note: The first six problems are designed to illustrate the application of the mass balance principle using examples from hydraulics with which the students should be familiar.

Problem Statement - See text, page 53

Solution

1. Write a materials balance on the water in the tank

Accumulation = inflow – outflow + generation

$$\frac{dV}{dt} = \frac{dh}{dt} A = Q_{in} - Q_{out} + 0$$

2. Substitute given values for variable items and solve for h

$$\frac{dh}{dt} A = 0.35 \left(1 + \cos \frac{\pi t}{43,200} \right) \text{ m}^3/\text{s} - 0.35 \text{ m}^3/\text{s}$$

$$A = 2000 \text{ m}^2$$

$$dh = 1.75 \times 10^{-4} \left(\cos \frac{\pi t}{43,200} \right) dt$$

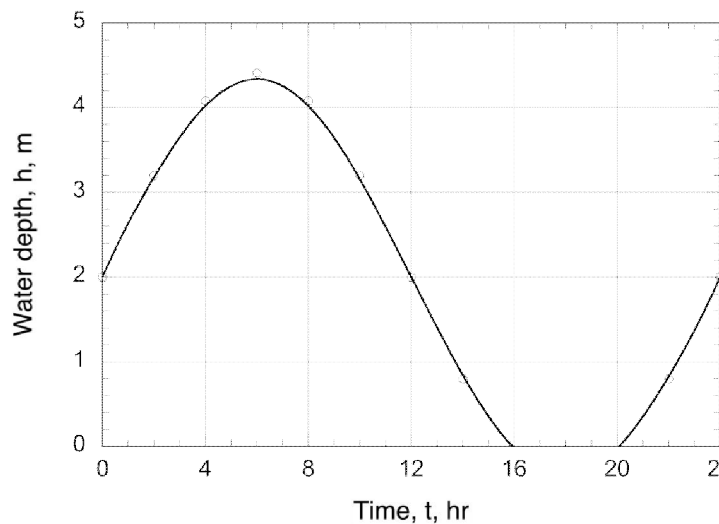
3. Integrating the above expression yields:

$$h - h_o = \left[\frac{(0.35 \text{ m}^3/\text{s})(43,200)}{\pi 2000 \text{ m}^2} \right] \left(\sin \frac{\pi t}{43,200} \right)$$

4. Determine h as a function of time for a 24 hour cycle

t, hr	t, s	h, m	t, hr	t, s	h, m
0	0	2.00	14	50,400	0.80
2	7200	3.20	16	57,600	-0.08
4	14,400	4.08	18	64,800	-0.41
6	21,600	4.41	20	72,000	-0.08
8	28,800	4.08	22	79,200	0.80
10	36,000	3.20	24	84,400	2.00
12	43,200	2.00			

5. Plot the water depth versus time



PROBLEM 1-5

Instructors Note: The first six problems are designed to illustrate the application of the mass balance principle using examples from hydraulics with which the students should be familiar.

Problem Statement - See text, page 53

Solution

1. Write a materials balance on the water in the tank

Accumulation = inflow – outflow + generation

$$\frac{dV}{dt} = \frac{dh}{dt} A = Q_{in} - Q_{out} + 0$$

2. Substitute given values for variable items and solve for h

$$\frac{dh}{dt} A = 0.5 \text{ m}^3 / \text{min} - [(2.1 \text{ m}^2 / \text{min})(h, \text{m})]$$

Integrating the above expression yields

$$\int_0^h \frac{dh}{0.5 - 2.1h} = \frac{1}{A} dt$$

$$-\frac{1}{2.1} \left(\ln \frac{0.5 - 2.1h}{0.5} \right) = \frac{t}{A}$$

Solving for h yields

$$h = \frac{1}{2.1} (0.5) (1 - e^{-2.1t/A})$$

$$h = 0.24 (1 - e^{-2.1t/A})$$

$$\text{Area} = (\pi/4) (4.2)^2 = 13.85 \text{ m}^2$$

$$h = 0.24 (1 - e^{-2.1t/13.85}) = 0.24 (1 - e^{-0.152t})$$

3. Determine the steady-state value of h

As $t \rightarrow \infty$

$h \rightarrow 0.24 \text{ m}$

PROBLEM 1-6

Instructors Note: The first six problems are designed to illustrate the application of the mass balance principle using examples from hydraulics with which the students should be familiar.

Problem Statement - See text, page 53

Solution

1. Write a materials balance on the water in the tank

Accumulation = inflow – outflow + generation

$$\frac{dV}{dt} = \frac{dh}{dt} A = Q_{in} - Q_{out} + 0$$

2. Substitute given values for variable items and solve for h

$$\frac{dh}{dt} A = 0.75 \text{ m}^3 / \text{min} - [(2.7 \text{ m}^2 / \text{min}) \times h(\text{m})]$$

Integrating the above expression yields

$$\int_0^h \frac{dh}{0.75 - 2.7 h} = \frac{1}{A} dt$$

$$-\frac{1}{2.7} \left(\ln \frac{0.75 - 2.7 h}{0.75} \right) = \frac{t}{A}$$

Solving for h yields

$$h = \frac{1}{2.7} (0.75) (1 - e^{-2.7 t/A})$$

$$h = 0.28 (1 - e^{-2.7 t/A})$$

$$\text{Area} = (\pi/4) (4.2)^2 = 13.85 \text{ m}^2$$

$$h = 0.28 (1 - e^{-2.7 t/13.85}) = 0.28 (1 - e^{-0.195t})$$

3. Determine the steady-state value of h

As $t \rightarrow \infty$

$h \rightarrow 0.28 \text{ m}$

PROBLEM 1-7

Problem Statement - See text, page 53

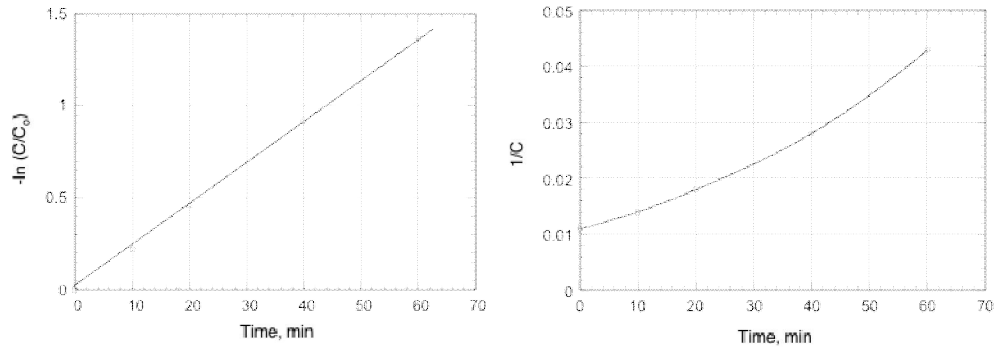
Solution: Graphical Approach

1. Determine the reaction order and the reaction rate constant using the integration method. Develop the data needed to plot the experimental data functionally for reactant 1, assuming the reaction is either first or second order.

Time, min	C, mg/L	$-\ln (C/C_0)$	1/C
0	90	0.000	0.011
10	72	0.223	0.014

20	57	0.457	0.018
40	36	0.916	0.028
60	23	1.364	0.043

2. To determine whether the reaction is first- or second-order, plot $-\ln(C/C_0)$ and $1/C$ versus t as shown below. Because the plot of $-\ln(C/C_0)$ versus t is a straight line, the reaction is first order with respect to the concentration C .



