1 MULTIPLE CHEMICAL REACTIONS IN PLUG FLOW TUBULAR REACTORS AND CONTINUOUS STIRRED TANK REACTORS

1-1 GAS-PHASE PLUG-FLOW TUBULAR REACTORS THAT PRODUCE TRIETHANOLAMINE FROM ETHYLENE OXIDE AND AMMONIA

Triethanolamine is produced from ethylene oxide and ammonia at 5 atm total pressure via three consecutive elementary chemical reactions in a gas-phase plug-flow tubular reactor (PFR) that is not insulated from the surroundings. Ethylene oxide must react with the products from the first and second reactions before triethanolamine is formed in the third elementary step. The reaction scheme is described below via equations (1-1) to (1-3). All reactions are elementary, irreversible, and occur in the gas phase. In the first reaction, ethylene oxide, which is a cyclic ether, and ammonia combine to form monoethanolamine:

\[ \text{CH}_2\text{CH}_2\text{O} + \text{NH}_3 \rightarrow \text{HOCH}_2\text{CH}_2\text{NH}_2 \]  

At 325 K, the kinetic rate constant for the first reaction is 5 L/g mol·min. In the second reaction, ethylene oxide and monoethanolamine combine to form diethanolamine:

\[ \text{CH}_2\text{CH}_2\text{O} + \text{HOCH}_2\text{CH}_2\text{NH}_2 \rightarrow (\text{HOCH}_2\text{CH}_2)_2\text{NH} \]  

At 325 K, the kinetic rate constant for the second reaction is 10 L/g mol·min. In the third reaction, ethylene oxide reacts with diethanolamine to generate triethanolamine:

\[ \text{CH}_2\text{CH}_2\text{O} + (\text{HOCH}_2\text{CH}_2)_2\text{NH} \rightarrow (\text{HOCH}_2\text{CH}_2)_3\text{N} \]
At 325 K, the kinetic rate constant for the third reaction is 7 L/g mol·min. Coupled mass and thermal energy transport with multiple reactions in a plug-flow reactor suggests that the temperature of the reactive mixture changes by about 4°C from inlet (323 K) to outlet (327 K).

The overall objective is to produce triethanolamine, which is featured in the third reaction. Which of the following alternatives is more desirable: a stoichiometric (1 : 1) feed of ethylene oxide and ammonia enters the reactor; or a 3 : 1 molar ratio of ethylene oxide to ammonia enters the reactor? Provide support for your answer by calculating the reactor volume in liters and the outlet molar flow rate of triethanolamine that correspond to your design.

1-1.1 **Strategy to Solve This Problem**

The solution to this problem requires an analysis of multiple gas-phase reactions in a differential plug-flow tubular reactor. Two different solution strategies are described here. In both cases, it is important to write mass balances in terms of molar flow rates and reactor volume. Molar densities and residence time are not appropriate for the convective mass-transfer-rate process because one cannot assume that the total volumetric flow rate is constant in the gas phase, particularly when the total number of moles is not conserved. In each reaction, 2 mol of reactants generates 1 mol of product. Furthermore, an overall mass balance suggests that the volumetric flow rate is constant only when the overall mass density does not change. This is a reasonable assumption for liquid-phase reactors but not for gas-phase problems when the total volume is not restricted. The exception is a constant-volume batch reactor.

A few comments are in order about the fact that the reactor does not operate isothermally and that there is at least a 4 K difference between the temperatures of the inlet and outlet streams. Since the wall of the reactor is not insulated, interactions with the surroundings will provide a heating or cooling mechanism to offset the endothermic or exothermic nature of the chemical reaction. In an adiabatically enclosed reactor, the bulk temperature will increase or decrease continuously for reactions that are exothermic or endothermic, respectively. In the absence of thermodynamic data for enthalpies of formation at 298 K and heat transfer coefficient information, it seems reasonable to neglect thermal effects as a first approximation. The problem statement indicates that the outlet temperature of the reactive mixture is 4 K higher than the inlet temperature. However, no information is provided about the actual temperature profile from inlet to outlet, and more information is required to predict the bulk temperature within the reactor as a function of reactor volume or axial coordinate. It could be incorrect to conclude that the maximum temperature of the mixture is 327 K at the outlet of the reactor. Consider the following scenario. If the sum of all three heats of reaction suggests that the multiple reaction scheme is exothermic, strong temperature increases within the reactor could trigger the phenomenon of thermal runaway, where the reaction rates increase dramatically. For irreversible chemical reactions, thermal runaway depletes the reactants rather quickly at high temperatures. Under these conditions, all reactions are essentially completed and
heat is no longer generated far upstream from the reactor outlet. The remainder of the reactor functions as a heat exchanger to decrease the bulk temperature to 327 K, which is slightly higher than the inlet temperature. The solution strategies neglect temperature variation within the reactor and use the kinetic rate constants at 325 K as provided in the problem description.

When multiple reactions occur in the gas phase, the mass balance for component \( i \) is written for an ideal tubular reactor at high mass transfer Peclet numbers in the following form, and each term has units of moles per volume per time:

\[
\frac{dF_i}{dV} = \sum_j v_{ij} \xi_j
\]

where \( F_i \) is the molar flow rate of component \( i \), \( dV \) the differential reactor volume, \( v_{ij} \) the stoichiometric coefficient of component \( i \) in reaction \( j \), and \( \xi_j \) the intrinsic rate law for reaction \( j \). There are three elementary irreversible chemical reactions, and the units of the kinetic rate constants suggest that each second-order rate law should be constructed in terms of molar densities. Partial pressures and mole fractions can be introduced via the ideal gas law and Dalton’s law as follows:

\[
C_i = \frac{N_i}{V_{total}} = \frac{y_i p}{RT}
\]

Finally, the mole fraction of component \( i \) is written as its molar flow rate divided by the total molar flow rate. The differential mass balance is written for each component in the mixture: \( A \) = ethylene oxide, \( B \) = ammonia, \( C \) = monoethanolamine, \( D \) = diethanolamine and \( E \) = triethanolamine. The matrix of stoichiometric coefficients is summarized as follows for five components that participate in three independent chemical reactions:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Component</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>First</td>
<td></td>
<td>−1</td>
<td>−1</td>
<td>+1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Second</td>
<td></td>
<td>−1</td>
<td>0</td>
<td>−1</td>
<td>+1</td>
<td>0</td>
</tr>
<tr>
<td>Third</td>
<td></td>
<td>−1</td>
<td>0</td>
<td>0</td>
<td>−1</td>
<td>+1</td>
</tr>
</tbody>
</table>

Five coupled ordinary differential equations (ODEs) can be written for the five unknowns \( F_i \), where \( i = A, B, C, D, E \):

\[
\frac{dF_A}{dV} = -\xi_1 - \xi_2 - \xi_3
\]

\[
\frac{dF_B}{dV} = -\xi_1
\]

\[
\frac{dF_C}{dV} = +\xi_1 - \xi_2
\]
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\[ \frac{d F_D}{dV} = +\mathbf{R}_2 - \mathbf{R}_3 \]
\[ \frac{d F_E}{dV} = +\mathbf{R}_3 \]  

(1-6)

The kinetic rate law for each elementary irreversible chemical reaction is written in terms of gas-phase molar densities (A, B, C, D, where A = C_A, etc.) as follows:

\[ \mathbf{R}_1 = k_1AB \]
\[ \mathbf{R}_2 = k_2AC \]
\[ \mathbf{R}_3 = k_3AD \]  

(1-7)

The relation between gas-phase molar density and molar flow rates for ideal gases is obtained via equation (1-5):

\[ C_i = \frac{p F_i}{RT \sum_j F_j} \]  

(1-8)

where the sum of molar flow rates in the denominator includes all components and represents the total molar flow rate. Five boundary conditions are required at \( V = 0 \) to define a unique solution of these highly coupled ODEs. For a stoichiometric (1:1) feed of ethylene oxide and ammonia at the reactor inlet, \( F_A = F_B = 1 \text{ g mol/min} \) and \( F_i = 0 \) for the three products C, D, and E. For a 3:1 molar ratio of ethylene oxide to ammonia, \( F_A/3 = F_B = 1 \text{ g mol/min} \) and all other \( F_i = 0 \). Since triethanolamine is the product desired, it is important to monitor its molar flow rate \( F_E \) as a function of reactor volume in each case. The reactor design strategy must consider both alternatives [i.e., a stoichiometric (1:1) feed vs. a 3:1 feed ratio of ethylene oxide to ammonia]. The final decision should address the need for a costly separation process to extract the desired product, triethanolamine, from the gas mixture, if necessary. Qualitatively, one must also consider the initial cost to build the reactor, the operating cost to supply ethylene oxide, and the rate of production of triethanolamine.

