

Chemical Reaction Engineering

Third Edition

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Preface

Chemical reaction engineering is that engineering activity concerned with the exploitation of chemical reactions on a commercial scale. Its goal is the successful design and operation of chemical reactors, and probably more than any other activity it sets chemical engineering apart as a distinct branch of the engineering profession.

In a typical situation the engineer is faced with a host of questions: what information is needed to attack a problem, how best to obtain it, and then how to select a reasonable design from the many available alternatives? The purpose of this book is to teach how to answer these questions reliably and wisely. To do this I emphasize qualitative arguments, simple design methods, graphical procedures, and frequent comparison of capabilities of the major reactor types. This approach should help develop a strong intuitive sense for good design which can then guide and reinforce the formal methods.

This is a teaching book; thus, simple ideas are treated first, and are then extended to the more complex. Also, emphasis is placed throughout on the development of a common design strategy for all systems, homogeneous and heterogeneous.

This is an introductory book. The pace is leisurely, and where needed, time is taken to consider why certain assumptions are made, to discuss why an alternative approach is not used, and to indicate the limitations of the treatment when applied to real situations. Although the mathematical level is not particularly difficult (elementary calculus and the linear first-order differential equation is all that is needed), this does not mean that the ideas and concepts being taught are particularly simple. To develop new ways of thinking and new intuitions is not easy.

Regarding this new edition: first of all I should say that in spirit it follows the earlier ones, and I try to keep things simple. In fact, I have removed material from here and there that I felt more properly belonged in advanced books. But I have added a number of new topics—biochemical systems, reactors with fluidized solids, gas/liquid reactors, and more on nonideal flow. The reason for this is my feeling that students should at least be introduced to these subjects so that they will have an idea of how to approach problems in these important areas.

I feel that problem-solving—the process of applying concepts to new situations—is essential to learning. Consequently this edition includes over 80 illustrative examples and over 400 problems (75% new) to help the student learn and understand the concepts being taught.

This new edition is divided into five parts. For the first undergraduate course, I would suggest covering Part 1 (go through Chapters 1 and 2 quickly—don't dawdle there), and if extra time is available, go on to whatever chapters in Parts 2 to 5 that are of interest. For me, these would be catalytic systems (just Chapter 18) and a bit on nonideal flow (Chapters 11 and 12).

For the graduate or second course the material in Parts 2 to 5 should be suitable.

Finally, I'd like to acknowledge Professors Keith Levien, Julio Ottino, and Richard Turton, and Dr. Amos Avidan, who have made useful and helpful comments. Also, my grateful thanks go to Pam Wegner and Peggy Blair, who typed and retyped—probably what seemed like *ad infinitum*—to get this manuscript ready for the publisher.

And to you, the reader, if you find errors—no, when you find errors—or sections of this book that are unclear, please let me know.

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Notation

Symbols and constants which are defined and used locally are not included here. SI units are given to show the dimensions of the symbols.

a	interfacial area per unit volume of tower (m^2/m^3), see Chapter 23
\mathbf{a}	activity of a catalyst, see Eq. 21.4
a, b, \dots, r, s, \dots	stoichiometric coefficients for reacting substances A, B, ..., R, S, ...
A	cross sectional area of a reactor (m^2), see Chapter 20
A, B, ...	reactants
A, B, C, D,	Geldart classification of particles, see Chapter 20
C	concentration (mol/m^3)
C_M	Monod constant (mol/m^3), see Chapters 28-30; or Michaelis constant (mol/m^3), see Chapter 27
C_p	heat capacity ($\text{J}/\text{mol}\cdot\text{K}$)
$\mathbf{C}'_{pA}, \mathbf{C}''_{pA}$	mean specific heat of feed, and of completely converted product stream, per mole of key entering reactant ($\text{J}/\text{mol A} + \text{all else with it}$)
d	diameter (m)
d	order of deactivation, see Chapter 22
d^*	dimensionless particle diameter, see Eq. 20.1
D	axial dispersion coefficient for flowing fluid (m^2/s), see Chapter 13
\mathcal{D}	molecular diffusion coefficient (m^2/s)
\mathcal{D}_e	effective diffusion coefficient in porous structures ($\text{m}^3/\text{m solid}\cdot\text{s}$)
$\text{ei}(x)$	an exponential integral, see Table 16.1

E	enhancement factor for mass transfer with reaction, see Eq. 23.6
E	concentration of enzyme (mol or gm/m ³), see Chapter 27
E	dimensionless output to a pulse input, the exit age distribution function (s ⁻¹), see Chapter 11
E, E^*, E^{**}	RTD for convective flow, see Chapter 15
$E_{oo}, E_{oc}, E_{co}, E_{cc}$	RTD for the dispersion model, see Chapter 13
$Ei(x)$	an exponential integral, see Table 16.1
\mathcal{E}	effectiveness factor (-), see Chapter 18
f	fraction of solids (m ³ solid/m ³ vessel), see Chapter 20
f_i	volume fraction of phase i (-), see Chapter 22
F	feed rate (mol/s or kg/s)
F	dimensionless output to a step input (-), see Fig. 11.12
G_A	free energy (J/mol A)
h	heat transfer coefficient (W/m ² ·K), see Chapter 18
h	height of absorption column (m), see Chapter 24
H	height of fluidized reactor (m), see Chapter 20
H	phase distribution coefficient or Henry's law constant; for gas phase systems $H = p/C$ (Pa·m ³ /mol), see Chapter 23
H_A	mean enthalpy of the flowing stream per mole of A flowing (J/mol A + all else with it), see Chapter 9
H'_A, H''_A	enthalpy of unreacted feed stream, and of completely converted product stream, per mole of A (J/mol A + all else), see Chapter 19
ΔH_r	heat of reaction at temperature T for the stoichiometry as written (J)
$\Delta H_r, \Delta H_f, \Delta H_c$	heat or enthalpy change of reaction, of formation, and of combustion (J or J/mol)
k	reaction rate constant (mol/m ³) ¹⁻ⁿ s ⁻¹ , see Eq. 2.2
k, k', k'', k''', k''''	reaction rate constants based on r, r', r'', r''', r'''' , see Eqs. 18.14 to 18.18
k_d	rate constant for the deactivation of catalyst, see Chapter 21
k_{eff}	effective thermal conductivity (W/m·K), see Chapter 18
k_g	mass transfer coefficient of the gas film (mol/m ² ·Pa·s), see Eq. 23.2
k_l	mass transfer coefficient of the liquid film (m ³ liquid/m ² surface·s), see Eq. 23.3
K	equilibrium constant of a reaction for the stoichiometry as written (-), see Chapter 9

K_{bc}	bubble-cloud interchange coefficient in fluidized beds (s^{-1}), see Eq. 20.13
K_{ce}	cloud-emulsion interchange coefficient in fluidized beds (s^{-1}), see Eq. 20.14
L	characteristic size of a porous catalyst particle (m), see Eq. 18.13
L	half thickness of a flat plate particle (m), see Table 25.1
\dot{m}	mass flow rate (kg/s), see Eq. 11.6
M	mass (kg), see Chapter 11
n	order of reaction, see Eq. 2.2
N	number of equal-size mixed flow reactors in series, see Chapter 6
N_A	moles of component A
p_A	partial pressure of component A (Pa)
p_A^*	partial pressure of A in gas which would be in equilibrium with C_A in the liquid; hence $p_A^* = H_A C_A$ (Pa)
Q	heat duty ($J/s = W$)
r, r', r'', r''', r''''	rate of reaction, an intensive measure, see Eqs. 1.2 to 1.6
r_c	radius of unreacted core (m), see Chapter 25
R	radius of particle (m), see Chapter 25
R, S, ...	products of reaction
R	ideal gas law constant, = 8.314 J/mol·K = 1.987 cal/mol·K = 0.08206 lit·atm/mol·K
R	recycle ratio, see Eq. 6.15
s	space velocity (s^{-1}); see Eqs. 5.7 and 5.8
S	surface (m^2)
t	time (s)
\bar{t}	= V/v , reactor holding time or mean residence time of fluid in a flow reactor (s), see Eq. 5.24
T	temperature (K or °C)
u^*	dimensionless velocity, see Eq. 20.2
U	carrier or inert component in a phase, see Chapter 24
v	volumetric flow rate (m^3/s)
V	volume (m^3)
W	mass of solids in the reactor (kg)
X_A	fraction of A converted, the conversion (-)

X_A	moles A/moles inert in the liquid (–), see Chapter 24
Y_A	moles A/moles inert in the gas (–), see Chapter 24