3. Determine the reaction rate coefficient.

Slope = k

The slope from the plot = $\frac{1.364 - 0.223}{60 \text{ min} - 10 \text{ min}} = 0.023/\text{min}$

$k = 0.023/\text{min}$

Summary of results for Problem 1-7

Reactant	Order	k, min^{-1}	$k, \text{m}^3/\text{g}\cdot\text{min}$
1	First	0.023	
2	Second		0.0121
3	Second		0.0003
4	First	0.035	

Solution: Mathematical Approach

- The following analysis is based on **reactant 1**
- For zero order kinetics the substrate utilization rate would remain constant. Because the utilization rate is not constant for reactant 1, the reaction rate is not zero order.

3. Assume first order kinetics are applicable and compute the value of the rate constant at various times.

Time, min	C/C ₀	ln C/C ₀	k, min ⁻¹
0	1.00	0.000	
10	0.80	-0.223	0.022
20	0.63	-0.457	0.023
40	0.40	-0.916	0.023
60	0.26	-1.364	0.023

3. Because the reaction rate constant is essentially constant, it can be concluded that the reaction is first order with respect to the utilization of reactant 1.

PROBLEM 1-8

Problem Statement - See text, page 53

Solution

1. Write a materials balance for the batch reactor

Accumulation = inflow – outflow + generation

$$\frac{d[A]}{dt} = 0 - 0 + (-k[A][B])$$

However, because [A] = [B]

$$\frac{d[A]}{dt} = -k[A]^2$$

2. Integrate the above expression

$$\int_{A_0}^A \frac{d[A]}{[A]^2} = -k \int_0^t dt$$

$$-\left(\frac{1}{A} - \frac{1}{A_0}\right) = -kt$$

3. Determine the reaction rate constant k

$$-\left[\frac{1}{0.9(1)} - \frac{1}{1}\right] = -k(10)$$

$$k = 0.011 \text{ L/mole}\cdot\text{min}$$

4. Determine the time at which the reaction will be 90 percent complete

$$-\left[\frac{1}{0.1(1)} - \frac{1}{1}\right] = -0.011(t)$$

$$t = 818 \text{ min}$$

PROBLEM 1-9

Problem Statement - See text, page 53

Solution

1. Write a materials balance for the batch reactor

Accumulation = inflow – outflow + generation

$$\frac{d[A]}{dt} = 0 - 0 + (-k[A][B])$$

However, because $[A] = [B]$

$$\frac{d[A]}{dt} = -k[A]^2$$

2. Integrate the above expression

$$\int_{A_0}^A \frac{d[A]}{[A]^2} = -k \int_0^t dt$$

$$-\left(\frac{1}{A} - \frac{1}{A_0}\right) = -kt$$

3. Determine the reaction rate constant k

$$-\left[\frac{1}{0.92(1.33)} - \frac{1}{1.33}\right] = -k(12)$$

$$k = 0.00545 \text{ L/mole}\cdot\text{min}$$

4. Determine the time at which the reaction will be 96 percent complete

$$-\left[\frac{1}{0.04(1.33)} - \frac{1}{1.33} \right] = -0.00545 (t)$$

$$t = 3313 \text{ min}$$

PROBLEM 1-10

Problem Statement - See text, page 53

Solution

1. Solve Eq. (1-41) for activation energy. The required equation is:

$$E = \frac{RT_1T_2}{(T_2 - T_1)} \left(\ln \frac{k_2}{k_1} \right) = \frac{R \ln(k_2/k_1)}{(1/T_1 - 1/T_2)}$$

where $k_2/k_1 = 2.75$

$$T_1 = 10^\circ\text{C} = 283.15 \text{ K}$$

$$T_2 = 25^\circ\text{C} = 298.15 \text{ K}$$

$$R = 8.314 \text{ J/mole}\cdot\text{K}$$

2. Solve for E given the above values:

$$E = \frac{(8.314)[\ln(2.75)]}{(1/298.15 - 1/283.15)} = 47,335 \text{ J/mole}$$

PROBLEM 1-11

Problem Statement - See text, page 53

Solution

1. Determine the activation energy using Eq. (1-41):

$$\ln \frac{k_2}{k_1} = \frac{E(T_2 - T_1)}{RT_1T_2} = \frac{E}{RT_1T_2} (T_2 - T_1)$$

where $k_2/k_1 = 2.4$

$$E = 58,000 \text{ J/mole}$$

$$R = 8.314 \text{ J/mole}\cdot\text{K}$$

2. Given $k_2 > k_1$, the lowest reaction rate is observed at k_1 . Therefore, $T_1 = 15^\circ\text{C}$. Insert known values into Eq. (1-41) and solve for T_2 to determine the temperature difference between T_1 and T_2 :

$$\begin{aligned} \ln \frac{k_2}{k_1} = 0.8755 &= \frac{E(T_2 - T_1)}{RT_1 T_2} = \frac{(58,000 \text{ J/mole})(T_2 - 288.15 \text{ K})}{(8.314 \text{ J/mole}\cdot\text{K})(288.15 \text{ K})T_2} \\ &= \frac{58,000T_2}{2395.68T_2} - \frac{16,712,700}{2395.68T_2} \\ &= 24.21 - 6976.18/T_2 \end{aligned}$$

$$\frac{1}{T_2} = \frac{24.21 - 0.8755}{6976.18} = 0.003345$$

$$T_2 = 298.96 \text{ K} = 26^\circ\text{C}$$

3. The temperature difference is therefore 11°C .

PROBLEM 1-12

Problem Statement - See text, page 53

Solution

1. Use Eq. (1-41) to determine $\ln(k_2/k_1)$:

$$\ln \frac{k_2}{k_1} = \frac{E(T_2 - T_1)}{RT_1 T_2} = \frac{E}{RT_1 T_2} (T_2 - T_1)$$

$$\text{where } T_1 = 27^\circ\text{C} - 15^\circ\text{C} = 12^\circ\text{C} = 285.15 \text{ K}$$

$$T_2 = 27^\circ\text{C} = 300.15 \text{ K}$$

$$E = 52,000 \text{ J/mole}$$

$$R = 8.314 \text{ J/mole}\cdot\text{K}$$

2. Solve for $\ln(k_2/k_1)$ given the above values:

$$\begin{aligned} \ln \frac{k_2}{k_1} &= \frac{(52,000 \text{ J/mole})}{(8.314 \text{ J/mole}\cdot\text{K})(285.15 \text{ K})(300.15 \text{ K})} (285.15 \text{ K} - 300.15 \text{ K}) \\ &= 1.0962 \end{aligned}$$

3. The difference in the reaction rates is:

$$\ln \frac{k_2}{k_1} = \ln(k_2) - \ln(k_1) = 1.0962$$

PROBLEM 1-13

Problem Statement - See text, page 54

Solution

1. Determine the activation energy using Eq. (1-41)

$$\ln \frac{k_2}{k_1} = \frac{E(T_2 - T_1)}{RT_1T_2} = \frac{E}{RT_1T_2} (T_2 - T_1)$$

where $k_{25^\circ\text{C}} = 1.5 \times 10^{-2}$ L/mole•min

$k_{45^\circ\text{C}} = 4.5 \times 10^{-2}$ L/mole•min

$T_1 = 25^\circ\text{C} = 298.15$ K

$T_2 = 45^\circ\text{C} = 318.15$ K

$R = 8.314$ J/mole•K

2. Solve the above expression for E

$$E = \frac{RT_1T_2}{(T_2 - T_1)} \left(\ln \frac{k_2}{k_1} \right)$$

$$E = \frac{(8.314)(298.15)(318.15)}{(318.15 - 298.15)} \left(\ln \frac{4.5 \times 10^{-2}}{1.5 \times 10^{-2}} \right) = 43,320 \text{ J/mole}$$