The solution strategy described above is based on writing a differential plug-flow reactor mass balance for each component in the mixture, and five coupled ODEs are solved directly for the five molar flow rates. The solution strategy described below is based on the extent of reaction for independent chemical reactions, and three coupled ODEs are solved for the three extents of reaction. Molar flow rates are calculated from the extents of reaction. The starting point is the same as before. The mass balance is written for component \( i \) based on molar flow rate and differential reactor volume in the presence of multiple chemical reactions:

\[ \frac{d F_i}{dV} = \sum_j v_{ij} \mathbf{R}_j \]  

(1-4)
However, the similarities end here. The differential change in the molar flow rate of component $i$, $dF_i$, is written as follows:

$$dF_i = \sum_j (dF_i)_{cRj}$$  \hspace{1cm} (1-9)

where the acronym “$cRj$” represents the contribution from reaction $j$. Hence, $(dF_i)_{cRj}$ represents the differential change in the molar flow rate of component $i$ due to the $j$th chemical reaction. The differential mass balance becomes

$$\frac{dF_i}{dV} = \sum_j \left(\frac{dF_i}{dV}\right)_{cRj} = \sum_j v_{ij} \xi_j$$  \hspace{1cm} (1-10)

When all terms are grouped on the left-hand side of equation (1-10), the rearranged mass balance for component $i$,

$$\sum_j \left[\left(\frac{dF_i}{dV}\right)_{cRj} - v_{ij} \xi_j\right] = 0$$  \hspace{1cm} (1-11)

can be written in standard form as

$$\sum_j \psi_j = 0$$  \hspace{1cm} (1-12)

$$\psi_j = \left(\frac{dF_i}{dV}\right)_{cRj} - v_{ij} \xi_j$$  \hspace{1cm} (1-13)

Now it is necessary to introduce the concept of independent chemical reactions. A reaction is classified as independent if it cannot be synthesized from a linear combination of the other chemical reactions. In other words, the backward reaction for a reversible scheme is not independent of the forward reaction because it is only necessary to multiply the forward step by $(-1)$ to obtain the backward step. Hence, a reversible chemical reaction represents only one independent step, and consequently, only one extent of reaction is defined for a reversible sequence. The theorem states that “if all chemical reactions are independent, $\sum_j \psi_j = 0$ if and only if each $\psi_j = 0$ for all values of $j$.” The differential mass balance for component $i$ focuses on the contribution from reaction $j$, and if reaction $j$ is independent,

$$\psi_j = \left(\frac{dF_i}{dV}\right)_{cRj} - v_{ij} \xi_j = 0$$  \hspace{1cm} (1-14)

This relation is rearranged such that all terms which involve component $i$ are grouped together. The result is

$$\frac{(dF_i)_{cRj}}{v_{ij}} = R_j dV = d\xi_j \text{ same for every component in reaction } j$$  \hspace{1cm} (1-15)
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where \( d \xi_j \) is the differential extent of the \( j \)th independent chemical reaction, with units of molar flow rate. Hence, the design equation for multiple chemical reactions in a gas-phase differential tubular reactor at high mass transfer Peclet numbers is

\[
\frac{d \xi_j}{dV} = \mathbf{R}_j \tag{1-16}
\]

and this design equation is written once for each independent chemical reaction, which is consistent with the fact that a different extent \( \xi \) is defined for each independent chemical reaction. For three independent reactions involving ethylene oxide in the gas phase, the following set of coupled ODEs must be solved:

\[
\frac{d \xi_1}{dV} = k_1AB \\
\frac{d \xi_2}{dV} = k_2AC \\
\frac{d \xi_3}{dV} = k_3AD \tag{1-17}
\]

where the molar density of component A is written as \( C_A = A \), and so on. Three boundary conditions are required to define a unique solution to these ODEs. By definition, each extent of reaction is zero at the inlet to the reactor, where \( V = 0 \). The similarities between the two approaches return when one relates molar densities, partial pressures, and mole fractions as

\[
C_i = y_i \frac{p}{RT} \tag{1-5}
\]

and the mole fraction of component \( i \) is

\[
y_i = \frac{F_i}{\sum_j F_j} \quad 1 \leq j \leq \text{total number of components} \tag{1-18}
\]

The final task, before solving the coupled ODEs for the extents of reaction \( \xi_1 \), \( \xi_2 \), and \( \xi_3 \) is to express component molar flow rates in terms of the extents of reaction.

Based on the definition of the differential extent of the \( j \)th chemical reaction via equation (1-15), and the fact that

\[
dF_i = \sum_j (dF_i)_{cRj} \tag{1-9}
\]

\[
\frac{(dF_i)_{cRj}}{v_{ij}} = \mathbf{R}_j dV = d\xi_j \tag{1-15}
\]
it follows that the differential of the total molar flow rate of component $i$ can be expressed as

$$ dF_i = \sum_j v_{ij} d\xi_j $$

When (1-19) is integrated from the reactor inlet, where $V = 0$, $F_i = F_{i0}$, and $\xi_j = 0$ for each independent chemical reaction ($j = 1, 2, 3$ for this particular problem) to any arbitrary position downstream from the inlet, one obtains the desired relation between a component molar flow rate and the extents of reaction:

$$ F_i = F_{i0} + \sum_j v_{ij}\xi_j \quad 1 \leq j \leq \text{total number of independent reactions} $$

(1-20)

This equation is written for each of the five components in the gas-phase reactor. Given the matrix of stoichiometric coefficients for the five gas-phase components in three chemical reactions (see page 5),

$$
\begin{align*}
F_A &= F_{A0} - \xi_1 - \xi_2 - \xi_3 \\
F_B &= F_{B0} - \xi_1 \\
F_C &= \xi_1 - \xi_2 \\
F_D &= \xi_2 - \xi_3 \\
F_E &= \xi_3 
\end{align*}
$$

(1-21)

The molar densities in the rate laws are expressed in terms of mole fractions for ideal gas behavior via

$$ C_i = y_i \frac{p}{RT} $$

(1-5)

and the mole fraction of component $i$ is written in terms of the extents of reaction via molar flow rates:

$$ y_i = \frac{F_i}{\sum_j F_j} \quad 1 \leq j \leq \text{total number of components} $$

(1-18)

One differential design equation,

$$ \frac{d\xi_j}{dV} = R_j $$

(1-16)

is written for each independent chemical reaction, and it is now possible to solve three coupled ODEs in terms of three unknowns: $\xi_1$, $\xi_2$, and $\xi_3$. Of course, both methods of solution produce the same final answers.
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Verify the claim that both methods of solution produce the same final answers, and hence the same reactor design strategy, when the two alternatives [i.e., stoichiometric (1 : 1) feed vs. the 3 : 1 feed ratio] are considered. A more rigorous addendum to both approaches employs the Hagen–Poiseuille equation for laminar flow or the Ergun equation if the tubular reactor is packed with porous solid catalysts to calculate the pressure drop through the reactor instead of assuming that \( p = \text{constant from inlet to outlet} \).