Greek symbols

α	m^3 wake/ m^3 bubble, see Eq. 20.9
δ	volume fraction of bubbles in a BFB
δ	Dirac delta function, an ideal pulse occurring at time $t = 0$ (s^{-1}), see Eq. 11.14
$\delta(t - t_0)$	Dirac delta function occurring at time t_0 (s^{-1})
ε_A	expansion factor, fractional volume change on complete conversion of A, see Eq. 3.64
ϵ	void fraction in a gas-solid system, see Chapter 20
\mathcal{E}	effectiveness factor, see Eq. 18.11
$\theta = t/\bar{t}$	dimensionless time units (–), see Eq. 11.5
K''	overall reaction rate constant in BFB (m^3 solid/ m^3 gas·s), see Chapter 20
μ	viscosity of fluid (kg/m·s)
μ	mean of a tracer output curve, (s), see Chapter 15
π	total pressure (Pa)
ρ	density or molar density (kg/ m^3 or mol/ m^3)
σ^2	variance of a tracer curve or distribution function (s^2), see Eq. 13.2
τ	$V/\nu = C_{A0}V/F_{A0}$, space-time (s), see Eqs. 5.6 and 5.8
τ	time for complete conversion of a reactant particle to product (s)
τ'	$= C_{A0}W/F_{A0}$, weight-time, (kg·s/ m^3), see Eq. 15.23
$\tau', \tau'', \tau''', \tau''''$	various measures of reactor performance, see Eqs. 18.42, 18.43
Φ	overall fractional yield, see Eq. 7.8
ϕ	sphericity, see Eq. 20.6
φ	instantaneous fractional yield, see Eq. 7.7
$\varphi(M/N) = \textcircled{M/N}$	instantaneous fractional yield of M with respect to N, or moles M formed/mol N formed or reacted away, see Chapter 7

Symbols and abbreviations

BFB	bubbling fluidized bed, see Chapter 20
BR	batch reactor, see Chapters 3 and 5
CFB	circulating fluidized bed, see Chapter 20
FF	fast fluidized bed, see Chapter 20

LFR	laminar flow reactor, see Chapter 15
MFR	mixed flow reactor, see Chapter 5
M-M	Michaelis Menten, see Chapter 27
$\textcircled{M/N} = \varphi(M/N)$	see Eqs. 28.1 to 28.4
<i>mw</i>	molecular weight (kg/mol)
PC	pneumatic conveying, see Chapter 20
PCM	progressive conversion model, see Chapter 25
PFR	plug flow reactor, see Chapter 5
RTD	residence time distribution, see Chapter 11
SCM	shrinking-core model, see Chapter 25
TB	turbulent fluidized bed, see Chapter 20

Subscripts

<i>b</i>	batch
<i>b</i>	bubble phase of a fluidized bed
<i>c</i>	of combustion
<i>c</i>	cloud phase of a fluidized bed
<i>c</i>	at unreacted core
<i>d</i>	deactivation
<i>d</i>	deadwater, or stagnant fluid
<i>e</i>	emulsion phase of a fluidized bed
<i>e</i>	equilibrium conditions
<i>f</i>	leaving or final
<i>f</i>	of formation
<i>g</i>	of gas
<i>i</i>	entering
<i>l</i>	of liquid
<i>m</i>	mixed flow
<i>mf</i>	at minimum fluidizing conditions
<i>p</i>	plug flow
<i>r</i>	reactor or of reaction
<i>s</i>	solid or catalyst or surface conditions
0	entering or reference
θ	using dimensionless time units, see Chapter 11

Superscripts

a, b, . . .	order of reaction, see Eq. 2.2
<i>n</i>	order of reaction
o	refers to the standard state

**Dimensionless
groups**

$$\frac{D}{uL}$$

vessel dispersion number, see Chapter 13

$$\frac{D}{ud}$$

intensity of dispersion number, see Chapter 13

$$M_H$$

Hatta modulus, see Eq. 23.8 and/or Figure 23.4

$$M_T$$

Thiele modulus, see Eq. 18.23 or 18.26

$$M_W$$

Wagner-Weisz-Wheeler modulus, see Eq. 18.24 or 18.34

$$\text{Re} = \frac{du\rho}{\mu}$$

Reynolds number

$$\text{Sc} = \frac{\mu}{\rho D}$$

Schmidt number

Chapter 1

Overview of Chemical Reaction Engineering

Every industrial chemical process is designed to produce economically a desired product from a variety of starting materials through a succession of treatment steps. Figure 1.1 shows a typical situation. The raw materials undergo a number of physical treatment steps to put them in the form in which they can be reacted chemically. Then they pass through the reactor. The products of the reaction must then undergo further physical treatment—separations, purifications, etc.—for the final desired product to be obtained.

Design of equipment for the physical treatment steps is studied in the unit operations. In this book we are concerned with the chemical treatment step of a process. Economically this may be an inconsequential unit, perhaps a simple mixing tank. Frequently, however, the chemical treatment step is the heart of the process, the thing that makes or breaks the process economically.

Design of the reactor is no routine matter, and many alternatives can be proposed for a process. In searching for the optimum it is not just the cost of the reactor that must be minimized. One design may have low reactor cost, but the materials leaving the unit may be such that their treatment requires a much higher cost than alternative designs. Hence, the economics of the overall process must be considered.

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.

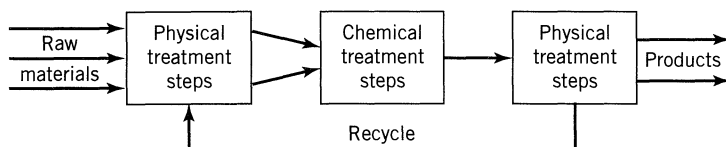


Figure 1.1 Typical chemical process.

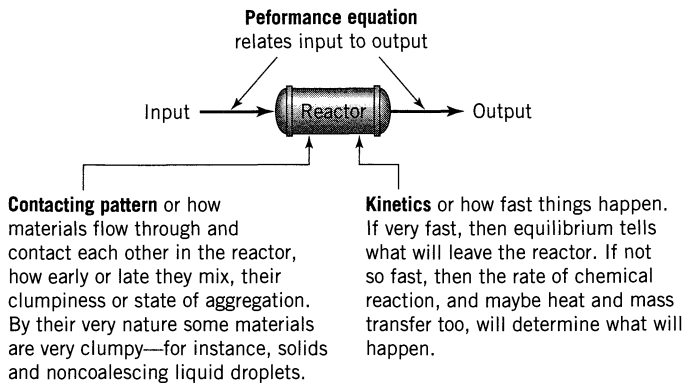


Figure 1.2 Information needed to predict what a reactor can do.

Much of this book deals with finding the expression to relate input to output for various kinetics and various contacting patterns, or

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

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.

Classification of Reactions

There are many ways of classifying chemical reactions. In chemical reaction engineering probably the most useful scheme is the breakdown according to the number and types of phases involved, the big division being between the *homogeneous* and *heterogeneous* systems. A reaction is homogeneous if it takes place in one phase alone. A reaction is heterogeneous if it requires the presence of at least two phases to proceed at the rate that it does. It is immaterial whether the reaction takes place in one, two, or more phases; at an interface; or whether the reactants and products are distributed among the phases or are all contained within a single phase. All that counts is that at least two phases are necessary for the reaction to proceed as it does.

Sometimes this classification is not clear-cut as with the large class of biological reactions, the enzyme-substrate reactions. Here the enzyme acts as a catalyst in the manufacture of proteins and other products. Since enzymes themselves are highly complicated large-molecular-weight proteins of colloidal size, 10–100 nm, enzyme-containing solutions represent a gray region between homogeneous and heterogeneous systems. Other examples for which the distinction between homogeneous and heterogeneous systems is not sharp are the very rapid chemical reactions, such as the burning gas flame. Here large nonhomogeneity in composition and temperature exist. Strictly speaking, then, we do not have a single phase, for a phase implies uniform temperature, pressure, and composition throughout. The answer to the question of how to classify these borderline cases is simple. It depends on how we *choose* to treat them, and this in turn depends on which

Table 1.1 Classification of Chemical Reactions Useful in Reactor Design

	Noncatalytic	Catalytic
Homogeneous	Most gas-phase reactions	Most liquid-phase reactions
	Fast reactions such as burning of a flame	Reactions in colloidal systems Enzyme and microbial reactions
	Burning of coal Roasting of ores Attack of solids by acids	Ammonia synthesis Oxidation of ammonia to produce nitric acid
Heterogeneous	Gas-liquid absorption with reaction Reduction of iron ore to iron and steel	Cracking of crude oil Oxidation of SO_2 to SO_3

description we think is more useful. Thus, only in the context of a given situation can we decide how best to treat these borderline cases.

Cutting across this classification is the catalytic reaction whose rate is altered by materials that are neither reactants nor products. These foreign materials, called *catalysts*, need not be present in large amounts. Catalysts act somehow as go-betweens, either hindering or accelerating the reaction process while being modified relatively slowly if at all.

Table 1.1 shows the classification of chemical reactions according to our scheme with a few examples of typical reactions for each type.

Variables Affecting the Rate of Reaction

Many variables may affect the rate of a chemical reaction. In homogeneous systems the temperature, pressure, and composition are obvious variables. In heterogeneous systems more than one phase is involved; hence, the problem becomes more complex. Material may have to move from phase to phase during reaction; hence, the rate of mass transfer can become important. For example, in the burning of a coal briquette the diffusion of oxygen through the gas film surrounding the particle, and through the ash layer at the surface of the particle, can play an important role in limiting the rate of reaction. In addition, the rate of heat transfer may also become a factor. Consider, for example, an exothermic reaction taking place at the interior surfaces of a porous catalyst pellet. If the heat released by reaction is not removed fast enough, a severe nonuniform temperature distribution can occur within the pellet, which in turn will result in differing point rates of reaction. These heat and mass transfer effects become increasingly important the faster the rate of reaction, and in very fast reactions, such as burning flames, they become rate controlling. Thus, heat and mass transfer may play important roles in determining the rates of heterogeneous reactions.

