University of Anbar

College of Engineering

Chemical and Petrochemical Engineering Department

Chemical Reacior Design

Third Year

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Lecture No. 1

Introduction:

Reactor design uses information, knowledge, and experience from a variety of areas-thermodynamics, chemical kinetics, fluid mechanics, heat transfer, mass transfer, and economics. Chemical reaction engineering is the synthesis of all these factors with the aim of properly designing a chemical reactor. To find what a reactor is able to do we need to know the kinetics, the contacting pattern and the performance equation. We show this schematically in Fig. 1.2.

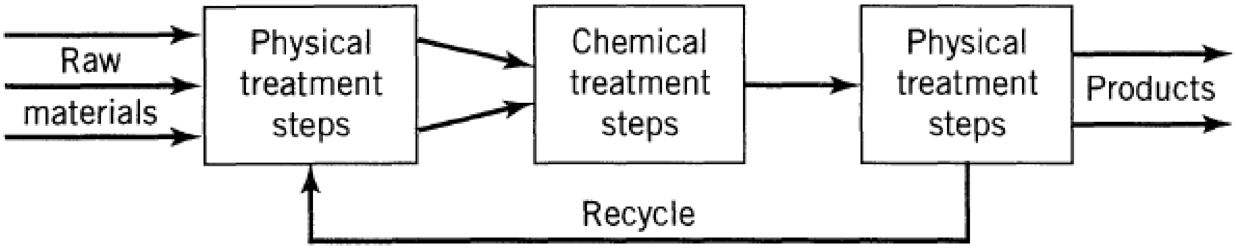
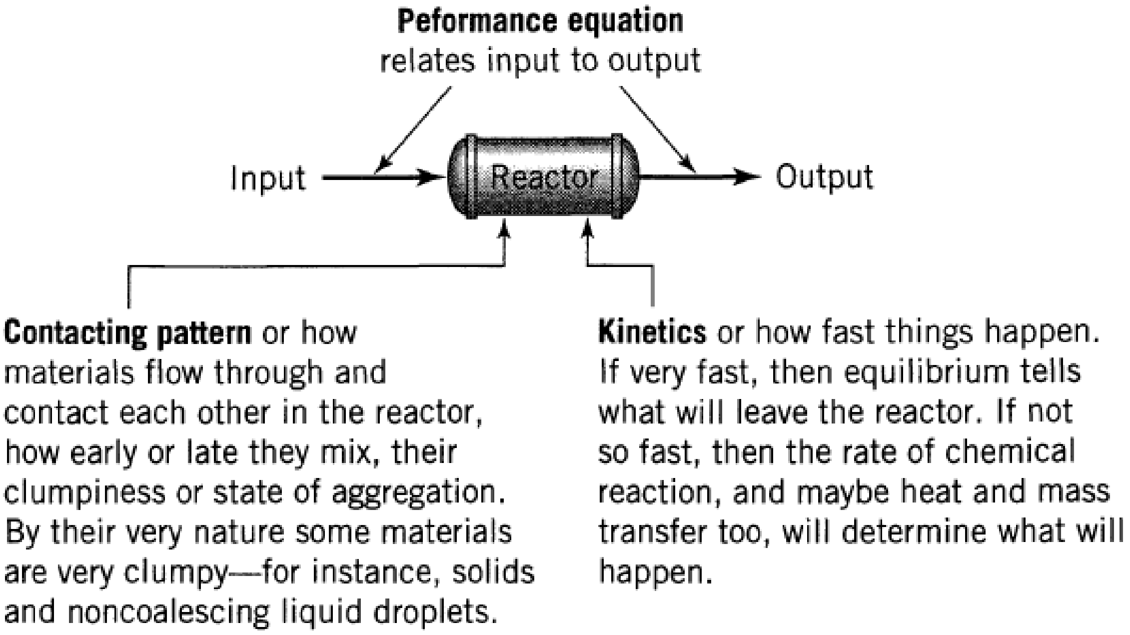


Figure 1.1 Typical chemical process.



Peformance equation relates input to output

Contacting pattern or how materials flow through and contact each other in the reactor, how early or late they mix, their clumpiness or state of aggregation. By their very nature some materials are very clumpy—for instance, solids and noncoalescing liquid droplets.

Kinetics or how fast things happen. If very fast, then equilibrium tells what will leave the reactor. If not so fast, then the rate of chemical reaction, and maybe heat and mass transfer too, will determine what will happen.

Figure 1.2 Information needed to predict what a reactor can do.

$$\text{output} = f[\text{input, kinetics, contacting}] \qquad \textbf{(1)}$$

This is called the performance equation. Why is this important? Because with this expression we can compare different designs and conditions, find which is best, and then scale up to larger units.

Definition of Reaction Rate:

If the rate of change in number of moles of this component due to reaction is dN_i/dt, then the rate of reaction in its various forms is defined as follows. Based on unit volume of reacting fluid,

$$\boxed{r_i = \frac{1}{V}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of fluid})\ (\text{time})}} \qquad \textbf{(2)}$$

Based on unit mass of solid in fluid-solid systems,

$$\boxed{r'_i = \frac{1}{W}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{mass of solid})\ (\text{time})}} \qquad \textbf{(3)}$$

Based on unit interfacial surface in two-fluid systems or based on unit surface of solid in gas-solid systems,

$$\boxed{r''_i = \frac{1}{S}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{surface})\ (\text{time})}} \qquad \textbf{(4)}$$

Based on unit volume of solid in gas-solid systems

$$\boxed{r'''_i = \frac{1}{V_s}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of solid})\ (\text{time})}} \qquad \textbf{(5)}$$

Based on unit volume of reactor, if different from the rate based on unit volume of fluid,

$$\boxed{r''''_i = \frac{1}{V_r}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of reactor})\ (\text{time})}} \qquad \textbf{(6)}$$

In homogeneous systems the volume of fluid in the reactor is often identical to the volume of reactor. In such a case V and Vr are identical and Eqs. 2 and 6 are used interchangeably. In heterogeneous systems all the above definitions of reaction rate are encountered, the definition used in any particular situation often being a matter of convenience.

EXAMPLE 1.1 THE ROCKET ENGINE

A rocket engine, Fig. E1.1, burns a stoichiometric mixture of fuel (liquid hydrogen) in oxidant (liquid oxygen). The combustion chamber is cylindrical, 75 cm long and 60 cm in diameter, and the combustion process produces 108 kg/s of exhaust gases. If combustion is complete, find the rate of reaction of hydrogen and of oxygen.

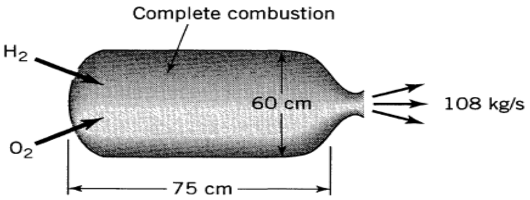


Figure E1.1

SOLUTION

We want to evaluate

$$-r_{H_2} = \frac{1}{V}\frac{dN_{H_2}}{dt} \quad \text{and} \quad -r_{O_2} = \frac{1}{V}\frac{dN_{O_2}}{dt}$$

Let us evaluate terms. The reactor volume and the volume in which reaction takes place are identical. Thus,

$$V = \frac{\pi}{4}(0.6)^2(0.75) = 0.2121 \text{ m}^3$$

Next, let us look at the reaction occurring.

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \qquad \textbf{(i)}$$

molecular weight: 2gm 16 gm 18 gm

Therefore,

$$H_2O \text{ produced/s} = 108 \text{ kg/s}\left(\frac{1 \text{ kmol}}{18 \text{ kg}}\right) = 6 \text{ kmol/s}$$

So from Eq. (i)

$$H_2 \text{ used} = 6 \text{ kmol/s}$$
$$O_2 \text{ used} = 3 \text{ kmol/s}$$

and the rate of reaction is

$$\underline{\underline{-r_{H_2}}} = -\frac{1}{0.2121 \text{ m}^3}\cdot\frac{6 \text{ kmol}}{\text{s}} = \underline{\underline{2.829\times10^4 \frac{\text{mol used}}{(\text{m}^3 \text{ of rocket})\cdot\text{s}}}}$$

$$\underline{\underline{-r_{O_2}}} = -\frac{1}{0.2121 \text{ m}^3}\cdot 3\frac{\text{kmol}}{\text{s}} = \underline{\underline{1.415\times10^4 \frac{\text{mol}}{\text{m}^3\cdot\text{s}}}}$$

EXAMPLE 1.2 THE LIVING PERSON

A human being (75 kg) consumes about 6000 kJ of food per day. Assume that the food is all glucose and that the overall reaction is

$$C_6H_{12}O_6 + \underset{\text{from air}}{6O_2} \rightarrow \underset{\text{breathed out}}{6CO_2} + 6H_2O, \quad -\Delta H_r = 2816\ \text{kJ}$$

Find man's metabolic rate (the rate of living, loving, and laughing) in terms of moles of oxygen used per m^3 of person per second.

SOLUTION

We want to find

$$-r'''_{O_2} = -\frac{1}{V_{\text{person}}}\frac{dN_{O_2}}{dt} = \frac{\text{mol } O_2 \text{ used}}{(\text{m}^3 \text{ of person})\text{s}} \qquad \textbf{(i)}$$

Let us evaluate the two terms in this equation. First of all, from our life experience we estimate the density of man to be

$$\rho = 1000\,\frac{\text{kg}}{\text{m}^3}$$

Therefore, for the person in question

$$V_{\text{person}} = \frac{75\ \text{kg}}{1000\ \text{kg/m}^3} = 0.075\ \text{m}^3$$

Next, noting that each mole of glucose consumed uses 6 moles of oxygen and releases 2816 kJ of energy, we see that we need

$$\frac{dN_{O_2}}{dt} = \left(\frac{6000\ \text{kJ/day}}{2816\ \text{kJ/mol glucose}}\right)\left(\frac{6\ \text{mol } O_2}{1\ \text{mol glucose}}\right) = 12.8\,\frac{\text{mol } O_2}{\text{day}}$$

Inserting into Eq. (i)

$$-r'''_{O_2} = \frac{1}{0.075\ \text{m}^3}\cdot\frac{12.8\ \text{mol } O_2 \text{ used}}{\text{day}}\,\frac{1\ \text{day}}{24 \times 3600\ \text{s}} = \underline{\underline{0.002\,\frac{\text{mol } O_2 \text{ used}}{\text{m}^3 \cdot \text{s}}}}$$

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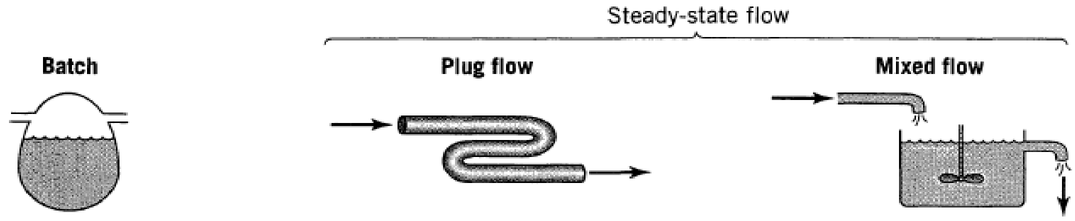
Lecture No. 2:

Kinetics of Homogeneous Reactions:

Simple Reactor Types:

Ideal reactors have three ideal flow or contacting patterns



Uniform composition everywhere in the reactor, but of course the composition changes with time.

Fluid passes through the reactor with no mixing of earlier and later entering fluid, and with no overtaking. It is as if the fluid moved in single file through the reactor.

Uniformly mixed, same composition everywhere, within the reactor and at the exit.

Figure 2.1 Ideal reactor types.

The Rate Equation:

Suppose a single-phase reaction $aA + bB \rightarrow rR + sS$. The most useful measure of reaction rate for reactant A is then

rate of disappearance of A

$$-r_A = -\frac{1}{V}\frac{dN_A}{dt} = \frac{\text{(amount of A disappearing)}}{\text{(volume) (time)}}, \quad \left[\frac{\text{mol}}{\text{m}^3 \cdot \text{s}}\right] \tag{1}$$

note that this is an intensive measure

the minus sign means disappearance

In addition, the rates of reaction of all materials are related by

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_R}{r} = \frac{r_S}{s}$$

Experience shows that the rate of reaction is influenced by the composition and the energy of the material. By energy we mean the temperature (random kinetic energy of the molecules), the light intensity within the system (this may affect the bond energy between atoms), the magnetic field intensity, etc. Ordinarily we only need to consider the temperature, so let us focus on this factor. Thus, we can write

$$\overset{\frac{\text{mol}}{\text{m}^3\cdot\text{s}}}{-r_A} = f\begin{bmatrix}\text{temperature} & & \text{concentration}\\ \text{dependent} & , & \text{dependent}\\ \text{terms} & & \text{terms}\end{bmatrix} \xrightarrow[\text{example}]{\text{as an}} \overset{\left(\frac{\text{mol}}{\text{m}^3}\right)^{1-a}\text{s}^{-1}}{k}C_A^{\underset{\text{reaction order}}{a}} = \underbrace{k_0 e^{-\overset{\text{activation energy}}{\mathbf{E}}/\mathbf{R}T}}_{\text{temperature dependent term}} C_A^a \qquad \textbf{(2)}$$

Single and Multiple Reactions:

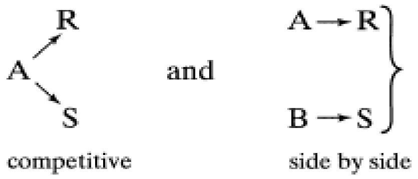
When a single stoichiometric equation and single rate equation are chosen to represent the progress of the reaction, we have a *single reaction.* When more than one stoichiometric equation is chosen to represent the observed changes, then more than one kinetic expression is needed to follow the changing composition of all the reaction components, and we have *multiple reactions.*

Multiple reactions may be classified as:

series reactions,

$$A \rightarrow R \rightarrow S$$

parallel reactions, which are of two types



competitive side by side

and more complicated schemes, an example of which is

$$A + B \rightarrow R$$
$$R + B \rightarrow S$$

Here, reaction proceeds in parallel with respect to B, but in series with respect to A, *R*, and **S.**

Elementary and Nonelementary Reactions:

Such reactions in which the rate equation corresponds to a stoichiometric equation are called *elementary reactions.*

$$A + B \rightarrow R \quad \Longrightarrow \quad -r_A = kC_AC_B$$

When there is no direct correspondence between stoichiometry and rate, then we have *nonelementary reactions.*

$$H_2 + Br_2 \rightarrow 2HBr$$

$$r_{HBr} = \frac{k_1[H_2][Br_2]^{1/2}}{k_2 + [HBr]/[Br_2]} \qquad (3)$$

Molecularity and Order of Reaction:

The molecularity of an elementary reaction is the number of molecules involved in the reaction, and this has been found to have the values of one, two, or occasionally three. Note that the molecularity refers only to an elementary reaction.

Often we find that the rate of progress of a reaction, involving, say, materials A, B, . . . , D, can be approximated by an expression of the following type:

$$-r_A = kC_A^aC_B^b\ldots C_D^d, \qquad a+b+\cdots+d=n \qquad (4)$$

We call the powers to which the concentrations are raised the order of the reaction. Thus, the reaction is

ath order with respect to A

bth order with respect to B

nth order overall

$$A \longrightarrow \text{products}$$

Order	Rate Equation	Units
Zero	$-r_A = k$	$mol.V^{-1}.s^{-1}$
First	$-r_A = kC_A$	s^{-1}
Second	$-r_A = kC_A^2$	$V.mol^{-1}.s^{-1}$
Third	$-r_A = kC_A^3$	$(V.mol^{-1})2.s^{-1}$
nth order	$-r_A = kC_A^n$	$(concentration)^{1-n}.s^{-1}$

Rate Constant k:

When the rate expression for a homogeneous chemical reaction is written in the form of Eq. 4, the dimensions of the rate constant k for the nth-order reaction are

$$(\text{time})^{-1}(\text{concentration})^{1-n} \qquad (5)$$

which for a first-order reaction becomes simply

$$(\text{time})^{-1} \qquad (6)$$

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Lecture No. 3

TEMPERATURE-DEPENDENT TERM OF A RATE EQUATION

Temperature Dependency from Arrhenius' Law

For many reactions, and particularly elementary reactions, the rate expression can be written as a product of a temperature-dependent term and a composition dependent term, or:

$$r_i = f_1(\text{temperature}) \cdot f_2(\text{composition}) \quad = k \cdot f_2(\text{composition}) \tag{7}$$

For such reactions the temperature-dependent term, the reaction rate constant, has been found in practically all cases to be well represented by **Arrhenius' law:**

$$k = k_0 e^{-\mathbf{E}/\mathbf{R}T} \tag{8}$$

where k_0, is called the frequency or pre-exponential factor and E is called the activation energy of the reaction

At the same concentration, but at two different temperatures, Arrhenius' law indicates that:

$$\ln\frac{r_2}{r_1} = \ln\frac{k_2}{k_1} = \frac{\mathbf{E}}{\mathbf{R}}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{9}$$

The temperature dependency of reactions is determined by the activation energy and temperature level of the reaction, as illustrated in Fig. 2.2

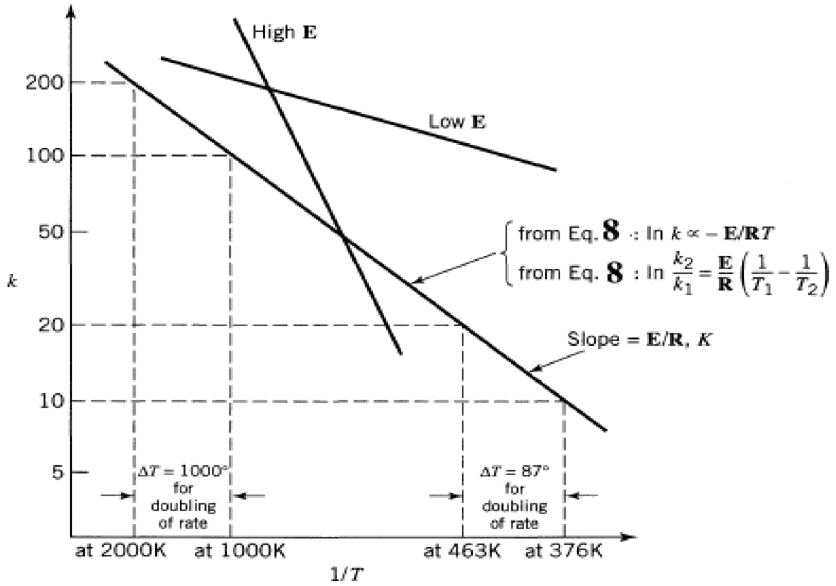
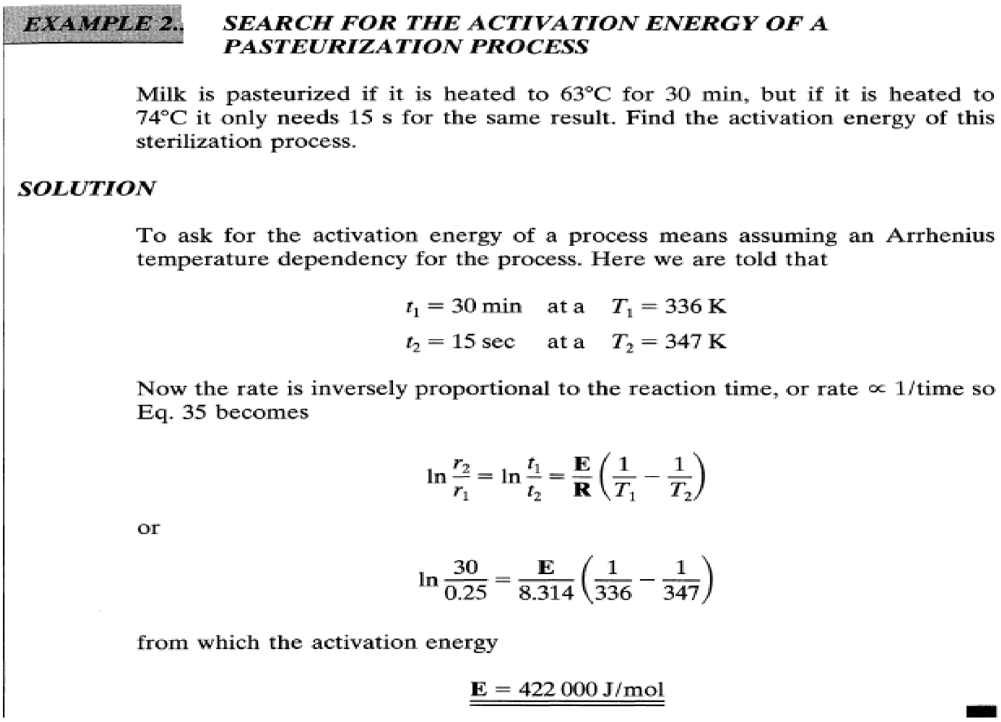


Figure 2.2 Sketch showing temperature dependency of the reaction rate.

These findings are summarized as follows:

1. From Arrhenius' law a plot of ***In k*** vs ***1/T*** gives a straight line, with large slope for large ***E*** and small slope for small ***E.***
2. Reactions with high activation energies are very temperature-sensitive; reactions, with low activation energies are relatively temperature-insensitive.
3. Any given reaction is much more temperature-sensitive at a low temperature than at a high temperature.
4. From the Arrhenius law, the value of the frequency factor k_0, does not affect the temperature sensitivity.



EXAMPLE 2.. ***SEARCH FOR THE ACTIVATION ENERGY OF A PASTEURIZATION PROCESS***

Milk is pasteurized if it is heated to 63°C for 30 min, but if it is heated to 74°C it only needs 15 s for the same result. Find the activation energy of this sterilization process.

SOLUTION

To ask for the activation energy of a process means assuming an Arrhenius temperature dependency for the process. Here we are told that

$$t_1 = 30 \text{ min} \quad \text{at a} \quad T_1 = 336 \text{ K}$$
$$t_2 = 15 \text{ sec} \quad \text{at a} \quad T_2 = 347 \text{ K}$$

Now the rate is inversely proportional to the reaction time, or rate ∝ 1/time so Eq. 35 becomes

$$\ln \frac{r_2}{r_1} = \ln \frac{t_1}{t_2} = \frac{\mathbf{E}}{\mathbf{R}} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

or

$$\ln \frac{30}{0.25} = \frac{\mathbf{E}}{8.314} \left(\frac{1}{336} - \frac{1}{347} \right)$$

from which the activation energy

$$\underline{\underline{\mathbf{E} = 422\,000 \text{ J/mol}}}$$

Interpretation of Batch Reactor Data:

There are two procedures for analyzing kinetic data, **the integral** and the **differential methods**.

- **In the integral method** of analysis after integration and mathematical manipulation, predict that the plot of a certain concentration function versus time should yield a straight line. The data are plotted, and if a reasonably good straight line is obtained, then the rate equation is said to satisfactorily fit the data
- **In the differential method** of analysis we test the fit of the rate expression to the data directly and without any integration. However, since the rate expression is a differential equation, we must first find (l/V)(dN/dt) from the data before attempting the fitting procedure

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CONSTANT-VOLUME BATCH REACTOR:

The constant-volume batch reactor we refer to the volume of reaction mixture, and not the volume of reactor. Thus, this term actually means a constant-density reaction system. Most liquid-phase reactions as well as all gas-phase reactions occurring in a constant-volume bomb fall in this class.

In a constant-volume system the measure of reaction rate of component *i* becomes

$$\boxed{r_i = \frac{1}{V}\frac{dN_i}{dt} = \frac{d(N_i/V)}{dt} = \frac{dC_i}{dt}} \qquad (10)$$

or for ideal gases, where ***C = P/RT***,

$$r_i = \frac{1}{\mathbf{R}T}\frac{dp_i}{dt} \qquad (11)$$

For gas reactions with changing numbers of moles, a simple way of finding the reaction rate is to follow the change in total pressure.$\boldsymbol{\pi}$ of the system.

	$a\mathrm{A}$	$+$	$b\mathrm{B}$	$+\cdots=$	$r\mathrm{R}$	$+$	$s\mathrm{S}$	$+\cdots$
At time 0:	N_{A0}		N_{B0}		N_{R0}		N_{S0}	N_{inert}
At time t:	$N_{\mathrm{A}} = N_{\mathrm{A0}} - ax$		$N_{\mathrm{B}} = N_{\mathrm{B0}} - bx$		$N_{\mathrm{R}} = N_{\mathrm{R0}} + rx$		$N_{\mathrm{S}} = N_{\mathrm{S0}} + sx$	N_{inert}

Initially the total number of moles present in the system is

$$N_0 = N_{\mathrm{A0}} + N_{\mathrm{B0}} + \cdots + N_{\mathrm{R0}} + N_{\mathrm{S0}} + \cdots + N_{\mathrm{inert}}$$

but at time t it is

$$N = N_0 + x(r + s + \cdots - a - b - \cdots) = N_0 + x\,\Delta n \qquad \mathbf{(3)}$$

where

$$\Delta n = r + s + \cdots - a - b - \cdots$$

Assuming that the ideal gas law holds, we may write for any reactant, say Ain the system of volume V

$$C_{\mathrm{A}} = \frac{p_{\mathrm{A}}}{\mathbf{R}T} = \frac{N_{\mathrm{A}}}{V} = \frac{N_{\mathrm{A0}} - ax}{V} \qquad \mathbf{(4)}$$

Combining Eqs. 3 and 4 we obtain

$$C_{\mathrm{A}} = \frac{N_{\mathrm{A0}}}{V} - \frac{a}{\Delta n}\frac{N - N_0}{V}$$

or

$$\boxed{p_{\mathrm{A}} = C_{\mathrm{A}}\mathbf{R}T = p_{\mathrm{A0}} - \frac{a}{\Delta n}(\pi - \pi_0)} \qquad \mathbf{(5)}$$

The Conversion:

Suppose that N_{Ao} is the initial amount of A in the reactor at time $t = 0$, and that N_A is the amount present at time t. Then the conversion of A in the constant volume system is given by:

$$X_{\mathrm{A}} = \frac{N_{\mathrm{A0}} - N_{\mathrm{A}}}{N_{\mathrm{A0}}} = 1 - \frac{N_{\mathrm{A}}/V}{N_{\mathrm{A0}}/V} = 1 - \frac{C_{\mathrm{A}}}{C_{\mathrm{A0}}} \qquad \mathbf{(7)} \qquad dX_{\mathrm{A}} = -\frac{dC_{\mathrm{A}}}{C_{\mathrm{A0}}}$$

Integral Method of Analysis of Data:

Irreversible Unimolecular-Type First-Order Reactions. Consider the reaction

$$A \rightarrow \text{products} \tag{9}$$

Suppose we wish to test the first-order rate equation of the following type,

$$-r_A = -\frac{dC_A}{dt} = kC_A \tag{10}$$

for this reaction. Separating and integrating we obtain

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = k\int_0^t dt$$

or

$$-\ln\frac{C_A}{C_{A0}} = kt \tag{11}$$

$$\frac{dX_A}{dt} = k(1 - X_A) \longrightarrow \int_0^{X_A} \frac{dX_A}{1 - X_A} = k\int_0^t dt$$

$$\boxed{-\ln(1 - X_A) = kt} \tag{12}$$

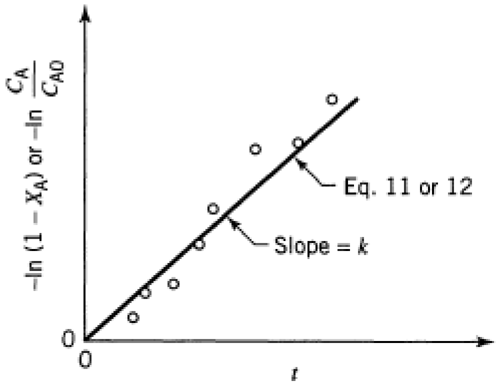

Figure 3.1 Test for the first-order rate equation, Eq. 10.