1-1.2 Computer-Aided Solution

Since triethanolamine is the desired product, it is important to monitor its molar flow rate \( F_E \) as a function of reactor volume in each case. Most differential equation solver software packages will integrate five coupled ODEs quickly and easily to generate the following results. The stoichiometric (1 : 1) feed in case 1 requires a 25- to 30-L reactor to produce 0.1 mol of triethanolamine per minute. If the reactor operates in this fashion, simulations indicate that the outlet molar flow rate of ethylene oxide is essentially zero. Furthermore, ammonia (B) and the three products (C > D > E) exit the reactor in measurable quantities. Hence, a costly separation process is required to extract the desired product, triethanolamine (E), from the gas mixture. The upper limit of \( F_E \) is 0.113 g mol/min if the reactor volume is increased significantly. For the stoichiometric (1 : 1) feed, the outlet molar flow rate of triethanolamine is always smallest, excluding, of course, ethylene oxide. The 3 : 1 feed ratio in case 2 generates the predictions of reactor performance in terms of the molar flow rate of triethanolamine that are listed in Table 1-1.

Hence, a 3 : 1 molar feed ratio of ethylene oxide to ammonia seems to be advantageous with a corresponding reactor volume between 75 and 100 L. The

<table>
<thead>
<tr>
<th>Reactor Volume (L)</th>
<th>Molar Flow Rate of Triethanolamine (g mol/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.13</td>
</tr>
<tr>
<td>50</td>
<td>0.49</td>
</tr>
<tr>
<td>75</td>
<td>0.75</td>
</tr>
<tr>
<td>100</td>
<td>0.87</td>
</tr>
<tr>
<td>125</td>
<td>0.92</td>
</tr>
<tr>
<td>150</td>
<td>0.94</td>
</tr>
<tr>
<td>175</td>
<td>0.95</td>
</tr>
<tr>
<td>200</td>
<td>0.96</td>
</tr>
</tbody>
</table>

\(^a\)The feed stream contains a 3 : 1 molar flow rate ratio of ethylene oxide to ammonia.
production rate of triethanolamine is between seven- and eight-fold larger than in case 1 with a stoichiometric (1:1) feed. The initial cost to build the reactor will be approximately three- or four-fold larger and the operating cost to supply ethylene oxide will be three-fold larger relative to the stoichiometric (1:1) feed. However, the increased rate of production of triethanolamine could be worth the larger capital investments for initial and operating costs. This decision strategy is qualitative in the absence of cost data, but one should weigh the factor of 3 to 4 from an investment viewpoint against the factor of 7 to 8 in terms of product revenue. Furthermore, when the reactor volume is greater than \( \approx 70 \text{ L} \) with a 3:1 molar feed ratio of ethylene oxide to ammonia, the outlet molar flow rate of triethanolamine is largest, and the cost of separating the desired product should be much smaller relative to the stoichiometric (1:1) feed. For example, the outlet mole fraction of triethanolamine is 93% when the reactor volume is 250 L. Once again, cost data are required to determine if this exceedingly large reactor is cost-effective with respect to the separation process required, which should be rather inexpensive.

1-2 Multiple Chemical Reactions in a Liquid-Phase CSTR

1-2.1 Steady-State Analysis Based on Extents of Reaction

If component \( i \) participates in several chemical reactions in a well-mixed continuous-stirred tank reactor (CSTR) with volume \( V_{\text{CSTR}} \), then the macroscopic mass balance at large mass transfer Peclet numbers is

\[
\frac{dN_i}{dt} = F_{i, \text{inlet}} - F_{i, \text{outlet}} + V_{\text{CSTR}} \sum_j \nu_{ij} R_j \tag{1-22}
\]

where \( N_i \) represents the moles of component \( i \) and the other notation is the same as described earlier on page 5. Since the left side of (1-22) vanishes at steady state, rates of convective mass transfer (i.e., \( F_{i, \text{outlet}} - F_{i, \text{inlet}} \)) are balanced by the production of component \( i \) in all the reactions (i.e., \( V_{\text{CSTR}} \sum_j \nu_{ij} R_j \)). As illustrated in the liquid-phase problem below, it is possible to:

1. Express the molar flow rate of component \( i \) as a product of total volumetric flow rate \( q_{\text{total}} \) and molar density \( C_i \) (i.e., \( F_i = q_{\text{total}} C_i \)).
2. Invoke a steady-state macroscopic mass balance for each component in the reactive mixture.
3. Use chemical kinetic principles to write the rate law for each reaction in terms of molar densities.
4. Solve coupled algebraic equations for all molar densities in the CSTR exit stream.

Our objective in this section is to introduce a complementary method of solution based on extents of reaction \( \xi_j \), which have units of molar density. To initiate
this approach, one manipulates the convective mass transfer terms for component

\[ F_{i, \text{inlet}} - F_{i, \text{outlet}} = \sum_j (F_{i, \text{inlet}} - F_{i, \text{outlet}}) \cdot c_{Rj} = q_{\text{total}} \sum_j (C_{i, \text{inlet}} - C_{i, \text{outlet}}) \cdot c_{Rj} \]

(1-23)

Now the steady-state mass balance for component \( i \) can be written as a sum of contributions from each chemical reaction:

\[ F_{i, \text{inlet}} - F_{i, \text{outlet}} + V_{\text{CSTR}} \sum_j v_{ij} \cdot R_j \]

\[ = \sum_j [q_{\text{total}} (C_{i, \text{inlet}} - C_{i, \text{outlet}}) \cdot c_{Rj} + V_{\text{CSTR}} v_{ij} \cdot R_j] = 0 \]  

(1-24)

Division by \( q_{\text{total}} \) and identification of residence time \( \tau = \frac{V_{\text{CSTR}}}{q_{\text{total}}} \) yields the final form of the complete mass balance for component \( i \):

\[ \sum_j [(C_{i, \text{inlet}} - C_{i, \text{outlet}}) \cdot c_{Rj} + \tau v_{ij} \cdot R_j] = 0 \]  

(1-25)

If each step in the multiple reaction sequence is independent and cannot be synthesized from a linear combination of the other reactions, each kinetic rate law \( R_j \) is unique and

\[ (C_{i, \text{inlet}} - C_{i, \text{outlet}}) \cdot c_{Rj} + \tau v_{ij} \cdot R_j = 0 \]  

(1-26)

The previous statement based on the contribution from reaction \( j \) obviously satisfies the complete mass balance for component \( i \). It is written for each independent reaction. Furthermore, one applies stoichiometry to the contribution from reaction \( j \) and groups all quantities that are specific to component \( i \). For example,

\[ \frac{(C_{i, \text{outlet}} - C_{i, \text{inlet}}) \cdot c_{Rj}}{v_{ij}} = \tau \cdot R_j \]  

(1-27)

Since each side of (1-27) is the same for each component in the mixture but unique to reaction \( j \), one defines the extent of the \( j \)th chemical reaction \( \xi_j \) such that:

1. \( \tau R_j = \xi_j \)
2. \( (C_{i, \text{outlet}} - C_{i, \text{inlet}}) \cdot c_{Rj} = v_{ij} \cdot \xi_j \)

Expression 1 represents the CSTR design equation for steady-state analysis in the presence of multiple chemical reactions. This design equation is written for each independent reaction. If there is only one chemical reaction and subscript \( j \) is not required, the extent of reaction \( \xi \) is analogous to \( \chi C_{A, \text{inlet}} \), where \( \chi \)
represents the conversion of reactant A based on molar flow rates, in general, and molar densities for liquid-phase reactions. Expression 2 is used to calculate molar densities in terms of the extents of reaction. For example,

\[
F_i,\text{outlet} - F_i,\text{inlet} = q_{\text{total}} (C_i,\text{outlet} - C_i,\text{inlet}) = q_{\text{total}} \sum_j (C_i,\text{outlet} - C_i,\text{inlet}) c_{Rj} = q_{\text{total}} \sum_j v_{ij} \xi_j
\]

(1-28)

Hence, molar densities are calculated as follows:

\[
C_i,\text{outlet} = C_i,\text{inlet} + \sum_j v_{ij} \xi_j
\]

(1-29)