Definition of Reaction Rate

We next ask how to *define* the rate of reaction in meaningful and useful ways. To answer this, let us adopt a number of definitions of rate of reaction, all

interrelated and all intensive rather than extensive measures. But first we must select one reaction component for consideration and define the rate in terms of this component i . 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,

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

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

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

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

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

Based on unit volume of solid in gas-solid systems

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

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

$$r_i'''' = \frac{1}{V_r} \frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of reactor}) (\text{time})} \quad (6)$$

In homogeneous systems the volume of fluid in the reactor is often identical to the volume of reactor. In such a case V and V_r 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.

From Eqs. 2 to 6 these intensive definitions of reaction rate are related by

$$\left(\begin{array}{c} \text{volume} \\ \text{of fluid} \end{array} \right) r_i = \left(\begin{array}{c} \text{mass of} \\ \text{solid} \end{array} \right) r'_i = \left(\begin{array}{c} \text{surface} \\ \text{of solid} \end{array} \right) r''_i = \left(\begin{array}{c} \text{volume} \\ \text{of solid} \end{array} \right) r'''_i = \left(\begin{array}{c} \text{volume} \\ \text{of reactor} \end{array} \right) r_i''''$$

or

$$Vr_i = Wr'_i = Sr''_i = V_s r'''_i = V_r r_i'''' \quad (7)$$

Speed of Chemical Reactions

Some reactions occur very rapidly; others very, very slowly. For example, in the production of polyethylene, one of our most important plastics, or in the production of gasoline from crude petroleum, we want the reaction step to be complete in less than one second, while in waste water treatment, reaction may take days and days to do the job.

Figure 1.3 indicates the relative rates at which reactions occur. To give you an appreciation of the relative rates or relative values between what goes on in sewage treatment plants and in rocket engines, this is equivalent to

1 sec to 3 yr

With such a large ratio, of course the design of reactors will be quite different in these cases.

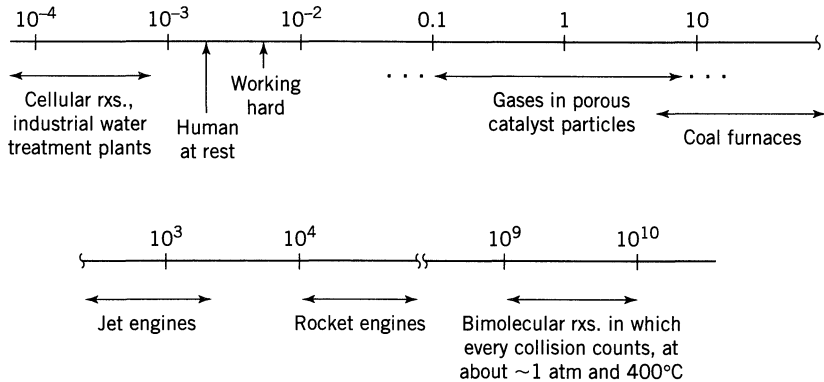


Figure 1.3 Rate of reactions $-r_A''' = \frac{\text{moles of A disappearing}}{\text{m}^3 \text{ of thing} \cdot \text{s}}$

Overall Plan

Reactors come in all colors, shapes, and sizes and are used for all sorts of reactions. As a brief sampling we have the giant cat crackers for oil refining; the monster blast furnaces for iron making; the crafty activated sludge ponds for sewage treatment; the amazing polymerization tanks for plastics, paints, and fibers; the critically important pharmaceutical vats for producing aspirin, penicillin, and birth control drugs; the happy-go-lucky fermentation jugs for moonshine; and, of course, the beastly cigarette.

Such reactions are so different in rates and types that it would be awkward to try to treat them all in one way. So we treat them by type in this book because each type requires developing the appropriate set of performance equations.

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.

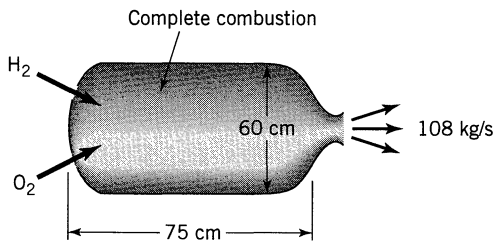


Figure E1.1

SOLUTION

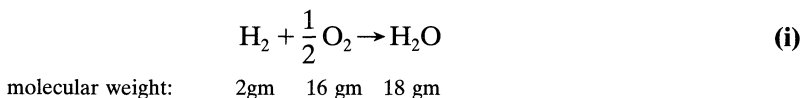
We want to evaluate

$$-r_{\text{H}_2} = \frac{1}{V} \frac{dN_{\text{H}_2}}{dt} \quad \text{and} \quad -r_{\text{O}_2} = \frac{1}{V} \frac{dN_{\text{O}_2}}{dt}$$

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.



Therefore,

$$\text{H}_2\text{O produced/s} = 108 \text{ kg/s} \left(\frac{1 \text{ kmol}}{18 \text{ kg}} \right) = 6 \text{ kmol/s}$$

So from Eq. (i)

$$\text{H}_2 \text{ used} = 6 \text{ kmol/s}$$

$$\text{O}_2 \text{ used} = 3 \text{ kmol/s}$$

and the rate of reaction is

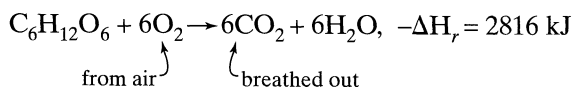
$$\underline{\underline{-r_{\text{H}_2}}} = -\frac{1}{0.2121 \text{ m}^3} \cdot \frac{6 \text{ kmol}}{\text{s}} = \underline{\underline{2.829 \times 10^4 \frac{\text{mol used}}{(\text{m}^3 \text{ of rocket}) \cdot \text{s}}}}$$

$$\underline{\underline{-r_{\text{O}_2}}} = -\frac{1}{0.2121 \text{ m}^3} \cdot 3 \frac{\text{kmol}}{\text{s}} = \underline{\underline{1.415 \times 10^4 \frac{\text{mol}}{\text{m}^3 \cdot \text{s}}}}$$

Note: Compare these rates with the values given in Figure 1.3. ■

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



Find man's metabolic rate (the rate of living, loving, and laughing) in terms of moles of oxygen used per m³ of person per second.

SOLUTION

We want to find

$$-r''_{\text{O}_2} = -\frac{1}{V_{\text{person}}} \frac{dN_{\text{O}_2}}{dt} = \frac{\text{mol O}_2 \text{ used}}{(\text{m}^3 \text{ of person})\text{s}} \quad (\text{i})$$

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

$$\frac{dN_{\text{O}_2}}{dt} = \left(\frac{6000 \text{ kJ/day}}{2816 \text{ kJ/mol glucose}} \right) \left(\frac{6 \text{ mol O}_2}{1 \text{ mol glucose}} \right) = 12.8 \frac{\text{mol O}_2}{\text{day}}$$

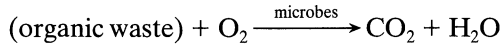
Inserting into Eq. (i)

$$-r_{O_2}''' = \frac{1}{0.075 \text{ m}^3} \cdot \frac{12.8 \text{ mol O}_2 \text{ used}}{\text{day}} \frac{1 \text{ day}}{24 \times 3600 \text{ s}} = \underline{\underline{0.002 \frac{\text{mol O}_2 \text{ used}}{\text{m}^3 \cdot \text{s}}}}$$

Note: Compare this value with those listed in Figure 1.3.

PROBLEMS

- 1.1. Municipal waste water treatment plant.** Consider a municipal water treatment plant for a small community (Fig. P1.1). Waste water, 32 000 m³/day, flows through the treatment plant with a mean residence time of 8 hr, air is bubbled through the tanks, and microbes in the tank attack and break down the organic material



A typical entering feed has a BOD (biological oxygen demand) of 200 mg O₂/liter, while the effluent has a negligible BOD. Find the rate of reaction, or decrease in BOD in the treatment tanks.

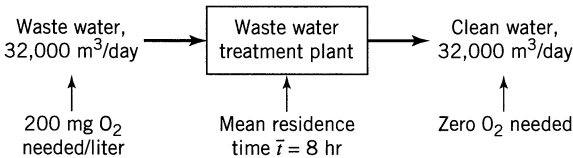


Figure P1.1

- 1.2. Coal burning electrical power station.** Large central power stations (about 1000 MW electrical) using fluidized bed combustors may be built some day (see Fig. P1.2). These giants would be fed 240 tons of coal/hr (90% C, 10%

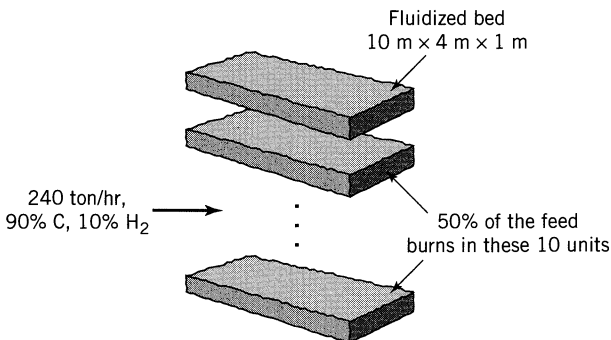
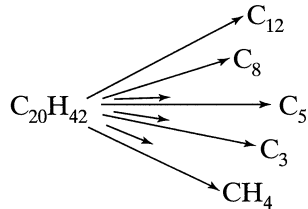


Figure P1.2

H_2), 50% of which would burn within the battery of primary fluidized beds, the other 50% elsewhere in the system. One suggested design would use a battery of 10 fluidized beds, each 20 m long, 4 m wide, and containing solids to a depth of 1 m. Find the rate of reaction within the beds, based on the oxygen used.