Irreversible Bimolecular-Type Second-Order Reactions. Consider the reaction:

$$A + B \rightarrow \text{products} \tag{13a}$$

$$-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_AC_B \tag{13b}$$

Noting that the amounts of A and B that have reacted at any time t are equal and given by $C_{A0}X_A$, we may write Eqs. 13a and b in terms of X_A as

$$-r_A = C_{A0}\frac{dX_A}{dt} = k(C_{A0} - C_{A0}X_A)(C_{B0} - C_{A0}X_A)$$

Letting $M = C_{B0}/C_{A0}$ be the initial molar ratio of reactants, we obtain

$$-r_A = C_{A0}\frac{dX_A}{dt} = kC_{A0}^2(1 - X_A)(M - X_A)$$

which on separation and formal integration becomes

$$\int_0^{X_A} \frac{dX_A}{(1 - X_A)(M - X_A)} = C_{A0}k \int_0^t dt$$

After breakdown into partial fractions, integration, and rearrangement, the final result in a number of different forms is

$$\boxed{\begin{aligned} \ln\frac{1 - X_B}{1 - X_A} &= \ln\frac{M - X_A}{M(1 - X_A)} = \ln\frac{C_B C_{A0}}{C_{B0}C_A} = \ln\frac{C_B}{MC_A} \\ &= C_{A0}(M - 1)kt = (C_{B0} - C_{A0})kt, \quad M \neq 1 \end{aligned}} \qquad \textbf{(14)}$$

Figure 3.2 shows two equivalent ways of obtaining a linear plot between the concentration function and time for this second-order rate law.

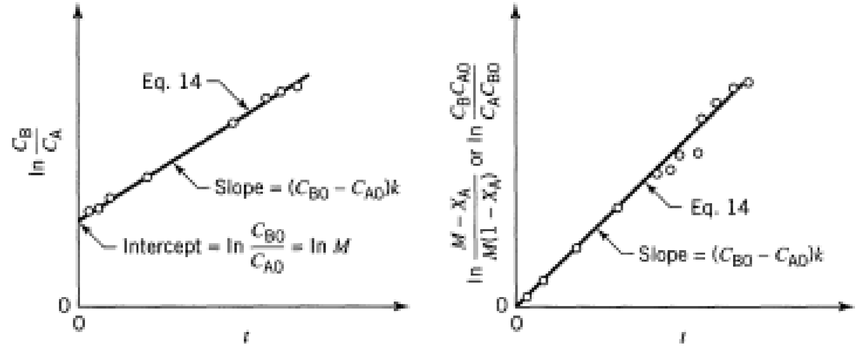

Figure 3.2 Test for the bimolecular mechanism $A + B \rightarrow R$ with $C_{A0} \neq C_{B0}$, or for the second-order reaction, Eq. 13.

Caution 1. In the special case where reactants are introduced in their stoichiometric ratio, the integrated rate expression becomes indeterminate and this requires taking limits of quotients for evaluation. This difficulty is avoided if we go back to the original differential rate expression and solve it for this particular reactant ratio. Thus, for the second-order reaction with equal initial concentrations of A and B, or for the reaction.

$$2A \rightarrow \text{products} \tag{15a}$$

the defining second-order differential equation becomes

$$-r_A = -\frac{dC_A}{dt} = kC_A^2 = kC_{A0}^2(1 - X_A)^2 \tag{15b}$$

which on integration yields

$$\boxed{\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{1}{C_{A0}}\frac{X_A}{1 - X_A} = kt} \tag{16}$$

Plotting the variables as shown in Fig. 3.3 provides a test for this rate expression. In practice we should choose reactant ratios either equal to or widely different from the stoichiometric ratio.

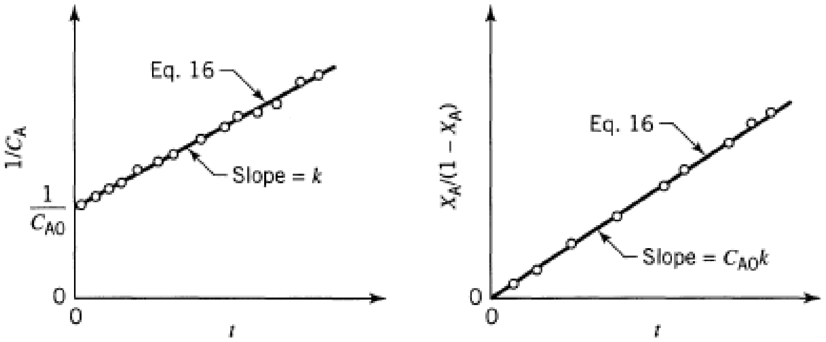

Figure 3.3 Test for the bimolecular mechanisms, A + B → R with $C_{A0} = C_{B0}$, or for the second-order reaction of Eq. 15.

Caution 2. The integrated expression depends on the stoichiometry as well as the kinetics. To illustrate, if the reaction:

$$A + 2B \rightarrow \text{products} \tag{17a}$$

is first order with respect to both A and B, hence second order overall, or

$$-r_A = -\frac{dC_A}{dt} = kC_AC_B = kC_{A0}^2(1 - X_A)(M - 2X_A) \tag{17b}$$

The integrated form is

$$\boxed{\ln\frac{C_BC_{A0}}{C_{B0}C_A} = \ln\frac{M - 2X_A}{M(1 - X_A)} = C_{A0}(M - 2)kt, \qquad M \neq 2} \tag{18}$$

When a stoichiometric reactant ratio is used the integrated form is

$$\boxed{\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{1}{C_{A0}}\frac{X_A}{1 - X_A} = 2kt, \qquad M = 2} \tag{19}$$

These two cautions apply to all reaction types. Thus, special forms for the integrated expressions appear whenever reactants are used in stoichiometric ratios, or when the reaction is not elementary.

Empirical Rate Equations of nth Order. When the mechanism of reaction is not known, we often attempt to fit the data with an nth-order rate equation of the form

$$-r_A = -\frac{dC_A}{dt} = kC_A^n \quad (20) \quad \longrightarrow \quad \boxed{C_A^{1-n} - C_{A0}^{1-n} = (n-1)kt, \qquad n \neq 1} \quad \ldots\ldots(21)$$

Select a value for n and calculate k. The value of n which minimizes the variation in k is the desired value of n.

Zero-Order Reactions. A reaction is of zero order when the rate of reaction is independent of the concentration of materials; thus

$$-r_A = -\frac{dC_A}{dt} = k \quad (22) \quad \longrightarrow \quad \begin{array}{r} C_{A0} - C_A = C_{A0}X_A = kt \quad \text{for} \quad t < \dfrac{C_{A0}}{k} \\ C_A = 0 \quad \text{for} \quad t \geq \dfrac{C_{A0}}{k} \end{array}$$

(23)

Which means that the conversion is proportional to time, as shown in Fig. 3.4. As a rule, reactions are of zero order only in certain concentration ranges-the higher concentrations. If the concentration is lowered far enough, we usually

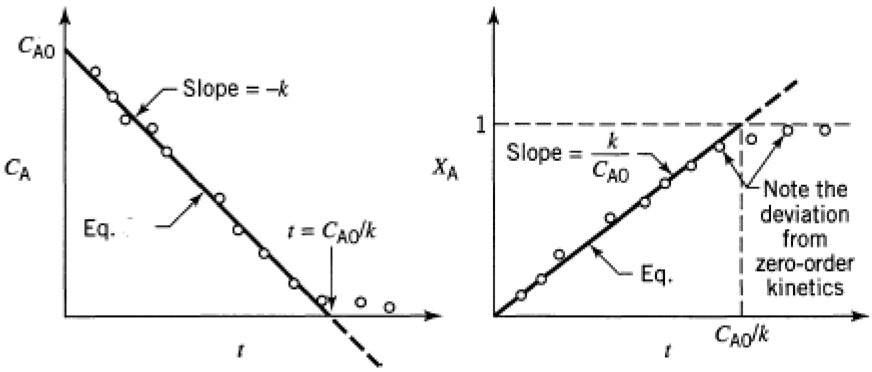

Figure 3.4 Test for a zero-order reaction, or rate equation, Eq. .

Find that the reaction becomes concentration-dependent, in which case the order rises from

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Third Year

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Lecture No.4:

Overall Order of Irreversible Reactions from the Half-Life $t_{,,}$. Sometimes, for the irreversible reaction

$$\alpha A + \beta B + \cdots \rightarrow \text{products} \qquad -r_A = -\frac{dC_A}{dt} = kC_A^a C_B^b \cdots$$

If the reactants are present in their stoichiometric ratios, they will remain at that ratio throughout the reaction. Thus, for reactants A and B at any time $C_B/C_A = \beta/\alpha$, and we may write

$$-r_A = -\frac{dC_A}{dt} = kC_A^a\left(\frac{\beta}{\alpha}C_A\right)^b \cdots = \underbrace{k\left(\frac{\beta}{\alpha}\right)^b \cdots}_{\tilde{k}} \underbrace{C_A^{a+b+\cdots}}_{C_A^n}$$

or

$$-\frac{dC_A}{dt} = \tilde{k}C_A^n$$

Integrating for $n \neq 1$ gives

$$C_A^{1-n} - C_{A0}^{1-n} = \tilde{k}(n-1)t \qquad (24)$$

Defining the half-life of the reaction, $t_{1/2}$, as the time needed for the concentration of reactants to drop to one-half the original value, we obtain

$$\boxed{t_{1/2} = \frac{(0.5)^{1-n} - 1}{\tilde{k}(n-1)} C_{A0}^{1-n}} \qquad (25)$$

This expression shows that a plot of log $t_{,,}$ vs. *log* C_{Ao} gives a straight line of slope *1 - n*, as shown in Fig. 3.5.

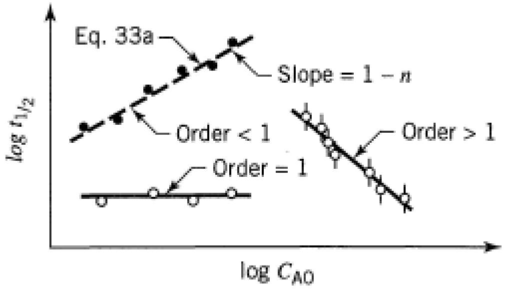

Figure 3.5 Overall order of reaction from a series of half-life experiments, each at a different initial concentration of reactant.

The half-life method requires making a series of runs, each at a different initial concentration ***fractional conversion*** in a given time ***rises with increased concentration*** for **orders greater than one**, ***drops*** with ***increased concentration*** for **orders less than one**, and is ***independent of initial concentration*** for **reactions of first order**

Fractional Life Method t_F. The half-life method can be extended to any fractional life method in which the concentration of reactant drops to any fractional value $F = C_A/C_{A0}$ in time t_F. The derivation is a direct extension of the half-life method giving

$$\boxed{t_F = \frac{F^{1-n} - 1}{k(n-1)} C_{A0}^{1-n}} \tag{33b}$$

Thus, a plot of log t_F versus log C_{A0}, as shown in Fig. 3.5, will give the reaction order.

Irreversible Reactions in Parallel. Consider the simplest case, A decomposing by two competing paths, both elementary reactions:

$$\left.\begin{array}{l} A \xrightarrow{k_1} R \\ A \xrightarrow{k_2} S \end{array}\right\}$$

$$-r_A = -\frac{dC_A}{dt} = k_1 C_A + k_2 C_A = (k_1 + k_2) C_A \tag{34}$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A \tag{35}$$

$$r_S = \frac{dC_S}{dt} = k_2 C_A \tag{36}$$

The ***k*** values are found using all three differential rate equations. First of all, Eq. 34, which is of simple first order, is integrated to give

$$\boxed{-\ln \frac{C_A}{C_{A0}} = (k_1 + k_2)t} \tag{37}$$

When plotted as in Fig. 3.6, the slope is $k_1 + k_2$. Then dividing Eq. 35 by Eq. 36 we obtain the following (Fig. 3.6).

$$\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_1}{k_2}$$

which when integrated gives simply

$$\boxed{\frac{C_R - C_{R0}}{C_S - C_{S0}} = \frac{k_1}{k_2}} \tag{38}$$

This result is shown in Fig. 3.6. Thus, the slope of a plot of C_R versus C_s gives the ratio k_1 / k_2. Knowing k_1 / k_2 as well as $k_1 + k_2$ gives k_1 and k_2. Typical concentration-time curves of the three components in a batch reactor for the case where CRo = Cso = 0 and $k_1 > k_2$, are shown in Fig. 3.7.

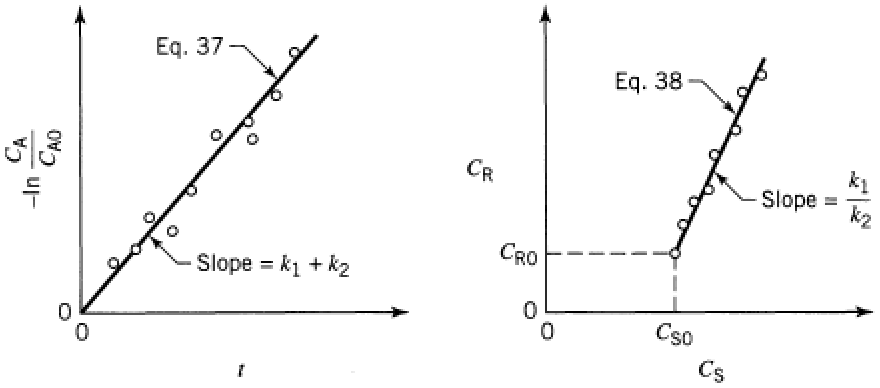

Figure 3.6 Evaluation of the rate constants for two competing elementary first-order reactions of the type $A \begin{smallmatrix} \nearrow R \\ \searrow S \end{smallmatrix}$.

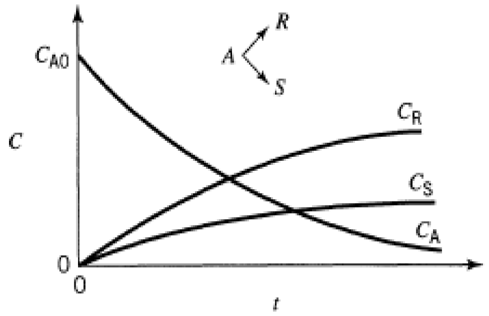

Figure 3.7 Typical concentration-time curves for competing reactions.

Homogeneous Catalyzed Reactions. Suppose the reaction rate for a homogeneous catalyzed system is the sum of rates of both the uncatalyzed and catalyzed reactions,

$$\left.\begin{aligned} A &\xrightarrow{k_1} R \\ A + C &\xrightarrow{k_2} R + C \end{aligned}\right\} \qquad \begin{aligned} -\left(\frac{dC_A}{dt}\right)_1 &= k_1 C_A \\ -\left(\frac{dC_A}{dt}\right)_2 &= k_2 C_A C_C \end{aligned}$$

The overall rate of disappearance of reactant A is then

$$-\frac{dC_A}{dt} = k_1 C_A + k_2 C_A C_C = (k_1 + k_2 C_C) C_A \qquad \textbf{(39)}$$

$$-\ln \frac{C_A}{C_{A0}} = -\ln(1 - X_A) = (k_1 + k_2 C_C)t = k_{\text{observed}}\, t \qquad \textbf{(40)}$$

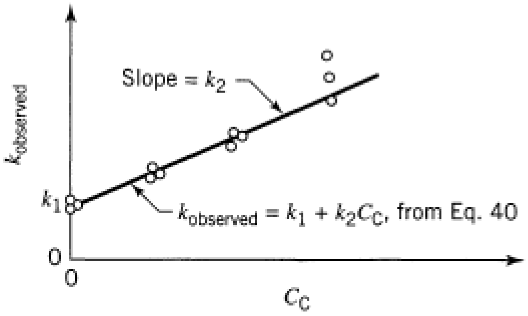

Figure 3.8 Rate constants for a homogeneous catalyzed reaction from a series of runs with different catalyst concentrations.

Making a series of runs with different catalyst concentrations allows us to find k_1 and k_2. This is done by plotting the observed k value against the catalyst concentrations as shown in Fig. 3.8. The slope of such a plot is k_2 and the intercept k_1.

Autocatalytic Reactions. A reaction in which one of the products of reaction acts as a catalyst is called an autocatalytic reaction. The simplest such reaction is

$$A + R \rightarrow R + R \tag{41a}$$

for which the rate equation is

$$-r_A = -\frac{dC_A}{dt} = kC_AC_R \tag{41b}$$

Because the total number of moles of A and R remain unchanged as A is consumed, we may write that at any time

$$C_0 = C_A + C_R = C_{A0} + C_{R0} = \text{constant}$$

Thus, the rate equation becomes

$$-r_A = -\frac{dC_A}{dt} = kC_A(C_0 - C_A)$$

Rearranging and breaking into partial fractions, we obtain

$$-\frac{dC_A}{C_A(C_0 - C_A)} = -\frac{1}{C_0}\left(\frac{dC_A}{C_A} + \frac{dC_A}{C_0 - C_A}\right) = k\,dt$$

which on integration gives

$$\boxed{\ln \frac{C_{A0}(C_0 - C_A)}{C_A(C_0 - C_{A0})} = \ln \frac{C_R/C_{R0}}{C_A/C_{A0}} = C_0 kt = (C_{A0} + C_{R0})\,kt} \qquad (42)$$

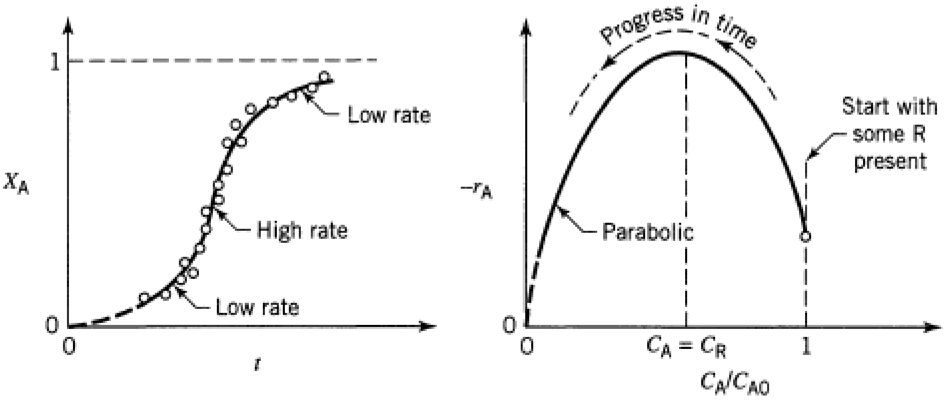

Figure 3.9 Conversion-time and rate-concentration curves for autocatalytic reaction of Eq. 41. This shape is typical for this type of reaction.

In terms of the initial reactant ratio $M = C_{R0}/C_{A0}$ and fractional conversion of A, this can be written as

$$\boxed{\ln \frac{M + X_A}{M(1 - X_A)} = C_{A0}(M + 1)kt = (C_{A0} + C_{R0})kt} \qquad (43)$$

For an autocatalytic reaction in a batch reactor some product R must be present if the reaction is to proceed at all. Starting with a very small concentration of R, we see qualitatively that the rate will rise as R is formed. At the other extreme, when A is just about used up the rate must drop to zero. This result is given in Fig. 3.9, which shows that the rate follows a parabola, with a maximum where the concentrations of A and R are equal.

To test for an autocatalytic reaction, plot the time and concentration coordinates of Eq. 42 or 43, as shown in Fig. 3.10 and see whether a straight line passing through zero is obtained.

Irreversible Reactions in Series. We first consider consecutive unimolecular type ***first-order*** reactions such as

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

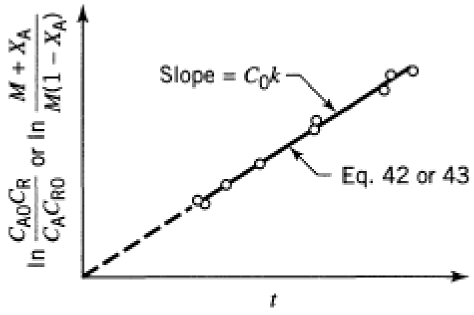

Figure 3.10 Test for the autocatalytic reaction of Eq. 41.

whose rate equations for the three components are

$$r_A = \frac{dC_A}{dt} = -k_1 C_A \qquad \textbf{(44)}$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A - k_2 C_R \qquad \textbf{(45)}$$

$$r_S = \frac{dC_S}{dt} = k_2 C_R \qquad \textbf{(46)}$$

Let us start with a concentration $\boldsymbol{C_{A0}}$ of A, no R or S present, and see how the concentrations of the components change with time. By integration of Eq. 44 we find the concentration of A to be

$$\boxed{-\ln \frac{C_A}{C_{A0}} = k_1 t \quad \text{or} \quad C_A = C_{A0} e^{-k_1 t}} \qquad \textbf{(47)}$$

To find the changing concentration of ***R***, substitute the concentration of A from Eq. 47 into the differential equation governing the rate of change of R, Eq. 45; thus

$$\frac{dC_R}{dt} + k_2 C_R = k_1 C_{A0} e^{-k_1 t} \qquad \textbf{(48)}$$

which is a first-order linear differential equation of the form

$$\frac{dy}{dx} + Py = Q$$

By multiplying through with the integrating factor $e^{\int PdX}$ the solution is

$$ye^{\int P\,dx} = \int Qe^{\int P\,dx}\,dx + \text{constant}$$

Applying this general procedure to the integration of Eq. 48:

The integrating factor=$e^{K_2 t}$, The constant of integration= $-k_1 C_{Ao} / (k_1 - k_2)$ from the initial conditions $C_{R0} = 0$ at t = 0, the final expression for the changing concentration of R is

$$\boxed{C_R = C_{A0} k_1 \left(\frac{e^{-k_1 t}}{k_2 - k_1} + \frac{e^{-k_2 t}}{k_1 - k_2} \right)} \qquad \textbf{(49)}$$

Noting that there is no change in total number of moles, the stoichiometry relates the concentrations of reacting components by

$$C_{A0} = C_A + C_R + C_S$$

which with Eqs. 47 and 49 gives

$$\boxed{C_S = C_{A0}\left(1 + \frac{k_2}{k_1 - k_2}e^{-k_1 t} + \frac{k_1}{k_2 - k_1}e^{-k_2 t}\right)} \qquad \textbf{(50)}$$

Thus, we have found how the concentrations of components A, R, and S vary with time.

Now if k_2 is much larger than k_1, Eq. 50 reduces to

$$C_S = C_{A0}(1 - e^{-k_1 t}), \qquad k_2 \gg k_1$$

In other words, the rate is determined by k_1 or the first step of the two-step reaction.

If k_1 is much larger than k_2, then

$$C_S = C_{A0}(1 - e^{-k_2 t}), \qquad k_1 \gg k_2$$

which is a first-order reaction governed by k_2, the slower step in the two-step reaction. Thus, in general, for any number of reactions in series it is the slowest step that has the greatest influence on the overall reaction rate.

As may be expected, the values of k_1 and k_2 also govern the location and maximum concentration of R. This may be found by differentiating Eq. 49 and setting $dC_R/dt = 0$. The time at which the maximum concentration of R occurs is thus

$$\boxed{t_{max} = \frac{1}{k_{\log mean}} = \frac{\ln(k_2/k_1)}{k_2 - k_1}} \qquad \textbf{(51)}$$

The maximum concentration of R is found by combining Eqs. 49 and 51 to give

$$\boxed{\frac{C_{R,max}}{C_{A0}} = \left(\frac{k_1}{k_2}\right)^{k_2/(k_2 - k_1)}} \qquad \textbf{(52)}$$

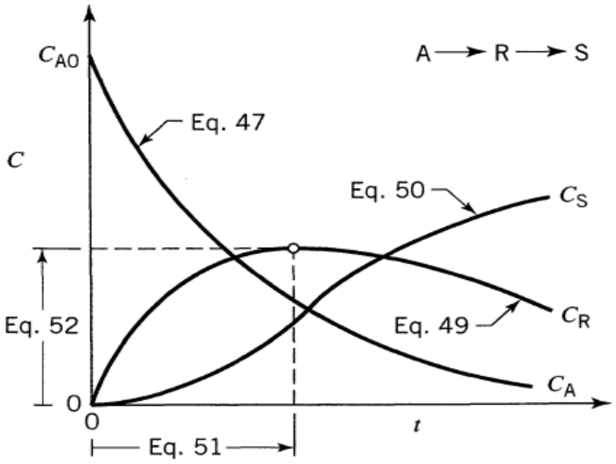

Figure 3.11 Typical concentration-time curves for consecutive first-order reactions.

Figure 3.11 shows the general characteristics of the concentration-time curves for the three components; A decreases exponentially, R rises to a maximum and then falls, and S raises continuously, the greatest rate of increase of S occurring where R is a maximum. In particular, this figure shows that one can evaluate ***k₁*** and ***k₂*** by noting the maximum concentration of intermediate and the time when this maximum is reached.

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Lecture No.5:

First-Order Reversible Reactions. Though no reaction ever goes to completion, we can consider many reactions to be essentially irreversible because of the large value of the equilibrium constant.. The simplest case is the opposed ***unimolecular***-type reaction:

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} R, \qquad K_C = K = \text{equilibrium constant} \qquad \textbf{(53}\boldsymbol{a}\textbf{)}$$

Starting with a concentration ratio $M = C_{R0}/C_{A0}$ the rate equation is

$$\frac{dC_R}{dt} = -\frac{dC_A}{dt} = C_{A0}\frac{dX_A}{dt} = k_1 C_A - k_2 C_R \qquad \textbf{(53}\boldsymbol{b}\textbf{)}$$

$$= k_1(C_{A0} - C_{A0}X_A) - k_2(MC_{A0} + C_{A0}X_A)$$

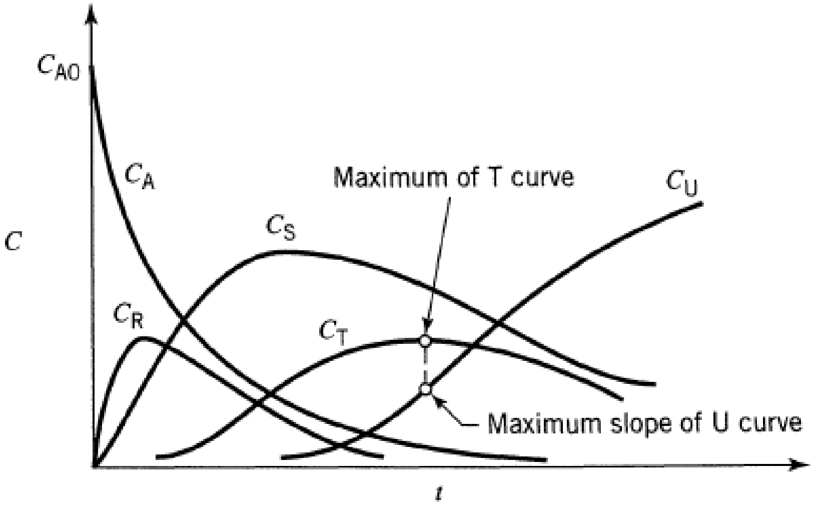


Figure 3.12 Concentration-time curves for a chain of successive first-order reactions. Only for the last two compounds do the maximum and the inflection points occur at the same time.