1.2.2 Chlorination of Benzene

We apply the concepts discussed above to design a CSTR that operates at 55 °C for the chlorination of benzene in the liquid phase. It is necessary to account for all three chlorination reactions. Chlorine gas is bubbled through the liquid mixture in the CSTR and it must diffuse across the gas–liquid interface before any of the reactions can occur. For this particular problem, it is reasonable to assume that chlorine is present as a solubilized liquid-phase component, and its molar density in the inlet liquid stream is given as a fraction \( \varepsilon \) of the inlet molar density of pure liquid benzene. In a subsequent example discussed in Chapter 24, a two-phase gas–liquid CSTR analysis is presented which accounts for the realistic fact that benzene enters the reactor in an undiluted liquid stream, and chlorine is actually bubbled through as a gas. It is sufficient to consider that the fraction \( \varepsilon = 0.25 \) remains constant for all simulations. In the first chlorination step, benzene reacts irreversibly with dissolved chlorine to produce monochlorobenzene and hydrogen chloride:

\[
C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl
\]

(1-30)

The inlet molar density of benzene is \( C_{\text{benzene, inlet}} = 11.28 \text{ g mol/L} \), and the kinetic rate constant for the first reaction is \( k_1 = 8.84 \times 10^{-3} \text{ L/mol·s at 55 °C} \). The overall objective is to design a CSTR that will maximize the rate of production of monochlorobenzene. Economics should be considered from a qualitative viewpoint. In the second reaction, the desired product, monochlorobenzene, reacts irreversibly with dissolved chlorine to produce dichlorobenzene and hydrogen chloride:

\[
C_6H_5Cl + Cl_2 \rightarrow C_6H_4Cl_2 + HCl
\]

(1-31)

The kinetic rate constant for the second reaction is a factor of 8 smaller than the kinetic rate constant for the first reaction at 55 °C. In the third reaction, dichlorobenzene reacts irreversibly with dissolved chlorine to generate trichlorobenzene and hydrogen chloride:

\[
C_6H_4Cl_2 + Cl_2 \rightarrow C_6H_3Cl_3 + HCl
\]

(1-32)
The kinetic rate constant for the third reaction is a factor of 30 smaller than the kinetic rate constant for the second reaction at 55 °C.

**Illustrative Problem.** Generate a CSTR performance curve for the molar density of the desired product, monochlorobenzene, in the outlet stream of the reactor vs. log \( \tau k_1 \), where \( \tau \) is the average residence time for convective mass transfer and \( k_1 \) is the kinetic rate constant for the first chlorination step. Identify your operating point on the CSTR performance curve. Design the CSTR by calculating the volume associated with this operating point if the volumetric flow rate is 50 L/min (i.e., \( \approx 12 \) to 13 gallons/min). Solve this problem by two different methods: (a) using extents of reaction \( \xi_j \), and (b) using only molar densities \( C_i \) without introducing \( \xi_j \)'s.

**SOLUTION.** (a) Molar density of pure liquid benzene (g mol/L):

\[
C_{\text{benzene, inlet}} = 11.28
\]

Ratio of kinetic rate constants for the first and second chlorination reactions at 55 °C:

\[
\frac{k_2}{k_1} = \frac{1}{8}
\]

Ratio of kinetic rate constants for the second and third chlorination reactions at 55 °C:

\[
\frac{k_3}{k_2} = \frac{1}{30}
\]

Ratio of dissolved chlorine to benzene on a molar basis in the inlet stream:

\[
\varepsilon = 0.25
\]

Inlet molar density of chlorine dissolved in the liquid phase:

\[
C_{\text{chlorine, inlet}} = \varepsilon C_{\text{benzene, inlet}}
\]

Matrix of stoichiometric coefficients:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Extent ( \xi_j )</th>
<th>( \xi_1 )</th>
<th>( \xi_2 )</th>
<th>( \xi_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
<td>( C_6H_6 )</td>
<td>( C_2H_4 )</td>
<td>( HCl )</td>
<td>( C_6H_5Cl )</td>
</tr>
<tr>
<td>First chlorination</td>
<td>( \xi_1 )</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
</tr>
<tr>
<td>Second chlorination</td>
<td>( \xi_2 )</td>
<td>0</td>
<td>-1</td>
<td>+1</td>
</tr>
<tr>
<td>Third chlorination</td>
<td>( \xi_3 )</td>
<td>0</td>
<td>-1</td>
<td>+1</td>
</tr>
</tbody>
</table>
Molar density of benzene in the CSTR exit stream (g mol/L):
\[ C_{\text{benzene, outlet}} = C_{\text{benzene, inlet}} - \xi_1 \]

Molar density of monochlorobenzene in the CSTR exit stream (g mol/L):
\[ C_{\text{monochlorobenzene, outlet}} = \xi_1 - \xi_2 \]

Molar density of dichlorobenzene in the CSTR exit stream (g mol/L):
\[ C_{\text{dichlorobenzene, outlet}} = \xi_2 - \xi_3 \]

Molar density of dissolved chlorine in the CSTR exit stream (g mol/L):
\[ C_{\text{chlorine, outlet}} = C_{\text{chlorine, inlet}} - \xi_1 - \xi_2 - \xi_3 \]

Kinetic rate laws, excluding rate constants, for the three chlorination reactions:
\[ \begin{align*}
R_1 &= C_{\text{benzene, outlet}}C_{\text{chlorine, outlet}} \\
R_2 &= C_{\text{monochlorobenzene, outlet}}C_{\text{chlorine, outlet}} \\
R_3 &= C_{\text{dichlorobenzene, outlet}}C_{\text{chlorine, outlet}}
\end{align*} \]

CSTR design equations with multiple chemical reactions and \( \tau k_1 \) as a parameter:
\[ \begin{align*}
\xi_1 &= (\tau k_1) R_1 \\
\xi_2 &= (\tau k_1) \frac{k_2}{k_1} R_2 \\
\xi_3 &= (\tau k_1) \frac{k_2 k_3}{k_1 k_2} R_3
\end{align*} \]

Volumetric flow rate (L/min):
\[ q_{\text{total}} = 50 \]

Kinetic rate constant for the first chlorination step at 55 °C (L/mol-min):
\[ k_1 = 0.00884 \times 60 \]

CSTR volume (L):
\[ V_{\text{CSTR}} = \frac{(\tau k_1) q_{\text{total}}}{k_1} \]

(b) Without introducing the extents for each independent chemical reaction, we have the following steady-state mass balance for each component (accumulation = input – output + rate of production = 0):
C₆H₆:

\[ 0 = C_{\text{benzene, inlet}} - C_{\text{benzene, outlet}} - (\tau k_1)R_1 \]

Cl₂:

\[ 0 = C_{\text{chlorine, inlet}} - C_{\text{chlorine, outlet}} - (\tau k_1)R_1 - (\tau k_1)\frac{k_2}{k_1}R_2 - (\tau k_1)\frac{k_2 k_3}{k_1 k_2}R_3 \]

C₆H₅Cl:

\[ 0 = -C_{\text{monochlorobenzene, outlet}} + (\tau k_1)R_1 - (\tau k_1)\frac{k_2}{k_1}R_2 \]

C₆H₄Cl₂:

\[ 0 = -C_{\text{dichlorobenzene, outlet}} + (\tau k_1)\frac{k_2}{k_1}R_2 - (\tau k_1)\frac{k_2 k_3}{k_1 k_2}R_3 \]

C₆H₃Cl₃:

\[ 0 = -C_{\text{trichlorobenzene, outlet}} + (\tau k_1)\frac{k_2 k_3}{k_1 k_2}R_3 \]

HCl:

\[ 0 = -C_{\text{hydrogen chloride}} + (\tau k_1)R_1 + (\tau k_1)\frac{k_2}{k_1}R_2 + (\tau k_1)\frac{k_2 k_3}{k_1 k_2}R_3 \]

The performance curve for the desired product, monochlorobenzene, and the CSTR volume required are presented in Figure 1-1 as a function of log(\(\tau k_1\)). The

![Figure 1-1](image-url)
two methodologies generate the same results, as expected. A reasonable design that considers economics qualitatively is as follows;

\[ 10^{-1} < \tau k_1 \ (L/g \ \text{mol}) < 10^0 \]
\[ 1.42 < C_{\text{monochlorobenzene, outlet}} \ (g \ \text{mol/L}) < 2.38 \]
\[ 10 < V_{CSTR} \ (L) < 96 \]

**Problem.** The following sequence of elementary irreversible reactions occurs in a liquid-phase CSTR with a feed stream that contains only reactant A.

\[ 2A \overset{k_1(T)}{\longrightarrow} B + C \quad A + C \overset{k_2(T)}{\longrightarrow} D \]

All components exhibit relatively low vapor pressures below 90°C. The activation energy for the first reaction is 15 kcal/mol, and the activation energy for the second reaction is 14 kcal/mol. The steady-state molar density ratio of reactive intermediate C to reactant A in the CSTR exit stream and in the well-mixed reactor is

\[ \frac{C}{A} = \frac{\tau k_1 A}{1 + \tau k_2 A} \]

(a) Are the two elementary steps independent?
(b) Calculate the selectivity of the final product D relative to the intermediate product B.

\[ S_{D/B} = \frac{F_{D,\text{outlet}} - F_{D,\text{inlet}}}{F_{B,\text{outlet}} - F_{B,\text{inlet}}} = \frac{D}{B} \]

where \( F_i \) is the molar flow rate of component \( i \).