1.3. Fluid cracking crackers (FCC). FCC reactors are among the largest processing units used in the petroleum industry. Figure P1.3 shows an example of such units. A typical unit is 4-10 m ID and 10-20 m high and contains about 50 tons of $\rho = 800 \text{ kg/m}^3$ porous catalyst. It is fed about 38 000 barrels of crude oil per day ($6000 \text{ m}^3/\text{day}$ at a density $\rho \cong 900 \text{ kg/m}^3$), and it cracks these long chain hydrocarbons into shorter molecules.

To get an idea of the rate of reaction in these giant units, let us simplify and suppose that the feed consists of just C_{20} hydrocarbon, or



If 60% of the vaporized feed is cracked in the unit, what is the rate of reaction, expressed as $-r'$ (mols reacted/kg cat · s) and as r''' (mols reacted/ $\text{m}^3 \text{ cat} \cdot \text{s}$)?

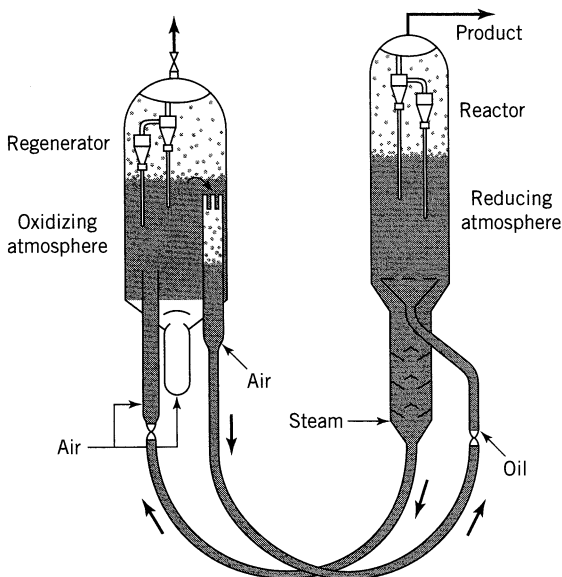


Figure P1.3 The Exxon Model IV FCC unit.

Part I

Homogeneous Reactions in Ideal Reactors

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- Chapter 4** Introduction to Reactor Design /83
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Chapter 2

Kinetics of Homogeneous Reactions

Simple Reactor Types

Ideal reactors have three ideal flow or contacting patterns. We show these in Fig. 2.1, and we very often try to make real reactors approach these ideals as closely as possible.

We particularly like these three flow or reacting patterns because they are easy to treat (it is simple to find their performance equations) and because one of them often is the best pattern possible (it will give the most of whatever it is we want). Later we will consider recycle reactors, staged reactors, and other flow pattern combinations, as well as deviations of real reactors from these ideals.

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

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

rate of disappearance of A

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

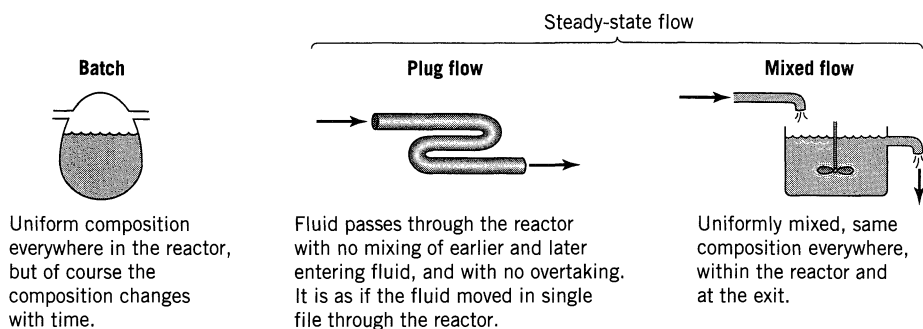


Figure 2.1 Ideal reactor types.

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

$$\begin{array}{c}
 \frac{\text{mol}}{\text{m}^3 \cdot \text{s}} \\
 \downarrow \\
 -r_A = f \left[\begin{array}{l} \text{temperature} \\ \text{dependent} \\ \text{terms} \end{array} , \begin{array}{l} \text{concentration} \\ \text{dependent} \\ \text{terms} \end{array} \right]
 \end{array}
 \quad \xrightarrow{\text{as an example}} \quad
 \begin{array}{c}
 \left(\frac{\text{mol}}{\text{m}^3} \right)^{1-a} \text{s}^{-1} \\
 \downarrow \\
 k C_A^a = k_0 e^{-\frac{E}{RT}} C_A^a
 \end{array}
 \quad (2)$$

activation energy \rightarrow E/RT
 reaction order \rightarrow a
 temperature dependent term \rightarrow $e^{-E/RT}$

Here are a few words about the concentration-dependent and the temperature-dependent terms of the rate.

2.1 CONCENTRATION-DEPENDENT TERM OF A RATE EQUATION

Before we can find the form of the concentration term in a rate expression, we must distinguish between different types of reactions. This distinction is based on the form and number of kinetic equations used to describe the progress of reaction. Also, since we are concerned with the concentration-dependent term of the rate equation, we hold the temperature of the system constant.

Single and Multiple Reactions

First of all, when materials react to form products it is usually easy to decide after examining the stoichiometry, preferably at more than one temperature, whether we should consider a single reaction or a number of reactions to be occurring.

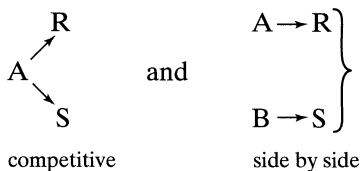
When a single stoichiometric equation and single rate equation are chosen to represent the progress of the reaction, we have a *single reaction*. When more than one stoichiometric equation is chosen to represent the observed changes,

then more than one kinetic expression is needed to follow the changing composition of all the reaction components, and we have *multiple reactions*.

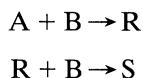
Multiple reactions may be classified as:
series reactions,



parallel reactions, which are of two types



and more complicated schemes, an example of which is



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

Elementary and Nonelementary Reactions

Consider a single reaction with stoichiometric equation

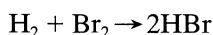


If we postulate that the rate-controlling mechanism involves the collision or interaction of a single molecule of A with a single molecule of B, then the number of collisions of molecules A with B is proportional to the rate of reaction. But at a given temperature the number of collisions is proportional to the concentration of reactants in the mixture; hence, the rate of disappearance of A is given by

$$-r_A = kC_A C_B$$

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

When there is no direct correspondence between stoichiometry and rate, then we have *nonelementary reactions*. The classical example of a nonelementary reaction is that between hydrogen and bromine,



which has a rate expression*

$$r_{\text{HBr}} = \frac{k_1[\text{H}_2][\text{Br}_2]^{1/2}}{k_2 + [\text{HBr}]/[\text{Br}_2]} \quad (3)$$

Nonelementary reactions are explained by assuming that what we observe as a single reaction is in reality the overall effect of a sequence of elementary reactions. The reason for observing only a single reaction rather than two or more elementary reactions is that the amount of intermediates formed is negligibly small and, therefore, escapes detection. We take up these explanations later.

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:

$$-r_A = kC_A^a C_B^b \dots C_D^d, \quad a + b + \dots + d = n \quad (4)$$

where a, b, \dots, d are not necessarily related to the stoichiometric coefficients. We call the powers to which the concentrations are raised the *order of the reaction*. Thus, the reaction is

a th order with respect to A

b th order with respect to B

n th order overall

Since the order refers to the empirically found rate expression, it can have a fractional value and need not be an integer. However, the molecularity of a reaction must be an integer because it refers to the mechanism of the reaction, and can only apply to an elementary reaction.

For rate expressions not of the form of Eq. 4, such as Eq. 3, it makes no sense to use the term reaction order.

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 n th-order reaction are

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

* To eliminate much writing, in this chapter we use square brackets to indicate concentrations. Thus,

$$C_{\text{HBr}} = [\text{HBr}]$$

which for a first-order reaction becomes simply

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

Representation of an Elementary Reaction

In expressing a rate we may use any measure equivalent to concentration (for example, partial pressure), in which case

$$r_A = k p_A^a p_B^b \dots p_D^d$$

Whatever measure we use leaves the order unchanged; however, it will affect the rate constant k .

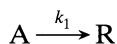
For brevity, elementary reactions are often represented by an equation showing both the molecularity and the rate constant. For example,



represents a bimolecular irreversible reaction with second-order rate constant k_1 , implying that the rate of reaction is

$$-r_A = r_R = k_1 C_A^2$$

It would not be proper to write Eq. 7 as



for this would imply that the rate expression is

$$-r_A = r_R = k_1 C_A$$

Thus, we must be careful to distinguish between the one particular equation that represents the elementary reaction and the many possible representations of the stoichiometry.