3. Determine the rate constant at 15°C

$$\ln \frac{k_2}{k_1} = \frac{E}{RT_1T_2} (T_2 - T_1)$$

where $k_{15^\circ\text{C}} = ?$ L/mole•min

$k_{25^\circ\text{C}} = 1.5 \times 10^{-2}$ L/mole•min

$T_1 = 25^\circ\text{C} = 298.15$ K

$T_2 = 15^\circ\text{C} = 288.15$ K

$$R = 8.314 \text{ J/mole}\cdot\text{K}$$

$$\ln \frac{k_{15^\circ\text{C}}}{1.5 \times 10^{-2}} = \frac{43,320}{(8.314)(298.15)(288.15)} (288.15 - 298.15)$$

$$\ln \frac{k_{15^\circ\text{C}}}{1.5 \times 10^{-2}} = -0.6065$$

$$k_{15^\circ\text{C}} = (1.5 \times 10^{-2})(0.5453) = 0.818 \times 10^{-2}$$

PROBLEM 1-14

Problem Statement - See text, page 54

Solution

1. Determine the activation energy using Eq. (1-41)

$$\ln \frac{k_2}{k_1} = \frac{E(T_2 - T_1)}{RT_1T_2} = \frac{E}{RT_1T_2} (T_2 - T_1)$$

where $k_{20^\circ\text{C}} = 1.25 \times 10^{-2} \text{ L/mole}\cdot\text{min}$

$$k_{35^\circ\text{C}} = 3.55 \times 10^{-2} \text{ L/mole}\cdot\text{min}$$

$$T_1 = 20^\circ\text{C} = 293.15 \text{ K}$$

$$T_2 = 35^\circ\text{C} = 308.15 \text{ K}$$

$$R = 8.314 \text{ J/mole}\cdot\text{K}$$

2. Solve the above expression for E

$$E = \frac{RT_1T_2}{(T_2 - T_1)} \left(\ln \frac{k_2}{k_1} \right)$$

$$E = \frac{(8.314)(293.15)(308.15)}{(308.15 - 293.15)} \left(\ln \frac{3.55 \times 10^{-2}}{1.25 \times 10^{-2}} \right) = 52,262 \text{ J/mole}$$

3. Determine the rate constant at 15°C

$$\ln \frac{k_2}{k_1} = \frac{E}{RT_1T_2} (T_2 - T_1)$$

where $k_{15^\circ\text{C}} = ? \text{ L/mole}\cdot\text{min}$

$$k_{20^{\circ}\text{C}} = 1.25 \times 10^{-2} \text{ L/mole}\cdot\text{min}$$

$$T_1 = 20^{\circ}\text{C} = 293.15 \text{ K}$$

$$T_2 = 15^{\circ}\text{C} = 288.15 \text{ K}$$

$$R = 8.314 \text{ J/mole}\cdot\text{K}$$

$$\ln \frac{k_{15^{\circ}\text{C}}}{1.25 \times 10^{-2}} = \frac{52,262}{(8.314)(293.15)(288.15)} (288.15 - 293.15)$$

$$\ln \frac{k_{15^{\circ}\text{C}}}{1.25 \times 10^{-2}} = -0.372$$

$$k_{15^{\circ}\text{C}} = (1.25 \times 10^{-2})(0.689) = 0.862 \times 10^{-2}$$

PROBLEM 1-15

Problem Statement - See text, page 53

Solution

1. Write a materials balance for a complete-mix reactor. Use the generic rate expression for chemical reactions given in Table 1-11.

Accumulation = inflow – outflow + generation

$$\frac{dC}{dt}V = QC_o - QC + (-kC^n)V$$

2. Solve the mass balance at steady-state for kC^n

From stoichiometry, $C = C_o - 1/2C_R$

Substituting for C yields:

$$0 = QC_o - Q(C_o - \frac{1}{2}C_R) + (-kC^n)V$$

$$0 = \frac{1}{2}QC_R - kC^nV$$

$$kC^n = \frac{QC_R}{2V}$$

3. Determine the reaction order and the reaction rate constant at 13°C

- a. Consider Run 1

$$k_{13^{\circ}\text{C}} [1 - 1/2(1.8)]^n = \frac{(2 \text{ cm/s})(1.8 \text{ mole/L})}{2(5 \text{ L})(10^3 \text{ cm}^3/\text{L})} = 3.6 \times 10^{-4} \text{ mole/L}\cdot\text{s}$$

b. Consider Run 2

$$k_{13^{\circ}\text{C}} [1 - 1/2(1.5)]^n = \frac{(15 \text{ cm/s})(1.5 \text{ mole/L})}{2(5 \text{ L})(10^3 \text{ cm}^3/\text{L})} = 2.25 \times 10^{-3} \text{ mole/L}\cdot\text{s}$$

c. Divide a by b

$$\frac{k_{13^{\circ}\text{C}} (0.1)^n}{k_{13^{\circ}\text{C}} (0.25)^n} = \frac{3.6 \times 10^{-4}}{2.25 \times 10^{-3}}$$

$$\left(\frac{0.1}{0.25}\right)^n = 0.16$$

$$n = 2$$

4. Determine the reaction rate constant at 84°C

$$k_{84^{\circ}\text{C}} = \frac{QC_R}{2VC^2} = \frac{(15 \text{ cm/s})(1.8 \text{ mole/L})}{2(5 \text{ L})(10^3 \text{ cm}^3/\text{L})(0.1)^2} = 2.7 \times 10^{-1} \text{ L/mole}\cdot\text{s}$$

5. Determine the temperature coefficient θ using Eq. (1-44)

$$\frac{k_{84^{\circ}\text{C}}}{k_{13^{\circ}\text{C}}} = \theta^{(T_2 - T_1)}$$

$$\text{where } k_{13^{\circ}\text{C}} = (k_{13^{\circ}\text{C}} C^2)/C^2 = 3.6 \times 10^{-2}$$

$$\frac{2.7 \times 10^{-1}}{3.6 \times 10^{-2}} = \theta^{(357.15 - 286.15)}$$

$$\ln(7.5) = 71 \ln \theta$$

$$\ln \theta = 2.015/71 = 0.0284$$

$$\theta = 1.029$$

PROBLEM 1-16

Problem Statement - See text, page 53

Solution

1. Write a materials balance for the batch reactor

Accumulation = inflow – outflow + generation

$$\frac{dC}{dt} V = 0 - 0 + \left(-\frac{kC}{K + C}\right) V$$

2. Solve the mass balance for t

$$\left(\frac{K + C}{C}\right) dC = -k dt$$

$$\int_{C_0}^C \left[\left(\frac{K}{C}\right) + 1\right] dC = -k \int_0^t dt$$

$$K \ln(C_0/C) + (C_0 - C) = kt$$

$$t = \frac{K \ln(C_0/C) + C_0 - C}{k}$$

3. Compute t for the given data:

$$C_0 = 1000 \text{ mg/m}^3$$

$$C = 100 \text{ mg/m}^3$$

$$k = 40 \text{ mg/m}^3 \cdot \text{min}$$

$$K = 100 \text{ mg/m}^3$$

$$t = \frac{100 \ln(1000/100) + (1000-100)}{40} = 28.3 \text{ min}$$

Comment

An explicit expression for the concentration C cannot be obtained as a function of time. The concentration C at any time t must be obtained by successive trials.