If component D is the desired product:

(c) Is it better to operate the CSTR at 30°C or 55°C?
(d) Is it advantageous to dilute the feed of reactant A with an inert solvent?
(e) Is it advantageous to increase the reactor volume?
(f) Is it advantageous to increase the volumetric flow rate?

If component B is the desired product:

(g) Is it better to operate the CSTR at 30°C or 55°C?
(h) Is it advantageous to dilute the feed of reactant A with an inert solvent?
(i) Is it advantageous to increase the reactor volume?
(j) Is it advantageous to increase the volumetric flow rate?

**SOLUTION.** *Answer (b) and verification of the molar density ratio, C/A.** Stoichiometric coefficients, extents of reaction, and kinetic rate laws are summarized
MULTIPLE CHEMICAL REACTIONS IN PFRs AND CSTRs

below. Four components participate in two independent elementary reactions. Hence, two extents of reaction are required.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Extent $\xi_j$</th>
<th>Component</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>Rate Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2A \rightarrow B + C$</td>
<td>$\xi_1$</td>
<td>A</td>
<td>$-2$</td>
<td>$+1$</td>
<td>$+1$</td>
<td>$0$</td>
<td>$k_1A^2$</td>
</tr>
<tr>
<td>$A + C \rightarrow D$</td>
<td>$\xi_2$</td>
<td>B</td>
<td>$-1$</td>
<td>$0$</td>
<td>$-1$</td>
<td>$+1$</td>
<td>$k_2AC$</td>
</tr>
</tbody>
</table>

Application of the CSTR design equation for each independent chemical reaction yields

$$
\xi_1 = \tau R_1 = \tau k_1A^2 \\
\xi_2 = \tau R_2 = \tau k_2AC
$$

The molar density of each component is expressed in terms of extents of reaction as

$$
A = A_0 - 2\xi_1 - \xi_2 \\
B = \xi_1 \\
C = \xi_1 - \xi_2 \\
D = \xi_2
$$

If one combines the two design equations with the expression for the molar density of reactive intermediate C, it is possible to verify the molar density ratio, C/A, which is given in the problem statement.

$$
C = \xi_1 - \xi_2 = \tau k_1A^2 - \tau k_2AC \\
C + \tau k_2AC = C(1 + \tau k_2A) = \tau k_1A^2
$$

Hence,

$$
\frac{C}{A} = \frac{\tau k_1A}{1 + \tau k_2A}
$$

This intermediate result is employed to calculate the selectivity of final product D relative to intermediate product B, and its inverse if B is the desired product. For example:

$$
S_{D/B} = \frac{D}{B} = \frac{\xi_2}{\xi_1} = \frac{\frac{\tau k_2AC}{\tau k_1A^2}}{\frac{k_2C}{k_1A}} = \frac{k_2}{k_1} \frac{C}{A} = \frac{\tau k_2A}{1 + \tau k_2A}
$$

$$
S_{B/D} = \frac{B}{D} = \frac{1}{S_{D/B}} = 1 + \frac{1}{\tau k_2A}
$$
Answers (c) through (j). Answers to parts (c) through (f) are based on analysis of \( S_{D/B} \). Answers to parts (g) through (j) are based on analysis of \( S_{B/D} \). Since the kinetic rate constant \( k_1 \) does not affect either selectivity, comparison of activation energies for the two reactions is not an important consideration in the final design. Final product D is favored at (1) higher temperature, (2) higher concentrations of reactant A in the exit stream, (3) larger reactor volume, and (4) slower volumetric flow rate. Intermediate product B is favored at (1) lower temperature, (2) lower concentration of reactant A in the CSTR exit stream, (3) smaller reactor volume, and (4) larger volumetric flow rate.

1-3 MULTIPLE CHEMICAL REACTIONS IN A CSTR TRAIN

1-3.1 Generalized Steady-State Analysis

Sequential application of the steady-state design equations is required when multiple chemical reactions occur in a series configuration of well-mixed tanks. If temperature, residence time, kinetic rate laws, and the characteristics of the feed to the first reactor are known, then it is possible to predict molar densities in the exit stream of the first reactor, which represent the feed to the second reactor, and so on. Subscripts are required to monitor:

- Components: \( i \)
- Independent chemical reactions: \( j \)
- Reactors in series: \( k \)

For example,

- \( C_{ik} \) molar density of component \( i \) in the exit stream of the \( k \)th tank
- \( \nu_{ij} \) stoichiometric coefficient of component \( i \) in the \( j \)th reaction. If the reaction scheme is modified by catalysts, etc., that differ in each tank, then subscript \( k \) is required
- \( R_{jk} \) rate of the \( j \)th chemical reaction using conditions in the exit stream of the \( k \)th tank
- \( \xi_{jk} \) extent of the \( j \)th chemical reaction in the \( k \)th tank
- \( \tau_k \) residence time for the \( k \)th reactor
- \( T_k \) operating temperature in the \( k \)th reactor

The CSTR design equation

\[
\xi_{jk} = \tau_k R_{jk}
\]

is written for each independent chemical reaction in each tank. If all reactions are \( n \)th-order and irreversible, the generic form of each rate law is

\[
R_{jk} = k_{j\infty} \exp \left( -\frac{E_{\text{act},j}}{RT_k} \right) \prod_{i \text{ reactants}} (C_{ik})^{-\nu_{ij}}
\]
Molar densities in the kinetic rate laws are expressed in terms of extents of reaction as follows:

\[ C_{ik} = C_{i,k-1} + \sum_j v_{ij} \xi_{jk} \]

1-3.2 Unrestricted Optimization of the Yield of a Reactive Intermediate

Consider the following generic complex multiple reaction scheme that occurs isothermally in a liquid-phase CSTR train. Both reactors operate at the same temperature. In the first elementary step, 1 mol of reactant A and 2 mol of reactant B reversibly produce intermediate product D, which is the desired product:

\[ A + 2B \rightleftharpoons D \]

The equilibrium constant for the first reaction, based on molar densities, is

\[ K_{eq,C/1} = \frac{k_{forward\ 1}}{k_{backward\ 1}} = 10 \ (L/mol)^2 \]

The third-order forward kinetic rate constant for the first reaction is

\[ k_{forward\ 1} = 0.05 \ (L/mol)^2/min \]

In the second elementary step, 1 mol of reactant B and 1 mol of intermediate product D irreversibly generate intermediate product E:

\[ B + D \rightarrow E \]

via the second-order kinetic rate constant

\[ k_2 = 0.01 \ L/mol-min \]

In the third elementary step, 1 mol each of intermediate products D and E irreversibly generate the final product F:

\[ D + E \rightarrow F \]

with the second-order kinetic rate constant

\[ k_3 = 0.02 \ L/mol-min \]

The feed stream to the first CSTR contains stoichiometric proportions (i.e., 1 : 2) of reactants A and B, and the molar density of reactant A in this inlet stream is

\[ C_{A,\text{inlet}} = 0.5 \ g \ mol/L \]
**Illustrative Problem.** As a reactor design engineer, your task is to design a train of two CSTRs in series that operate at the same temperature, which will maximize the yield of intermediate product D in the exit stream of the second reactor. What yield is expected for intermediate product D in the exit stream of the second CSTR? The yield of intermediate product D is defined as

\[
\text{yield}(D_2) \equiv \frac{F_{D_2} - F_{D,\text{inlet}}}{F_{A,\text{inlet}}} = \frac{C_{D_2} - C_{D,\text{inlet}}}{C_{A,\text{inlet}}}
\]

where \( F_{ik} \) is the molar flow rate of component \( i \) in the exit stream of the \( k \)th reactor.