We should note that writing the elementary reaction with the rate constant, as shown by Eq. 7, may not be sufficient to avoid ambiguity. At times it may be necessary to specify the component in the reaction to which the rate constant is referred. For example, consider the reaction,



If the rate is measured in terms of B, the rate equation is

$$-r_B = k_B C_B C_D^2$$

If it refers to D, the rate equation is

$$-r_D = k_D C_B C_D^2$$

Or if it refers to the product T, then

$$r_T = k_T C_B C_D^2$$

But from the stoichiometry

$$-r_B = -\frac{1}{2}r_D = \frac{1}{3}r_T$$

hence,

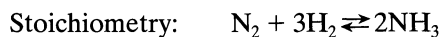
$$k_B = \frac{1}{2}k_D = \frac{1}{3}k_T \quad (9)$$

In Eq. 8, which of these three k values are we referring to? We cannot tell. Hence, to avoid ambiguity when the stoichiometry involves different numbers of molecules of the various components, we must specify the component being considered.

To sum up, the condensed form of expressing the rate can be ambiguous. To eliminate any possible confusion, write the stoichiometric equation followed by the complete rate expression, and give the units of the rate constant.

Representation of a Nonelementary Reaction

A nonelementary reaction is one whose stoichiometry does not match its kinetics. For example,

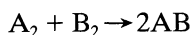


Rate:
$$r_{\text{NH}_3} = k_1 \frac{[\text{N}_2][\text{H}_2]^{3/2}}{[\text{NH}_3]^2} - k_2 \frac{[\text{NH}_3]}{[\text{H}_2]^{3/2}}$$

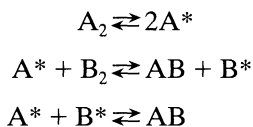
This nonmatch shows that we must try to develop a multistep reaction model to explain the kinetics.

Kinetic Models for Nonelementary Reactions

To explain the kinetics of nonelementary reactions we assume that a sequence of elementary reactions is actually occurring but that we cannot measure or observe the intermediates formed because they are only present in very minute quantities. Thus, we observe only the initial reactants and final products, or what appears to be a single reaction. For example, if the kinetics of the reaction



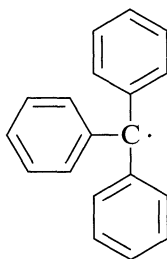
indicates that the reaction is nonelementary, we may postulate a series of elementary steps to explain the kinetics, such as



where the asterisks refer to the unobserved intermediates. To test our postulation scheme, we must see whether its predicted kinetic expression corresponds to experiment.

The types of intermediates we may postulate are suggested by the chemistry of the materials. These may be grouped as follows.

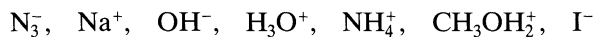
Free Radicals. Free atoms or larger fragments of stable molecules that contain one or more unpaired electrons are called free radicals. The unpaired electron is designated by a dot in the chemical symbol for the substance. Some free radicals are relatively stable, such as triphenylmethyl,



but as a rule they are unstable and highly reactive, such as



Ions and Polar Substances. Electrically charged atoms, molecules, or fragments of molecules, such as



are called ions. These may act as active intermediates in reactions.

Molecules. Consider the consecutive reactions

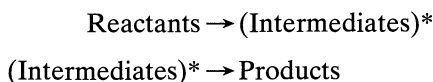


Ordinarily these are treated as multiple reactions. However, if the intermediate R is highly reactive its mean lifetime will be very small and its concentration in the reacting mixture can become too small to measure. In such a situation R may not be observed and can be considered to be a reactive intermediate.

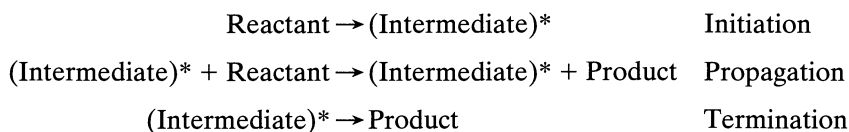
Transition Complexes. The numerous collisions between reactant molecules result in a wide distribution of energies among the individual molecules. This can result in strained bonds, unstable forms of molecules, or unstable association of molecules which can then either decompose to give products, or by further collisions return to molecules in the normal state. Such unstable forms are called transition complexes.

Postulated reaction schemes involving these four kinds of intermediates can be of two types.

Nonchain Reactions. In the nonchain reaction the intermediate is formed in the first reaction and then disappears as it reacts further to give the product. Thus,



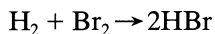
Chain Reactions. In chain reactions the intermediate is formed in a first reaction, called the *chain initiation step*. It then combines with reactant to form product and more intermediate in the chain propagation step. Occasionally the intermediate is destroyed in the chain termination step. Thus,



The essential feature of the chain reaction is the propagation step. In this step the intermediate is not consumed but acts simply as a catalyst for the conversion of material. Thus, each molecule of intermediate can catalyze a long chain of reactions, even thousands, before being finally destroyed.

The following are examples of mechanisms of various kinds.

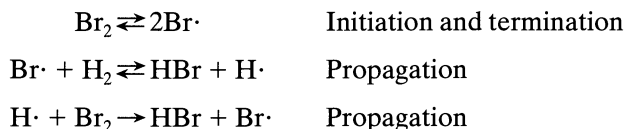
1. Free radicals, chain reaction mechanism. The reaction



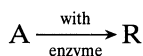
with experimental rate

$$r_{\text{HBr}} = \frac{k_1[\text{H}_2][\text{Br}_2]^{1/2}}{k_2 + [\text{HBr}]/[\text{Br}_2]}$$

can be explained by the following scheme which introduces and involves the intermediates $\text{H}\cdot$ and $\text{Br}\cdot$,

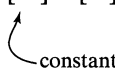


2. **Molecular intermediates, nonchain mechanism.** The general class of enzyme-catalyzed fermentation reactions



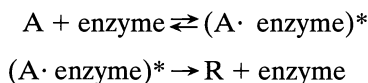
with experimental rate

$$r_R = \frac{k[A][E_0]}{[M] + [A]}$$



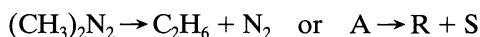
constant

is viewed to proceed with intermediate (A· enzyme)* as follows:

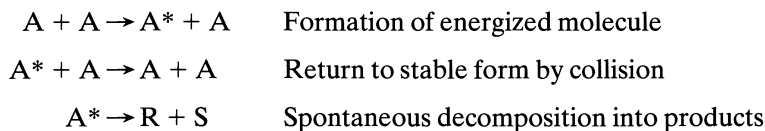


In such reactions the concentration of intermediate may become more than negligible, in which case a special analysis, first proposed by Michaelis and Menten (1913), is required.

3. **Transition complex, nonchain mechanism.** The spontaneous decomposition of azomethane



exhibits under various conditions first-order, second-order, or intermediate kinetics. This type of behavior can be explained by postulating the existence of an energized and unstable form for the reactant, A*. Thus,



Lindemann (1922) first suggested this type of intermediate.

Testing Kinetic Models

Two problems make the search for the correct mechanism of reaction difficult. First, the reaction may proceed by more than one mechanism, say free radical and ionic, with relative rates that change with conditions. Second, more than one mechanism can be consistent with kinetic data. Resolving these problems is difficult and requires an extensive knowledge of the chemistry of the substances involved. Leaving these aside, let us see how to test the correspondence between experiment and a proposed mechanism that involves a sequence of elementary reactions.

In these elementary reactions we hypothesize the existence of either of two types of intermediates.

Type 1. An unseen and unmeasured intermediate X usually present at such small concentration that its rate of change in the mixture can be taken to be zero. Thus, we assume

$$[X] \text{ is small and } \frac{d[X]}{dt} \cong 0$$

This is called the *steady-state approximation*. Mechanism types 1 and 2, above, adopt this type of intermediate, and Example 2.1 shows how to use it.

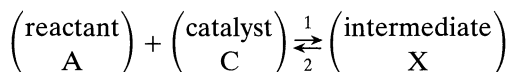
Type 2. Where a homogeneous catalyst of initial concentration C_0 is present in two forms, either as free catalyst C or combined in an appreciable extent to form intermediate X, an accounting for the catalyst gives

$$[C_0] = [C] + [X]$$

We then also assume that either

$$\frac{dX}{dt} = 0$$

or that the intermediate is in equilibrium with its reactants; thus,



where

$$K = \frac{k_1}{k_2} = \frac{[X]}{[A][C]}$$

Example 2.2 and Problem 2.23 deal with this type of intermediate.

The trial-and-error procedure involved in searching for a mechanism is illustrated in the following two examples.

EXAMPLE 2.1 SEARCH FOR THE REACTION MECHANISM

The irreversible reaction



has been studied kinetically, and the rate of formation of product has been found to be well correlated by the following rate equation:

$$r_{AB} = kC_B^2 \dots \text{independent of } C_A. \quad (11)$$

What reaction mechanism is suggested by this rate expression if the chemistry of the reaction suggests that the intermediate consists of an association of reactant molecules and that a chain reaction does not occur?