Now at equilibrium $dC_A/dt = 0$. Hence from Eq. 53 we find the fractional conversion of A at equilibrium conditions to be

$$K_C = \frac{C_{Re}}{C_{Ae}} = \frac{M + X_{Ae}}{1 - X_{Ae}} \longrightarrow K_C = \frac{k_1}{k_2}$$

Combining the above three equations we obtain, in terms of the equilibrium conversion,

$$\frac{dX_A}{dt} = \frac{k_1(M+1)}{M + X_{Ae}}(X_{Ae} - X_A)$$

With conversions measured in terms of X_{Ae}, this may be looked on as a pseudo first-order irreversible reaction which on integration gives

$$\boxed{-\ln\left(1-\frac{X_A}{X_{Ae}}\right) = -\ln\frac{C_A - C_{Ae}}{C_{A0} - C_{Ae}} = \frac{M+1}{M+X_{Ae}}k_1 t} \qquad \textbf{(54)}$$

A plot of $-\ln(1 - X_A/X_{Ae})$ vs. t, as shown in Fig. 3.13, gives a straight line.

Thus, the irreversible reaction is simply the special case of the reversible reaction in which $C_{Ae} = 0$, or $X_{Ae} = 1$, or $K_C = \infty$.

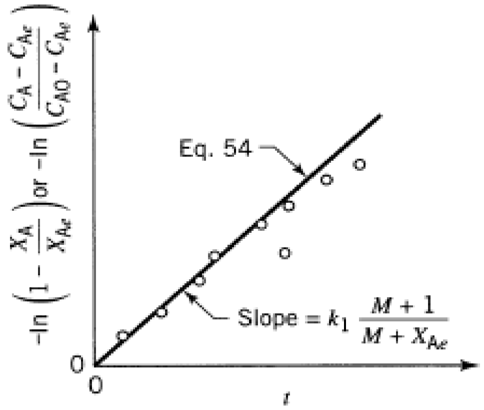


Figure 3.13 Test for the unimolecular type reversible reactions of Eq. 53.

EXAMPLE 3.1 FIND A RATE EQUATION USING THE INTEGRAL METHOD

Reactant A decomposes in a batch reactor

$$A \rightarrow \text{products}$$

The composition of A in the reactor is measured at various times with results shown in the following columns 1 and 2. Find a rate equation to represent the data.

Column 1	Column 2	Column 3	Column 4
Time t, s	Concentration C_A, mol/liter	$\ln\frac{C_{A0}}{C_A}$	$\frac{1}{C_A}$
0	$C_{A0} = 10$	ln 10/10 = 0	0.1
20	8	ln 10/8 = 0.2231	0.125
40	6	0.511	0.167
60	5	0.6931	0.200
120	3	1.204	0.333
180	2	1.609	0.500
300	1	2.303	1.000
Reported data		Calculated	

SOLUTION

Guess First-Order Kinetics. Start by guessing the simplest rate form, or first-order kinetics. This means that ln C_{A0}/C_A vs. t should give a straight line, see Eq. 11 or 12, or Fig. 3.1. So column 3 is calculated and the plot of Fig. E3.1*a* is made. Unfortunately, this does not give a straight line, so first-order kinetics cannot reasonably represent the data, and we must guess another rate form.

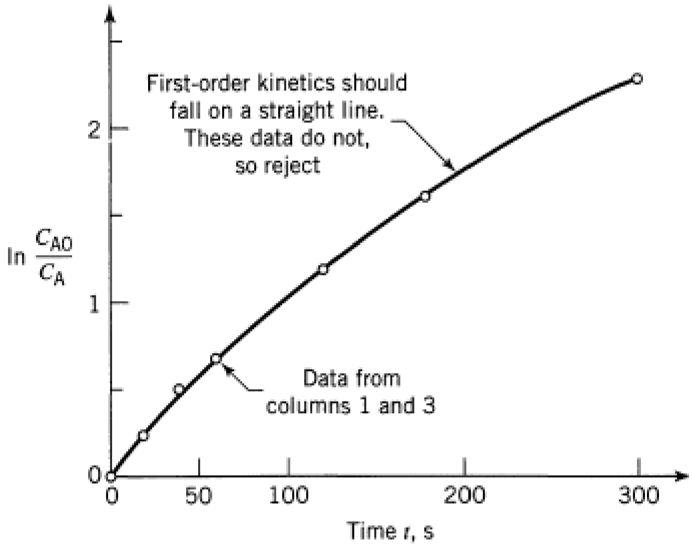


Figure E3.1*a*

Guess Second-Order Kinetics. Equation 16 tells that $1/C_A$ vs. t should give a straight line. So calculate column 4, plot column 1 vs. column 4, as shown in Fig. E3.1*b*. Again, this does not give a straight line, so a second-order kinetic form is rejected.

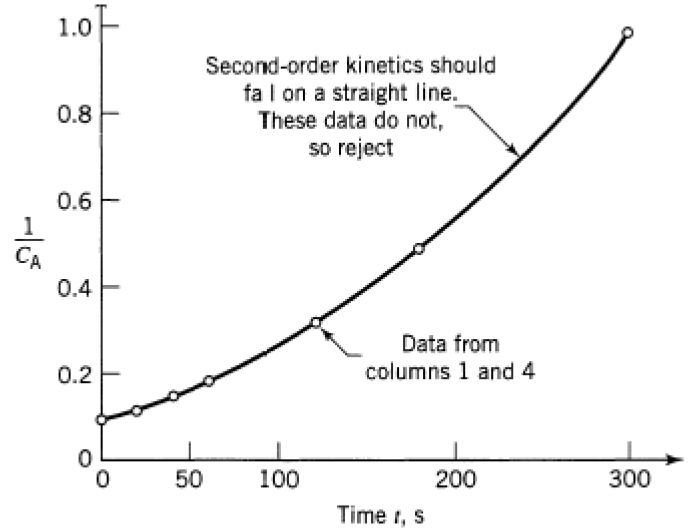


Figure E3.1*b*

Guess nth-Order Kinetics. Let's plan to use the fractional life method with F = 80%. Then Eq. 33*b* becomes

$$t_F = \frac{(0.8)^{1-n} - 1}{k(n-1)} C_{A0}^{1-n} \qquad \textbf{(i)}$$

Next take logarithms

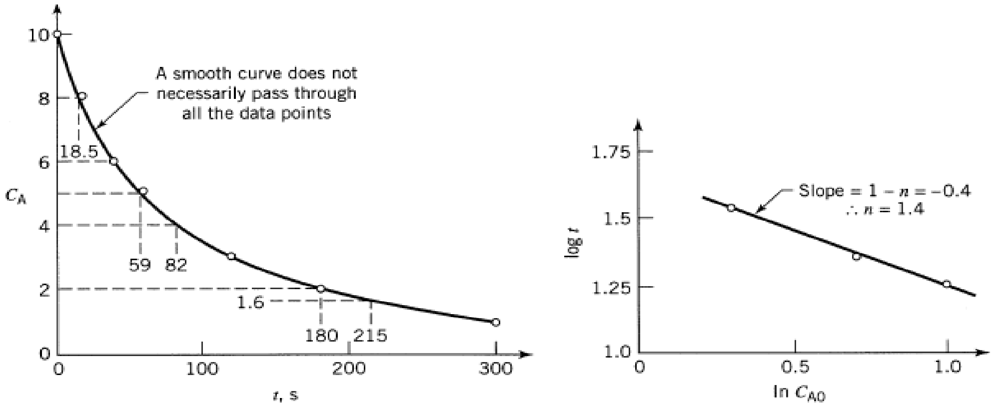
$$\underbrace{\log t_F}_{y} = \overbrace{\underbrace{\log\left(\frac{0.8^{1-n}-1}{k(n-1)}\right)}_{a}}^{\text{a constant}} + \underbrace{(1-n)\log C_{A0}}_{bx} \qquad \textbf{(ii)}$$

The procedure is as follows. First accurately plot the C_A vs. t data, draw a smooth curve to represent the data (most important) as shown in Fig. E3.1c, then pick C_{A0} = 10, 5, and 2 and fill in the following table from this figure.

C_{A0}	$C_{A\,end}$ (= $0.8C_{A0}$)	Time needed t_F, s	$\log t_F$	$\log C_{A0}$
10	8	0 → 18.5 = 18.5	log 18.5 = 1.27	1.00
5	4	59 → 82 = 23	1.36	0.70
2	1.6	180 → 215 = 35	1.54	0.30

From the curve, not the data

Next, plot $\log t_F$ vs. $\log C_{A0}$, as shown in Fig. E3.1d and find the slope.



Figures E3.1*c* and *E3.1d*

We now have the reaction order. To evaluate the rate constant, take any point on the C_A vs. t curve. Pick $C_{A0} = 10$, for which $t_F = 18.5$ s. Replacing all values into Eq. (i) gives

$$18.5 = \frac{(0.8)^{1-1.4} - 1}{k(1.4 - 1)} 10^{1-1.4}$$

from which

$$k = 0.005$$

Therefore, the rate equation that represents this reaction is

$$\underline{\underline{-r_A = \left(0.005 \frac{\text{liter}^{0.4}}{\text{mol}^{0.4} \cdot \text{s}}\right) C_A^{1.4}, \qquad \frac{\text{mol}}{\text{liter} \cdot \text{s}}}}$$

VARYING-VOLUME BATCH REACTOR

These reactors are much more complex than the simple constant-volume batch reactor. Their main use would be in the microprocessing field where a capillary tube with a movable bead would represent the reactor (see Fig. 3.20). The progress of the reaction is followed by noting the movement of the bead with time, a much simpler procedure than trying to measure the composition of the mixture, especially for microreactors. Thus,

V_0 = initial volume of the reactor

V = the volume at time t.

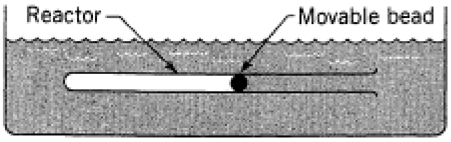


Figure 3.20 A varying-volume batch reactor.

This kind of reactor can be used for isothermal constant pressure operations, of reactions having a single stoichiometry. For such systems the volume is linearly related to the conversion, or

$$V = V_0(1 + \varepsilon_A X_A) \quad \text{or} \quad X_A = \frac{V - V_0}{V_0 \varepsilon_A} \qquad \textbf{(63a)}$$

$$dX_A = \frac{dV}{V_0 \varepsilon_A} \qquad \textbf{(63b)}$$

where ε_A is the fractional change in volume of the system between no conversion and complete conversion of reactant A. Thus

$$\boxed{\varepsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}}} \qquad \textbf{(64)}$$

As an example of the use of ε_A, consider the isothermal gas-phase reaction

$$A \rightarrow 4R$$

By starting with pure reactant A,

$$\varepsilon_A = \frac{4-1}{1} = 3$$

but with 50% inerts present at the start, two volumes of reactant mixture yield, on complete conversion, five volumes of product mixture. In this case

$$\varepsilon_A = \frac{5-2}{2} = 1.5$$

We see, then, that ε_A accounts for both the reaction stoichiometry and the presence of inerts. Noting that

$$N_A = N_{A0}(1 - X_A) \qquad \textbf{(65)}$$

we have, on combining with Eq. 63,

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X_A)}{V_0(1+\varepsilon_A X_A)} = C_{A0}\frac{1-X_A}{1+\varepsilon_A X_A}$$

Thus

$$\frac{C_A}{C_{A0}} = \frac{1-X_A}{1+\varepsilon_A X_A} \quad \text{or} \quad X_A = \frac{1 - C_A/C_{A0}}{1+\varepsilon_A C_A/C_{A0}} \qquad \textbf{(66)}$$

which is the relationship between conversion and concentration for isothermal varying-volume (or varying-density) systems satisfying the linearity assumption of Eq. 63.

The rate of reaction (disappearance of component A), is, in general

$$-r_A = -\frac{1}{V}\frac{dN_A}{dt}$$

Replacing V from Eq. 63*a* and N_A from Eq. 65 we end up with the rate in terms of the conversion

$$-r_A = \frac{C_{A0}}{(1 + \varepsilon_A X_A)}\frac{dX_A}{dt}$$

or in terms of volume, from Eqs. 63

$$-r_A = \frac{C_{A0}}{V\varepsilon_A}\cdot\frac{dV}{dt} = \frac{C_{A0}}{\varepsilon_A}\cdot\frac{d(\ln V)}{dt} \tag{67}$$

Zero-Order Reactions For a homogeneous zero-order reaction the rate of change of any reactant A is independent of the concentration of materials, or

$$-r_A = \frac{C_{A0}}{\varepsilon_A}\frac{d(\ln V)}{dt} = k \tag{69}$$

Integrating gives

$$\boxed{\frac{C_{A0}}{\varepsilon_A}\ln\frac{V}{V_0} = kt} \tag{70}$$

As shown in Fig. 3.21, the logarithm of the fractional change in volume versus time yields a straight line of slope $k\varepsilon_A/C_{A0}$.

First-Order Reactions. For a unimolecular-type first-order reaction the rate of change of reactant A is

$$-r_A = \frac{C_{A0}}{\varepsilon_A}\frac{d(\ln V)}{dt} = kC_A = kC_{A0}\left(\frac{1 - X_A}{1 + \varepsilon_A X_A}\right) \tag{71}$$

Replacing X_A by V from Eqs. 63 and integrating gives

$$\boxed{-\ln\left(1 - \frac{\Delta V}{\varepsilon_A V_0}\right) = kt,\ \Delta V = V - V_0} \tag{72}$$

A semilogarithmic plot of Eq. 72, as shown in Fig. 3.22, yields a straight line of slope k.

Second-Order Reactions. For a bimolecular-type second-order reaction

$$2A \rightarrow \text{products}$$

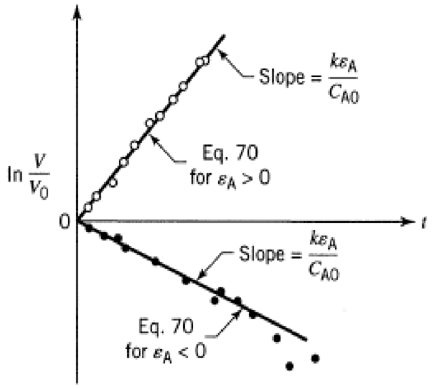


Figure 3.21 Test for a homogeneous zero-order reaction, Eq. 69, in a constant-pressure, varying volume reactor.

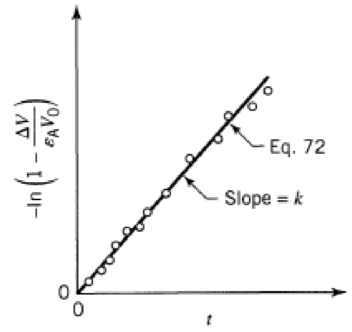


Figure 3.22 Test for a first-order reaction, Eq. 71, in a constant-pressure, varying-volume reactor.

$$A + B \rightarrow \text{products}, \quad \text{with} \quad C_{A0} = C_{B0}$$

the rate is given by

$$-r_A = \frac{C_{A0}}{\varepsilon_A}\frac{d\ln V}{dt} = kC_A^2 = kC_{A0}^2\left(\frac{1-X_A}{1+\varepsilon_A X_A}\right)^2$$

Replacing X_A by V from Eqs. 63 and then integrating gives, after much algebraic manipulation,

$$\boxed{\frac{(1+\varepsilon_A)\,\Delta V}{V_0\varepsilon_A - \Delta V} + \varepsilon_A \ln\left(1-\frac{\Delta V}{V_0\varepsilon_A}\right) = kC_{A0}t} \qquad \textbf{(73)}$$

Figure 3.23 shows how to test for those kinetics.

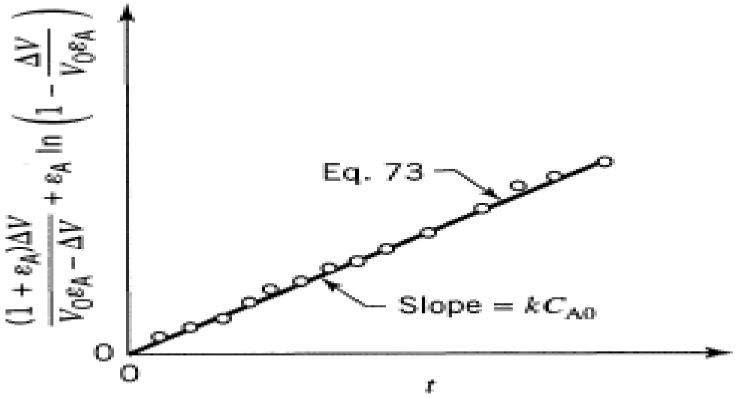


Figure 3.23 Test for the second-order reaction, Eq. 73, in a constant-pressure, varying-volume reactor.

EXAMPLE .4 CORRECT AND INCORRECT E VALUES

Experimental studies of a specific decomposition of A in a batch reactor using pressure units show exactly the same rate at two different temperatures:

$$\begin{aligned} &\text{at } 400\text{ K} \quad -r_A = 2.3\,p_A^2 \\ &\text{at } 500\text{ K} \quad -r_A = 2.3\,p_A^2 \end{aligned} \qquad \text{where} \quad \begin{cases} -r_A = \left[\dfrac{\text{mol}}{\text{m}^3\cdot\text{s}}\right] \\ p_A = [\text{atm}] \end{cases}$$

(a) Evaluate the activation using these units

(b) Transform the rate expressions into concentration units and then evaluate the activation energy.

The pressure is not excessive, so the ideal gas law can be used.

SOLUTION

(a) ***Using Pressure Units.*** We see right away that a change in temperature does not affect the rate of reaction. This means that

$$\underline{\underline{\mathbf{E} = 0}}$$

Alternatively, we can find **E** by going through the calculations. Thus

$$\ln\frac{k_2}{k_1} = \ln\frac{2.3}{2.3} = 0$$

hence replacing in Eq. 75 shows that

$$\underline{\underline{\mathbf{E} = 0}}$$

(b) ***Transform p_A into C_A, then find* E.** First write the rate equations with all units shown:

$$-r_A, \frac{\text{mol}}{\text{m}^3\cdot\text{s}} = \left(2.3, \frac{\text{mol}}{\text{m}^3\cdot\text{s}\cdot\text{atm}^2}\right)(p_A^2, \text{atm}^2)$$

Next change p_A to C_A. From ideal gas law

$$p_A = \frac{n_A}{V}\mathbf{R}T = C_A\mathbf{R}T$$

Combining the two preceding equations

$$-r_A = 2.3 C_A^2 \mathbf{R}^2 T^2$$

At 400 K

$$-r_{A1} = 2.3 \frac{\text{mol}}{\text{m}^3 \cdot \text{s} \cdot \text{atm}^2} \cdot C_A^2 \left(82.06 \times 10^{-6} \frac{\text{m}^3 \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)^2 (400\ \text{K})^2$$

$$= 0.0025 C_A^2 \quad \text{where} \quad k_1 = 0.0025 \frac{\text{m}^3}{\text{mol} \cdot \text{s}}$$

At 500 K, similarly

$$-r_{A2} = 0.0039 C_A^2 \quad \text{where} \quad k_2 = 0.0039 \frac{\text{m}^3}{\text{mol} \cdot \text{s}}$$

Here we see that in concentration units the rate constants are not independent of temperature. Evaluating the activation energy from Eq. 75, and replacing numbers gives

$$\mathbf{E} = \frac{(8.314)(400)(500)}{500 - 400} \ln \frac{0.0039}{0.0025}$$

or

$$\underline{\underline{\mathbf{E} = 7394 \frac{\text{J}}{\text{mol}}}}$$

This example shows that **E** values differ when either p or C used to measure concentrations of materials. ■

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Third Year

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Lecture No.6

Introduction to Reactor Design:

In reactor design, we want to know what size and type of reactor and method of operation are best for a given job. Equipment in which homogeneous reactions are effected can be one of three general types; the batch, the steady-state flow, and the unsteady-state flow or semibatch reactor The last classification includes all reactors that do not fall into the first two categories. These types are shown in Fig. 4.1.

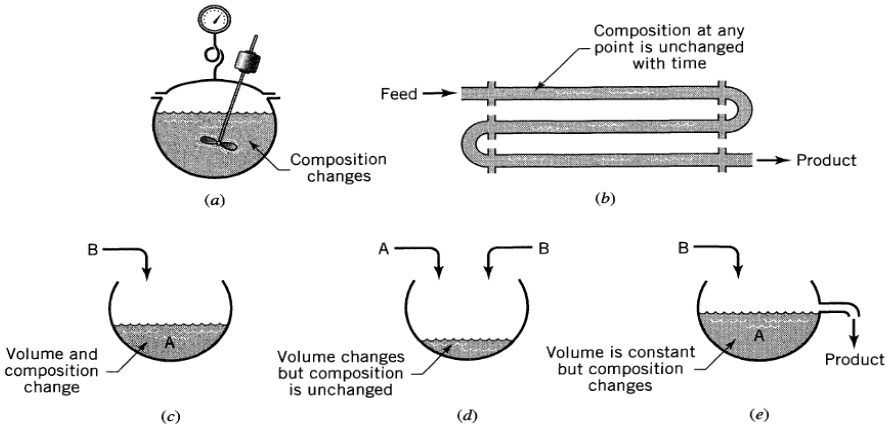

Figure 4.1 Broad classification of reactor types. (*a*) The batch reactor. (*b*) The steady-state flow reactor. (*c*), (*d*), and (*e*) Various forms of the semibatch reactor.

The starting point for all design is the *material balance* expressed for any reactant (or product). Thus, as illustrated in Fig. 4.2, we have

$$\begin{pmatrix}\text{rate of}\\ \text{reactant}\\ \text{flow into}\\ \text{element}\\ \text{of volume}\end{pmatrix} = \begin{pmatrix}\text{rate of}\\ \text{reactant}\\ \text{flow out}\\ \text{of element}\\ \text{of volume}\end{pmatrix} + \begin{pmatrix}\text{rate of reactant}\\ \text{loss due to}\\ \text{chemical reaction}\\ \text{within the element}\\ \text{of volume}\end{pmatrix} + \begin{pmatrix}\text{rate of}\\ \text{accumulation}\\ \text{of reactant}\\ \text{in element}\\ \text{of volume}\end{pmatrix} \qquad \textbf{(1)}$$

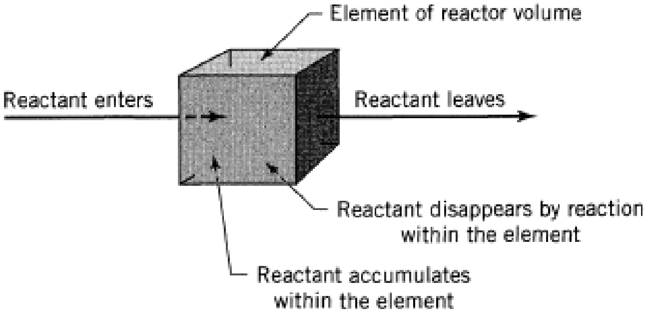

Figure 4.2 Material balance for an element of volume of the reactor.

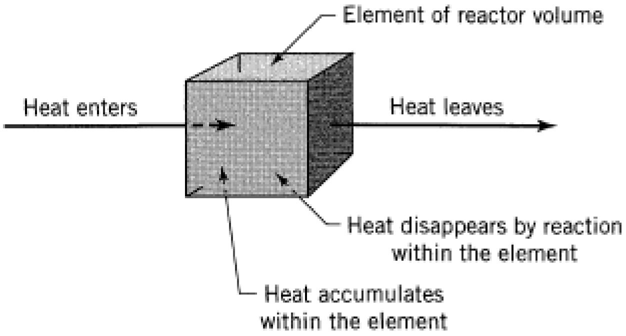

Figure 4.3 Energy balance for an element of volume of the reactor.

In nonisothermal operations *energy balances* must be used in conjunction with material balances. Thus, as illustrated in Fig. 4.3, we have

$$\begin{pmatrix}\text{rate of heat}\\ \text{flow into}\\ \text{element of}\\ \text{volume}\end{pmatrix} = \begin{pmatrix}\text{rate of heat}\\ \text{flow out of}\\ \text{element of}\\ \text{volume}\end{pmatrix} + \begin{pmatrix}\text{rate of}\\ \text{disappearance}\\ \text{of heat by}\\ \text{reaction within}\\ \text{element of}\\ \text{volume}\end{pmatrix} + \begin{pmatrix}\text{rate of}\\ \text{accumulation}\\ \text{of heat within}\\ \text{element of}\\ \text{volume}\end{pmatrix} \qquad \textbf{(2)}$$

Symbols and Relationship between C_A and X_A

For the reaction $aA + bB \rightarrow rR$, with inerts iI, Figs. 4.4 and 4.5 show the symbols commonly used to tell what is happening in the batch and flow reactors. These figures show that there are two related measures of the extent of reaction, the concentration C_A and the conversion X_A. However, the relationship between C_A and X_A is often not obvious but depends on a number of factors. This leads to three special cases, as follows.

Special Case 1. Constant Density Batch and Flow Systems. This includes most liquid reactions and also those gas reactions run at constant temperature and density. Here C_A and X_A are related as follows:

$$\left.\begin{aligned} X_A &= 1 - \frac{C_A}{C_{A0}} \quad \text{and} \quad dX_A = -\frac{dC_A}{C_{A0}} \\ \frac{C_A}{C_{A0}} &= 1 - X_A \quad \text{and} \quad dC_A = -C_{A0}dX_A \end{aligned}\right\} \text{for} \quad \varepsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}} = 0 \qquad \textbf{(3)}$$

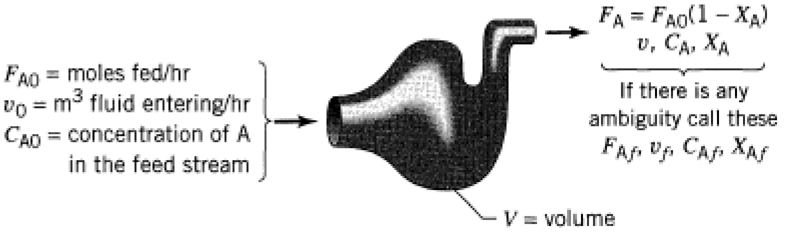

Figure 4.5 Symbols used for flow reactors.