PROBLEM 1-17

Problem Statement - See text, page 54

Solution

1. Write a materials balance for the batch reactor

Accumulation = inflow – outflow + generation

$$\frac{dC}{dt}V = 0 - 0 + \left(-\frac{kC}{K+C}\right)V$$

2. Solve the mass balance for t

$$\left(\frac{K+C}{C}\right)dC = -k dt$$

$$\int_{C_0}^C \left[\left(\frac{K}{C}\right) + 1 \right] dC = -k \int_0^t dt$$

$$K \ln(C_0/C) + C_0 - C = kt$$

$$t = \frac{K \ln(C_0/C) + C_0 - C}{k}$$

3. Compute t for the given data:

$$C_0 = 1000 \text{ g/m}^3$$

$$C = 100 \text{ g/m}^3$$

$$k = 28 \text{ g/m}^3 \cdot \text{min}$$

$$K = 116 \text{ g/m}^3$$

$$t = \frac{116 \ln(1000/100) + (1000-100)}{28} = 41.7 \text{ min}$$

Comment

An explicit expression for the concentration C cannot be obtained as a function of time. The concentration C at any time t must be obtained by successive trials.

PROBLEM 1-18

Problem Statement - See text, page 54

Solution

1. Write a materials balance on the water in the complete-mix reactor

$$\text{Accumulation} = \text{inflow} - \text{outflow} + \text{generation}$$

$$\frac{dC}{dt} = QC_0 - QC + (-kC)V$$

2. Determine the flowrate at steady state

$$0 = QC_0 - QC + (-kC)V$$

solve for C/C_0

$$\frac{C}{C_0} = \frac{Q}{Q + kV}$$

Substitute known values and solve for Q at 98 percent conversion

$$(C/C_0 = 0.02)$$

$$0.02 = \frac{Q}{Q + (0.15 / d)(20 \text{ m}^3)}$$

$$Q = 0.02Q + 0.06$$

$$Q = 0.0612 \text{ m}^3/\text{d}$$

3. Determine the corresponding reactor volume required for 92 percent conversion at a flowrate of 0.0612 m³/d

$$0.08 = \frac{(0.0612 \text{ m}^3 / \text{d})}{(0.0612 \text{ m}^3 / \text{d}) + (0.15 / \text{d})V}$$

$$V = 4.7 \text{ m}^3$$

PROBLEM 1-19

Problem Statement - See text, page 54

Solution

1. The general expression for reactors in series for first order kinetics is:

- a. For reactors of the same size the expression [Eq. (1-75)] is:

$$C_n = \frac{C_0}{[1 + (kV / nQ)]^n} = \frac{C_0}{[1 + (k\tau)]^n}$$

where τ = hydraulic detention time of individual reactors

- b. For reactors of unequal size the expression is:

$$C_n = \left[\frac{C_o}{1 + (k\tau_1)} \right] \left[\frac{C_o}{1 + (k\tau_2)} \right] \cdots \left[\frac{C_o}{1 + (k\tau_n)} \right]$$

where $\tau_1, \tau_2, \dots, \tau_n$ = hydraulic detention of individual reactors

2. Demonstrate that the maximum treatment efficiency in a series of complete-mix reactors occurs when all the reactors are the same size.

- a. Determine efficiency for three reactors in series when the reactors are of the same size.

Assume $C_o = 1, V_T = 3, \tau = 1, k = 1,$ and $n = 3$

$$\frac{C_3}{C_o} = \frac{1}{[1 + (k\tau)]^n} = \frac{1}{[1 + (1 \times 1)]^3} = 0.125$$

- b. Determine efficiency for three reactors in series when the reactors are not of the same size.

Assume $C_o = 1, V_T = 3, \tau_1 = 2, \tau_2 = 0.5, \tau_3 = 0.5,$ and $k = 1$

$$\frac{C_3}{C_o} = \left[\frac{1}{1 + (1 \times 2)} \right] \left[\frac{1}{1 + (1 \times 0.5)} \right] \left[\frac{1}{1 + (1 \times 0.5)} \right] = 0.148$$

- c. Determine efficiency for three reactors in series when the reactors are not of the same size and are of a different configuration from b

Assume $C_o = 1, V_T = 3, \tau_1 = 1, \tau_2 = 1.5, \tau_3 = 0.5, k = 1,$ and $n = 3$

$$\frac{C_3}{C_o} = \left[\frac{1}{1 + (1 \times 1)} \right] \left[\frac{1}{1 + (1 \times 1.5)} \right] \left[\frac{1}{1 + (1 \times 0.5)} \right] = 0.133$$

3. Demonstrate mathematically that the maximum treatment efficiency in a series of complete-mix reactors occurs when all the reactors are the same size.

- a. For two reactors in series

$$\frac{C_o}{C_2} = (1 + k\tau_1)(1 + k\tau_2)$$

- b. Determine τ_1 and τ_2 such that C_o/C_2 will be maximized

$$\nabla(C_o / C_2) = (1 + k^2\tau_1) \hat{i} + (1 + k^2\tau_2) \hat{j}$$

- c. To maximize the above expression let $\nabla(C_o/C_2) = 0$

$$0 = (1 + k^2\tau_1)\hat{i} + (1 + k^2\tau_2)\hat{j}$$

$$1 + k^2\tau_1 = 0$$

$$1 + k^2\tau_2 = 0$$

thus, $\tau_1 = \tau_2$ for $k \neq 0$

d. Check to identify maximum or minimum

Let $\tau_1 + \tau_2 = 2$ and $k = 1$

If $\tau_1 = \tau_2 = 1$

$$\text{Then } \frac{C_o}{C_2} = (1 + k\tau_1)(1 + k\tau_2) = [1 + (1 \times 1)][1 + (1 \times 1)] = 4$$

e. For any other combination of $\tau_1 + \tau_2$, C_o/C_2 will be less than 4. Thus,

C_o/C_2 will be maximized when $\tau_1 = \tau_2$.

f. By extension it can be shown that the maximum treatment efficiency in a series of complete-mix reactors occurs when all of the reactors are of the same size.

PROBLEM 1-20

Problem Statement - See text, page 54

Solution

1. For n complete-mix reactors in series the corresponding expression is given by Eq. (1-75)

$$\frac{C_n}{C_o} = \frac{1}{[1 + (kV/nQ)]^n} = \frac{1}{[1 + (k/\tau)]^n}$$

where τ = hydraulic detention time for individual reactors

2. Determine the number of reactors in series

$$[1 + (k/\tau)]^n = \frac{C_o}{C_n}$$

Substitute the given values and solve for n , the number of reactors in series

$$[1 + (6.1/h)/(0.5 h)]^n = \frac{10^6}{14.5}$$

$$n \log [1 + (6.1/h) / (0.5 h)] = \log \left(\frac{10^6}{14.5} \right)$$

$n \approx 10.2$, Use 10 reactors

PROBLEM 1-21

Problem Statement - See text, page 54

Solution

1. The expression for an ideal plug flow reactor is given in Eq. (1-21)

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x}$$

The influent concentration must be equal to the effluent concentration and the change with respect to distance is equal to zero by definition.