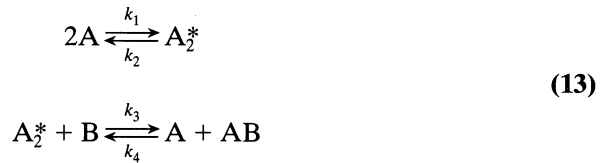
SOLUTION

If this were an elementary reaction, the rate would be given by

$$r_{AB} = kC_A C_B = k[A][B] \quad (12)$$

Since Eqs. 11 and 12 are not of the same type, the reaction evidently is nonelementary. Consequently, let us try various mechanisms and see which gives a rate expression similar in form to the experimentally found expression. We start with simple two-step models, and if these are unsuccessful we will try more complicated three-, four-, or five-step models.

Model 1. Hypothesize a two-step reversible scheme involving the formation of an intermediate substance A_2^* , not actually seen and hence thought to be present only in small amounts. Thus,



which really involves four elementary reactions



Let the k values refer to the components disappearing; thus, k_1 refers to A , k_2 refers to A_2^* , etc.

Now write the expression for the rate of formation of AB . Since this component is involved in Eqs. 16 and 17, its overall rate of change is the sum of the individual rates. Thus,

$$r_{AB} = k_3[A_2^*][B] - k_4[A][AB] \quad (18)$$

Because the concentration of intermediate A_2^* is so small and not measurable, the above rate expression cannot be tested in its present form. So, replace $[A_2^*]$ by concentrations that can be measured, such as $[A]$, $[B]$, or $[AB]$. This is done in the following manner. From the four elementary reactions that all involve A_2^* we find

$$r_{A_2^*} = \frac{1}{2} k_1[A]^2 - k_2[A_2^*] - k_3[A_2^*][B] + k_4[A][AB] \quad (19)$$

Because the concentration of A_2^* is always extremely small we may assume that its rate of change is zero or

$$r_{A_2^*} = 0 \quad (20)$$

This is the steady-state approximation. Combining Eqs. 19 and 20 we then find

$$[A_2^*] = \frac{\frac{1}{2} k_1[A]^2 + k_4[A][AB]}{k_2 + k_3[B]} \quad (21)$$

which, when replaced in Eq. 18, simplifying and cancelling two terms (two terms will always cancel if you are doing it right), gives the rate of formation of AB in terms of measurable quantities. Thus,

$$r_{AB} = \frac{\frac{1}{2} k_1 k_3 [A]^2 [B] - k_2 k_4 [A][AB]}{k_2 + k_3 [B]} \quad (22)$$

In searching for a model consistent with observed kinetics we may, if we wish, restrict a more general model by arbitrarily selecting the magnitude of the various rate constants. Since Eq. 22 does not match Eq. 11, let us see if any of its simplified forms will. Thus, if k_2 is very small, this expression reduces to

$$r_{AB} = \frac{1}{2} k_1 [A]^2 \quad (23)$$

If k_4 is very small, r_{AB} reduces to

$$r_{AB} = \frac{(k_1 k_3 / 2k_2) [A]^2 [B]}{1 + (k_3 / k_2) [B]} \quad (24)$$

Neither of these special forms, Eqs. 23 and 24, matches the experimentally found rate, Eq. 11. Thus, the hypothesized mechanism, Eq. 13, is incorrect, so another needs to be tried.

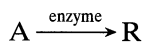
Model 2. First note that the stoichiometry of Eq. 10 is symmetrical in A and B, so just interchange A and B in Model 1, put $k_2 = 0$ and we will get $r_{AB} = k[B]^2$, which is what we want. So the mechanism that will match the second-order rate equation is



We are fortunate in this example to have represented our data by a form of equation which happened to match exactly that obtained from the theoretical mechanism. Often a number of different equation types will fit a set of experimental data equally well, especially for somewhat scattered data. Hence, to avoid rejecting the correct mechanism, it is advisable to test the fit of the various theoretically derived equations to the raw data using statistical criteria whenever possible, rather than just matching equation forms.

EXAMPLE 2.2 SEARCH FOR A MECHANISM FOR THE ENZYME-SUBSTRATE REACTION

Here, a reactant, called the *substrate*, is converted to product by the action of an enzyme, a high molecular weight ($mw > 10\,000$) protein-like substance. An enzyme is highly specific, catalyzing one particular reaction, or one group of reactions. Thus,



Many of these reactions exhibit the following behavior:

1. A rate proportional to the concentration of enzyme introduced into the mixture $[E_0]$.
2. At low reactant concentration the rate is proportional to the reactant concentration, $[A]$.
3. At high reactant concentration the rate levels off and becomes independent of reactant concentration.

Propose a mechanism to account for this behavior.

SOLUTION

Michaelis and Menten (1913) were the first to solve this puzzle. (By the way, Michaelis received the Nobel prize in chemistry.) They guessed that the reaction proceeded as follows



with the two assumptions

$$[E_0] = [E] + [X] \quad (27)$$

and

$$\frac{dX}{dt} \cong 0 \quad (28)$$

First write the rates for the pertinent reaction components of Eq. 26. This gives

$$\frac{d[R]}{dt} = k_3[X] \quad (29)$$

and

$$\frac{d[X]}{dt} = k_1[A][E] - k_2[X] - k_3[X] = 0 \quad (30)$$

Eliminating $[E]$ from Eqs. 27 and 30 gives

$$[X] = \frac{k_1[A][E_0]}{(k_2 + k_3) + k_1[A]} \quad (31)$$

and when Eq. 31 is introduced into Eq. 29 we find

$$\frac{d[R]}{dt} = \frac{k_1 k_3 [A][E_0]}{(k_2 + k_3) + k_1 [A]} = \frac{k_3 [A][E_0]}{[M] + [A]} \quad (32)$$

$[M] = \left(\frac{k_2 + k_3}{k_1} \right)$ is called
 the Michaelis constant

By comparing with experiment, we see that this equation fits the three reported facts:

$$\frac{-d[A]}{dt} = \frac{d[R]}{dt} \begin{cases} \propto [E_0] \\ \propto [A] \text{ when } [A] \ll [M] \\ \text{is independent of } [A] \text{ when } [A] \gg [M] \end{cases}$$

For more discussion about this reaction, see Problem 2.23.

2.2 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

$$\begin{aligned} r_i &= f_1(\text{temperature}) \cdot f_2(\text{composition}) \\ &= k \cdot f_2(\text{composition}) \end{aligned} \quad (33)$$

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:

$$k = k_0 e^{-E/RT} \quad (34)$$

where k_0 is called the frequency or pre-exponential factor and E is called the activation energy of the reaction.* This expression fits experiment well over wide temperature ranges and is strongly suggested from various standpoints as being a very good approximation to the true temperature dependency.

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

$$\ln \frac{r_2}{r_1} = \ln \frac{k_2}{k_1} = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (35)$$

provided that E stays constant.

Comparison of Theories with Arrhenius' Law

The expression

$$k = k_0' T^m e^{-E/RT}, \quad 0 \leq m \leq 1 \quad (36)$$

summarizes the predictions of the simpler versions of the collision and transition state theories for the temperature dependency of the rate constant. For more complicated versions m can be as great as 3 or 4. Now, because the exponential term is so much more temperature-sensitive than the pre-exponential term, the variation of the latter with temperature is effectively masked, and we have in effect

$$k = k_0 e^{-E/RT} \quad (34)$$

* There seems to be a disagreement in the dimensions used to report the activation energy; some authors use joules and others use joules per mole. However, joules per mole are clearly indicated in Eq. 34.

But what moles are we referring to in the units of E ? This is unclear. However, since E and R always appear together, and since they both refer to the same number of moles, this bypasses the problem. This whole question can be avoided by using the ratio E/R throughout.

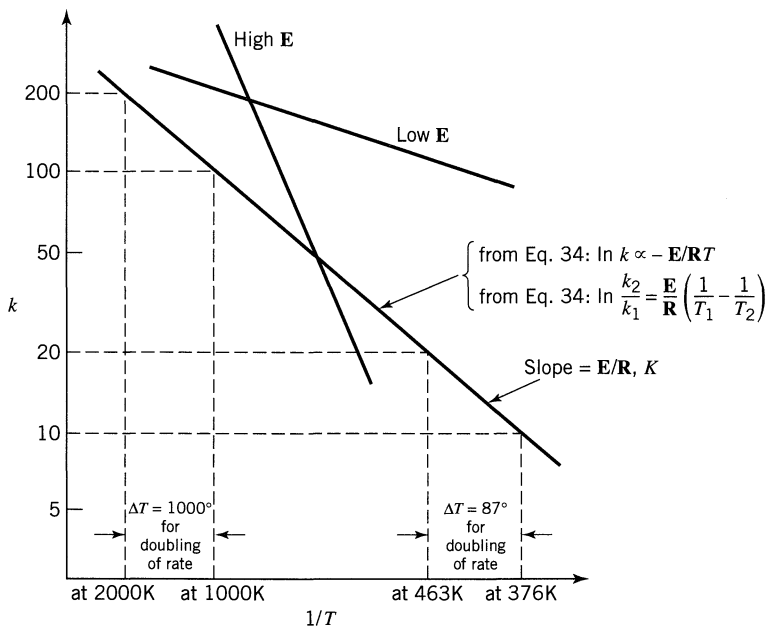


Figure 2.2 Sketch showing temperature dependency of the reaction rate.

This shows that Arrhenius' law is a good approximation to the temperature dependency of both collision and transition-state theories.