**Helpful hints.** Use the conjugate gradient method of optimization with 2 degrees of freedom. In other words, you should develop a set of \( n \) equations in terms of \( n + 2 \) variables that describe the steady-state operation of three independent chemical reactions in a train of two chemical reactors. Maximization algorithms implicitly use two additional equations to determine optimum performance of the CSTR train:

\[
\frac{\partial \text{[yield}(D_2)\text{]}_1}{\partial \tau_1} = 0 \quad \text{at constant } \tau_2
\]

\[
\frac{\partial \text{[yield}(D_2)\text{]}_2}{\partial \tau_2} = 0 \quad \text{at constant } \tau_1
\]

These two additional restrictions are implemented numerically. Identify two key independent design variables and provide realistic upper and lower bounds for these variables to assist the maximization algorithm in finding the best answer. The conjugate gradient optimization method should converge in approximately 20 iterations.

**Matrix of stoichiometric coefficients.** Five components participate in three independent elementary reactions. Hence, three extents of reaction are required. The kinetic rate law for each elementary step is included in the following table.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Extent ( \xi_j )</th>
<th>A</th>
<th>B</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>Rate Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A + 2B \leftrightarrow D )</td>
<td>( \xi_1 )</td>
<td>-1</td>
<td>-2</td>
<td>+1</td>
<td>0</td>
<td>0</td>
<td>( k_1(2AB^2 - D/K_{eq}) )</td>
</tr>
<tr>
<td>( B + D \rightarrow E )</td>
<td>( \xi_2 )</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
<td>0</td>
<td>( k_2BD )</td>
</tr>
<tr>
<td>( D + E \rightarrow F )</td>
<td>( \xi_3 )</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
<td>( k_3DE )</td>
</tr>
</tbody>
</table>

**SOLUTION.** Concentrations \( C_{i,\text{inlet}} \) of the five reactive species in the inlet stream to the first reactor, in units of g mol/L:

\[
A_{\text{inlet}} = 0.5
\]

\[
B_{\text{inlet}} = \Theta_B A_{\text{inlet}} \quad \Theta_B = 2
\]

\[
D_{\text{inlet}} = E_{\text{inlet}} = F_{\text{inlet}} = 0
\]
Concentrations $C_{i1}$ of the five reactive species in the exit stream of the first reactor, in terms of the extents of reaction $\xi_{j1}$ in the first CSTR:

\[
\begin{align*}
A_1 &= A_{\text{inlet}} - \xi_{11} \\
B_1 &= B_{\text{inlet}} - 2\xi_{11} - \xi_{21} \\
D_1 &= D_{\text{inlet}} + \xi_{11} - \xi_{21} - \xi_{31} \\
E_1 &= E_{\text{inlet}} + \xi_{21} - \xi_{31} \\
F_1 &= F_{\text{inlet}} + \xi_{31}
\end{align*}
\]

Kinetic rate laws $R_{j1}$ for three independent elementary reactions in the first CSTR:

\[
\begin{align*}
R_{11} &= k_{\text{forward 1}}(T_1) \left[ A_1(B_1)^2 - \frac{D_1}{K_{eq,C/1}(T_1)} \right] \\
R_{21} &= k_2(T_1)B_1D_1 \\
R_{31} &= k_3(T_1)D_1E_1
\end{align*}
\]

CSTR design equations, $\xi_{j1} = \tau_1 R_{j1}$, for three independent reactions in the first reactor:

\[
\begin{align*}
\xi_{11} &= \tau_1 R_{11} \\
\xi_{21} &= \tau_1 R_{21} \\
\xi_{31} &= \tau_1 R_{31}
\end{align*}
\]

Concentrations $C_{i2}$ of the five reactive species in the exit stream of the second reactor, in terms of the extents of reaction $\xi_{j2}$ in the second CSTR:

\[
\begin{align*}
A_2 &= A_1 - \xi_{12} \\
B_2 &= B_1 - 2\xi_{12} - \xi_{22} \\
D_2 &= D_1 + \xi_{12} - \xi_{22} - \xi_{32} \\
E_2 &= E_1 + \xi_{22} - \xi_{32} \\
F_2 &= F_1 + \xi_{32}
\end{align*}
\]

Kinetic rate laws $R_{j2}$ for three independent elementary reactions in the second CSTR:

\[
\begin{align*}
R_{12} &= k_{\text{forward 1}}(T_2) \left[ A_2(B_2)^2 - \frac{D_2}{K_{eq,C/1}(T_2)} \right] \\
R_{22} &= k_2(T_2)B_2D_2 \\
R_{32} &= k_3(T_2)D_2E_2
\end{align*}
\]
CSTR design equations, $\xi_{j2} = \tau_2 \hat{x}_{j2}$, for three independent reactions in the second reactor:

$$
\begin{align*}
\xi_{12} &= \tau_2 \hat{x}_{12} \\
\xi_{22} &= \tau_2 \hat{x}_{22} \\
\xi_{32} &= \tau_2 \hat{x}_{32}
\end{align*}
$$

There are 2 degrees of freedom, $\tau_1$ and $\tau_2$, in this unrestricted optimization problem. The yield of intermediate product D in the exit stream of the second CSTR achieves a maximum of 35.4% when $\tau_1 = 26.9$ min and $\tau_2 = 27$ min.

1-3.3 CSTR Design Strategies

Four CSTR design strategies are summarized below when simple third-order irreversible chemical kinetics convert reactants to products.

1. It is advantageous to employ a longer residence time for the last reactor in series. This claim is justified by the following results, which have been generated by the supporting numerical algorithms.
   a. Two CSTRs in series (see Figure 1-2 and Table 1-2). The sequence of equations on page 24 calculates the conversion of reactant A in both exit streams for two CSTRs in series. The kinetics are $n$th-order irreversible and depend only on the molar density of reactant A. Both reactors operate at the same temperature, so that the $n$th-order kinetic rate constant is the same in both CSTRs. Furthermore, the characteristic chemical reaction

![Figure 1-2](image)

**Figure 1-2** Example of restricted isothermal optimization for two CSTRs in series. This graph illustrates the effect of residence time in the first reactor on the outlet conversion from the second reactor in series for simple $n$th-order kinetics, where $n = 1, 2, 3$. 
### TABLE 1-2 Restricted Residence-Time Optimization for Two CSTRs in Series Operating at the Same Temperature

<table>
<thead>
<tr>
<th>Reaction Order</th>
<th>τ_1 (min)</th>
<th>τ_2 (min)</th>
<th>χ_1 (%)</th>
<th>χ_2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>25</td>
<td>71</td>
<td>92</td>
</tr>
<tr>
<td>1.5</td>
<td>23</td>
<td>27</td>
<td>59</td>
<td>81</td>
</tr>
<tr>
<td>2</td>
<td>22</td>
<td>28</td>
<td>52</td>
<td>73</td>
</tr>
<tr>
<td>3</td>
<td>21</td>
<td>29</td>
<td>42</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>30</td>
<td>35</td>
<td>52</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>30</td>
<td>31</td>
<td>46</td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>30</td>
<td>28</td>
<td>41</td>
</tr>
<tr>
<td>7</td>
<td>19</td>
<td>31</td>
<td>25</td>
<td>37</td>
</tr>
<tr>
<td>8</td>
<td>19</td>
<td>31</td>
<td>23</td>
<td>34</td>
</tr>
<tr>
<td>9</td>
<td>19</td>
<td>31</td>
<td>22</td>
<td>32</td>
</tr>
<tr>
<td>10</td>
<td>19</td>
<td>31</td>
<td>20</td>
<td>30</td>
</tr>
</tbody>
</table>

*a* Includes the effect of reaction order \( n \) for simple \( n \)th-order chemical kinetics on optimum residence times and outlet reactant conversions in each CSTR. \( k(T_1) = k(T_2) = 0.1 \) (L/mol)\(^n\)min\(^{-1}\); \( τ_1 + τ_2 \approx 50 \) min; \( C_{A, \text{inlet}} = 1 \) mol/L.