To relate the changes in B and R to A we have

$$\frac{C_{A0} - C_A}{a} = \frac{C_{B0} - C_B}{b} = \frac{C_R - C_{R0}}{r} \quad \text{or} \quad \frac{C_{A0}X_A}{a} = \frac{C_{B0}X_B}{b} \qquad \textbf{(4)}$$

Special Case 2. Batch and Flow Systems of Gases of Changing Density but with T and π Constant. Here the density changes because of the change in number of moles during reaction. In addition, we require that the volume of a fluid element changes linearly with conversion, or $V = V_0(1 + \varepsilon_A X_A)$.

$$\left.\begin{aligned} X_A &= \frac{C_{A0} - C_A}{C_{A0} + \varepsilon_A C_A} \quad \text{and} \quad dX_A = -\frac{C_{A0}(1 + \varepsilon_A)}{(C_{A0} + \varepsilon_A C_A)^2} dC_A \\ \frac{C_A}{C_{A0}} &= \frac{1 - X_A}{1 + \varepsilon_A X_A} \quad \text{and} \quad \frac{dC_A}{C_{A0}} = -\frac{1 + \varepsilon_A}{(1 + \varepsilon_A X_A)^2} dX_A \end{aligned}\right\} \text{for}$$

$$\varepsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}} \neq 0 \qquad \textbf{(5)}$$

To follow changes in the other components we have

$$\text{between reactants}\begin{cases}\varepsilon_A X_A = \varepsilon_B X_B\\[4pt] \dfrac{a\varepsilon_A}{C_{A0}} = \dfrac{b\varepsilon_B}{C_{B0}}\end{cases}\qquad \text{for products and inerts}\begin{cases}\dfrac{C_R}{C_{A0}} = \dfrac{(r/a)X_A + C_{R0}/C_{A0}}{1+\varepsilon_A X_A}\\[8pt] \dfrac{C_I}{C_{I0}} = \dfrac{1}{1+\varepsilon_A X_A}\end{cases}\qquad \textbf{(6)}$$

Special Case 3. Batch and Flow Systems for Gases in General (varying ρ, T, π) which react according to

$$aA + bB \rightarrow rR, \qquad a + b \neq r$$

Pick one reactant as the basis for determining the conversion. We call this the *key reactant*. Let A be the key. Then for *ideal gas* behavior,

$$X_A = \frac{1 - \dfrac{C_A}{C_{A0}}\left(\dfrac{T\pi_0}{T_0\pi}\right)}{1 + \varepsilon_A \dfrac{C_A}{C_{A0}}\left(\dfrac{T\pi_0}{T_0\pi}\right)} \quad \text{or} \quad \frac{C_A}{C_{A0}} = \frac{1 - X_A}{1 + \varepsilon_A X_A}\left(\frac{T_0\pi}{T\pi_0}\right)$$

$$X_A = \frac{\dfrac{C_{B0}}{C_{A0}} - \dfrac{C_B}{C_{A0}}\left(\dfrac{T\pi_0}{T_0\pi}\right)}{\dfrac{b}{a} + \varepsilon_A \dfrac{C_B}{C_{A0}}\left(\dfrac{T\pi_0}{T_0\pi}\right)} \quad \text{or} \quad \frac{C_B}{C_{A0}} = \frac{\dfrac{C_{B0}}{C_{A0}} - \dfrac{b}{a}X_A}{1 + \varepsilon_A X_A}\left(\frac{T_0\pi}{T\pi_0}\right)$$

$$\frac{C_R}{C_{A0}} = \frac{\dfrac{C_{R0}}{C_{A0}} + \dfrac{r}{a}X_A}{1 + \varepsilon_A X_A}\left(\frac{T_0\pi}{T\pi_0}\right)$$

For high-pressure nonideal gas behavior replace $\left(\dfrac{T_0\pi}{\tau_0\pi_0}\right)$ by $\left(\dfrac{z_0T_0\pi}{zT\pi}\right)$, where z is the compressibility factor. To change to another key reactant, say B, note that

$$\frac{a\varepsilon_A}{C_{A0}} = \frac{b\varepsilon_B}{C_{B0}} \quad \text{and} \quad \frac{C_{A0}X_A}{a} = \frac{C_{B0}X_B}{b}$$

For liquids or isothermal gases with no change pressure and density

$$\varepsilon_A \rightarrow 0 \quad \text{and} \quad \left(\frac{T_0\pi}{T\pi_0}\right) \rightarrow 1$$

and the preceding expressions simplify greatly.

EXAMPLE 4.1 ***A BALANCE FROM STOICHIOMETRY***

Consider a feed $C_{A0} = 100$, $C_{B0} = 200$, $C_{i0} = 100$ to a steady-flow reactor. The isothermal gas-phase reaction is

$$A + 3B \rightarrow 6R$$

If $C_A = 40$ at the reactor exit, what is C_B, X_A, and X_B there?

SOLUTION

First sketch what is known (see Fig. E4.1).

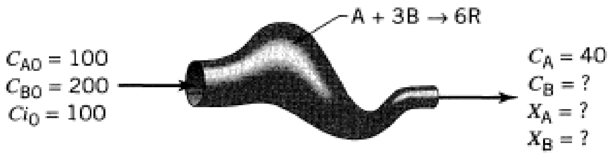

Figure E4.1

Next recognize that this problem concerns Special Case 2. So evaluate ε_A and ε_B. For this take 400 volumes of gas

$$\left.\begin{array}{ll} \text{at } X_A = 0 & V = 100A + 200B + 100i = 400 \\ \text{at } X_A = 1 & V = 0A - 100B + 600R + 100i = 600 \end{array}\right\} \quad \varepsilon_A = \frac{600-400}{400} = \frac{1}{2}$$

Then from the equations in the text

$$\varepsilon_B = \frac{\varepsilon_A C_{B0}}{bC_{A0}} = \frac{(1/2)(200)}{3(100)} = \frac{1}{3}$$

$$X_A = \frac{C_{A0} - C_A}{C_{A0} + \varepsilon_A C_A} = \frac{100 - 40}{100 + (1/2)40} = \frac{60}{120} = \underline{\underline{0.5}}$$

$$X_B = \frac{bC_{A0}X_A}{C_{B0}} = \frac{3(100)(0.5)}{200} = \underline{\underline{0.75}}$$

$$C_B = C_{B0}\left(\frac{1 - X_B}{1 + \varepsilon_B X_B}\right) = \frac{200(1 - 0.75)}{1 + (1/3)(0.75)} = \underline{\underline{40}}$$

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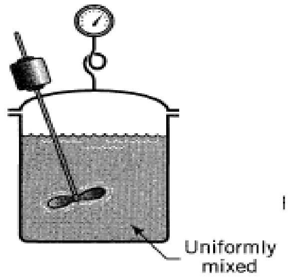
1. Ideal Reactors for a Single Reaction:



A. IDEAL BATCH REACTOR:

Make a material balance for any component A

$$\overset{=0}{\cancel{\text{input}}} = \overset{=0}{\cancel{\text{output}}} + \text{disappearance} + \text{accumulation}$$

or

$$+\begin{pmatrix}\text{rate of loss of reactant A}\\ \text{within reactor due to}\\ \text{chemical reaction}\end{pmatrix} = -\begin{pmatrix}\text{rate of accumulation}\\ \text{of reactant A}\\ \text{within the reactor}\end{pmatrix} \qquad \textbf{(1)}$$

Evaluating the terms of Eq. 1, we find

$$\begin{matrix}\text{disappearance of A}\\ \text{by reaction,}\\ \text{moles/time}\end{matrix} = (-r_A)V = \left(\frac{\text{moles A reacting}}{(\text{time})(\text{volume of fluid})}\right)(\text{volume of fluid})$$

$$\begin{matrix}\text{accumulation of A,}\\ \text{moles/time}\end{matrix} = \frac{dN_A}{dt} = \frac{d[N_{A0}(1-X_A)]}{dt} = -N_{A0}\frac{dX_A}{dt}$$

By replacing these two terms in Eq. 1, we obtain

$$(-r_A)V = N_{A0}\frac{dX_A}{dt} \qquad \textbf{(2)}$$

Rearranging and integrating then gives

$$t = N_{A0}\int_0^{X_A}\frac{dX_A}{(-r_A)V} \qquad \textbf{(3)}$$

This equation may be simplified for a number of situations. If the density of the fluid remains constant, we obtain

$$\boxed{t = C_{A0}\int_0^{X_A}\frac{dX_A}{-r_A} = -\int_{C_{A0}}^{C_A}\frac{dC_A}{-r_A} \qquad \text{for } \varepsilon_A = 0} \qquad \textbf{(4)}$$

For all reactions in which the volume of reacting mixture changes proportionately with conversion, such as in single gas-phase reactions with significant density changes, Eq. 3 becomes

$$t = N_{A0}\int_0^{X_A}\frac{dX_A}{(-r_A)V_0(1+\varepsilon_A X_A)} = C_{A0}\int_0^{X_A}\frac{dX_A}{(-r_A)(1+\varepsilon_A X_A)} \qquad \textbf{(5)}$$

In one form or another, Eqs. 2 to 5 they are applicable to both isothermal and nonisothermal operations.

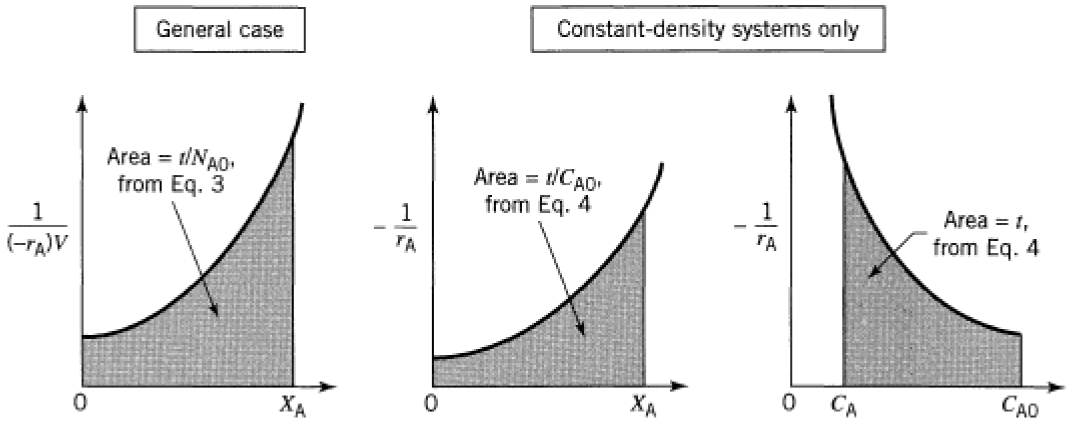


Figure 5.2 Graphical representation of the performance equations for batch reactors, isothermal or nonisothermal.

Space-Time and Space-Velocity

Space-time:

$$\tau = \frac{1}{s} = \begin{pmatrix} \text{time required to process one} \\ \text{reactor volume of feed measured} \\ \text{at specified conditions} \end{pmatrix} = [\text{time}] \qquad \textbf{(6)}$$

Space-velocity:

$$s = \frac{1}{\tau} = \begin{pmatrix} \text{number of reactor volumes of} \\ \text{feed at specified conditions which} \\ \text{can be treated in unit time} \end{pmatrix} = [\text{time}^{-1}] \qquad \textbf{(7)}$$

If they are of the stream entering the reactor, the relation between ***s*** and ***τ*** and the other pertinent variables is

$$\tau = \frac{1}{s} = \frac{C_{A0}V}{F_{A0}} = \frac{\left(\frac{\text{moles A entering}}{\text{volume of feed}}\right)(\text{volume of reactor})}{\left(\frac{\text{moles A entering}}{\text{time}}\right)} \qquad \textbf{(8)}$$

$$= \frac{V}{v_0} = \frac{(\text{reactor volume})}{(\text{volumetric feed rate})}$$

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Lecture No. 7

B STEADY-STATE MIXED FLOW REACTOR:

$$\text{input} = \text{output} + \text{disappearance by reaction} + \overset{=0}{\cancel{\text{accumulation}}} \qquad \textbf{(10)}$$

As shown in Fig. 5.3, if $F_{A0} = v_0 C_{A0}$ is the molar feed rate of component A to the reactor, then considering the reactor as a whole we have

$$\text{input of A, moles/time} = F_{A0}(1 - X_{A0}) = F_{A0}$$

$$\text{output of A, moles/time} = F_A = F_{A0}(1 - X_A)$$

$$\begin{array}{c}\text{disappearance of A}\\ \text{by reaction,}\\ \text{moles/time}\end{array} = (-r_A)V = \left(\frac{\text{moles A reacting}}{(\text{time})(\text{volume of fluid})}\right)\left(\begin{array}{c}\text{volume of}\\ \text{reactor}\end{array}\right)$$

Introducing these three terms into Eq. 10, we obtain

$$F_{A0}X_A = (-r_A)V$$

which on rearrangement becomes

$$\boxed{\begin{aligned}\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \frac{\Delta X_A}{-r_A} = \frac{X_A}{-r_A}\\ \tau = \frac{1}{s} = \frac{V}{v_0} = \frac{VC_{A0}}{F_{A0}} = \frac{C_{A0}X_A}{-r_A}\end{aligned}} \qquad \text{any } \varepsilon_A \qquad \textbf{(11)}$$

or

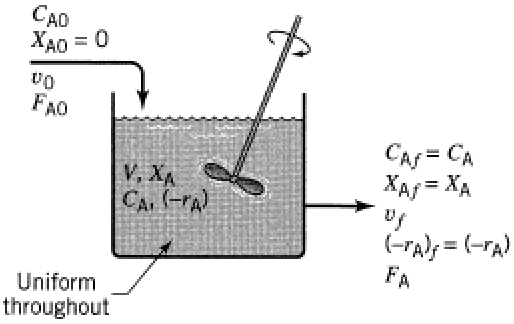

Figure 5.3 Notation for a mixed reactor.

For the special case of constant-density systems $X_A = 1 - C_A/C_{A0}$, in which case the performance equation for mixed reactors can also be written in terms of concentrations or

$$\boxed{\begin{aligned}\frac{V}{F_{A0}} = \frac{X_A}{-r_A} = \frac{C_{A0} - C_A}{C_{A0}(-r_A)}\\ \tau = \frac{V}{v} = \frac{C_{A0}X_A}{-r_A} = \frac{C_{A0} - C_A}{-r_A}\end{aligned}} \qquad \varepsilon_A = 0 \qquad \textbf{(13)}$$

or

Figure 5.4 is a graphical representation of these mixed flow performance equations. For any specific kinetic form the equations can be written out directly.

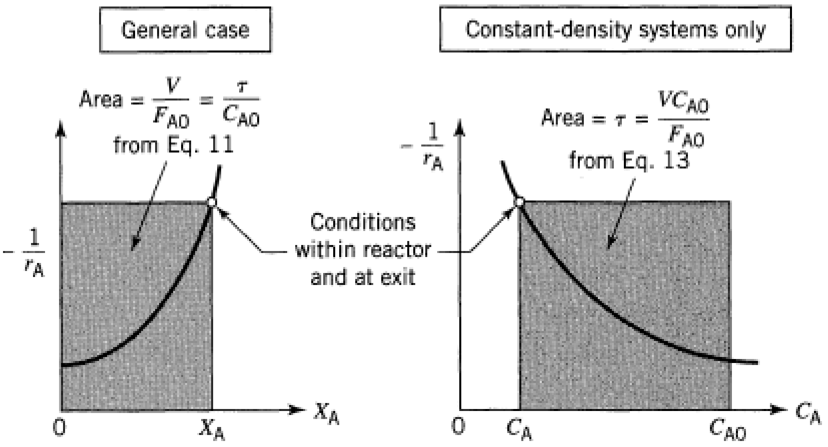

Figure 5.4 Graphical representation of the design equations for mixed flow reactor.

As an example, for constant density systems $C_A/C_{A0} = 1 - X_A$, thus the performance expression *for first-order reaction* becomes

$$\boxed{k\tau = \frac{X_A}{1 - X_A} = \frac{C_{A0} - C_A}{C_A} \qquad \text{for } \varepsilon_A = 0} \tag{14a}$$

On the other hand, for linear expansion

$$V = V_0(1 + \varepsilon_A X_A) \quad \text{and} \quad \frac{C_A}{C_{A0}} = \frac{1 - X_A}{1 + \varepsilon_A X_A}$$

thus *for first-order reaction* the performance expression of Eq. 11 becomes

$$\boxed{k\tau = \frac{X_A(1 + \varepsilon_A X_A)}{1 - X_A} \qquad \text{for any } \varepsilon_A} \tag{14b}$$

For *second-order reaction*, A → products, $-r_A = kC_A^2$, $\varepsilon_A = 0$, the performance equation of Eq. 11 becomes

$$\boxed{k\tau = \frac{C_{A0} - C_A}{C_A^2} \quad \text{or} \quad C_A = \frac{-1 + \sqrt{1 + 4k\tau C_{A0}}}{2k\tau}} \tag{15}$$

EXAMPLE 5.1 REACTION RATE IN A MIXED FLOW REACTOR

One liter per minute of liquid containing A and B (C_{A0} = 0.10 mol/liter, C_{B0} = 0.01 mol/liter) flow into a mixed reactor of volume V = 1 liter. The materials react in a complex manner for which the stoichiometry is unknown. The outlet stream from the reactor contains A, B, and C (C_{Af} = 0.02 mol/liter, C_{Bf} = 0.03 mol/liter, C_{Cf} = 0.04 mol/liter), as shown in Fig. E5.1. Find the rate of reaction of A, B, and C for the conditions within the reactor.

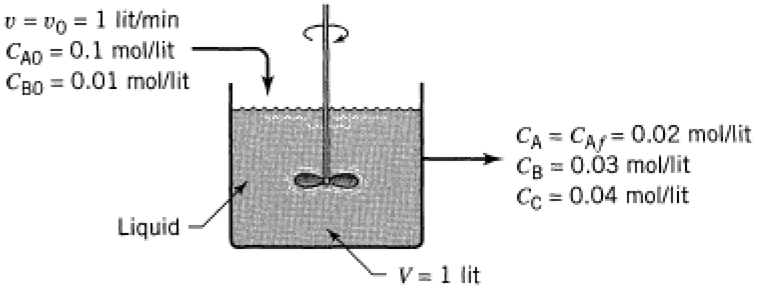

Figure E5.1

SOLUTION

For a liquid in a mixed flow reactor $\varepsilon_A = 0$ and Eq. 13 applies to each of the reacting components, giving for the rate of disappearance:

$$-r_A = \frac{C_{A0} - C_A}{\tau} = \frac{C_{A0} - C_A}{V/v} = \frac{0.10 - 0.02}{1/1} = \underline{\underline{0.08 \text{ mol/liter} \cdot \text{min}}}$$

$$-r_B = \frac{C_{B0} - C_B}{\tau} = \frac{0.01 - 0.03}{1} = \underline{\underline{-0.02 \text{ mol/liter} \cdot \text{min}}}$$

$$-r_C = \frac{C_{C0} - C_C}{\tau} = \frac{0 - 0.04}{1} = \underline{\underline{-0.04 \text{ mol/liter} \cdot \text{min}}}$$

Thus A is disappearing while B and C are being formed. ■

EXAMPLE 5.2 KINETICS FROM A MIXED FLOW REACTOR

Pure gaseous reactant A ($C_{A0} = 100$ millimol/liter) is fed at a steady rate into a mixed flow reactor ($V = 0.1$ liter) where it dimerizes ($2A \rightarrow R$). For different gas feed rates the following data are obtained:

Run number	1	2	3	4
v_0, liter/hr	10.0	3.0	1.2	0.5
C_{Af}, millimol/liter	85.7	66.7	50	33.4

Find a rate equation for this reaction.

SOLUTION

For this stoichiometry, $2A \rightarrow R$, the expansion factor is

$$\varepsilon_A = \frac{1-2}{2} = -\frac{1}{2}$$

and the corresponding relation between concentration and conversion is

$$\frac{C_A}{C_{A0}} = \frac{1 - X_A}{1 + \varepsilon_A X_A} = \frac{1 - X_A}{1 - \frac{1}{2}X_A}$$

or

$$X_A = \frac{1 - C_A/C_{A0}}{1 + \varepsilon_A C_A/C_{A0}} = \frac{1 - C_A/C_{A0}}{1 - C_A/2C_{A0}}$$

The conversion for each run is then calculated and tabulated in column 4 of Table E5.2.

Table E5.2

	Given		Calculated			
Run	v_0	C_A	X_A	$(-r_A) = \frac{v_0 C_{A0} X_A}{V}$	$\log C_A$	$\log(-r_A)$
1	10.0	85.7	0.25	$\frac{(10)(100)(0.25)}{0.1} = 2500$	1.933	3.398
2	3.0	66.7	0.50	1500	1.824	3.176
3	1.2	50	0.667	800	1.699	2.903
4	0.5	33.3	0.80	400	1.522	2.602

From the performance equation, Eq. 11, the rate of reaction for each run is given by

$$(-r_A) = \frac{v_0 C_{A0} X_A}{V}, \qquad \left[\frac{\text{millimol}}{\text{liter}\cdot\text{hr}}\right]$$

$$\log(-r_A) = \log k + n \log C_A$$

For *n*th-order kinetics this data should give a straight line on a log $(-r_A)$ vs. log C_A plot. From columns 6 and 7 of Table E5.2 and as shown in Fig. E5.2, the four data points are reasonably represented by a straight line of slope 2, so the rate equation for this dimerization is

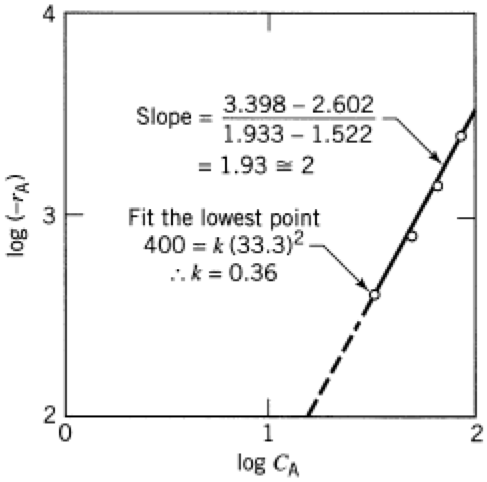

Figure E5.2

$$-r_A = \left(0.36 \frac{\text{liter}}{\text{hr}\cdot\text{millimol}}\right) C_A^2, \qquad \left[\frac{\text{millimol}}{\text{liter}\cdot\text{hr}}\right]$$

Comment. If we ignore the density change in our analysis (or put $\varepsilon_A = 0$ and use $C_A/C_{A0} = 1 - X_A$) we end up with an incorrect rate equation (reaction order $n \cong 1.6$) which when used in design would give wrong performance predictions.

EXAMPLE 5.3 MIXED FLOW REACTOR PERFORMANCE

The elementary liquid-phase reaction

$$A + 2B \underset{k_2}{\overset{k_1}{\rightleftarrows}} R$$

with rate equation

$$-r_A = -\frac{1}{2} r_B = (12.5\ \text{liter}^2/\text{mol}^2\cdot\text{min}) C_A C_B^2 - (1.5\ \text{min}^{-1}) C_R, \qquad \left[\frac{\text{mol}}{\text{liter}\cdot\text{min}}\right]$$

is to take place in a 6-liter steady-state mixed flow reactor. Two feed streams, one containing 2.8 mol A/liter and the other containing 1.6 mol B/liter, are to be introduced at equal volumetric flow rates into the reactor, and 75% conversion of limiting component is desired (see Fig. E5.3). What should be the flow rate of each stream? Assume a constant density throughout.

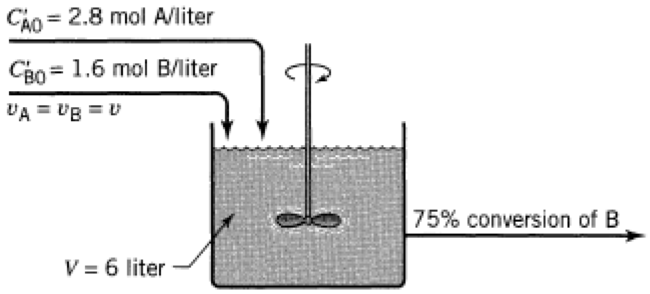

Figure E5.3

SOLUTION

The concentration of components in the mixed feed stream is

$C_{A0} = 1.4$ mol/liter , $C_{B0} = 0.8$ mol/liter , $C_{R0} = 0$

These numbers show that B is the limiting component, so for 75% conversion of B and $\varepsilon = 0$, the composition in the reactor and in the exit stream is

$C_A = 1.4 - 0.6/2 = 1.1$ mol/liter

$C_B = 0.8 - 0.6 = 0.2$ mol/liter or 75% conversion

$C_R = 0.3$ mol/liter

Writing the rate and solving the problem in terms of B we have at the conditions within the reactor

$$-r_B = 2(-r_A) = (2 \times 12.5)C_A C_B^2 - (2 \times 1.5)C_R$$

$$= \left(25\,\frac{\text{liter}^2}{\text{mol}^2\cdot\text{min}}\right)\left(1.1\,\frac{\text{mol}}{\text{liter}}\right)\left(0.2\,\frac{\text{mol}}{\text{liter}}\right)^2 - (3\ \text{min}^{-1})\left(0.3\,\frac{\text{mol}}{\text{liter}}\right)$$

$$= (1.1 - 0.9)\frac{\text{mol}}{\text{liter}\cdot\text{min}} = 0.2\,\frac{\text{mol}}{\text{liter}\cdot\text{min}}$$

For no density change, the performance equation of Eq. 13 gives

$$\tau = \frac{V}{v} = \frac{C_{B0} - C_B}{-r_B}$$

Hence the volumentric flow rate into and out of the reactor is

$$v = \frac{V(-r_B)}{C_{B0} - C_B}$$

$$\underline{\underline{v}} = \frac{(6\text{ liter})(0.2\text{ mol/liter}\cdot\text{min})}{(0.8-0.6)\text{ mol/liter}} = \underline{\underline{6\text{ liter/min}}}$$

or

$$\underline{\underline{3\text{ liter/min of each of the two feed streams}}}$$

■

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C STEADY-STATE PLUG FLOW REACTOR:

$$\text{input} = \text{output} + \text{disappearance by reaction} + \overset{=0}{\cancel{\text{accumulation}}} \qquad \textbf{(10)}$$

Referring to Fig. 5.5, we see for volume dV that

input of A, moles/time $= F_A$

output of A, moles/time $= F_A + dF_A$

disappearance of A by reaction, moles/time $= (-r_A)dV$

$$= \left(\frac{\text{moles A reacting)}}{\text{(time)(volume of fluid)}}\right)\left(\begin{matrix}\text{volume of}\\ \text{element}\end{matrix}\right)$$

Introducing these three terms in Eq. 10, we obtain

$$F_A = (F_A + dF_A) + (-r_A)dV$$

Noting that

$$dF_A = d[F_{A0}(1 - X_A)] = -F_{A0}dX_A$$

We obtain on replacement

$$F_{A0}dX_A = (-r_A)dV \qquad \textbf{(16)}$$

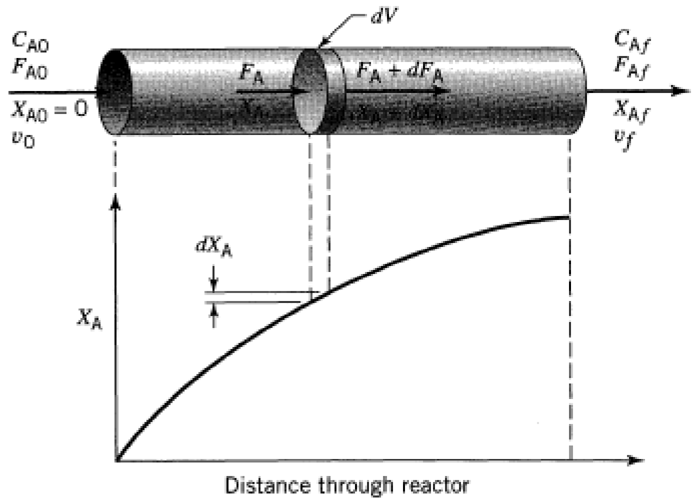

Figure 5.5 Notation for a plug flow reactor.

This, then, is the equation which accounts for A in the differential section of reactor of volume dV. For the reactor as a whole the expression must be integrated. Now F_{A0}, the feed rate, is constant, but r_A is certainly dependent on the concentration or conversion of materials. Grouping the terms accordingly, we obtain

$$\int_0^V \frac{dV}{F_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A}$$

, Thus;

or

$$\boxed{\begin{gathered}\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A} \\ \tau = \frac{V}{v_0} = \frac{VC_{A0}}{F_{A0}} = C_{A0}\int_0^{X_{Af}} \frac{dX_A}{-r_A}\end{gathered}} \quad \text{any } \varepsilon_A \qquad \textbf{(17)}$$

$$\frac{V}{F_{A0}} = \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{-r_A}$$

(18)

$$\tau = C_{A0}\int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{-r_A}$$

in which case the performance equation can be expressed in terms of concentrations, or

$$\boxed{\begin{gathered}\frac{V}{F_{A0}} = \frac{\tau}{C_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A} = -\frac{1}{C_{A0}}\int_{C_{A0}}^{C_{Af}} \frac{dC_A}{-r_A} \\ \tau = \frac{V}{v_0} = C_{A0}\int_0^{X_{Af}} \frac{dX_A}{-r_A} = -\int_{C_{A0}}^{C_{Af}} \frac{dC_A}{-r_A}\end{gathered}} \quad \varepsilon_A = 0 \qquad \textbf{(19)}$$

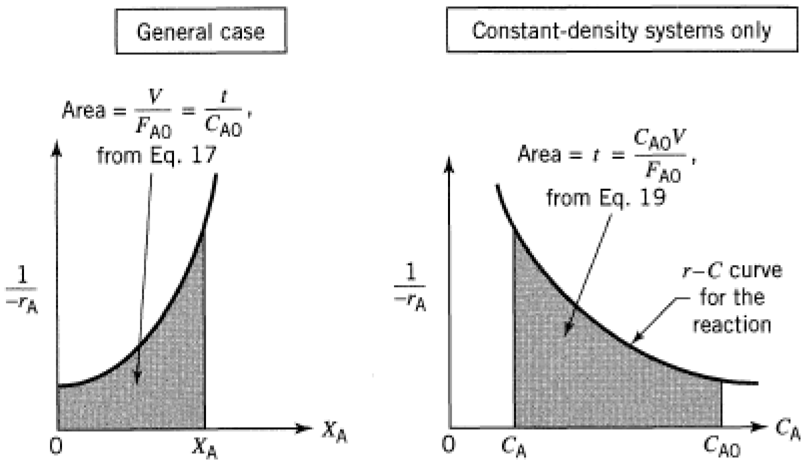

Figure 5.6 Graphical representation of the performance equations for plug flow reactors.