2. The rate of reaction is defined as retarded first order given in Eq. (1-53),

$$\frac{dC}{dt} = -\frac{kC}{(1+r_t t)^n}$$

Bringing like terms together, integrate between the limits $C = C_o$ and $C = C$ and $t = 0$ and $t = t$,

$$\int_{C=C_o}^{C=C} \frac{dC}{C} = - \int_{t=0}^{t=t} \frac{k}{(1+r_t t)^n} dt$$

3. For $n = 1$,

$$\ln \left(\frac{C}{C_o} \right) = -\frac{k}{r_t} \ln(1+r_t t)$$

$$C = C_o \exp \left[-\frac{k}{r_t} \ln(1+r_t t) \right]$$

4. For $n \neq 1$,

$$\ln \left(\frac{C}{C_o} \right) = -\frac{k}{r_t(n-1)} \left[1 - \frac{1}{(1+r_t t)^{n-1}} \right]$$

$$C = C_o \exp \left\{ -\frac{k}{r_t(n-1)} \left[1 - \frac{1}{(1+r_t t)^{n-1}} \right] \right\}$$

PROBLEM 1-22

Problem Statement - See text, page 54

Solution

1. Develop basic materials balance formulations for a complete-mix reactor (CMR) and a plug-flow reactor (PFR).

- a. CMR

Accumulation = inflow – outflow + generation

$$\frac{dC}{dt}V = QC_o - QC + r_c V \quad \text{Eq. (1-57)}$$

At steady state

$$0 = QC_o - QC + r_c V$$

- b. PFR

Accumulation = inflow – outflow + generation

$$\frac{\partial C}{\partial t} \Delta V = QC|_x - QC|_{x+\Delta x} + r_c dV \quad \text{Eq. (1-79)}$$

Taking the limit as Δx goes to zero and considering steady-state yields

$$0 = -\frac{Q}{A} \frac{dC}{dx} + r_c$$

For a rate of reaction defined as $r_c = -kC^n$ the above expression can be written as follows. See.

$$\int_{C_o}^C \frac{dC}{C^n} = -k \frac{A}{Q} \int_0^L dx = -k \frac{AL}{Q} = -k \frac{V}{Q} = -k\tau \quad \text{Eq. (1-83)}$$

2. Solve the complete-mix and plug-flow expressions for $r = -k$ and determine ratio of volumes

- a. Complete-mix reactor

$$0 = QC_o - QC - kV$$

$$V_{CMR} = \frac{Q(C_o - C)}{k}$$

- b. Plug-flow reactor

$$\int_{C_o}^C dC = -k \frac{V}{Q} = C - C_o$$

$$V_{\text{PFR}} = \frac{Q(C_o - C)}{k}$$

c. Ratio of volumes

$$\frac{V_{\text{PFR}}}{V_{\text{CMR}}} = \frac{\left[\frac{Q(C_o - C)}{k} \right]}{\left[\frac{Q(C_o - C)}{k} \right]} = 1$$

3. Solve the complete-mix and plug-flow expressions for $r = -kC^{0.5}$ and determine ratio of volumes

a. Complete-mix reactor

$$0 = QC_o - QC - kC^{0.5}V$$

$$V_{\text{CMR}} = \frac{Q}{k} \left(\frac{C_o}{C^{0.5}} - C^{0.5} \right)$$

b. Plug-flow reactor

$$\int_{C_o}^C \frac{dC}{C^{0.5}} = -k \frac{V}{Q}$$

$$V_{\text{PFR}} = \frac{2Q}{k} (C_o^{0.5} - C^{0.5})$$

c. Ratio of volumes

$$\frac{V_{\text{PFR}}}{V_{\text{CMR}}} = \frac{2C^{0.5}(C_o^{0.5} - C^{0.5})}{(C_o - C)}$$

4. Solve the complete-mix and plug-flow expressions for $r = -kC$ and determine ratio of volumes

a. Complete-mix reactor

$$0 = QC_o - QC - kCV$$

$$V_{\text{CMR}} = \frac{Q(C_o - C)}{kC}$$

b. Plug-flow reactor

$$\int_{C_o}^C \frac{dC}{C} = -k \frac{V}{Q}$$

$$V_{PFR} = \frac{Q}{k} \ln(C_o / C)$$

c. ratio of volumes

$$\frac{V_{PFR}}{V_{CMR}} = \frac{C [\ln(C_o / C)]}{(C_o - C)}$$

5. Solve the complete-mix and plug-flow expressions for $r = -kC^2$ and determine ratio of volumes

a. Complete-mix reactor

$$0 = QC_o - QC - kC^2V$$

$$V_{CMR} = \frac{Q(C_o - C)}{kC^2}$$

b. Plug-flow reactor

$$\int_{C_o}^C \frac{dC}{C^2} = -k \frac{V}{Q}$$

$$V_{PFR} = \frac{Q}{k} \left(\frac{1}{C} - \frac{1}{C_o} \right)$$

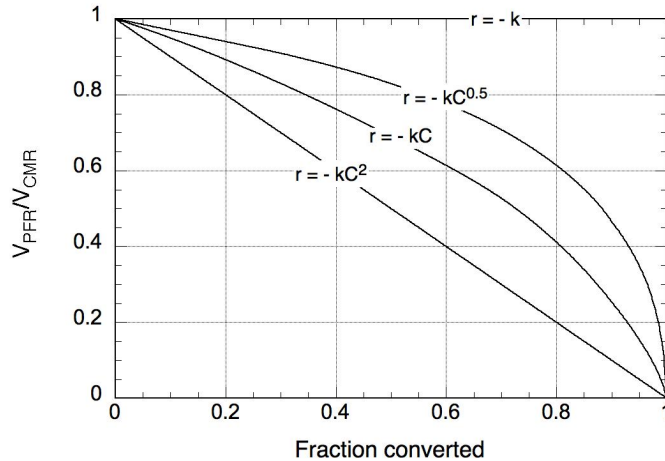
c. Ratio of volumes

$$\frac{V_{PFR}}{V_{CMR}} = \frac{C}{C_o}$$

6. Set up computation table to determine the ratio of volumes (V_{PFR}/V_{CMR}) versus the fraction of the original substrate that is converted

Fraction converted	V_{PFR}/V_{CMR}			
	$r = -k$	$r = -kC^{0.5}$	$r = -kC$	$r = -kC^2$
0.1	1	0.97	0.95	0.90
0.3	1	0.91	0.83	0.70
0.5	1	0.83	0.69	0.50
0.7	1	0.71	0.52	0.30
0.9	1	0.48	0.26	0.10
0.95	1	0.37	0.16	0.05
0.99	1	0.18	0.05	0.01

7. Plot the ratio of volumes versus the fraction of the original substrate that is converted.



8. Determine the ratio of volumes for each rate when $C = 0.25 \text{ g/m}^3$ and $C_0 = 1.0 \text{ g/m}^3$ (fraction converted = 0.75). From the plot in Step 7 the required values are:

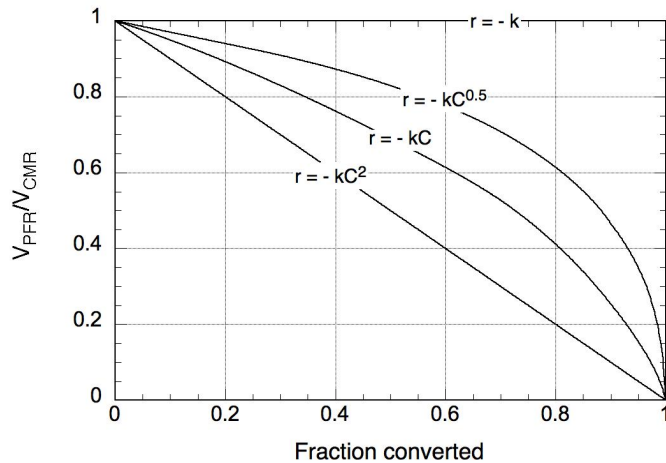
Rate	V_{PFR}/V_{CMR}
$r = -k$	1.00
$r = -kC^{0.5}$	0.67
$r = -kC$	0.46
$r = -kC^2$	0.25

PROBLEM 1-23

Problem Statement - See text, page 54

Solution

1. The ratio of volumes (V_{PFR}/V_{CMR}) versus the fraction of the original substrate converted is given in the following plot (see Problem 1-22).



2. Determine the ratio of volumes for each rate when $C = 0.17 \text{ g/m}^3$ and $C_0 = 1.25 \text{ g/m}^3$ (fraction converted = 0.86). From the plot in Step 7 the required values are:

Rate	V_{PFR}/V_{CMR}
$r = -k$	1.00
$r = -kC^{0.5}$	0.54
$r = -kC$	0.31
$r = -kC^2$	0.14

PROBLEM 1-24

Problem Statement - See text, page 54

Solution: Part 1 ($r = -kC^2$)

1. Solve the complete-mix and plug-flow expressions for C for $r = -kC^2$
- Complete-mix reactor

$$C^2 - \frac{Q}{kV}C - \frac{Q}{kV}C_0 = 0$$

$$C_{CMR} = \frac{Q/kV \left[\sqrt{1 + 4(kV/Q)C_0} - 1 \right]}{2}$$

- Plug-flow reactor

$$\int_{C_0}^C \frac{dC}{C^2} = -k \frac{V}{Q}$$

$$V_{PFR} = \frac{Q}{k} \left(\frac{1}{C} - \frac{1}{C_0} \right)$$

$$C_{PFR} = \left(\frac{kV}{Q} + \frac{1}{C_0} \right)^{-1}$$

2. Determine the effluent concentration from the combined reactor systems

a. PFR-CMR

$$C_{PFR} = \left(\frac{kQ}{V} + \frac{1}{C_0} \right)^{-1} = \left(\frac{1 \times 1}{1} + \frac{1}{1} \right)^{-1} = 0.5 \text{ kg/m}^3$$

$$C_{CMR} = \frac{Q/kV \left[\sqrt{1 + 4(kV/Q)C_0} - 1 \right]}{2} = \frac{(1/1 \times 1) \left[\sqrt{1 + 4(1 \times 1/1)(0.5)} - 1 \right]}{2}$$

$$= 0.366 \text{ kg/m}^3$$

b. CMR-PFR

$$C_{CMR} = \frac{Q/kV \left[\sqrt{1 + 4(kV/Q)C_0} - 1 \right]}{2} = \frac{(1/1 \times 1) \left[\sqrt{1 + 4(1 \times 1/1)(1)} - 1 \right]}{2}$$

$$= 0.618 \text{ kg/m}^3$$

$$C_{PFR} = \left(\frac{kQ}{V} + \frac{1}{C_0} \right)^{-1} = \left(\frac{1 \times 1}{1} + \frac{1}{0.618} \right)^{-1} = 0.382 \text{ kg/m}^3$$

c. Because the effluent concentration C is not directly proportional to C_0 for second order kinetics, the final concentrations are different

Solution: Part 2 ($r = -kC$)

1. Solve the complete-mix and plug-flow expressions for C for $r = -kC$

a. Complete-mix reactor

$$0 = QC_0 - QC - kCV$$

$$C = \frac{C_0}{(1 + kV/Q)}$$

b. Plug-flow reactor

$$\int_{C_0}^C \frac{dC}{C} = -k \frac{V}{Q}$$

$$C = C_0 e^{-kV/Q}$$

2. Determine the effluent concentration from the combined reactor systems

a. PFR-CMR

$$C_{\text{PFR}} = C_0 e^{-kV/Q} = (1) e^{-(1 \times 1)/1} = 0.368 \text{ kg/m}^3$$

$$C_{\text{CMR}} = \frac{C_0}{(1 + kV/Q)} = \frac{0.368}{[1 + (1 \times 1)/1]} = 0.184 \text{ kg/m}^3$$

b. CMR-PFR

$$C_{\text{CMR}} = \frac{C_0}{(1 + kV/Q)} = \frac{1}{[1 + (1 \times 1)/1]} = 0.5 \text{ kg/m}^3$$

$$C_{\text{PFR}} = C_0 e^{-kV/Q} = (0.5) e^{-(1 \times 1)/1} = 0.184 \text{ kg/m}^3$$

c. Because the effluent concentration C is directly proportional to C_0 for first order kinetics, the final concentrations are the same

Solution: Part 3 ($r = -k$)

1. Solve the complete-mix and plug-flow expressions for C for $r = -k$

a. Complete-mix reactor

$$0 = QC_0 - QC - kV$$

$$C = C_0 - k(V/Q)$$

b. Plug-flow reactor

$$\int_{C_0}^C dC = -k \frac{V}{Q}$$

$$C = C_0 - k(V/Q)$$

2. Determine the effluent concentration from the combined reactor systems

a. The two expressions derived above are identical.

b. Because the two expressions are identical, for the given data the concentration in the second reactor is equal to zero.

PROBLEM 1-25**Problem Statement** - See text, page 54**Solution**

1. Develop basic mass balance formulation for plug-flow reactor with recycle

Accumulation = inflow – outflow + generation

$$\frac{\partial C}{\partial t} \Delta V = Q' C_o' \Big|_x - Q' C_o' \Big|_{x+\Delta x} + r_c dV \quad (1-18)$$

where $Q' = Q(1 + \alpha)$

$$C_o' = \frac{\alpha C + C_o}{1 + \alpha}$$

$\alpha = \text{recycle ratio} = Q/Q_R$

2. Solve the mass balance equation for C/C_o

$$\int_{C_o'}^C \frac{dC}{C} = -k \frac{V}{Q'}$$

$$\ln C/C_o' = -k \frac{V}{Q'}$$

$$C = C_o' e^{-kV/Q'} = \frac{\alpha C + C_o}{1 + \alpha} e^{-k \frac{V}{Q} \left(\frac{1}{1 + \alpha} \right)}$$

With some manipulation,

$$C/C_o = \frac{e^{-k \frac{V}{Q} \left(\frac{1}{1 + \alpha} \right)}}{1 + \alpha \left[1 - e^{-k \frac{V}{Q} \left(\frac{1}{1 + \alpha} \right)} \right]}$$

Remembering that $e^x = 1 + x + \frac{x^2}{2!} + \dots$

$$C/C_o = \frac{1 + \left(-k \frac{V}{Q} \frac{1}{1 + \alpha} \right)}{1 + \alpha \left(1 - 1 + k \frac{V}{Q} \frac{1}{1 + \alpha} \right)} = \frac{\left(1 - k \frac{V}{Q} \frac{1}{1 + \alpha} \right)}{\left(1 + k \frac{V}{Q} \frac{\alpha}{1 + \alpha} \right)}$$