Time constant \( \lambda \) is the same in both CSTRs when they operate at the same temperature. When the kinetics are first order, the optimum strategy requires that both reactors be of equal size. For higher-order kinetics where \( n > 1 \), the optimum strategy suggests that the first reactor should be slightly smaller. *Note*: There is only one independent variable, \( τ_1 \) or \( τ_2 \), due to the restricted optimization nature of this formulation.

\[
\begin{align*}
τ_1 R_1 - C_{A0}(x_1 - x_0) &= 0 \quad \text{design equation for the first CSTR} \\
τ_2 R_2 - C_{A0}(x_2 - x_1) &= 0 \quad \text{design equation for the second CSTR in series} \\
τ_1 + τ_2 &= 50 \quad \text{example of restricted optimization, residence times are in minutes} \\
R_1 &= k_{\text{forward}}(T_1)[C_{A0}(1 - x_1)]^n \quad \text{\( n \)th-order rate law in the first CSTR} \\
R_2 &= k_{\text{forward}}(T_2)[C_{A0}(1 - x_2)]^n \quad \text{\( n \)th-order rate law in the second CSTR in series} \\
k_{\text{forward}}(T_1) &= k_{\text{forward}}(T_2) \quad \text{units depend on \( n \), time units are in minutes} \\
k_{\text{forward}}(T_1) &= 0.1 \quad \text{\( \lambda \) is 10 min} \\
x_0 &= 0 \quad \text{conversion of reactant A in the inlet stream to} \\
& \quad \text{the first CSTR} \\
C_{A0} &= 1 \quad \text{molar density of reactant A in the inlet stream to} \\
& \quad \text{the first CSTR, moles per volume} 
\end{align*}
\]
MULTIPLE CHEMICAL REACTIONS IN A CSTR TRAIN

TABLE 1-3 Restricted Residence-Time Optimization for Three CSTRs in Series Operating at the Same Temperature

<table>
<thead>
<tr>
<th>Reaction Order</th>
<th>Residence Time (min)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau_1$</td>
<td>$\tau_2$</td>
</tr>
<tr>
<td>1</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>1.5</td>
<td>28</td>
<td>36</td>
</tr>
<tr>
<td>2</td>
<td>26</td>
<td>37</td>
</tr>
<tr>
<td>3</td>
<td>24</td>
<td>38</td>
</tr>
<tr>
<td>4</td>
<td>23</td>
<td>38</td>
</tr>
<tr>
<td>5</td>
<td>22</td>
<td>39</td>
</tr>
<tr>
<td>6</td>
<td>22</td>
<td>39</td>
</tr>
<tr>
<td>7</td>
<td>21</td>
<td>39</td>
</tr>
<tr>
<td>8</td>
<td>21</td>
<td>39</td>
</tr>
<tr>
<td>9</td>
<td>20</td>
<td>39</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>39</td>
</tr>
</tbody>
</table>

*a*Includes the effect of reaction order $n$ for simple $n$th-order chemical kinetics on the optimum residence times and outlet reactant conversions in each CSTR. $k(T_1) = k(T_2) = k(T_3) = 0.1 \text{ (L/mol)}^{n-1}/\text{min}$; $\tau_1 + \tau_2 + \tau_3 \approx 99$ to 100 min; $C_{A_{\text{inlet}}} = 1 \text{ mol/L}$.

b. Three CSTRs in series (see Table 1-3). This strategy can be extended rather easily to a longer train of reactors, all of which operate at the same temperature. For higher-order kinetics where $n > 1$ in a train of three well-mixed reactors, the optimum strategy suggests that the last two reactors in the train should be larger than the first. Numerical results from this restricted optimization are summarized in Table 1-3. *Note:* This is an example of restricted optimization because the sum of all three residence times is fixed, but there are two independent variables, or 2 degrees of freedom, in the numerical algorithm.

2. The same reactant conversion can be achieved in the exit stream of the last reactor in series when the total volume of a CSTR train is less than the volume of the one-CSTR setup.

3. If the total volume of a CSTR train is the same as the volume of the one-CSTR setup, the final conversion in the exit stream of the last reactor in the train is greater than the final conversion in the exit stream of the one-CSTR setup.

4. When two CSTRs in series operate at different temperatures, it is advantageous to employ a longer residence time for the higher-temperature reactor. This strategy should be employed for reversible exothermic reactions, even though the equilibrium conversion decreases at higher temperature, because most reactors do not operate in the “near-equilibrium” regime (see Problem 1-7).
MULTIPLE CHEMICAL REACTIONS IN PFRs AND CSTRs

Let’s revisit the previous unrestricted optimization problem described on pages 20–23 in two CSTRs with 2 degrees of freedom and apply strategy 4. Since both reactors operate at the same temperature (i.e., \( T_1 = T_2 \)), it might seem reasonable that an optimum design should keep the mixture in each CSTR for the same amount of time, on average. Hence, \( \tau_1 = \tau_2 \). Now, this problem conforms to unrestricted optimization with 1 degree of freedom (i.e., either \( \tau_1 \) or \( \tau_2 \)). The behavior of the system of equations that describe the yield of intermediate product D in the exit stream of the second CSTR can be analyzed as a function of residence time. Optimum performance is obvious in Figure 1-3 when the reactive mixture remains in each CSTR for 25 to 29 min.

**PROBLEMS**

1-1. Draw the flow configuration for two CSTRs in series when the chemical kinetics are third order and irreversible. The objective is to maximize reactant conversion in the exit stream of the last CSTR. One CSTR operates at 75°C and the other CSTR operates at 30°C. Which reactor should be larger? Which reactor should be first in the train?

1-2. For a particular liquid-phase chemical reaction, the kinetic rate law is zeroth order:

\[
\dot{R} = k_\infty \exp\left(\frac{E_{\text{act}}}{RT}\right)
\]

**Figure 1-3** Example of unrestricted optimization in a train of two CSTRs that operate at the same temperature. This graph illustrates the effect of residence time for each reactor (i.e., \( \tau_1 = \tau_2 \)) on the yield of intermediate product D in the exit stream of the second reactor.
In other words, $R$ is not a function of conversion or molar densities. The characteristic chemical reaction time constant is 25 min. The temperature is the same in each case. The following reactor configurations are employed.

(1) One CSTR: $V_1 = 50$ L, $q = 5$ L/min
(2) One CSTR: $V_1 = 100$ L, $q = 5$ L/min
(3) Two CSTRs in series: $V_1 + V_2 = 50$ L, $q = 5$ L/min
(4) Two CSTRs in series: $V_1 + V_2 = 100$ L, $q = 5$ L/min

From highest to lowest, rank the conversion of reactant A to products in the CSTR exit stream for the four configurations described above.

1-3. One liquid-phase chemical reaction occurs in an isothermal configuration of PFRs. The chemical kinetics are second order and irreversible [i.e., $R = k_2(C_A)^2$], and the characteristic chemical reaction time constant $\lambda$ is 5 min. Rank the configurations listed in Table P1-3 from highest final conversion of reactant A in the exit stream of the last PFR in series to lowest final conversion in the exit stream of the last PFR. In each case, the volumetric flow rate is 10 L/min and $C_{A_{\text{inlet}}}$ is the same. Calculate the final conversion of reactant A in the exit stream of the third PFR in series for case 7.