To do this, insert the kinetic expression for r_A in Eq. 17 and integrate. Some of the simpler integrated forms for ***plug flow*** are as follows:

Zero-order homogeneous reaction, any constant ε_A

$$k\tau = \frac{kC_{A0}V}{F_{A0}} = C_{A0}X_A \qquad \textbf{(20)}$$

First-order irreversible reaction, A → products, any constant ε_A,

$$\boxed{k\tau = -(1+\varepsilon_A)\ln(1-X_A) - \varepsilon_A X_A} \qquad \textbf{(21)}$$

First-order reversible reaction, $A \rightleftarrows rR$, $C_{R0}/C_{A0} = M$, kinetics approximated or fitted by $-r_A = k_1C_A - k_2C_R$ with an observed equilibrium conversion X_{Ae}, any constant ε_A,

$$k_1\tau = \frac{M + rX_{Ae}}{M + r}\left[-(1+\varepsilon_A X_{Ae})\ln\left(1 - \frac{X_A}{X_{Ae}}\right) - \varepsilon_A X_A\right] \qquad \textbf{(22)}$$

Second-order irreversible reaction, A + B → products with equimolar feed or 2A → products, any constant ε_A,

$$C_{A0}k\tau = 2\varepsilon_A(1+\varepsilon_A)\ln(1-X_A) + \varepsilon_A^2 X_A + (\varepsilon_A + 1)^2\frac{X_A}{1-X_A} \qquad \textbf{(23)}$$

EXAMPLE 5.4 PLUG FLOW REACTOR PERFORMANCE

A homogeneous gas reaction $A \rightarrow 3R$ has a reported rate at 215°C

$$-r_A = 10^{-2}C_A^{1/2}, \qquad [\text{mol/liter}\cdot\text{sec}]$$

Find the space-time needed for 80% conversion of a 50% A–50% inert feed to a plug flow reactor operating at 215°C and 5 atm ($C_{A0} = 0.0625$ mol/liter).

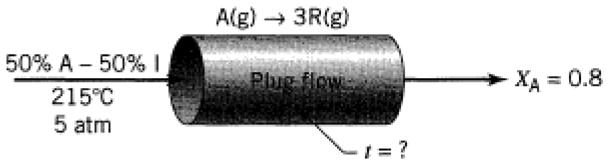

Figure E5.4*a*

SOLUTION

For this stoichiometry and with 50% inerts, two volumes of feed gas would give four volumes of completely converted product gas; thus

$$\varepsilon_A = \frac{4-2}{2} = 1$$

in which case the plug flow performance equation, Eq. 17, becomes

$$\tau = C_{A0}\int_0^{X_{Af}} \frac{dX_A}{-r_A} = C_{A0}\int_0^{X_{Af}} \frac{dX_A}{kC_{A0}^{1/2}\left(\frac{1-X_A}{1+\varepsilon_A X_A}\right)^{1/2}} = \frac{C_{A0}^{1/2}}{k}\int_0^{0.8}\left(\frac{1+X_A}{1-X_A}\right)^{1/2} dX_A \qquad \textbf{(i)}$$

The integral can be evaluated in any one of three ways: graphically, numerically, or analytically. Let us illustrate these methods.

Table E5.4

X_A	$\frac{1+X_A}{1-X_A}$	$\left(\frac{1+X_A}{1-X_A}\right)^{1/2}$
0	1	1
0.2	$\frac{1.2}{0.8} = 1.5$	1.227
0.4	2.3	1.528
0.6	4	2
0.8	9	3

Graphical Integration. First evaluate the function to be integrated at selected values (see Table E5.4) and plot this function (see Fig. E5.4*b*).

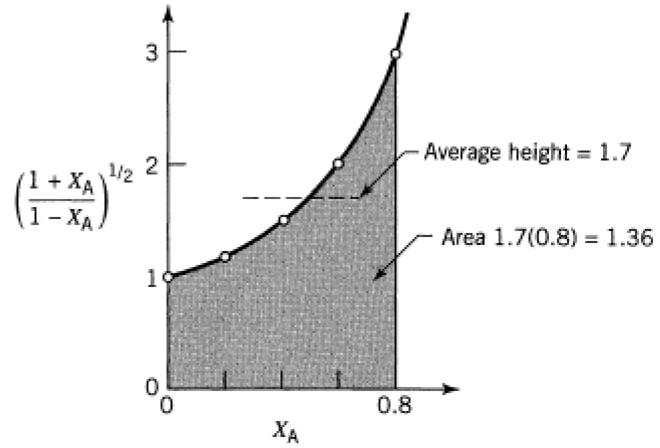

Figure E5.4*b*

Counting squares or estimating by eye we find

$$\text{Area} = \int_0^{0.8} \left(\frac{1+X_A}{1-X_A}\right)^{1/2} dX_A = (1.70)(0.8) = \underline{\underline{1.36}}$$

Numerical Integration. Using Simpson's rule, applicable to an even number of uniformly spaced intervals on the X_A axis, we find for the data of Table E5.4,

$$\int_0^{0.8} \left(\frac{1+X_A}{1-X_A}\right)^{1/2} dX_A = \text{(average height)(total width)}$$

$$= \left[\frac{1(1) + 4(1.227) + 2(1.528) + 4(2) + 1(3)}{12}\right](0.8)$$

$$= \underline{\underline{1.331}}$$

Analytical Integration. From a table of integrals

$$\int_0^{0.8} \left(\frac{1+X_A}{1-X_A}\right)^{1/2} dX_A = \int_0^{0.8} \frac{1+X_A}{\sqrt{1-X_A^2}}\, dX_A$$

$$= \left(\arcsin X_A - \sqrt{1-X_A^2}\right)\Big|_0^{0.8} = \underline{\underline{1.328}}$$

The method of integration recommended depends on the situation. In this problem probably the numerical method is the quickest and simplest and gives a good enough answer for most purposes.

So with the integral evaluated, Eq. (i) becomes

$$\underline{\underline{\tau}} = \frac{(0.0625\ \text{mol/liter})^{1/2}}{(10^{-2}\ \text{mol}^{1/2}/\text{liter}^{1/2}\cdot\text{sec})}(1.33) = \underline{\underline{33.2\ \text{sec}}}$$

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EXAMPLE 5.5 PLUG FLOW REACTOR VOLUME

The homogeneous gas decomposition of phosphine

$$4PH_3(g) \rightarrow P_4(g) + 6H_2$$

proceeds at 649°C with the first-order rate

$$-r_{PH_3} = (10/hr)\, C_{PH_3}$$

What size of plug flow reactor operating at 649°C and 460 kPa can produce 80% conversion of a feed consisting of 40 mol of pure phosphine per hour?

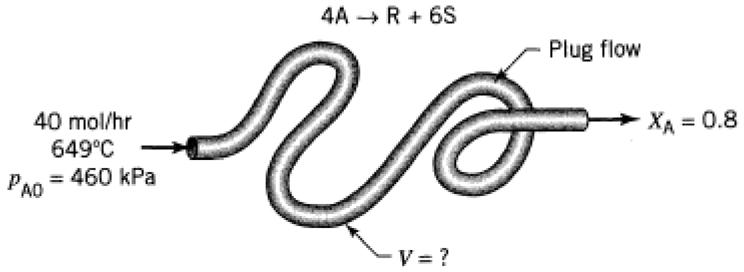

Figure E5.5

SOLUTION

Let A = PH_3, R = P_4, S = H_2. Then the reaction becomes

$$4A \rightarrow R + 6S$$

With

$$-r_A = (10/\text{hr})\ C_A$$

The volume of plug flow reactor is given by Eq. 21

$$V = \frac{F_{A0}}{kC_{A0}}\left[(1+\varepsilon_A)\ln\frac{1}{1-X_A} - \varepsilon_A X_A\right]$$

Evaluating the individual terms in this expression gives

$$F_{A0} = 40\ \text{mol/hr}$$

$$k = 10/\text{hr}$$

$$C_{A0} = \frac{p_{A0}}{\mathbf{R}T} = \frac{460\,000\ \text{Pa}}{(8.314\ \text{Pa}\cdot\text{m}^3/\text{mol}\cdot\text{K})(922\ \text{K})} = 60\ \text{mol/m}^3$$

$$\varepsilon_A = \frac{7-4}{4} = 0.75$$

$$X_A = 0.8$$

hence the volume of reactor

$$\underline{\underline{V}} = \frac{40\ \text{mol/hr}}{(10/\text{hr})(60\ \text{mol/m}^3)}\left[(1+0.75)\ln\frac{1}{0.2} - 0.75(0.8)\right] = 0.148\ \text{m}^3$$

$$= \underline{\underline{148\ \text{liters}}}$$

■

EXAMPLE 5.6 TEST OF A KINETIC EQUATION IN A PLUG FLOW REACTOR

We suspect that the gas reaction between A, B, and R is an elementary reversible reaction

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} R$$

and we plan to test this with experiments in an isothermal plug flow reactor.

(*a*) Develop the isothermal performance equation for these kinetics for a feed of A, B, R, and inerts.

(*b*) Show how to test this equation for an equimolar feed of A and B.

SOLUTION

(a) Feed of A, B, R, and inerts. For this elementary reaction the rate is

$$-r_A = k_1 C_A C_B - k_2 C_R = k_1 \frac{N_A}{V}\frac{N_B}{V} - k_2 \frac{N_R}{V}$$

At constant pressure, basing expansion and conversion on substance A,

$$-r_A = k_1 \frac{N_{A0} - N_{A0}X_A}{V_0(1+\varepsilon_A X_A)} \frac{N_{B0} - N_{A0}X_A}{V_0(1+\varepsilon_A X_A)} - k_2 \frac{N_{R0} + N_{A0}X_A}{V_0(1+\varepsilon_A X_A)}$$

Letting $M = C_{B0}/C_{A0}$, $M' = C_{R0}/C_{A0}$, we obtain

$$-r_A = k_1 C_{A0}^2 \frac{(1-X_A)(M-X_A)}{(1+\varepsilon_A X_A)^2} - k_2 C_{A0} \frac{M' + X_A}{1+\varepsilon_A X_A}$$

Hence, the design equation for plug flow, Eq. 17, becomes

$$\tau = C_{A0}\int_0^{X_{Af}} \frac{dX_A}{-r_A} = \int_0^{X_{Af}} \frac{(1+\varepsilon_A X_A)^2 dX_A}{k_1 C_{A0}(1-X_A)(M-X_A) - k_2(M'+X_A)(1+\varepsilon_A X_A)}$$

In this expression ε_A accounts for the stoichiometry and for inerts present in the feed.

(b) Equimolar feed of A and B. For $C_{A0} = C_{B0}$, $C_{R0} = 0$, and no inerts, we have $M = 1$, $M' = 0$, $\varepsilon_A = -0.5$; hence the expression for part a reduces to

$$\tau = \int_0^{X_{Af}} \frac{(1-0.5X_A)^2\, dX_A}{k_1 C_{A0}(1-X_A)^2 - k_2 X_A(1-0.5X_A)} \overset{\text{call}}{\underset{\text{this}}{=\!=}} \int_0^{X_{Af}} f(X_A) dX_A \qquad \textbf{(i)}$$

Having V, v_0, and X_A data from a series of experiments, separately evaluate the left side and the right side of Eq. (i). For the right side, at various X_A

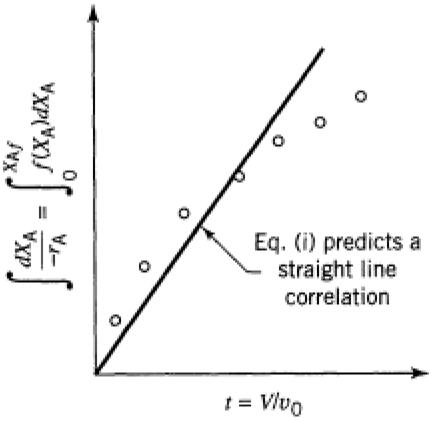

Figure E5.6

evaluate $f(X_A)$, then integrate graphically to give $\int f(X_A)dX_A$ and then make the plot of Fig. E5.6. If the data fall on a reasonably straight line, then the suggested kinetic scheme can be said to be satisfactory in that it fits the data.

Holding Time and Space Time for Flow Reactors

We should be clearly aware of the distinction between these two measures of time, $\bar{t}$ and τ. They are defined as follows:

$$\tau = \begin{pmatrix} \text{time needed to} \\ \text{treat one reactor} \\ \text{volume of feed} \end{pmatrix} = \frac{V}{v_0} = \frac{C_{A0}V}{F_{A0}}, \quad [\text{hr}] \qquad \textbf{(6) or (8)}$$

$$\bar{t} = \begin{pmatrix} \text{mean residence time} \\ \text{of flowing material} \\ \text{in the reactor} \end{pmatrix} = C_{A0}\int_0^{X_A} \frac{dX_A}{(-r_A)(1+\varepsilon_A X_A)}, \quad [\text{hr}] \qquad \textbf{(24)}$$

For constant density systems (all liquids and constant density gases)

$$\tau = \bar{t} = \frac{V}{v}$$

For changing density systems $\bar{t} \neq \tau$ and $\bar{t} \neq V/v_0$ in which case it becomes difficult to find how these terms are related.

Consider three cases, called X, Y, and Z, which are shown in Fig. 5.7. In the first case (case X) all the popping occurs at the back end of the reactor. In the second case (case Y) all the popping occurs at the front end of the reactor. In the third case (case Z) the popping occurs somewhere between entrance and exit. In all three cases

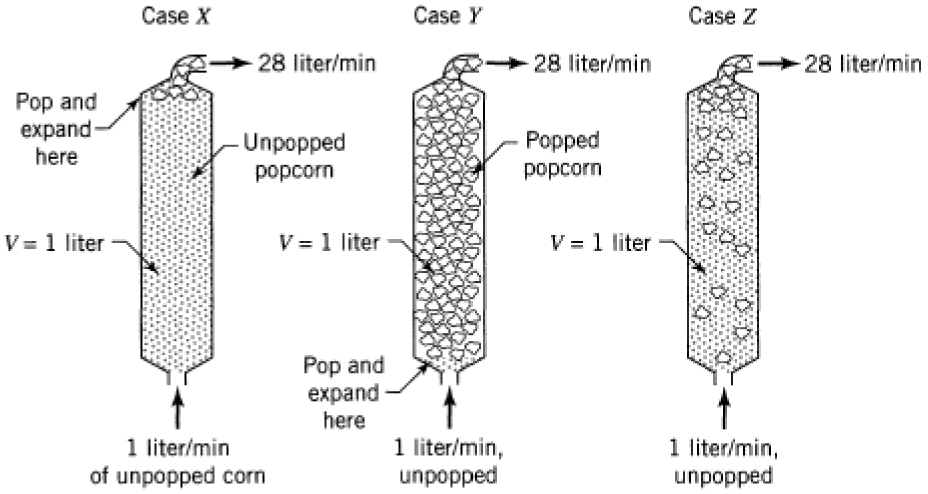

Figure 5.7 For the same τ value the $\bar{t}$ values differ in these three cases.

$$\tau_X = \tau_Y = \tau_Z = \frac{V}{v_0} = \frac{1\ \text{liter}}{1\ \text{liter/min}} = 1\ \text{min}$$

irrespective of where the popping occurs. However, we see that the residence time in the three cases is very different, or

$$\bar{t}_X = \frac{1\ \text{liter}}{1\ \text{liter/min}} = 1\ \text{min}$$

$$\bar{t}_Y = \frac{1\ \text{liter}}{28\ \text{liter/min}} \cong 2\ \text{sec}$$

$\bar{t}_Z$ is somewhere between 2 and 60 s, depending on the kinetics

Table 5.1 Performance Equations for nth-order Kinetics and $\varepsilon_A = 0$

	Plug Flow or Batch		Mixed Flow	
$n = 0$ $-r_A = k$	$\frac{k\tau}{C_{A0}} = \frac{C_{A0} - C_A}{C_{A0}} = X_A$	**(20)**	$\frac{k\tau}{C_{A0}} = \frac{C_{A0} - C_A}{C_{A0}} = X_A$	
$n = 1$ $-r_A = kC_A$	$k\tau = \ln\frac{C_{A0}}{C_A} = \ln\frac{1}{1 - X_A}$	**(3.12)**	$k\tau = \frac{C_{A0} - C_A}{C_A} = \frac{X_A}{1 - X_A}$	**(14*a*)**
$n = 2$ $-r_A = kC_A^2$	$k\tau C_{A0} = \frac{C_{A0} - C_A}{C_A} = \frac{X_A}{1 - X_A}$	**(3.16)**	$k\tau = \frac{(C_{A0} - C_A)}{C_A^2} = \frac{X_A}{C_{A0}(1 - X_A)^2}$	**(15)**
any n $-r_A = kC_A^n$	$(n-1)C_{A0}^{n-1}k\tau = \left(\frac{C_A}{C_{A0}}\right)^{1-n} - 1 = (1 - X_A)^{1-n} - 1$	**(3.29)**	$k\tau = \frac{C_{A0} - C_A}{C_A^n} = \frac{X_A}{C_{A0}^{n-1}(1 - X_A)^n}$	
$n = 1$ $A \underset{2}{\overset{1}{\rightleftarrows}} R$ $C_{R0} = 0$	$k_1\tau = \left(1 - \frac{C_{Ae}}{C_{A0}}\right)\ln\left(\frac{C_{A0} - C_{Ae}}{C_A - C_{Ae}}\right) = X_{Ae}\ln\left(\frac{X_{Ae}}{X_{Ae} - X_A}\right)$		$k_1\tau = \frac{(C_{A0} - C_A)(C_{A0} - C_{Ae})}{C_{A0}(C_A - C_{Ae})} = \frac{X_A X_{Ae}}{X_{Ae} - X_A}$	
General rate	$\tau = \int_{C_A}^{C_{A0}} \frac{dC_A}{-r_A} = C_{A0}\int_0^{X_{Af}} \frac{dX_A}{-r_A}$	**(19)**	$\tau = \frac{C_{A0} - C_A}{-r_{Af}} = \frac{C_{A0}X_A}{-r_{Af}}$	**(13)**

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SIZE COMPARISON OF SINGLE REACTORS

Mixed Versus Plug Flow Reactors, First- and Second-Order Reactions:

The **ratio of sizes** of mixed and plug flow reactors will depend on the **extent of reaction, the stoichiometry, and the form of the rate equation.**
For the general case ,a comparison of Eqs. 5.11 and 5.17 will give this size ratio. Let us make this comparison for the large class of reactions approximated by the simple ***nth***-order rate law

$$-r_A = -\frac{1}{V}\frac{dN_A}{dt} = kC_A^n$$

where n varies anywhere from zero to three. For mixed flow Eq. 5.11 gives

$$\tau_m = \left(\frac{C_{A0}V}{F_{A0}}\right)_m = \frac{C_{A0}X_A}{-r_A} = \frac{1}{kC_{A0}^{n-1}}\frac{X_A(1+\varepsilon_A X_A)^n}{(1-X_A)^n}$$

whereas for plug flow Eq. 5.17 gives

$$\tau_p = \left(\frac{C_{A0}V}{F_{A0}}\right)_p = C_{A0}\int_0^{X_A}\frac{dX_A}{-r_A} = \frac{1}{kC_{A0}^{n-1}}\int_0^{X_A}\frac{(1+\varepsilon_A X_A)^n dX_A}{(1-X_A)^n}$$

Dividing we find that

$$\frac{(\tau C_{A0}^{n-1})_m}{(\tau C_{A0}^{n-1})_p} = \frac{\left(\frac{C_{A0}^n V}{F_{A0}}\right)_m}{\left(\frac{C_{A0}^n V}{F_{A0}}\right)_p} = \frac{\left[X_A\left(\frac{1+\varepsilon_A X_A}{1-X_A}\right)^n\right]_m}{\left[\int_0^{X_A}\left(\frac{1+\varepsilon_A X_A}{1-X_A}\right)^n dX_A\right]_p} \qquad \textbf{(1)}$$

With constant density, or $\varepsilon = 0$, this expression integrates to

$$\frac{(\tau C_{A0}^{n-1})_m}{(\tau C_{A0}^{n-1})_p} = \frac{\left[\frac{X_A}{(1-X_A)^n}\right]_m}{\left[\frac{(1-X_A)^{1-n}-1}{n-1}\right]_p}, \qquad n \neq 1$$

or **(2)**

$$\frac{(\tau C_{A0}^{n-1})_m}{(\tau C_{A0}^{n-1})_p} = \frac{\left(\frac{X_A}{1-X_A}\right)_m}{-\ln(1-X_A)_p}, \qquad n = 1$$

Equations 1 and 2 are displayed in graphical form in Fig. 6.1 to provide a quick comparison of the performance of plug flow with mixed flow reactors. For

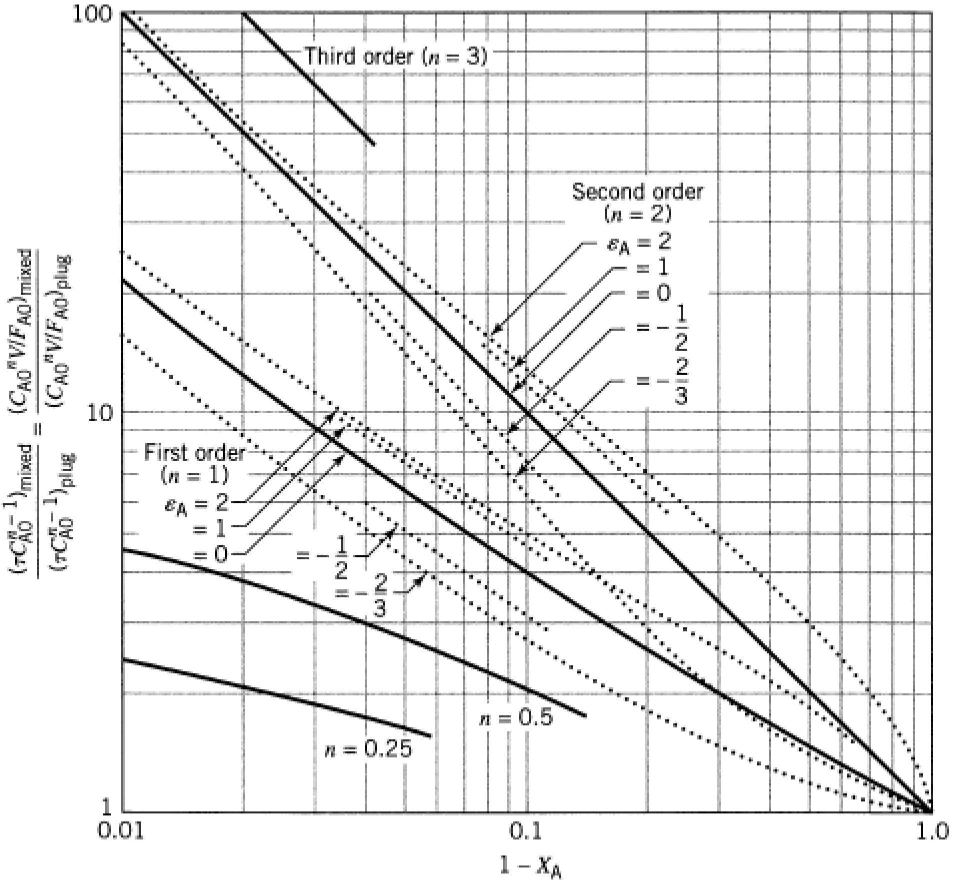

Figure 6.1 Comparison of performance of single mixed flow and plug flow reactors for the nth-order reactions

$$A \rightarrow \text{products}, \quad -r_A = kC_A^n$$

The ordinate becomes the volume ratio V_m/V_p or space-time ratio τ_m/τ_p if the same quantities of identical feed are used.

identical feed composition C_{A0} and flow rate F_{A0} the ordinate of this figure gives directly the volume ratio required for any specified conversion. Figure 6.1 shows the following.

1. For any particular duty and for all positive reaction orders the mixed reactor is always larger than the plug flow reactor. The ratio of volumes increases with reaction order.
2. When conversion is small, the reactor performance is only slightly affected by flow type. The performance ratio increases very rapidly at high conversion; consequently, a proper representation of the flow becomes very important in this range of conversion.
3. Density variation during reaction affects design; however, it is normally of secondary importance compared to the difference in flow type.

Variation of Reactant Ratio for Second-Order Reactions

Second-order reactions of two components and of the type

$$A + B \rightarrow \text{products}, \qquad M = C_{B0}/C_{A0} \qquad \textbf{(3.13)}$$

$$-r_A = -r_B = kC_AC_B$$

behave as second-order reactions of one component when the reactant ratio is unity. Thus

$$-r_A = kC_AC_B = kC_A^2 \qquad \text{when } M = 1 \qquad \textbf{(3)}$$

when a large excess of reactant B is used then its concentration does not change appreciably ($C_B \cong C_{B0}$) and the reaction approaches first-order behavior with respect to the limiting component A, or

$$-r_A = kC_AC_B = (kC_{B0})C_A = k'C_A \qquad \text{when } M \gg 1 \qquad \textbf{(4)}$$

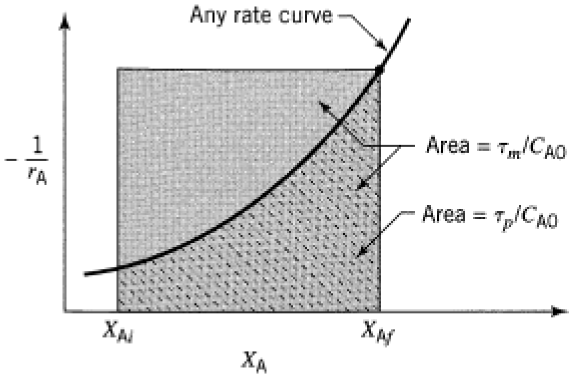

Figure 6.2 Comparison of performance of mixed flow and plug flow reactors for any reaction kinetics.

For reactions with arbitrary but known rate the performance capabilities of mixed and plug flow reactors are best illustrated in Fig. 6.2. The ratio of shaded and of hatched areas gives the ratio of space-times needed in these two reactors.

The rate curve drawn in Fig. 6.2 is typical of the large class of reactions whose rate decreases continually on approach to equilibrium (this includes all *n*th-order reactions, $n > 0$). For such reactions it can be seen that mixed flow always needs a larger volume than does plug flow for any given duty.