Activation Energy and Temperature Dependency

The temperature dependency of reactions is determined by the activation energy and temperature level of the reaction, as illustrated in Fig. 2.2 and Table 2.1. These findings are summarized as follows:

1. From Arrhenius' law a plot of $\ln k$ 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.

Table 2.1 Temperature Rise Needed to Double the Rate of Reaction for Activation Energies and Average Temperatures Shown^a

Average Temperature	Activation Energy E			
	40 kJ/mol	160 kJ/mol	280 kJ/mol	400 kJ/mol
0°C	11°C	2.7°C	1.5°C	1.1°C
400°C	65	16	9.3	6.5
1000°C	233	58	33	23
2000°C	744	185	106	74

^a Shows temperature sensitivity of reactions.

- Any given reaction is much more temperature-sensitive at a low temperature than at a high temperature.
- From the Arrhenius law, the value of the frequency factor k_0 does not affect the temperature sensitivity.

EXAMPLE 2.3 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 $\propto 1/\text{time}$ 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

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

2.3 SEARCHING FOR A MECHANISM

The more we know about what is occurring during reaction, what the reacting materials are, and how they react, the more assurance we have for proper design. This is the incentive to find out as much as we can about the factors influencing a reaction within the limitations of time and effort set by the economic optimization of the process.

There are three areas of investigation of a reaction, the *stoichiometry*, the *kinetics*, and the *mechanism*. In general, the stoichiometry is studied first, and when this is far enough along, the kinetics is then investigated. With empirical rate expressions available, the mechanism is then looked into. In any investigative

program considerable feedback of information occurs from area to area. For example, our ideas about the stoichiometry of the reaction may change on the basis of kinetic data obtained, and the form of the kinetic equations themselves may be suggested by mechanism studies. With this kind of relationship of the many factors, no straightforward experimental program can be formulated for the study of reactions. Thus, it becomes a matter of shrewd scientific detective work, with carefully planned experimental programs especially designed to discriminate between rival hypotheses, which in turn have been suggested and formulated on the basis of all available pertinent information.

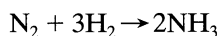
Although we cannot delve into the many aspects of this problem, a number of clues that are often used in such experimentation can be mentioned.

1. Stoichiometry can tell whether we have a single reaction or not. Thus, a complicated stoichiometry



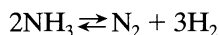
or one that changes with reaction conditions or extent of reaction is clear evidence of multiple reactions.

2. Stoichiometry can suggest whether a single reaction is elementary or not because no elementary reactions with molecularity greater than three have been observed to date. As an example, the reaction



is not elementary.

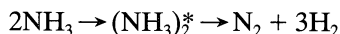
3. A comparison of the stoichiometric equation with the experimental kinetic expression can suggest whether or not we are dealing with an elementary reaction.
4. A large difference in the order of magnitude between the experimentally found frequency factor of a reaction and that calculated from collision theory or transition-state theory may suggest a nonelementary reaction; however, this is not necessarily true. For example, certain isomerizations have very low frequency factors and are still elementary.
5. Consider two alternative paths for a simple reversible reaction. If one of these paths is preferred for the forward reaction, the same path must also be preferred for the reverse reaction. This is called the *principle of microscopic reversibility*. Consider, for example, the forward reaction of



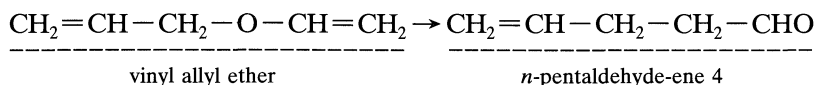
At a first sight this could very well be an elementary bimolecular reaction with two molecules of ammonia combining to yield directly the four product molecules. From this principle, however, the reverse reaction would then also have to be an elementary reaction involving the direct combination of three molecules of hydrogen with one of nitrogen. Because such a process is rejected as improbable, the bimolecular forward mechanism must also be rejected.

6. The principle of microreversibility also indicates that changes involving bond rupture, molecular syntheses, or splitting are likely to occur one at a

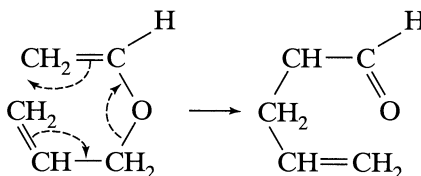
time, each then being an elementary step in the mechanism. From this point of view, the simultaneous splitting of the complex into the four product molecules in the reaction



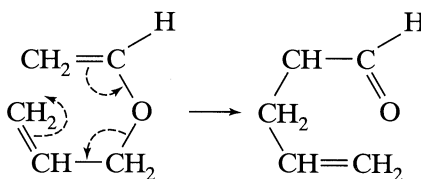
is very unlikely. This rule does not apply to changes that involve a shift in electron density along a molecule, which may take place in a cascade-like manner. For example, the transformation



can be expressed in terms of the following shifts in electron density:



or



7. For multiple reactions a change in the observed activation energy with temperature indicates a shift in the controlling mechanism of reaction. Thus, for an increase in temperature E_{obs} rises for reactions or steps in parallel, E_{obs} falls for reactions or steps in series. Conversely, for a decrease in temperature E_{obs} falls for reactions in parallel, E_{obs} rises for reactions in series. These findings are illustrated in Fig. 2.3.

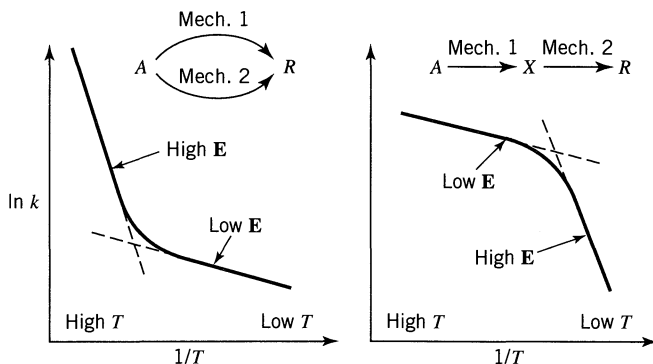


Figure 2.3 A change in activation energy indicates a shift in controlling mechanism of reaction.

2.4 PREDICTABILITY OF REACTION RATE FROM THEORY

Concentration-Dependent Term

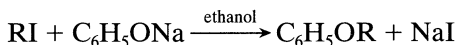
If a reaction has available a number of competing paths (e.g., noncatalytic and catalytic), it will in fact proceed by all of these paths, although primarily by the one of least resistance. This path usually dominates. Only a knowledge of the energies of all possible intermediates will allow prediction of the dominant path and its corresponding rate expression. As such information cannot be found in the present state of knowledge, a priori prediction of the form of the concentration term is not possible. Actually, the form of the experimentally found rate expression is often the clue used to investigate the energies of the intermediates of a reaction.

Temperature-Dependent Term

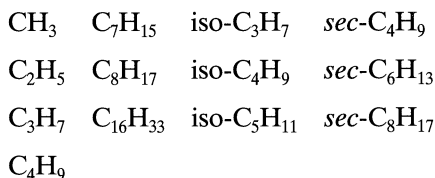
Assuming that we already know the mechanism of reaction and whether or not it is elementary, we may then proceed to the prediction of the frequency factor and activation energy terms of the rate constant.

If we are lucky, frequency factor predictions from either collision or transition-state theory may come within a factor of 100 of the correct value; however, in specific cases predictions may be much further off.

Though activation energies can be estimated from transition-state theory, reliability is poor, and it is probably best to estimate them from the experimental findings for reactions of similar compounds. For example, the activation energies of the following homologous series of reactions



where R is



all lie between 90 and 98 kJ.

Use of Predicted Values in Design

The frequent order-of-magnitude predictions of the theories tend to confirm the correctness of their representations, help find the form and the energies of various intermediates, and give us a better understanding of chemical structure. However, theoretical predictions rarely match experiment by a factor of two. In addition, we can never tell beforehand whether the predicted rate will be in the order of magnitude of experiment or will be off by a factor of 10^6 . Therefore, for engi-

neering design, this kind of information should not be relied on and experimentally found rates should be used in all cases. Thus, theoretical studies may be used as a supplementary aid to suggest the temperature sensitivity of a given reaction from a similar type of reaction, to suggest the upper limits of reaction rate, etc. Design invariably relies on experimentally determined rates.

RELATED READING

Jungers, J. C., et al., *Cinétique chimique appliquée*, Technip, Paris, 1958.
 Laidler, K. J., *Chemical Kinetics*, 2nd ed., Harper and Row, New York, 1987.
 Moore, W. J., *Basic Physical Chemistry*, Prentice-Hall, Upper Saddle River, NJ, 1983.

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Lindemann, F. A., *Trans. Faraday Soc.*, **17**, 598 (1922).
 Michaelis, L., and Menten, M. L., *Biochem. Z.*, **49**, 333 (1913). This treatment is discussed by Laidler (1987), see Related Readings.

PROBLEMS

- 2.1. A reaction has the stoichiometric equation $A + B = 2R$. What is the order of reaction?
- 2.2. Given the reaction $2NO_2 + \frac{1}{2} O_2 = N_2O_5$, what is the relation between the rates of formation and disappearance of the three reaction components?
- 2.3. 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 $A + 2B = 2R + S$?