Thus when $\alpha \rightarrow \infty$, the above expression is approximately equal to

$$C/C_o \approx \frac{1}{1 + k \frac{V}{Q}}$$

which is the expression for a complete-mix reactor

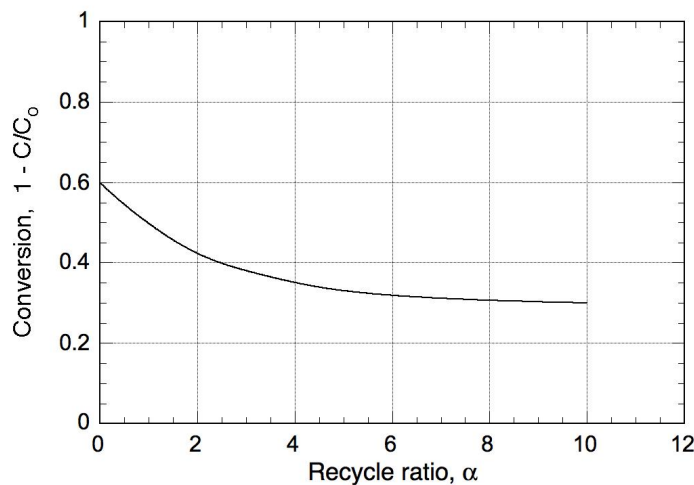
3. Sketch the generalized curve of conversion versus the recycle ratio.

a. At $\alpha = 0$

$$1 - C/C_o = 1 - e^{-kV/Q}$$

b. As $\alpha \rightarrow \infty$

$1 - C/C_o \rightarrow$ the conversion of a CMR



4. Sketch a family of curves to illustrate the effect of the recycle ratio on the longitudinal concentration gradient.

a. From Step 2

$$C/C_o' = e^{-k \frac{V}{Q} \left(\frac{1}{1 + \alpha} \right)}$$

b. The relative conversion is:

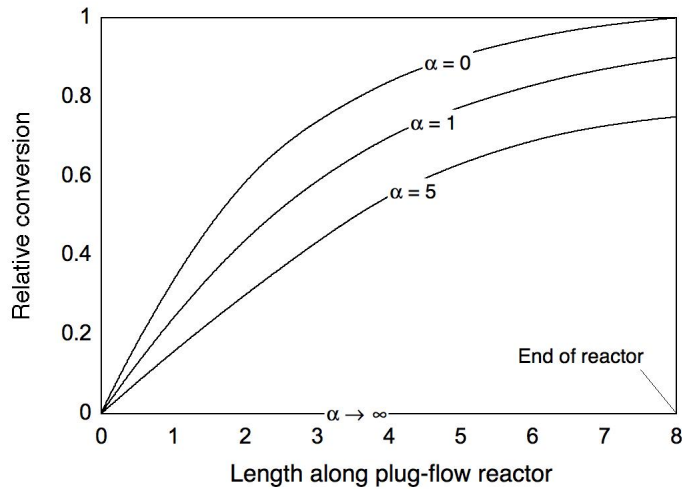
$$1 - C/C_o' = 1 - e^{-k \frac{V}{Q} \left(\frac{1}{1 + \alpha} \right)}$$

c. When $\alpha = 0$, the longitudinal concentration gradient is given by

$$1 - C/C_o = 1 - e^{-k \frac{V}{Q}}$$

d. When $\alpha \rightarrow \infty$, the longitudinal concentration gradient is given by

$$1 - C/C_0 = 1 - 1 = 0$$



5. Write a materials balance for a complete mix-reactor with recycle

Accumulation = inflow - outflow + generation

$$\frac{dC}{dt} = QC_0 + Q_R C - (Q + Q_R)C + (-r_C)V$$

At steady-state

$$0 = QC_0 + Q_R C - (Q + Q_R)C + (-r_C)V$$

Because Q_R drops out of the above expression, recycle flow has no effect.

PROBLEM 1-26

Problem Statement - See text, page 54

Solution

1. Write a materials balance for a complete mix-reactor with effluent recycle with first order reaction kinetics

Accumulation = inflow - outflow + generation

$$\frac{dC}{dt} = QC_0 + Q_R C - (Q + Q_R)C + (-r_C)V$$

2. At steady-state

$$0 = QC_0 + Q_R C - (Q + Q_R)C + (-r_C)V$$

Because Q_R drops out of the above expression, recycle flow has no effect for first or second order reactions.

PROBLEM 1-27

Problem Statement - See text, page 54

Solution

1. Starting with Eq. (1-53), derive an expression that can be used to compute the effluent concentration assuming a retarded second order removal rate coefficient.

$$\int_{C=C_0}^{C=C} \frac{dC}{C^2} = - \int_{t=0}^{t=t} \frac{k}{(1+r_t t)} dt$$

- a. Integrating the above expression yields

$$\frac{1}{C} \Big|_{C=C_0}^{C=C} = \frac{k}{r_t} \ln(1+r_t t) \Big|_{t=0}^{t=t}$$

- b. Carrying out the above substitutions and solving for C yields

$$C = \frac{r_t C_0}{r_t + k C_0 \ln(1+r_t t)}$$

2. Determine the effect of retardation.
 - a. The expression for the effluent concentration for second-order removal kinetics without retardation is (see Problem 1-24, Part 1 for plug-flow reactor):

$$C = \frac{1}{\left(k\tau + \frac{1}{C_0} \right)}$$

- b. Compare effluent concentrations for the following conditions

$C_0 = 1.0$

$k = 0.1$

$$r_t = 0.2$$

$$\tau = 1.0$$

$$C_{\text{eff (retarded)}} = \frac{0.2(1.0)}{0.2 + 0.1(1.0)\ln[1 + 0.2(1.0)]} = 0.92$$

$$C_{\text{eff (unretarded)}} = \frac{1}{\left[0.1(1.0) + \frac{1}{(1.0)}\right]} = 0.91$$

3. From the above computations it can be seen that the effect of retardation is not as significant for a second order reaction. The impact is much greater for first order reactions.

CONSTITUENTS IN WASTEWATER

PROBLEM 2-1

Problem Statement - See text, page 171

Solution

- Set up a computation table to determine the sum of milliequivalents per liter for both cations and anions for **Sample 3**, for example.