<table>
<thead>
<tr>
<th>Case</th>
<th>No. PFRs in Series</th>
<th>Volume (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$V_1$</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>45</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>45</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>15</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
<td>20</td>
</tr>
</tbody>
</table>

1-4. Three components (A,B,C) participate in two independent elementary chemical reactions:

\[
A \rightarrow B \rightarrow C
\]

in isothermal liquid-phase reactors. The kinetic rate constant for the first irreversible chemical reaction (A $\rightarrow$ B) is $k_1 = 0.15$ min$^{-1}$. The kinetic rate constant for the second irreversible chemical reaction (B $\rightarrow$ C) is $k_2 = 0.05$ min$^{-1}$. The feed stream contains only 1 mol of reactant A per litre.
All reactors operate at the same temperature. The reactor types and configurations are described below. Notice that the total residence time for each configuration is 1 min, whereas the chemical reaction time constants are \( \approx 7 \) minutes for the first reaction and 20 min for the second reaction.

1. One CSTR with a reactor volume of 10 L. The flow rate is 10 L/min.
2. Two CSTRs in series. The volume of each reactor is 5 L and the volumetric flow rate is 10 L/min.
3. Two CSTRs in parallel. The volume of each reactor is 5 L and the volumetric flow rate in each reactor is 5 L/min.
4. One PFR with a volume of 10 L and a volumetric flow rate of 10 L/min.
5. Two PFRs in series. The volume of each reactor is 5 L and the volumetric flow rate is 10 L/min.

The rate of production of intermediate product B in the final exit stream of each configuration has been calculated for the five cases described above. When two CSTRs are arranged in parallel, both exit streams contribute to the overall rate of production. In units of moles of B per minute, five correct answers and two incorrect answer for \( \dot{q}_{\text{total}}C_B \) are

\[ 1.42 \quad 1.36 \quad 1.36 \quad 1.24 \quad 1.24 \quad 1.18 \]

Associate a numerical answer for the rate of production of intermediate product B with each of the five configurations and reactor types described above.

1-5. The following multiple-reaction scheme converts reactants A and B to final product E via intermediate D in the liquid phase. Each reaction represents an elementary step. The feed contains a 1 : 1 molar ratio of reactants A and B. The kinetic rate constant is indicated for each step in the chemical reaction.

\[
\begin{align*}
\text{Step 1.} & \quad A + B \rightarrow D \quad \text{via} \quad k_1(T) \\
\text{Step 2.} & \quad D \rightarrow A + B \quad \text{via} \quad k_2(T) \\
\text{Step 3.} & \quad B + D \rightarrow E \quad \text{via} \quad k_3(T)
\end{align*}
\]

(a) How many independent chemical reactions occur?
(b) Use one graph and sketch the molar density of each component vs. time in a constant-volume batch reactor. Put four curves on one graph and label each curve.
(c) Use the pseudo-steady-state approximation (PSSA) to obtain an expression for the molar density of reactive intermediate D.
(d) Elementary step 3 is the slowest one in the mechanism. Use your answer to part (c) and express the rate law in terms of measurable quantities for the rate of conversion of reactants to products.
(e) Use the extents of reaction ξ_j and write all of the equations that must be solved to design a liquid-phase CSTR based on the three-step mechanism described above.

(f) Use the extents of reaction ξ_j and write an expression for the selectivity of intermediate product D with respect to final product E in a CSTR. 

S_{D/E} = ?

(g) Write all of the equations that must be solved, including the initial conditions, to analyze the startup behavior of one CSTR based on the three-step mechanism described above.

1-6. (a) Use the extents of reaction ξ_j and write all eight equations that must be solved to design an ideal gas-phase PFR in which the following three independent elementary reactions occur.

Step 1. A + 2B → D via \( k_1(T) \), (volume/mol)^2/time
Step 2. D → A + 2B via \( k_2(T) \), 1/time
Step 3. A + 2D → E via \( k_3(T) \), (volume/mol)^2/time
Step 4. 2A + E → F via \( k_4(T) \), (volume/mol)^2/time

The feed stream contains a 1 : 2 molar flow rate ratio of reactants A and B. The overall objective is to identify the PFR volume that maximizes the molar flow rate of intermediate product E. 

(b) Use only one set of axes and sketch the molar flow rates of intermediate product E and final product F as a function of reactor volume \( V_{PFR} \). Qualitatively identify the optimum reactor volume (i.e., \( V_{PFR, optimum} \)) on the horizontal axis of your graph.

1-7. This exercise deals with the restricted optimization of a train of two CSTRs with variable temperature options when the chemical reaction is reversible and exothermic. Consider the following third-order non-elementary reversible chemical reaction, which occurs in a train of two liquid-phase CSTRs:

\[ 2A \rightleftharpoons B \]

The catalyst is most effective when the reactors operate between 350 and 370 K. Under these conditions, the forward kinetic rate constant is described by a preexponential factor of \( 1 \times 10^9 \) (L/mol)^2/min and an activation energy of 17,000 cal/mol. The feed stream to the first CSTR contains reactant A at a molar density of 0.4 mol/L. Economic considerations restrict the total residence time of both reactors to be \( 10^3 \) min or less. The temperature dependence of the dimensionless equilibrium constant is modeled as follows (see pages 57–60):
MULTIPLE CHEMICAL REACTIONS IN PFRs AND CSTRs

\[ K_{equilibrium, C} = \exp \left( \frac{A + B}{T} \right) \]

\[ A = \frac{\Delta S_{Rx, 298}^c}{R} \]

\[ B = -\frac{\Delta H_{Rx, 298}^c}{R} \]

The reaction is exothermic because a chemical bond is formed and thermal energy is liberated when 2 molecules of reactant A combine to produce 1 molecule of product B. The entropy change is negative due to the reduction in total moles as the reaction proceeds. Hence, the following thermodynamic data are applicable when the stoichiometric coefficient of reactant A is -1:

\[ \Delta H_{Rx, 298}^c = -9000 \text{ cal/mol} \]

\[ \Delta S_{Rx, 298}^c = -15 \text{ cal/mol-K} \]

Design the CSTR train by specifying the residence time \( \tau \) in minutes and the temperature \( T \) in Kelvin for each reactor that maximize the conversion of reactant A in the exit stream of the second CSTR. The gas constant \( R \) is 1.987 cal/mol-K.

1-8. Calculate the CSTR operating temperature that maximizes the yield of a reactive intermediate. Consider the following multiple reaction scheme that occurs in one liquid-phase CSTR:

A \[\right\rightarrow\] B \[\right\rightarrow\] C

The overall objective is to determine the CSTR operating temperature that maximizes the yield of intermediate product B. The pre-exponential factor and Arrhenius activation energy for each reaction are:

A \[\right\rightarrow\] B: \( k_{1\infty} = 1 \times 10^7 \text{ (L/mol)}^{n-1} \text{/s} \quad E_{act, 1} = 15 \text{ kcal/mol} \)

B \[\right\rightarrow\] C: \( k_{2\infty} = 4 \times 10^6 \text{ (L/mol)}^{n-1} \text{/s} \quad E_{act, 2} = 12 \text{ kcal/mol} \)

The feed stream contains reactant A at a total mass flow rate of 250 g/s. The reactor volume is 100 L, and the overall density of the reactive mixture is 1 g/cm\(^3\) or 1 kg/L.

(a) Identify the operating temperature that maximizes the yield of intermediate product B if both reactions represent elementary steps and

(i) \( C_{A, \text{inlet}} = 1 \text{ mol/L} \)

(ii) \( C_{A, \text{inlet}} = 2 \text{ mol/L} \)
(b) Identify the operating temperature that maximizes the yield of intermediate product B if both reactions follow second-order irreversible kinetics, and

(i) \( C_{A,\text{inlet}} = 1 \text{ mol/L} \)

(ii) \( C_{A,\text{inlet}} = 2 \text{ mol/L} \)

(c) Identify the operating temperature that maximizes the yield of intermediate product B if both reactions follow second-order irreversible kinetics, the total mass flow rate is reduced to 100 g/s, and \( C_{A,\text{inlet}} = 1 \text{ mol/L} \).