6.2 MULTIPLE-REACTOR SYSTEMS

Plug Flow Reactors in Series and/or in Parallel

Consider N plug flow reactors connected in series, and let $X_1, X_2, \ldots, X_N$ be the fractional conversion of component A leaving reactor $1, 2, \ldots, N$. Basing the material balance on the feed rate of A to the first reactor, we find for the ith reactor from Eq. 5.18

$$\frac{V_i}{F_0} = \int_{X_{i-1}}^{X_i} \frac{dX}{-r}$$

or for the N reactors in series

$$\frac{V}{F_0}=\sum_{i=1}^{N}\frac{V_i}{F_0}=\frac{V_1+V_2+\cdot\cdot\cdot+V_N}{F_0}$$

$$=\int_{X_0=0}^{X_1}\frac{dX}{-r}+\int_{X_1}^{X_2}\frac{dX}{-r}+\cdot\cdot\cdot+\int_{X_{N-1}}^{X_N}\frac{dX}{-r}=\int_0^{X_N}\frac{dX}{-r}$$

Hence, N plug flow reactors in series with a total volume V gives the same conversion as a single plug flow reactor of volume V.

EXAMPLE 6.1 OPERATING A NUMBER OF PLUG FLOW REACTORS

The reactor setup shown in Fig. E6.1 consists of three plug flow reactors in two parallel branches. Branch D has a reactor of volume 50 liters followed by a reactor of volume 30 liters. Branch E has a reactor of volume 40 liters. What fraction of the feed should go to branch D?

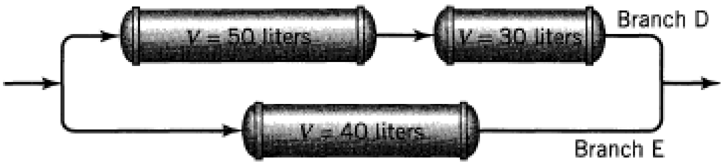

Figure E6.1

SOLUTION

Branch D consists of two reactors in series; hence, it may be considered to be a single reactor of volume

$$V_D = 50 + 30 = 80 \text{ liters}$$

Now for reactors in parallel V/F must be identical if the conversion is to be the same in each branch. Therefore,

$$\left(\frac{V}{F}\right)_D=\left(\frac{V}{F}\right)_E$$

Therefore, two-thirds of the feed must be fed to branch D.

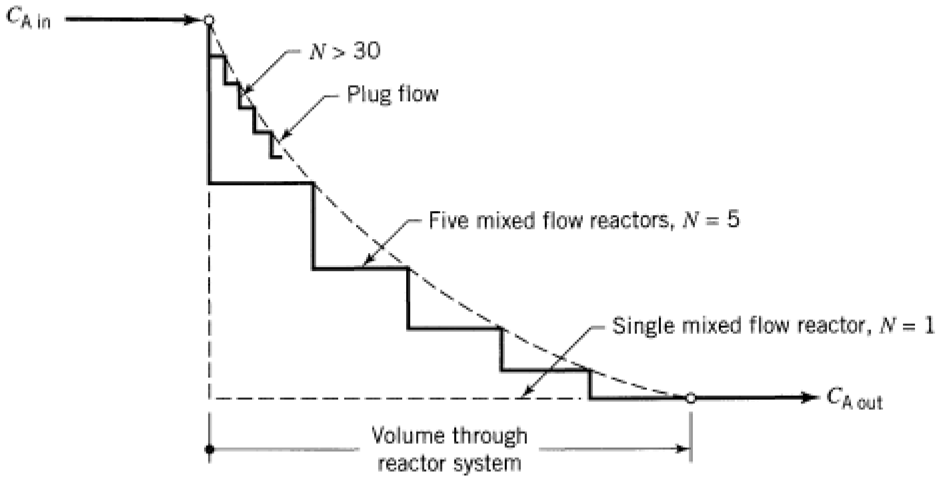

Figure 6.3 Concentration profile through an N-stage mixed flow reactor system compared with single flow reactors.

Equal-Size Mixed Flow Reactors in Series:

Consider a system of N mixed flow reactors connected in series. Though the concentration is uniform in each reactor, there is, nevertheless, a change in concentration as fluid moves from reactor to reactor. This stepwise drop in concentration, illustrated in Fig. 6.3, suggests that the larger the number of units in series, the closer should the behavior of the system approach plug flow. This will be shown to be so.

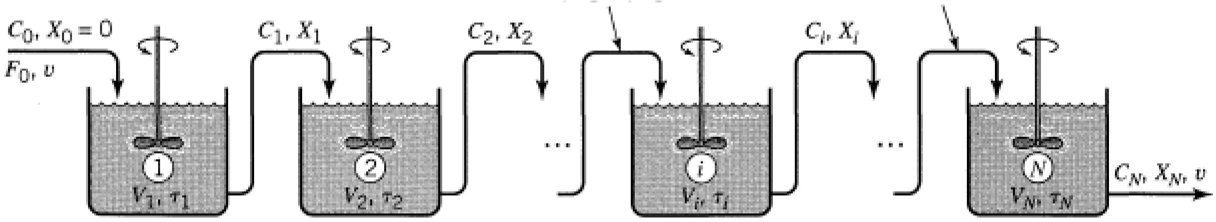

Figure 6.4 Notation for a system of N equal-size mixed reactors in series.

First-Order Reactions. From Eq. 5.12 a material balance for component A about vessel i gives

$$\tau_i = \frac{C_0 V_i}{F_0} = \frac{V_i}{v} = \frac{C_0(X_i - X_{i-1})}{-r_{Ai}}$$

Because $\varepsilon = 0$ this may be written in terms of concentrations. Hence

$$\tau_i = \frac{C_0[(1 - C_i/C_0) - (1 - C_{i-1}/C_0)]}{kC_i} = \frac{C_{i-1} - C_i}{kC_i}$$

Or

$$\frac{C_{i-1}}{C_i} = 1 + k\tau_i \qquad \textbf{(5)}$$

Now the space-time τ (or mean residence time t) is the same in all the equal-size reactors of volume V. Therefore

$$\frac{C_0}{C_N} = \frac{1}{1 - X_N} = \frac{C_0}{C_1}\frac{C_1}{C_2} \cdots \frac{C_{N-1}}{C_N} = (1 + k\tau_i)^N \qquad \textbf{(6a)}$$

Rearranging, we find for the system as a whole

$$\tau_{N\,\text{reactors}} = N\tau_i = \frac{N}{k}\left[\left(\frac{C_0}{C_N}\right)^{1/N} - 1\right] \qquad \textbf{(6b)}$$

In the limit, for $N \rightarrow \infty$, this equation reduces to the plug flow equation

$$\tau_p = \frac{1}{k}\ln\frac{C_0}{C} \qquad \textbf{(7)}$$

With Eqs. 6b and 7 compare performance of N reactors in series with a plug flow reactor or with a single mixed flow reactor. This comparison is shown in Fig. 6.5 for first-order reactions in which density variations are negligible.

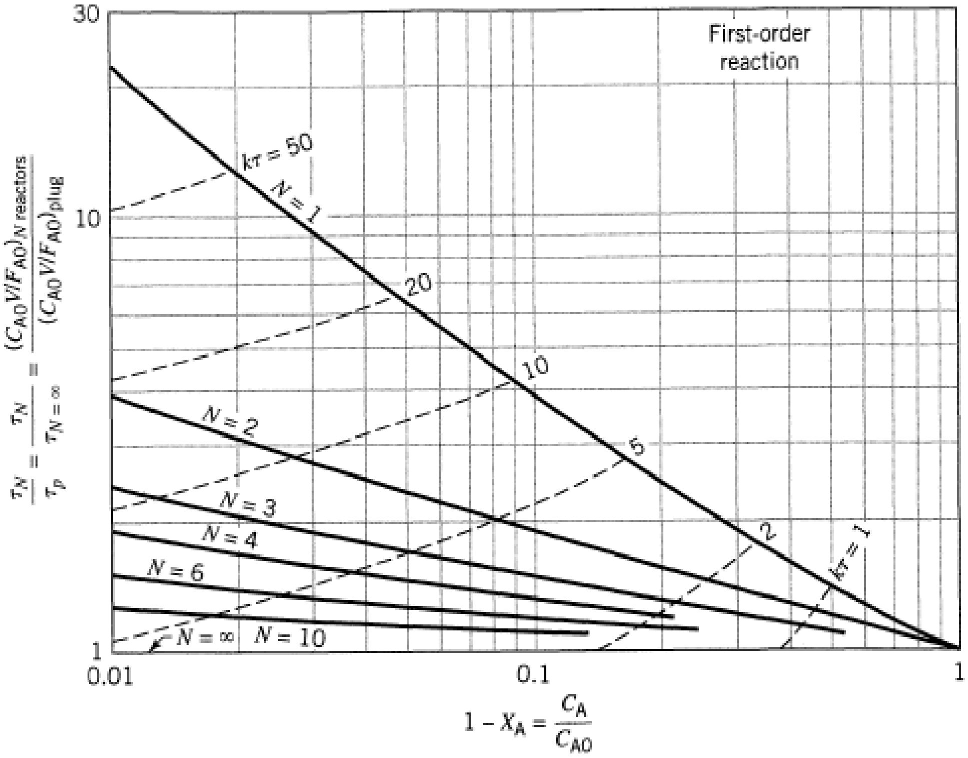

Figure 6.5 Comparison of performance of a series of N equal-size mixed flow reactors with a plug flow reactor for the first-order reaction

Second-Order Reactions. : the performance of a series of mixed flow reactors for a second-order, bimolecular-type reaction, no excess of either reactant, by a procedure similar to that of a first-order reaction

$A \rightarrow R, \qquad \varepsilon = 0$

For the same processing rate of identical feed the ordinate measures the volume ratio V_N/V_p directly.

N reactors in series we find

$$C_N = \frac{1}{4k\tau_i}\left(-2 + 2\sqrt{\overset{\vdots}{-1 \cdots + 2\sqrt{-1 + 2\sqrt{1 + 4C_0 k\tau_i}}}}\ \Big\}N\right) \qquad \textbf{(8a)}$$

whereas for plug flow

$$\frac{C_0}{C} = 1 + C_0 k\tau_p \qquad \textbf{(8b)}$$

A comparison of the performance of these reactors is shown in Fig. 6.6.

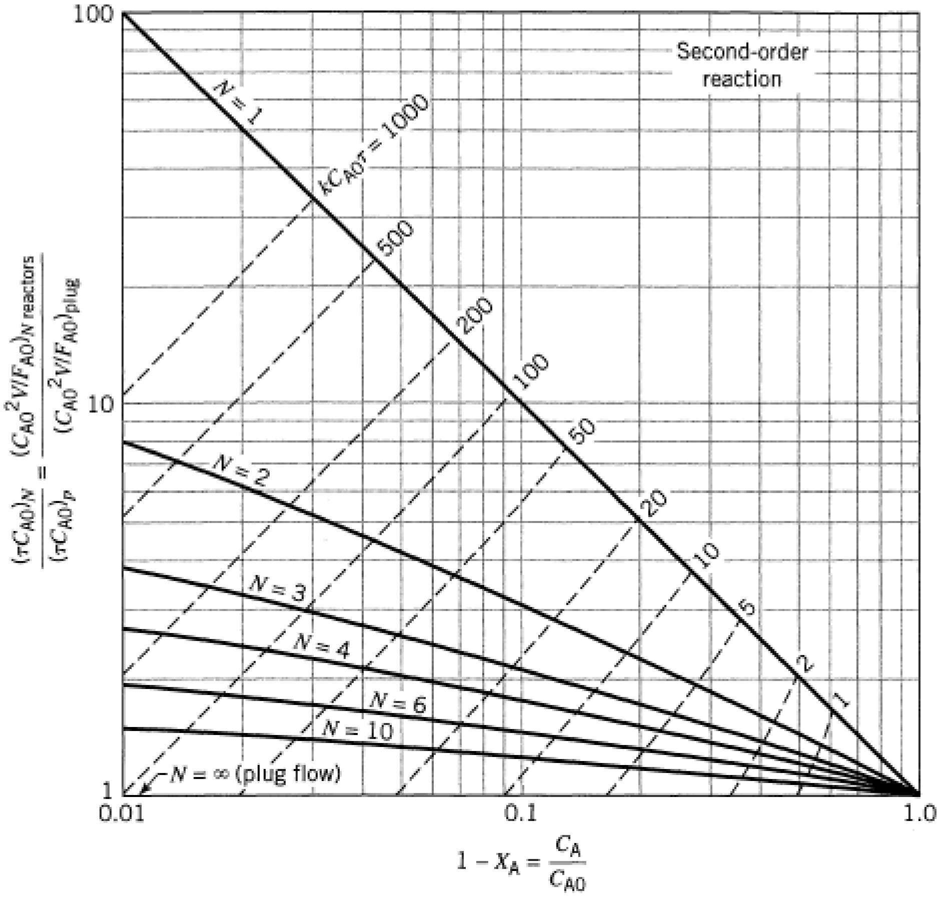

Figure 6.6 Comparison of performance of a series of N equal-size mixed flow reactors with a plug flow reactor for elementary second-order reactions

$$2A \rightarrow \text{products}$$

$$A + B \rightarrow \text{products}, \qquad C_{A0} = C_{B0}$$

with negligible expansion. For the same processing rate of identical feed the ordinate measures the volume ratio V_N/V_p or space-time ratio τ_N/τ_p directly.

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EXAMPLE 6.2 MIXED FLOW REACTORS IN SERIES

At present 90% of reactant A is converted into product by a second-order reaction in a single mixed flow reactor. We plan to place a second reactor similar to the one being used in series with it.

(a) For the same treatment rate as that used at present, how will this addition affect the conversion of reactant?

(b) For the same 90% conversion, by how much can the treatment rate be increased?

SOLUTION

The sketch of Fig. E6.2 shows how the performance chart of Fig. 6.6 can be used to help solve this problem.

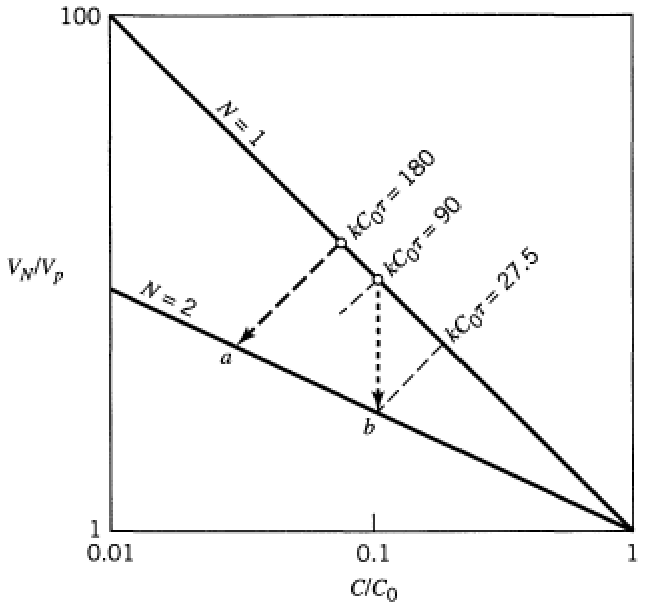


Figure E6.2

(a) Find the conversion for the same treatment rate. For the single reactor at 90% conversion we have from Fig. 6.6

$$kC_0\tau = 90$$

For the two reactors the space-time or holding time is doubled; hence, the operation will be represented by the dashed line of Fig. 6.6 where

$kC_0\tau = 180$

This line cuts the $N = 2$ line at a conversion $\underline{\underline{X = 97.4\%}}$, point *a*.

(b) Find the treatment rate for the same conversion. Staying on the 90% conversion line, we find for $N = 2$ that

$kC_0\tau = 27.5,$ point b

Comparing the value of the reaction rate group for $N = 1$ and $N = 2$, we find

$$\frac{(kC_0\tau)_{N=2}}{(kC_0\tau)_{N=1}} = \frac{\tau_{N=2}}{\tau_{N=1}} = \frac{(V/v)_{N=2}}{(V/v)_{N=1}} = \frac{27.5}{90}$$

Since $V_{N=2} = 2V_{N=1}$ the ratio of flow rates becomes

$$\frac{v_{N=1}}{v_{N=1}} = \frac{90}{27.5}(2) = 6.6$$

Thus, the treatment rate can be raised to 6.6 times the original.

Note. If the second reactor had been operated in parallel with the original unit then the treatment rate could only be doubled. Thus, there is a definite advantage in operating these two units in series. This advantage becomes more pronounced at higher conversions. ■

Mixed Flow Reactors of Different Sizes in Series:

For arbitrary kinetics in mixed flow reactors of different size, two types of questions may be asked:

A. how to find the outlet conversion from a given reactor system,
B. how to find the best setup to achieve a given conversion

Different procedures are used for these two problems

Finding the Conversion in a Given System A graphical procedure for finding the outlet composition from a series of mixed flow reactors of various sizes for reactions with negligible density change has been presented by Jones (1951). All that is needed is an r versus C curve for component A to represent the reaction rate at various concentrations.

$$\tau_1 = \bar{t}_1 = \frac{V_1}{v} = \frac{C_0 - C_1}{(-r)_1}$$

or

$$-\frac{1}{\tau_1} = \frac{(-r)_1}{C_1 - C_0} \qquad \textbf{(9)}$$

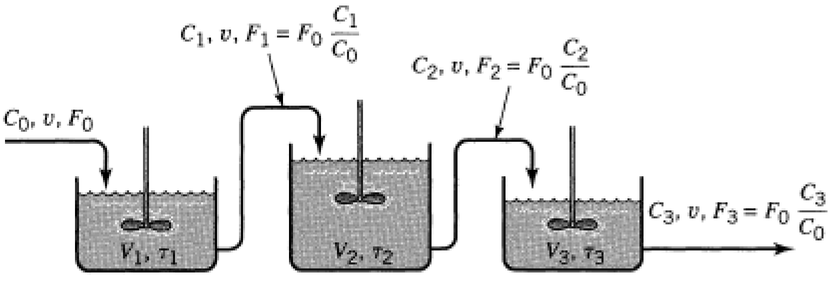


Figure 6.7 Notation for a series of unequal-size mixed flow reactors.

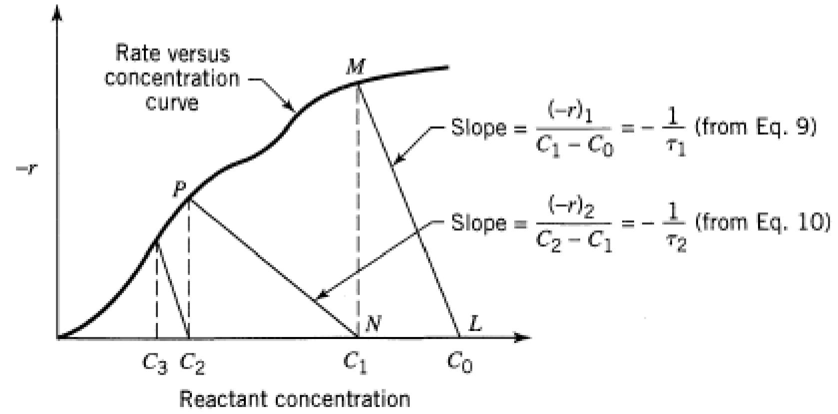


Figure 6.8 Graphical procedure for finding compositions in a series of mixed flow reactors.

$$-\frac{1}{\tau_i} = \frac{(-r)_i}{C_i - C_{i-1}} \qquad \textbf{(10)}$$

Plot the C versus r curve for component A and suppose that it is as shown in Fig. 6.8. To find the conditions in the first reactor note that the inlet concentration C_0 is known (point L), that C_1 and $(-r)_1$ correspond to a point on the curve to be found (point M), and that the slope of the line $LM = MN/NL = (-r)_1/(C_1 - C_0) = -(1/\tau_1)$ from Eq. 6.9. Hence, from C_0 draw a line of slope $-(1/\tau_1)$ until it cuts the rate curve; this gives C_1. Similarly, we find from Eq. 6.10 that a line of slope $-(1/\tau_2)$ from point N cuts the curve at P, giving the concentration C_2 of material leaving the second reactor. This procedure is then repeated as many times as needed.

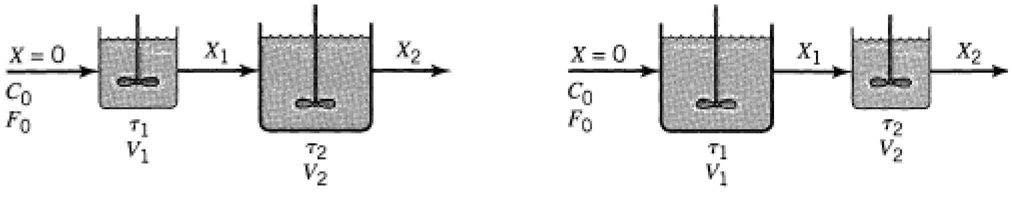
Determining the Best System for a Given Conversion. Suppose we want to find the minimum size of two mixed flow reactors in series to achieve a specified conversion of feed which reacts with arbitrary but known kinetics. The basic performance expressions, Eqs. 5.11 and 5.12, then give, in turn, for the first reactor

$$\frac{\tau_1}{C_0} = \frac{X_1}{(-r)_1} \qquad \textbf{(11)}$$

and for the second reactor

$$\frac{\tau_2}{C_0} = \frac{X_2 - X_1}{(-r)_2} \qquad \textbf{(12)}$$

These relationships are displayed in Fig. 6.9 for two alternative reactor arrangements, both giving the same final conversion X_2. Note, as the intermediate



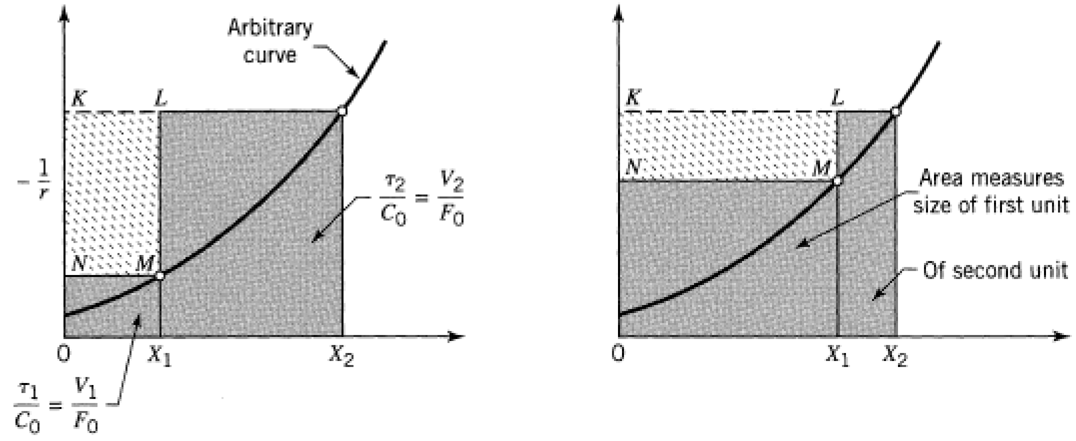


Figure 6.9 Graphical representation of the variables for two mixed flow reactors in series.

conversion X_1 changes, so does the size ratio of the units (represented by the two shaded areas) as well as the total volume of the two vessels required (the total area shaded).

Figure 6.9 shows that the total reactor volume is as small as possible (total shaded area is minimized) when the rectangle $KLMN$ is as large as possible. This brings us to the problem of choosing X_1 (or point M on the curve) so as to maximize the area of this rectangle. Consider this general problem.

Maximization of Rectangles. In Fig. 6.10, construct a rectangle between the x-y axes and touching the arbitrary curve at point $M(x, y)$. The area of the rectangle is then

$$A = xy \tag{13}$$

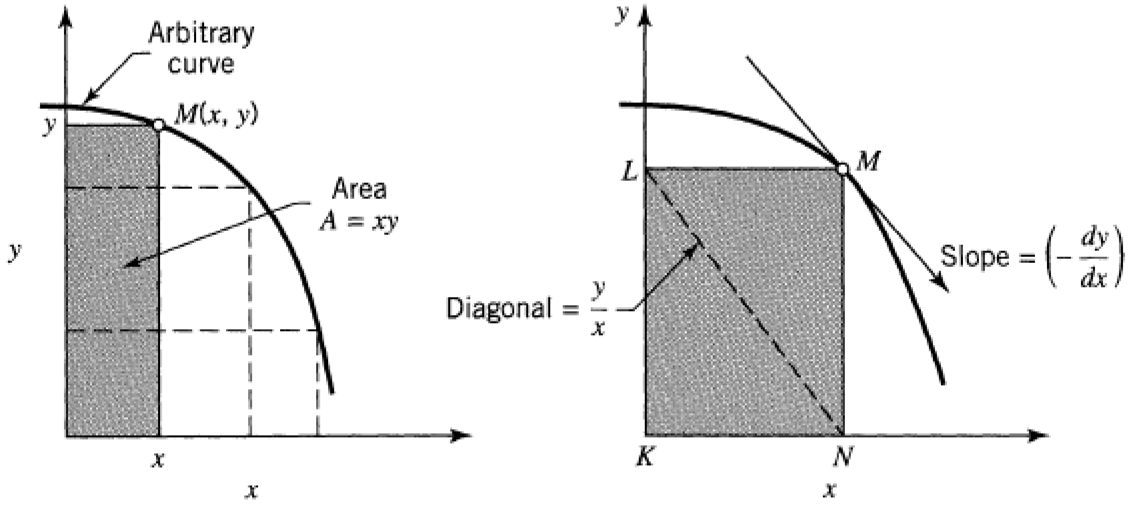


Figure 6.10 Graphical procedure for maximizing the area of a rectangle.

This area is maximized when

$$dA = 0 = y\,dx + x\,dy$$

or when

$$-\frac{dy}{dx} = \frac{y}{x} \tag{14}$$

this condition means that the area is maximized when M is at that point where the slope of the curve equals the slope of the diagonal NL of the rectangle Depending on the shape of the curve, there may be more than one or there may be no "best" point.
However, for nth-order kinetics, $n > 0$, there always is just one "best" point.

The optimum size ratio for two mixed flow reactors in series is found in general to be dependent on the kinetics of the reaction and on the conversion level.

- the special case of first-order reactions equal-size reactors are best;
- reaction orders $n > 1$ the smaller reactor should come first
- for $n < 1$ the larger should come first

The above procedure can be extended directly to multistage operations; however, here the argument for equal-size units is stronger still than for the two-stage system.

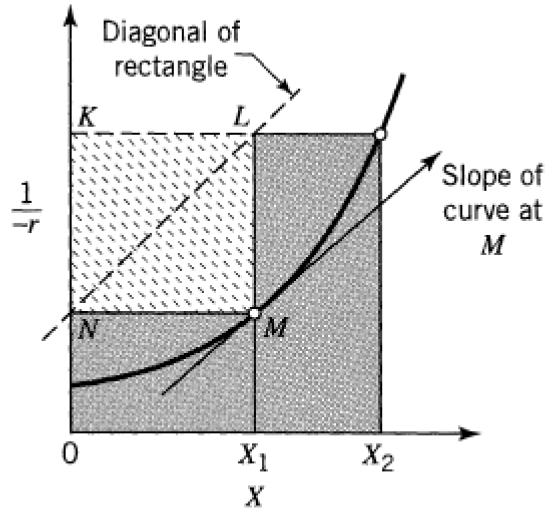


Figure 6.11 Maximization of rectangles applied to find the optimum intermediate conversion and optimum sizes of two mixed flow reactors in series.