Cation	Concentration			Anion	Concentration		
	mg/meq	mg/L	meq/L		mg/meq	mg/L	meq/L
Ca ²⁺	20.04	190.2	9.49	HCO ₃ ⁻	61.02	260.0	4.26
Mg ²⁺	12.15	84.1	6.92	SO ₄ ²⁻	48.03	64.0	1.33
Na ⁺	23.00	75.2	3.27	Cl ⁻	35.45	440.4	12.41
K ⁺	39.10	5.1	0.13	NO ₃ ⁻	62.01	35.1	0.58
Fe ²⁺		0.2	0.01	CO ₃ ²⁻		30.0	1.00
Sum	-	-	19.82	Sum	-	-	19.58

- Check the accuracy of the cation-anion balance using Eq. (2-5).

$$\text{Percent difference} = 100 \times \left(\frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} \right)$$

$$\text{Percent difference} = 100 \times \left(\frac{19.82 - 19.58}{19.82 + 19.58} \right) = -0.6\% \text{ (ok)}$$

PROBLEM 2-2

Problem Statement - See text, page 171

Solution

- Determine the mole fraction of each cation and anion in **Sample 1** using Eq. (2-2) written as follows:

$$x_{\text{Ca}^{2+}} = \frac{n_{\text{Ca}^{2+}}}{n_{\text{Ca}^{2+}} + n_{\text{Mg}^{2+}} + n_{\text{Na}^{+}} + n_{\text{K}^{+}} + n_{\text{HCO}_3^{-}} + n_{\text{SO}_4^{2-}} + n_{\text{Cl}^{-}} + n_{\text{NO}_3^{-}} + n_w}$$

a. Determine the moles of the solutes.

$$n_{\text{Ca}^{2+}} = \frac{(206.6 \text{ mg/L})}{(40.08 \times 10^3 \text{ mg/mole Ca}^{2+})} = 5.155 \times 10^{-3} \text{ mole/L}$$

$$n_{\text{Mg}^{2+}} = \frac{(95.3 \text{ mg/L})}{(24.305 \times 10^3 \text{ mg/mole of Mg}^{2+})} = 3.921 \times 10^{-3} \text{ mole/L}$$

$$n_{\text{Na}^{+}} = \frac{(82.3 \text{ mg/L})}{(23.000 \times 10^3 \text{ mg/mole of Na}^{+})} = 3.578 \times 10^{-3} \text{ mole/L}$$

$$n_{\text{K}^{+}} = \frac{(5.9 \text{ mg/L})}{(39.098 \times 10^3 \text{ mg/mole of K}^{+})} = 1.509 \times 10^{-4} \text{ mole/L}$$

$$n_{\text{HCO}_3^{-}} = \frac{(525.4 \text{ mg/L})}{(61.017 \times 10^3 \text{ mg/mole of HCO}_3^{-})} = 8.611 \times 10^{-3} \text{ mole/L}$$

$$n_{\text{SO}_4^{2-}} = \frac{(219.0 \text{ mg/L})}{(96.058 \times 10^3 \text{ mg/mole of SO}_4^{2-})} = 2.280 \times 10^{-3} \text{ mole/L}$$

$$n_{\text{Cl}^{-}} = \frac{(303.8 \text{ mg/L})}{(35.453 \times 10^3 \text{ mg/mole of Cl}^{-})} = 8.569 \times 10^{-3} \text{ mole/L}$$

$$n_{\text{NO}_3^{-}} = \frac{(19.2 \text{ mg/L})}{(62.005 \times 10^3 \text{ mg/mole of NO}_3^{-})} = 3.097 \times 10^{-4} \text{ mole/L}$$

c. Determine the moles of the water.

$$n_w = \frac{(1000 \text{ g/L})}{(18 \text{ g/mole of water})} = 55.556 \text{ mole/L}$$

d. The mole fraction of calcium in **Sample 1** is:

$$X_{\text{Ca}^{2+}} = \frac{5.16 \times 10^{-3}}{(5.16 + 3.92 + 3.58 + 0.151 + 8.61 + 2.28 + 8.57 + 3.10) \times 10^{-3} + 55.56}$$

$$= 9.28 \times 10^{-5}$$

2. Similarly, the mole fractions of Mg^{2+} and SO_4^{2-} in **Sample 1** are:

$$X_{\text{Mg}^{2+}} = \frac{3.92 \times 10^{-3}}{(5.16 + 3.92 + 3.58 + 0.151 + 8.61 + 2.28 + 8.57 + 3.10) \times 10^{-3} + 55.56}$$

$$= 7.05 \times 10^{-5}$$

$$X_{\text{SO}_4^{2-}} = \frac{2.28 \times 10^{-3}}{(5.16 + 3.92 + 3.58 + 0.151 + 8.61 + 2.28 + 8.57 + 3.10) \times 10^{-3} + 55.56}$$

$$= 4.10 \times 10^{-5}$$

PROBLEM 2-3

Problem Statement - See text, page 171

Solution

1. Determine the ionic strength of the wastewater using Eq. (2-11)
 - a. Prepare a computation table to determine the summation term in Eq. (2-11) using the data for **Sample 3** in **Problem 2-1**

Ion	Conc., C, mg/L	C x 10 ³ , mole/L	Z ²	CZ ² x 10 ³
Ca ²⁺	190.2	4.75	4	19.00
Mg ²⁺	84.1	3.46	4	13.84
Na ⁺	75.2	3.27	1	3.27
K ⁺	5.1	0.13	1	0.13
Fe ²⁺	0.2	-	4	-
HCO ₃ ⁻	260.0	4.26	1	4.26
SO ₄ ²⁻	64.0	0.67	4	2.68
Cl ⁻	440.4	12.42	1	12.42
NO ₃ ⁻	35.1	0.57	1	0.57
CO ₃ ²⁻	30.0	0.50	4	2.00

Sum	58.17
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- b. Determine the ionic strength for the concentration C using Eq. (2-10)

$$I = \frac{1}{2} \sum C_i Z_i^2 = \frac{1}{2} (58.17 \times 10^{-3}) = 29.09 \times 10^{-3}$$

2. Determine the activity coefficients for monovalent and divalent ions using Eq. (2-12)

- a. For monovalent ions

$$\log \gamma = -0.5 (Z_i)^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 I \right) = -0.5 (1)^2 \left[\frac{\sqrt{29.09 \times 10^{-3}}}{1 + \sqrt{29.09 \times 10^{-3}}} - 0.3 (29.09 \times 10^{-3}) \right]$$

$$= -0.0685$$

$$\gamma = 0.8541$$

- b. For divalent ions

$$\log \gamma = -0.5 (Z_i)^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 I \right) = -0.5 (2)^2 \left[\frac{\sqrt{29.09 \times 10^{-3}}}{1 + \sqrt{29.09 \times 10^{-3}}} - 0.3 (29.09 \times 10^{-3}) \right]$$

$$= -0.2739$$

$$\gamma = 0.5322$$

2. Continue the computation table from Part 1 to determine the activity for each ion using Eq. (2-8)

Ion	C x 10 ³ , mole/L	Activity a _i , mole/L
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Ca ²⁺	4.75	2.53
Mg ²⁺	3.46	1.84
Na ⁺	3.27	2.79
K ⁺	0.13	0.11
Fe ²⁺	-	-
HCO ₃ ⁻	4.26	3.64
SO ₄ ²⁻	0.67	0.36
Cl ⁻	12.42	10.61
NO ₃ ⁻	0.57	0.49
CO ₃ ²⁻	0.50	0.27

PROBLEM 2-4

Problem Statement - See text, page 171

Solution

1. Estimate the TDS for **Sample 3** from **Problem 2-1** using Eq. (2-11)

$$I = 2.5 \times 10^{-5} \times \text{TDS}$$

where TDS = total dissolved solids, mg/L or g/m³

$$\text{TDS} = \frac{I \times 10^5}{2.5} = \frac{(0.02909) \times 10^5}{2.5} = 1163 \text{ mg/L}$$

2. Estimate the TDS for **Sample 3** from by summing the solids concentrations

Ion	Conc., C, mg/L
Ca ²⁺	190.2
Mg ²⁺	84.1
Na ⁺	75.2
K ⁺	5.1
Fe ²⁺	0.2