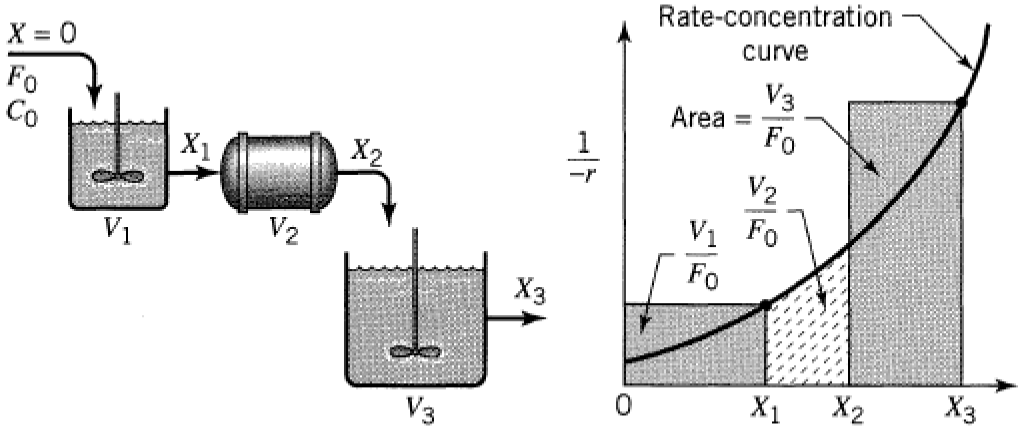


Figure 6.12 Graphical design procedure for reactors in series.

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Reactors of Different Types in Series

If reactors of different types are put in series, such as a mixed flow reactor followed by a plug flow reactor which in turn is followed by another mixed flow reactor, we may write for the three reactors

$$\frac{V_1}{F_0}=\frac{X_1-X_0}{(-r)_1},\quad \frac{V_2}{F_0}=\int_{X_1}^{X_2}\frac{dX}{-r},\quad \frac{V_3}{F_0}=\frac{X_3-X_2}{(-r)_3}$$

These relationships are represented in graphical form in Fig. 6.12.

Best Arrangement of a Set of Ideal Reactors. For the most effective use of a given set of ideal reactors we have the following general rules:

1. For a reaction whose rate-concentration curve rises monotonically (any nth-order reaction, $n > 0$) the reactors should be connected in series. They should be ordered so as to keep the concentration of reactant as high as possible if the rate-concentration curve is concave ($n > 1$), and as low as possible if the curve is convex ($n < 1$). As an example, for the case of Fig. 6.12 the ordering of units should be plug, small mixed, large mixed, for $n > 1$; the reverse order should be used when $n < 1$.
2. For reactions where the rate-concentration curve passes through a maximum or minimum the arrangement of units depends on the actual shape of curve, the conversion level desired, and the units available. No simple rules can be suggested.
3. Whatever may be the kinetics and the reactor system, an examination of the $1/(-r_A)$ vs. C_A curve is a good way to find the best arrangement of units.

RECYCLE REACTOR

In certain situations it is found to be advantageous to divide the product stream from a plug flow reactor and return a portion of it to the entrance of the reactor. Let the *recycle ratio* $\boldsymbol{R}$ be defined as

$$\boldsymbol{R} = \frac{\text{volume of fluid returned to the reactor entrance}}{\text{volume leaving the system}} \qquad \textbf{(15)}$$

This recycle ratio can be made to vary from zero to infinity. Reflection suggests that as the recycle ratio is raised the behavior shifts from plug flow ($\boldsymbol{R} = 0$) to mixed flow ($\boldsymbol{R} = \infty$). Thus, recycling provides a means for obtaining various degrees of backmixing with a plug flow reactor. Let us develop the performance equation for the recycle reactor.

Consider a recycle reactor with nomenclature as shown in Fig. 6.13. Across the reactor itself Eq. 5.18 for plug flow gives

$$\frac{V}{F'_{A0}} = \int_{X_{A1}}^{X_{A2}=X_{Af}} \frac{dX_A}{-r_A} \qquad \textbf{(16)}$$

where F'_{A0} would be the feed rate of A if the stream entering the reactor (fresh feed plus recycle) were unconverted. Since F'_{A0} and X_{A1} are not known directly, they must be written in terms of known quantities before Eq. 16 can be used.

The flow entering the reactor includes both fresh feed and the recycle stream. Measuring the flow split at point L (point K will not do if $\varepsilon \neq 0$) we then have

$$F'_{A0} = \begin{pmatrix}\text{A which would enter in an}\\ \text{unconverted recycle stream}\end{pmatrix} + \begin{pmatrix}\text{A entering in}\\ \text{fresh feed}\end{pmatrix}$$

$$= \boldsymbol{R}F_{A0} + F_{A0} = (\boldsymbol{R} + 1)F_{A0} \qquad \textbf{(17)}$$

Now to the evaluation of X_{A1}: from Eq. 4.5 we may write

$$X_{A1} = \frac{1 - C_{A1}/C_{A0}}{1 + \varepsilon_A C_{A1}/C_{A0}} \qquad \textbf{(18)}$$

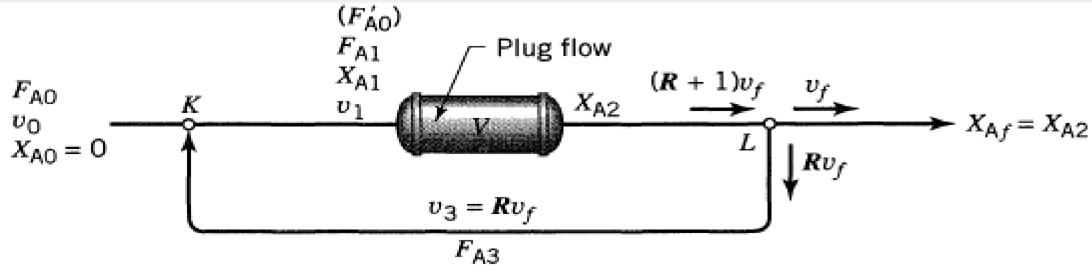

Figure 6.13 Nomenclature for the recycle reactor.

$$C_{A1} = \frac{F_{A1}}{v_1} = \frac{F_{A0} + F_{A3}}{v_0 + \boldsymbol{R}v_f} = \frac{F_{A0} + \boldsymbol{R}F_{A0}(1 - X_{Af})}{v_0 + \boldsymbol{R}v_0(1 + \varepsilon_A X_{Af})} = C_{A0}\left(\frac{1 + \boldsymbol{R} - \boldsymbol{R}X_{Af}}{1 + \boldsymbol{R} + \boldsymbol{R}\varepsilon_A X_{Af}}\right) \qquad \textbf{(19)}$$

Combining Eqs. 18 and 19 gives X_{A1} in terms of measured quantities, or

$$X_{A1} = \left(\frac{\boldsymbol{R}}{\boldsymbol{R} + 1}\right) X_{Af} \qquad \textbf{(20)}$$

Finally, on replacing Eqs. 17 and 20 in Eq. 16 we obtain the useful form for the performance equation for recycle reactors, good for any kinetics, any ε value and for $X_{A0} = 0$.

$$\frac{V}{F_{A0}} = (\boldsymbol{R} + 1) \int_{\left(\frac{\boldsymbol{R}}{\boldsymbol{R}+1}\right) X_{Af}}^{X_{Af}} \frac{dX_A}{-r_A} \quad \ldots \text{any } \varepsilon_A \qquad \textbf{(21)}$$

For the special case where density changes are negligible we may write this equation in terms of concentrations, or

$$\tau = \frac{C_{A0}V}{F_{A0}} = -(\boldsymbol{R} + 1) \int_{\frac{C_{A0} + \boldsymbol{R}C_{Af}}{\boldsymbol{R} + 1}}^{C_{Af}} \frac{dC_A}{-r_A} \quad \ldots \varepsilon_A = 0 \qquad \textbf{(22)}$$

These expressions are represented graphically in Fig. 6.14.

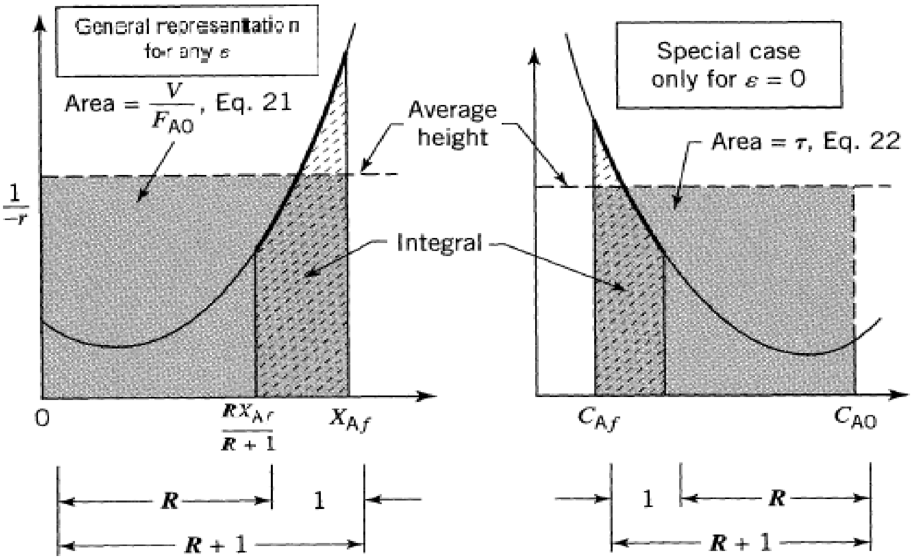

Figure 6.14 Representation of the performance equation for recycle reactors.

For the extremes of negligible and infinite recycle the system approaches plug flow and mixed flow, or

$$\begin{tikzcd}
& \dfrac{V}{F_{A0}} = (\boldsymbol{R}+1)\displaystyle\int_{\frac{\boldsymbol{R}}{\boldsymbol{R}+1}X_{Af}}^{X_{Af}} \frac{dX_A}{-r_A} \arrow[dl, "\boldsymbol{R}=0"'] \arrow[dr, "\boldsymbol{R}=\infty"] & \\
\underset{\text{plug flow}}{\dfrac{V}{F_{A0}} = \displaystyle\int_{A}^{X_{Af}} \frac{dX_A}{-r_A}} & & \underset{\text{mixed flow}}{\dfrac{V}{F_{A0}} = \dfrac{X_{Af}}{-r_{Af}}}
\end{tikzcd}$$

The approach to these extremes is shown in Fig. 6.15.

Integration of the recycle equation gives, for *first-order reaction*, $\varepsilon_A = 0$,

$$\boxed{\frac{k\tau}{\boldsymbol{R}+1} = \ln\left[\frac{C_{A0}+\boldsymbol{R}C_{Af}}{(\boldsymbol{R}+1)C_{Af}}\right]} \qquad \textbf{(23)}$$

and for *second-order reaction*, 2A → products, $-r_A = kC_A^2$, $\varepsilon_A = 0$,

$$\boxed{\frac{kC_{A0}\tau}{\boldsymbol{R}+1} = \frac{C_{A0}(C_{A0}-C_{Af})}{C_{Af}(C_{A0}+\boldsymbol{R}C_{Af})}} \qquad \textbf{(24)}$$

The expressions for $\varepsilon_A \neq 0$ and for other reaction orders can be evaluated, but are more cumbersome.

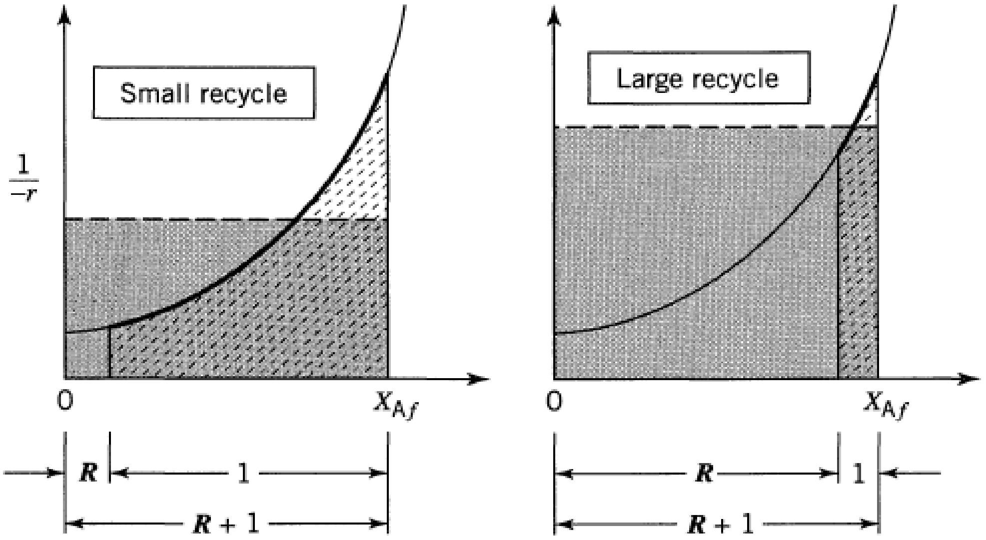

Figure 6.15 The recycle extremes approach plug flow ($\boldsymbol{R} \rightarrow 0$) and mixed flow ($\boldsymbol{R} \rightarrow \infty$).

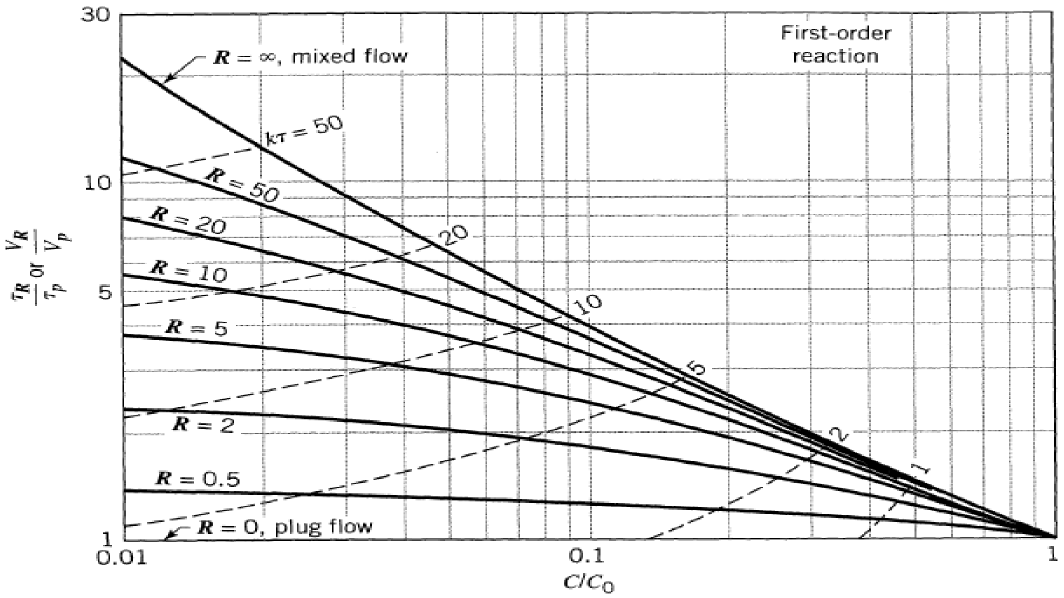

Figure 6.16 Comparison of performance of recycle and plug flow for first-order reactions

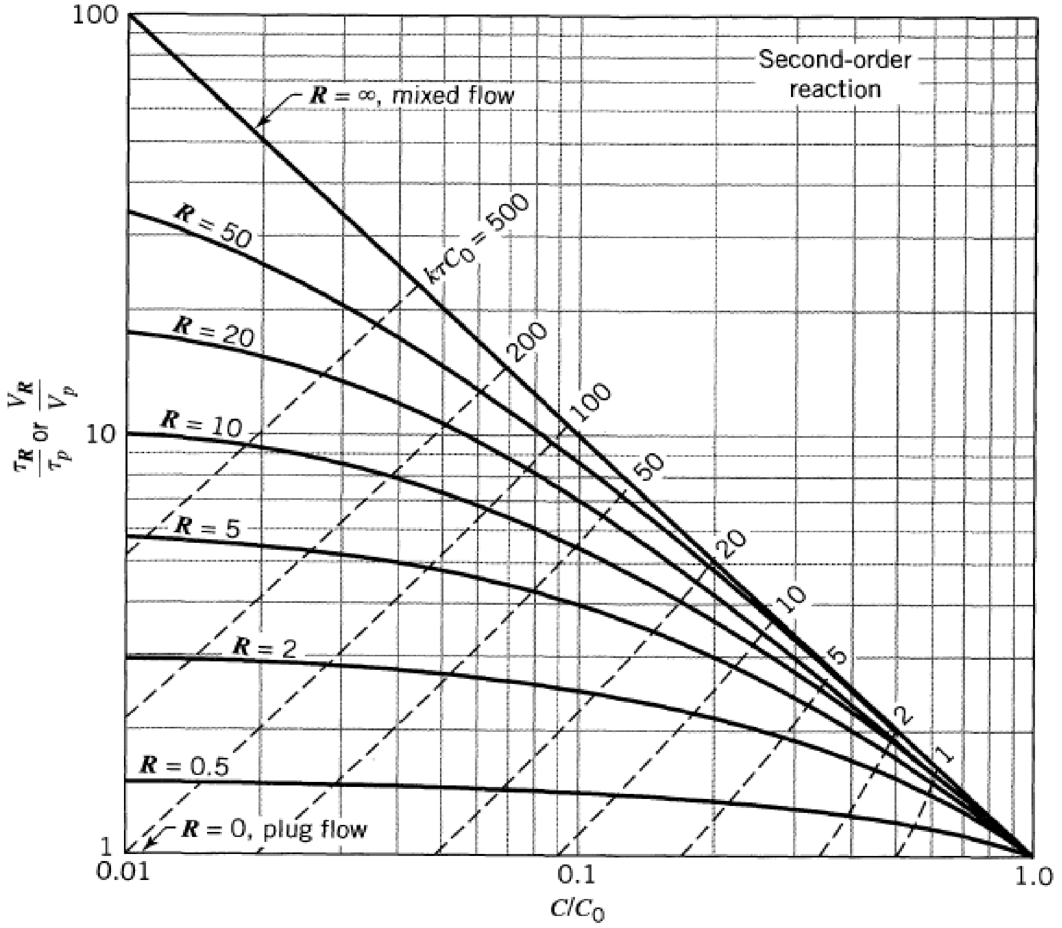

Figure 6.17 Comparison of performance of recycle reactors with plug flow reactors for elementary second-order reactions (Personal communication, from T. J. Fitzgerald and P. Fillesi):

Figures 6.16 and 6.17 show the transition from plug to mixed flow as ***R*** increases, and a match of these curves with those for *N* tanks in series (Figs. 6.5 and 6.6)

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Dr. Suha Akram

Lecture No. 13

Autocatalytic Reactions:

In our approach we deal exclusively with their $1/(-r_A)$ versus X_A curves with their characteristic minima, as shown in Fig. 6.18.

Plug Flow Versus Mixed Flow Reactor, No Recycle. For any particular rate-concentration curve a comparison of areas in Fig. 6.19 will show which reactor is superior (which requires a smaller volume) for a given job. We thus find

1. At low conversion the mixed reactor is superior to the plug flow reactor.
2. At high enough conversions the plug flow reactor is superior.

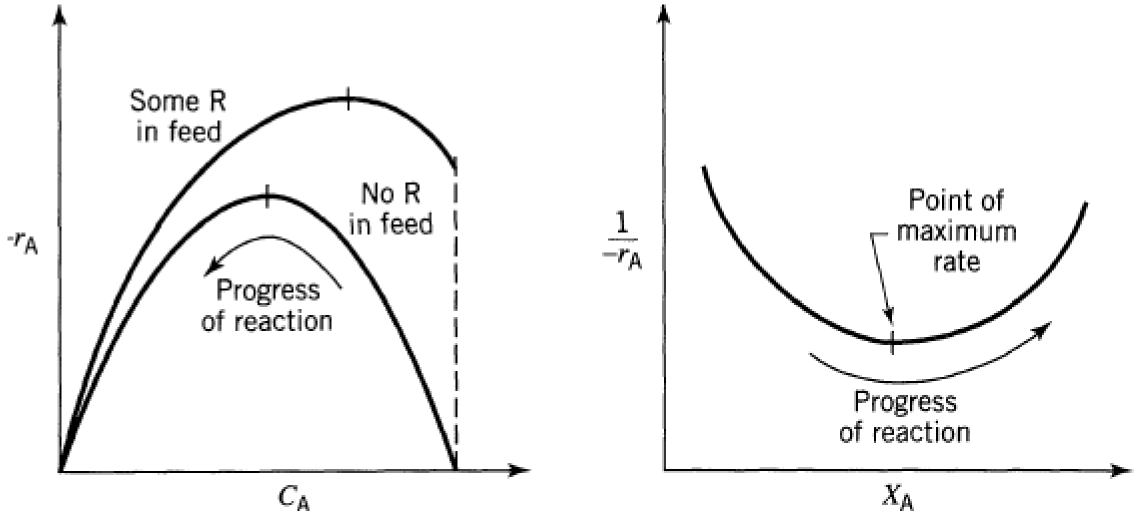


Figure 6.18 Typical rate-concentration curve for autocatalytic reactions, for example:

$$A + R \rightarrow R + R, \qquad -r_A = kC_A^a C_R^r$$

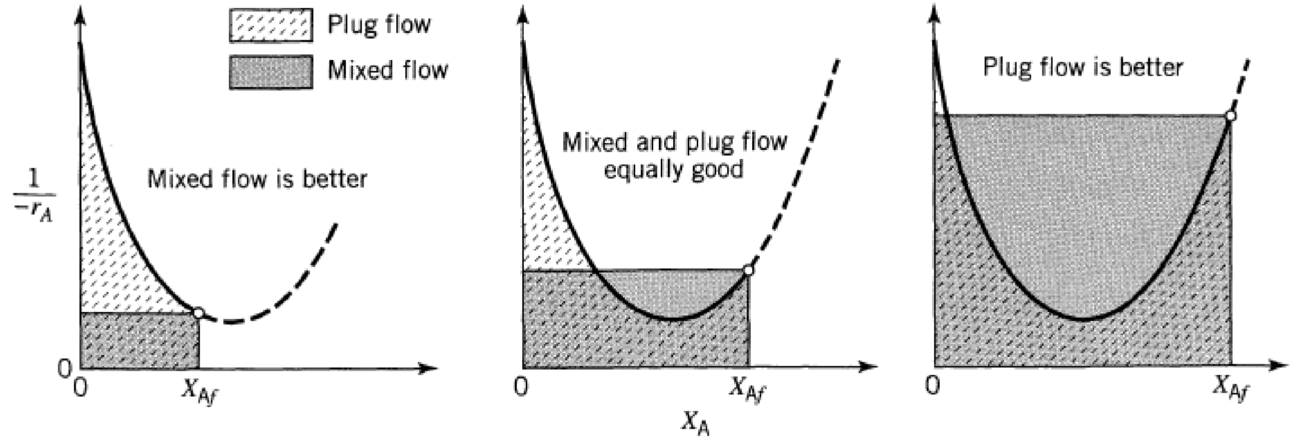


Figure 6.19 For autocatalytic reactions mixed flow is more efficient at low conversions, plug flow is more efficient at high conversions.

These findings differ from ordinary nth-order reactions ($n > 0$) where the plug flow reactor is always more efficient than the mixed flow reactor.

In addition, that a plug flow reactor will not operate at all with a feed of pure reactant. In such a situation the feed must be continually primed with product, an ideal opportunity for using a recycle reactor.

Optimum Recycle Operations. When material is to be processed to some fixed final conversion X_{Af} in a recycle reactor, reflection suggests that there must be a particular recycle ratio which is optimum in that it minimizes the reactor volume or space-time. Let us determine this value of $\boldsymbol{R}$.

The *optimum recycle ratio* is found by differentiating Eq. 21 with respect to $\boldsymbol{R}$ and setting to zero, thus

$$\text{take} \quad \frac{d(\tau/C_{A0})}{d\boldsymbol{R}} = 0 \quad \text{for} \quad \frac{\tau}{C_{A0}} = \int_{X_{Ai}=\frac{\boldsymbol{R}X_{Af}}{\boldsymbol{R}+1}}^{X_{Af}} \frac{\boldsymbol{R}+1}{(-r_A)} dX_A \qquad \textbf{(25)}$$

This operation requires differentiating under an integral sign. From the theorems of calculus, if

$$F(\boldsymbol{R}) = \int_{a(\boldsymbol{R})}^{b(\boldsymbol{R})} f(x, \boldsymbol{R})\, dx \qquad \textbf{(26)}$$

then

$$\frac{dF}{d\boldsymbol{R}} = \int_{a(\boldsymbol{R})}^{b(\boldsymbol{R})} \frac{\partial f(x, \boldsymbol{R})}{\partial \boldsymbol{R}} dx + f(\mathrm{b}, \boldsymbol{R}) \frac{db}{d\boldsymbol{R}} - f(a, \boldsymbol{R}) \frac{da}{d\boldsymbol{R}} \qquad \textbf{(27)}$$

For our case, Eq. 25, we then find

$$\frac{d(\tau/C_{A0})}{d\boldsymbol{R}} = 0 = \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{(-r_A)} + 0 - \left.\frac{\boldsymbol{R}+1}{(-r_A)}\right|_{X_{Ai}} \frac{dX_{Ai}}{d\boldsymbol{R}}$$

where

$$\frac{dX_{Ai}}{d\boldsymbol{R}} = \frac{X_{Af}}{(\boldsymbol{R}+1)^2}$$

Combining and rearranging then gives for the optimum

$$\boxed{\left.\frac{1}{-r_A}\right|_{X_{Ai}} = \frac{\int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{-r_A}}{(X_{Af} - X_{Ai})}} \qquad \textbf{(28)}$$

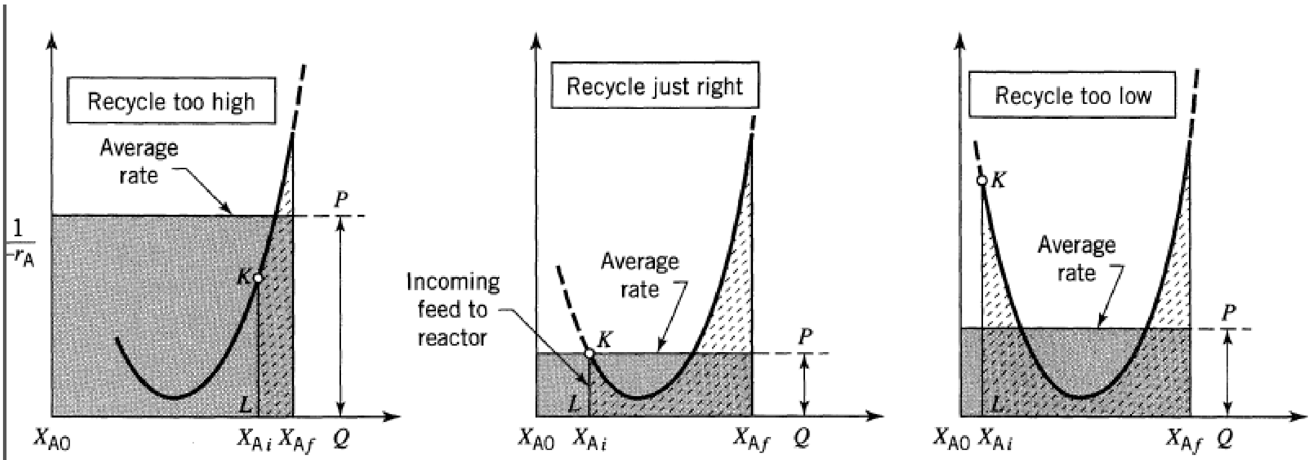


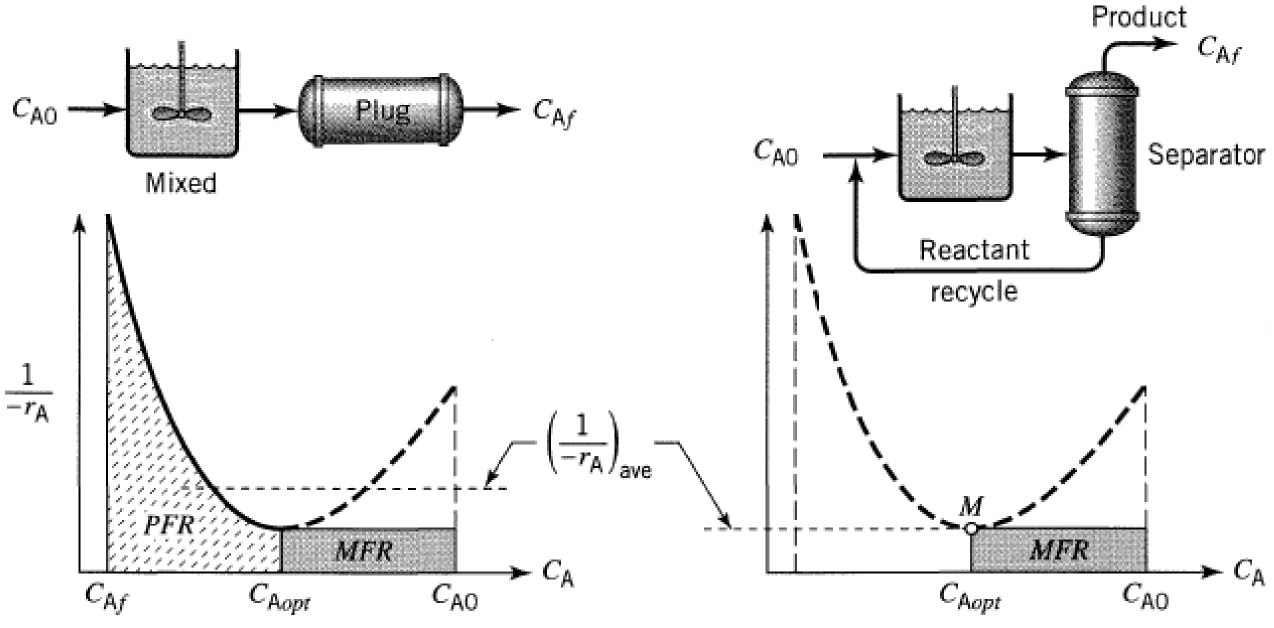
Figure 6.20 Correct recycle ratio for an autocatalytic reaction compared with recycle ratios which are too high and too low.

Reactor Combinations

For autocatalytic reactions all sorts of reactor arrangements are to be considered if product recycle or product separation with recycle is allowable. In general, for a rate-concentration curve as shown in Fig. 6.21 one should always try to reach point M in one step (using mixed flow in a single reactor), then follow with plug flow or as close to plug flow as possible. This procedure is shown as the shaded area in Fig. 6.21a.

When separation and reuse of unconverted reactant is possible, operate at point *M* (see Fig. 6.21*b*).

The volume required is now the very minimum, less than any of the previous ways of operating. However, the overall economics, including the cost of separation and of recycle, will determine which scheme is the optimum overall.



(*a*) (*b*)

Figure 6.21 (*a*) The best multiple reactor scheme. (*b*) The best scheme when unconverted reactant can be separated and recycled.

EXAMPLE 6.3 FINDING THE BEST REACTOR SETUP

In the presence of a specific enzyme E, which acts as a homogeneous catalyst, a harmful organic A present in industrial waste water degrades into harmless chemicals. At a given enzyme concentration C_E tests in a laboratory mixed flow reactor give the following results:

C_{A0}, mmol/m^3	2	5	6	6	11	14	16	24
C_A, mmol/m^3	0.5	3	1	2	6	10	8	4
τ, min	30	1	50	8	4	20	20	4

We wish to treat 0.1 m³/min of this waste water having $C_{A0} = 10$ mmol/m³ to 90% conversion with this enzyme at concentration C_E.

(a) One possibility is to use a long tubular reactor (assume plug flow) with possible recycle of exit fluid. What design do you recommend? Give the size of the reactor, tell if it should be used with recycle, and if so determine the recycle flow rate in cubic meters per minute (m³/min). Sketch your recommended design.

(b) Another possibility is to use one or two stirred tanks (assume ideal). What two-tank design do you recommend, and how much better is it than the one-tank arrangement?

(c) What arrangement of plug flow and mixed flow reactors would you use to minimize the total volume of reactors needed? Sketch your recommended design and show the size of units selected. We should mention that separation and recycle of part of the product stream is not allowed.

SOLUTION

First calculate and tabulate $1/-r_A$ at the measured C_A. This is shown as the last line of Table E6.3. Next, draw the $1/-r_A$ vs. C_A curve. This is seen to be U-shaped (see Figs. E6.3*a*, *b*, *c*) so we must prepare to deal with an autocatalytic type reacting system.

Table E6.3

C_{A0}, mmol/m³	2	5	6	6	11	14	16	24
C_A, mmol/m³	0.5	3	1	2	6	10	8	4
τ, min	30	1	50	8	4	20	20	4
$\frac{1}{-r_A} = \frac{\tau}{C_{A0} - C_A}, \frac{\text{m}^3 \cdot \text{min}}{\text{mmol}}$	20	0.5	10	2	0.8	5	2.5	0.2

Part* (a) *Solution. From the $-1/r_A$ vs. C_A curve we see that we should use plug flow with recycle. From Fig. E6.3*a* we find

$$C_{Ain} = 6.6 \text{ mmol/m}^3$$

$$\boldsymbol{R} = \frac{10 - 6.6}{6.6 - 1} = 0.607$$

$$V = \tau v_0 = \text{area}\,(v_0) = [(10-1)(1.2)](0.1) = \underline{\underline{1.08\ \text{m}^3}}$$

$$v_R = v_0 R = 0.1(0.607) = \underline{\underline{0.0607\ \text{m}^3/\text{min}}}$$

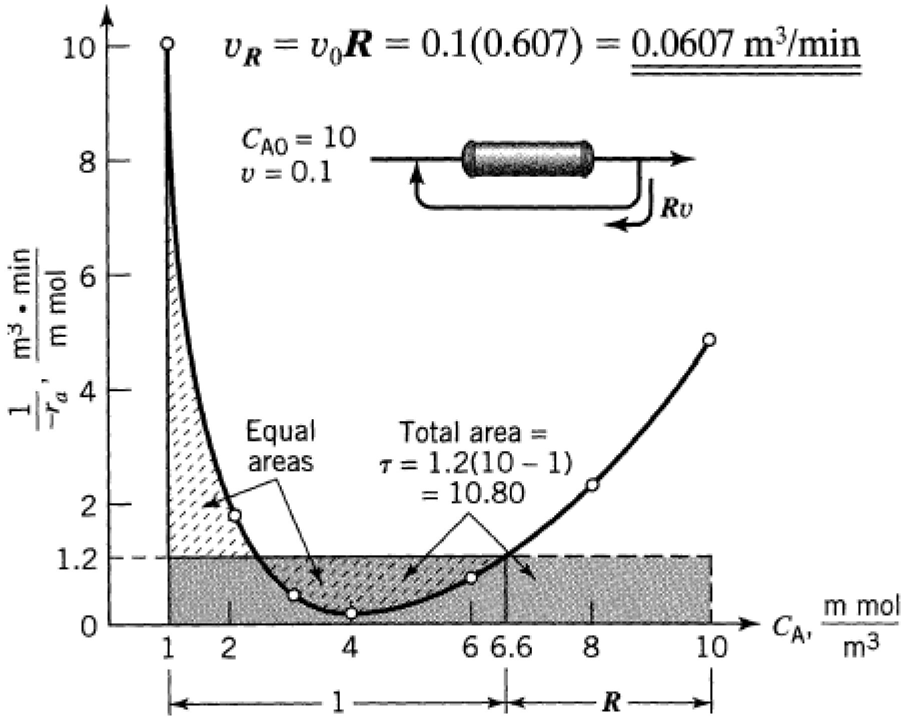


Figure E6.3*a* Plug flow with recycle.

Part* (b) *Solution. Drawing slopes and diagonals according to the method of maximization of rectangles we end up with Fig. E6.3*b*.

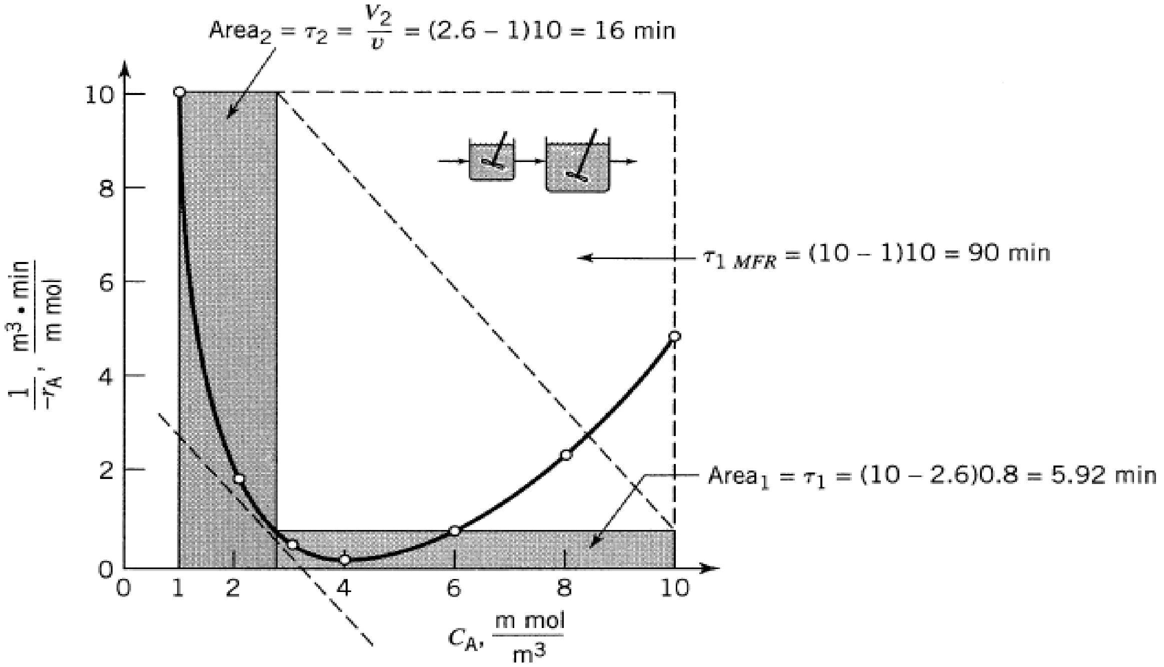


Figure E6.3*b* One and two mixed flow reactors in series.

For 1 tank $\quad V = \tau v = 90(0.1) = \underline{\underline{9.0\ \text{m}^3}}$

$$\text{For 2 tanks} \quad \left.\begin{aligned} V_1 &= \tau_1 v = 5.92(0.1) = 0.59 \\ V_2 &= \tau_2 v = 16(0.1) = 1.6\ \text{m}^3 \end{aligned}\right\} V_{\text{total}} = \underline{\underline{2.19\ \text{m}^3}}$$

Part* (c) *Solution. Following the reasoning in this chapter we should use a mixed flow reactor followed by a plug flow reactor. So with Fig. E6.3*c* we find

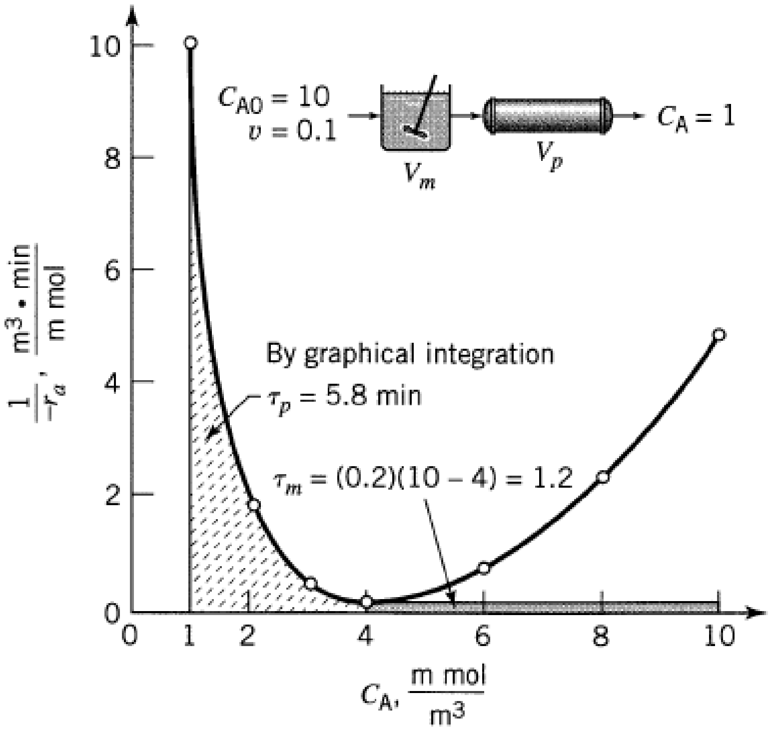


Figure E6.3*c* Arrangement with smallest volume.

$$\left.\begin{array}{ll}\text{For the MFR} & V_m = v\tau_m = 0.1(1.2) = 0.12\ \text{m}^3 \\ \text{For the PFR} & V_p = v\tau_p = 0.1(5.8) = 0.58\ \text{m}^3\end{array}\right\} V_{\text{total}} = \underline{\underline{0.7\ \text{m}^3}}$$

Note which scheme (a) or (b) or (c) gives the smallest size of reactors.

what should be the mean residence time of gas in this tube for the same extent of radioactive decay?

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Lecture No. 14

1-

A reaction with stoichiometric equation $\frac{1}{2}$ A + B = R + $\frac{1}{2}$ S has the following rate expression

$$-r_A = 2C_A^{0.5}C_B$$

What is the rate expression for this reaction if the stoichiometric equation is written as A + 2B = 2R + S?

2-

A certain reaction has a rate given by

$$-r_A = 0.005C_A^2, \qquad \text{mol/cm}^3 \cdot \text{min}$$

If the concentration is to be expressed in mol/liter and time in hours, what would be the value and units of the rate constant?

3-

The pyrolysis of ethane proceeds with an activation energy of about 300 kJ/mol. How much faster is the decomposition at 650°C than at 500°C?

4-

A 1100-K *n*-nonane thermally cracks (breaks down into smaller molecules) 20 times as rapidly as at 1000 K. Find the activation energy for this decomposition.

5-

A 10-minute experimental run shows that 75% of liquid reactant is converted to product by a ½-order rate. What would be the fraction converted in a half-hour run?

6-

In a homogeneous isothermal liquid polymerization, 20% of the monomer disappears in 34 minutes for initial monomer concentration of 0.04 and also for 0.8 mol/liter. What rate equation represents the disappearance of the monomer?

7-

After 8 minutes in a batch reactor, reactant (C_{A0} = 1 mol/liter) is 80% converted; after 18 minutes, conversion is 90%. Find a rate equation to represent this reaction.

8-

The first-order reversible liquid reaction

$$A \rightleftarrows R, \quad C_{A0} = 0.5 \text{ mol/liter}, \quad C_{R0} = 0$$

takes place in a batch reactor. After 8 minutes, conversion of A is 33.3% while equilibrium conversion is 66.7%. Find the rate equation for this reaction.

9-

Aqueous A reacts to form R ($A \rightarrow R$) and in the first minute in a batch reactor its concentration drops from $C_{A0} = 2.03$ mol/liter to $C_{Af} = 1.97$ mol/liter. Find the rate equation for the reaction if the kinetics are second-order with respect to A.

10-

For the elementary reactions in series

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S, \quad k_1 = k_2, \quad \text{at } t = 0 \quad \begin{cases} C_A = C_{A0}, \\ C_{R0} = C_{S0} = 0 \end{cases}$$

find the maximum concentration of R and when it is reached.

11-

At room temperature sucrose is hydrolyzed by the catalytic action of the enzyme sucrase as follows:

$$\text{sucrose} \xrightarrow{\text{sucrase}} \text{products}$$

Starting with a sucrose concentration $C_{A0} = 1.0$ millimol/liter and an enzyme concentration $C_{E0} = 0.01$ millimol/liter, the following kinetic data are obtained in a batch reactor (concentrations calculated from optical rotation measurements):

C_A, millimol/liter	0.84	0.68	0.53	0.38	0.27	0.16	0.09	0.04	0.018	0.006	0.0025
t, hr	1	2	3	4	5	6	7	8	9	10	11

Determine whether these data can be reasonably fitted by a kinetic equation of the Michaelis–Menten type, or

$$-r_A = \frac{k_3 C_A C_{E0}}{C_A + C_M} \quad \text{where} \quad C_M = \text{Michaelis constant}$$

If the fit is reasonable, evaluate the constants k_3 and C_M. Solve by the integral method.

12-

Enzyme E catalyzes the transformation of reactant A to product R as follows:

$$A \xrightarrow{\text{enzyme}} R, \qquad -r_A = \frac{200 C_A C_{E0}}{2 + C_A} \frac{\text{mol}}{\text{liter} \cdot \text{min}}$$

If we introduce enzyme ($C_{E0} = 0.001$ mol/liter) and reactant ($C_{A0} = 10$ mol/liter) into a batch reactor and let the reaction proceed, find the time needed for the concentration of reactant to drop to 0.025 mol/liter. Note that the concentration of enzyme remains unchanged during the reaction.

13-

An ampoule of radioactive Kr-89 (half life = 76 minutes) is set aside for a day. What does this do to the activity of the ampoule? Note that radioactive decay is a first-order process.

14-

Find the conversion after 1 hour in a batch reactor for

$$A \rightarrow R, \quad -r_A = 3C_A^{0.5} \frac{\text{mol}}{\text{liter} \cdot \text{hr}}, \quad C_{A0} = 1 \text{ mol/liter}$$

15-

$$H_2SO_4 + (C_2H_5)_2SO_4 \rightarrow 2C_2H_5SO_4H$$

Initial concentrations of H_2SO_4 and $(C_2H_5)_2SO_4$ are each 5.5 mol/liter. Find a rate equation for this reaction.

t, min	$C_2H_5SO_4H$, mol/liter	t, min	$C_2H_5SO_4H$, mol/liter
0	0	180	4.11
41	1.18	194	4.31
48	1.38	212	4.45
55	1.63	267	4.86
75	2.24	318	5.15
96	2.75	368	5.32
127	3.31	379	5.35
146	3.76	410	5.42
162	3.81	∞	(5.80)

16-

A small reaction bomb fitted with a sensitive pressure-measuring device is flushed out and then filled with pure reactant A at 1-atm pressure. The operation is carried out at 25°C, a temperature low enough that the reaction does not proceed to any appreciable extent. The temperature is then raised as rapidly as possible to 100°C by plunging the bomb into boiling water, and the readings in Table are obtained. The stoichiometry of the reaction is 2A → B, and after leaving the bomb in the bath over the weekend the contents are analyzed for A; none can be found. Find a rate equation in units of moles, liters, and minutes which will satisfactorily fit the data.

T, min	π, atm	T, min	π, atm
1	1.14	7	0.850
2	1.04	8	0.832
3	0.982	9	0.815
4	0.940	10	0.800
5	0.905	15	0.754
6	0.870	20	0.728

17-

For the reaction A → R, second-order kinetics and $C_{A0} = 1$ mol/liter, we get 50% conversion after 1 hour in a batch reactor. What will be the conversion and concentration of A after 1 hour if $C_{A0} = 10$ mol/liter?

18-

For the decomposition A → R, $C_{A0} = 1$ mol/liter, in a batch reactor conversion is 75% after 1 hour, and is just complete after 2 hours. Find a rate equation to represent these kinetics.

19-

In the presence of a homogeneous catalyst of given concentration, aqueous reactant A is converted to product at the following rates, and C_A alone determines this rate:

C_A, mol/liter	1	2	4	6	7	9	12
$-r_A$, mol/liter · hr	0.06	0.1	0.25	1.0	2.0	1.0	0.5

We plan to run this reaction in a batch reactor at the same catalyst concentration as used in getting the above data. Find the time needed to lower the concentration of A from $C_{A0} = 10$ mol/liter to $C_{Af} = 2$ mol/liter.

20-

The following data are obtained at 0°C in a constant-volume batch reactor using pure gaseous A:

Time, min	0	2	4	6	8	10	12	14	∞
Partial pressure of A, mm	760	600	475	390	320	275	240	215	150

The stoichiometry of the decomposition is A → 2.5R. Find a rate equation which satisfactorily represents this decomposition.

21-

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Lecture No. 15

1-

In an isothermal batch reactor 70% of a liquid reactant is converted in 13 min. What space-time and space-velocity are needed to effect this conversion in a plug flow reactor and in a mixed flow reactor?

2-

We plan to replace our present mixed flow reactor with one having double the volume. For the same aqueous feed (10 mol A/liter) and the same feed rate find the new conversion. The reaction kinetics are represented by

$$A \rightarrow R, \qquad -r_A = kC_A^{1.5}$$

and present conversion is 70%.

3-

An aqueous feed of A and B (400 liter/min, 100 mmol A/liter, 200 mmol B/liter) is to be converted to product in a plug flow reactor. The kinetics of the reaction is represented by

$$A + B \rightarrow R, \qquad -r_A = 200\, C_A C_B \frac{\text{mol}}{\text{liter} \cdot \text{min}}$$

Find the volume of reactor needed for 99.9% conversion of A to product.

4-

A plug flow reactor (2 m^3) processes an aqueous feed (100 liter/min) containing reactant A (C_{A0} = 100 mmol/liter). This reaction is reversible and represented by

$$A \rightleftharpoons R, \qquad -r_A = (0.04\ \text{min}^{-1})C_A - (0.01\ \text{min}^{-1})C_R$$

First find the equilibrium conversion and then find the actual conversion of A in the reactor.

5-

The off gas from a boiling water nuclear power reactor contains a whole variety of radioactive trash, one of the most troublesome being Xe-133 (half life = 5.2 days). This off gas flows continuously through a large holdup tank in which its mean residence time is 30 days, and where we can assume that the contents are well mixed. Find the fraction of activity removed in the tank.

6-

A specific enzyme acts as catalyst in the fermentation of reactant A. At a given enzyme concentration in the aqueous feed stream (25 liter/min) find the volume of plug flow reactor needed for 95% conversion of reactant A (C_{A0} = 2 mol/liter). The kinetics of the fermentation at this enzyme concentration is given by

$$A \xrightarrow{\text{enzyme}} R, \qquad -r_A = \frac{0.1\,C_A}{1 + 0.5\,C_A} \; \frac{\text{mol}}{\text{liter}\cdot\text{min}}$$

7-

A gaseous feed of pure A (2 mol/liter, 100 mol/min) decomposes to give a variety of products in a plug flow reactor. The kinetics of the conversion is represented by

$$A \rightarrow 2.5\,(\text{products}), \qquad -r_A = (10\,\text{min}^{-1})C_A$$

Find the expected conversion in a 22-liter reactor.

8-

A stream of pure gaseous reactant A (C_{A0} = 660 mmol/liter) enters a plug flow reactor at a flow rate of F_{A0} = 540 mmol/min and polymerizes there as follows

$$3A \rightarrow R, \qquad -r_A = 54\; \frac{\text{mmol}}{\text{liter}\cdot\text{min}}$$

How large a reactor is needed to lower the concentration of A in the exit stream to C_{Af} = 330 mmol/liter?

9-

A gaseous feed of pure A (1 mol/liter) enters a mixed flow reactor (2 liters) and reacts as follows:

$$2A \rightarrow R, \qquad -r_A = 0.05\, C_A^2 \ \frac{\text{mol}}{\text{liter} \cdot \text{sec}}$$

Find what feed rate (liter/min) will give an outlet concentration $C_A = 0.5$ mol/liter.

10-

Gaseous reactant A decomposes as follows:

$$A \rightarrow 3R, \qquad -r_A = (0.6\ \text{min}^{-1})C_A$$

Find the conversion of A in a 50% A–50% inert feed ($v_0 = 180$ liter/min, $C_{A0} = 300$ mmol/liter) to a 1 m^3 mixed flow reactor.

11-

An aqueous feed containing A (1 mol/liter) enters a 2-liter plug flow reactor and reacts away ($2A \rightarrow R$, $-r_A = 0.05\, C_A^2$ mol/liter · s). Find the outlet concentration of A for a feed rate of 0.5 liter/min.

12-

A mixed flow reactor is being used to determine the kinetics of a reaction whose stoichiometry is $A \rightarrow R$. For this purpose various flow rates of an aqueous solution of 100 mmol A/liter are fed to a 1-liter reactor, and for each run the outlet concentration of A is measured. Find a rate equation to represent the following data. Also assume that reactant alone affects the rate.

v, liter/min	1	6	24
C_A, mmol/liter	4	20	50

13-

We are planning to operate a batch reactor to convert A into R. This is a liquid reaction, the stoichiometry is $A \rightarrow R$, and the rate of reaction is given in Table. How long must we react each batch for the concentration to drop from $C_{A0} = 1.3$ mol/liter to $C_{Af} = 0.3$ mol/liter?

C_A, mol/liter	$-r_A$, mol/liter · min
0.1	0.1
0.2	0.3
0.3	0.5
0.4	0.6
0.5	0.5
0.6	0.25
0.7	0.10
0.8	0.06
1.0	0.05
1.3	0.045
2.0	0.042

14-

For the reaction of Problem 13 , what size of plug flow reactor would be needed for 80% conversion of a feed stream of 1000 mol A/hr at C_{A0} = 1.5 mol/liter?

15-

(a) For the reaction of Problem 13 , what size of mixed flow reactor is needed for 75% conversion of a feed stream of 1000 mol A/hr at C_{A0} = 1.2 mol/liter?

(b) Repeat part (a) with the modification that the feed rate is doubled, thus 2000 mol A/hr at C_{A0} = 1.2 mol/liter are to be treated.

(c) Repeat part (a) with the modification that C_{A0} = 2.4 mol/liter; however, 1000 mol A/hr are still to be treated down to C_{Af} = 0.3 mol/liter.

16-

A high molecular weight hydrocarbon gas A is fed continuously to a heated high temperature mixed flow reactor where it thermally cracks (homogeneous gas reaction) into lower molecular weight materials, collectively called R, by a stoichiometry approximated by $A \rightarrow 5R$. By changing the feed rate different extents of cracking are obtained as follows:

F_{A0}, millimol/hr	300	1000	3000	5000
$C_{A,out}$, millimol/liter	16	30	50	60

The internal void volume of the reactor is V = 0.1 liter, and at the temperature of the reactor the feed concentration is C_{A0} = 100 millimol/liter. Find a rate equation to represent the cracking reaction.

17-

The data in Table have been obtained on the decomposition of gaseous reactant A in a constant volume batch reactor at 100°C.

t, sec	p_A, atm	t, sec	p_A, atm
0	1.00	140	0.25
20	0.80	200	0.14
40	0.68	260	0.08
60	0.56	330	0.04
80	0.45	420	0.02
100	0.37		

stoichiometry of the reaction is $2A \rightarrow R + S$. What size plug flow reactor (in liters) operating at 100°C and 1 atm can treat 100 mol A/hr in a feed consisting of 20% inerts to obtain 95% converson of A?

18-

Repeat the previous problem for a mixed flow reactor.

19-

The aqueous decomposition of A produces R as follows:

$$A \rightleftharpoons R$$

The following results are obtained in a series of steady state runs, all having no R in the feed stream.

Space Time, τ, sec	C_{A0}, In Feed, mol/liter	C_{Af}, In Exit Stream, mol/liter
50	2.0	1.00
16	1.2	0.80
60	2.0	0.65
22	1.0	0.56
4.8	0.48	0.42
72	1.00	0.37
40	0.48	0.28
112	0.48	0.20

From this kinetic information, find the size of reactor needed to achieve 75% conversion of a feed stream of $v = 1$ liter/sec and $C_{A0} = 0.8$ mol/liter. In the reactor the fluid follows

(a) plug flow
(b) mixed flow