- 2.4. For the enzyme-substrate reaction of Example 2, the rate of disappearance of substrate is given by

$$-r_A = \frac{1760[A][E_0]}{6 + C_A}, \quad \text{mol/m}^3 \cdot \text{s}$$

What are the units of the two constants?

- 2.5. For the complex reaction with stoichiometry $A + 3B \rightarrow 2R + S$ and with second-order rate expression

$$-r_A = k_1[A][B]$$

are the reaction rates related as follows: $r_A = r_B = r_R$? If the rates are not so related, then how are they related? Please account for the signs, + or -.

- 2.6. A certain reaction has a rate given by

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

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?

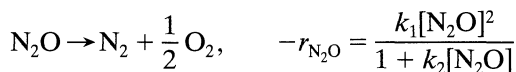
- 2.7. For a gas reaction at 400 K the rate is reported as

$$-\frac{dp_A}{dt} = 3.66p_A^2, \quad \text{atm/hr}$$

- (a) What are the units of the rate constant?
 (b) What is the value of the rate constant for this reaction if the rate equation is expressed as

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt} = kC_A^2, \quad \text{mol/m}^3 \cdot \text{s}$$

- 2.8. The decomposition of nitrous oxide is found to proceed as follows:



What is the order of this reaction with respect to N_2O , and overall?

- 2.9. 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?
- 2.10. 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.
- 2.11. In the mid-nineteenth century the entomologist Henri Fabre noted that French ants (garden variety) busily bustled about their business on hot

days but were rather sluggish on cool days. Checking his results with Oregon ants, I find

Running speed, m/hr		150	160	230	295	370
Temperature, °C		13	16	22	24	28

What activation energy represents this change in bustliness?

2.12. The maximum allowable temperature for a reactor is 800 K. At present our operating set point is 780 K, the 20-K margin of safety to account for fluctuating feed, sluggish controls, etc. Now, with a more sophisticated control system we would be able to raise our set point to 792 K with the same margin of safety that we now have. By how much can the reaction rate, hence, production rate, be raised by this change if the reaction taking place in the reactor has an activation energy of 175 kJ/mol?

2.13. Every May 22 I plant one watermelon seed. I water it, I fight slugs, I pray, I watch my beauty grow, and finally the day comes when the melon ripens. I then harvest and feast. Of course, some years are sad, like 1980, when a bluejay flew off with the seed. Anyway, six summers were a pure joy and for these I've tabulated the number of growing days versus the mean daytime temperature during the growing season. Does the temperature affect the growth rate? If so, represent this by an activation energy.

Year		1976	1977	1982	1984	1985	1988
Growing days		87	85	74	78	90	84
Mean temp, °C		22.0	23.4	26.3	24.3	21.1	22.7

2.14. On typical summer days, field crickets nibble, jump, and chirp now and then. But at a night when great numbers congregate, chirping seems to become a serious business and tends to be in unison. In 1897, A. E. Dolbear (*Am. Naturalist*, **31**, 970) reported that this social chirping rate was dependent on the temperature as given by

$$(\text{number of chirps in 15 s}) + 40 = (\text{temperature, } ^\circ\text{F})$$

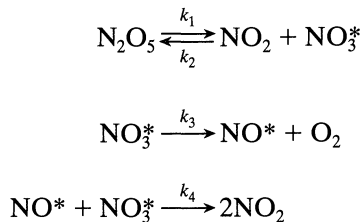
Assuming that the chirping rate is a direct measure of the metabolic rate, find the activation energy in kJ/mol of these crickets in the temperature range 60–80°F.

2.15. On doubling the concentration of reactant, the rate of reaction triples. Find the reaction order.

For the stoichiometry $A + B \rightarrow (\text{products})$ find the reaction orders with respect to A and B.

$$\begin{array}{l}
 C_A \\
 \mathbf{2.16.} \quad C_B \\
 -r_A
 \end{array}
 \left| \begin{array}{ccc}
 4 & 1 & 1 \\
 1 & 1 & 8 \\
 2 & 1 & 4
 \end{array} \right.
 \quad
 \begin{array}{l}
 C_A \\
 \mathbf{2.17.} \quad C_B \\
 -r_A
 \end{array}
 \left| \begin{array}{ccc}
 2 & 2 & 3 \\
 125 & 64 & 64 \\
 50 & 32 & 48
 \end{array} \right.$$

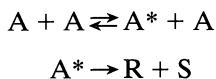
2.18. Show that the following scheme



proposed by R. Ogg, *J. Chem. Phys.*, **15**, 337 (1947) is consistent with, and can explain, the observed first-order decomposition of N_2O_5 .

2.19. The decomposition of reactant A at 400°C for pressures between 1 and 10 atm follows a first-order rate law.

(a) Show that a mechanism similar to azomethane decomposition, p. 21,



is consistent with the observed kinetics.

Different mechanisms can be proposed to explain first-order kinetics. To claim that this mechanism is correct in the face of the other alternatives requires additional evidence.

(b) For this purpose, what further experiments would you suggest we run and what results would you expect to find?

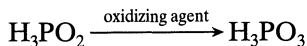
2.20. Experiment shows that the homogeneous decomposition of ozone proceeds with a rate

$$-r_{\text{O}_3} = k[\text{O}_3]^2 [\text{O}_2]^{-1}$$

(a) What is the overall order of reaction?

(b) Suggest a two-step mechanism to explain this rate and state how you would further test this mechanism.

2.21. Under the influence of oxidizing agents, hypophosphorous acid is transformed into phosphorous acid:



The kinetics of this transformation present the following features. At a low concentration of oxidizing agent,

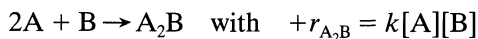
$$r_{\text{H}_3\text{PO}_3} = k[\text{oxidizing agent}][\text{H}_3\text{PO}_2]$$

At a high concentration of oxidizing agent,

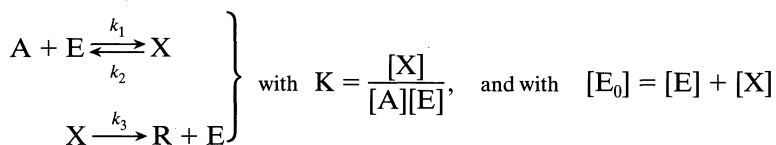
$$r_{\text{H}_3\text{PO}_3} = k'[\text{H}^+][\text{H}_3\text{PO}_2]$$

To explain the observed kinetics, it has been postulated that, with hydrogen ions as catalyst, normal unreactive H_3PO_2 is transformed reversibly into an active form, the nature of which is unknown. This intermediate then reacts with the oxidizing agent to give H_3PO_3 . Show that this scheme does explain the observed kinetics.

- 2.22.** Come up with (guess and then verify) a mechanism that is consistent with the experimentally found rate equation for the following reaction

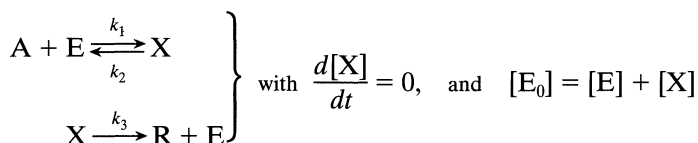


- 2.23.** *Mechanism for enzyme catalyzed reactions.* To explain the kinetics of enzyme-substrate reactions, Michaelis and Menten (1913) came up with the following mechanism, which uses an equilibrium assumption



and where $[\text{E}_0]$ represents the total enzyme and $[\text{E}]$ represents the free unattached enzyme.

G. E. Briggs and J. B. S. Haldane, *Biochem J.*, **19**, 338 (1925), on the other hand, employed a steady-state assumption in place of the equilibrium assumption



What final rate form $-r_{\text{A}}$ in terms of $[\text{A}]$, $[\text{E}_0]$, k_1 , k_2 , and k_3 does

- (a) the Michaelis-Menten mechanism give?
 (b) the Briggs-Haldane mechanism give?

Chapter 3

Interpretation of Batch Reactor Data

A rate equation characterizes the rate of reaction, and its form may either be suggested by theoretical considerations or simply be the result of an empirical curve-fitting procedure. In any case, the value of the constants of the equation can only be found by experiment; predictive methods are inadequate at present.

The determination of the rate equation is usually a two-step procedure; first the concentration dependency is found at fixed temperature and then the temperature dependence of the rate constants is found, yielding the complete rate equation.

Equipment by which empirical information is obtained can be divided into two types, the *batch* and *flow* reactors. The batch reactor is simply a container to hold the contents while they react. All that has to be determined is the extent of reaction at various times, and this can be followed in a number of ways, for example:

1. By following the concentration of a given component.
2. By following the change in some physical property of the fluid, such as the electrical conductivity or refractive index.
3. By following the change in total pressure of a constant-volume system.
4. By following the change in volume of a constant-pressure system.

The experimental batch reactor is usually operated isothermally and at constant volume because it is easy to interpret the results of such runs. This reactor is a relatively simple device adaptable to small-scale laboratory set-ups, and it needs but little auxiliary equipment or instrumentation. Thus, it is used whenever possible for obtaining homogeneous kinetic data. This chapter deals with the batch reactor.

The flow reactor is used primarily in the study of the kinetics of heterogeneous reactions. Planning of experiments and interpretation of data obtained in flow reactors are considered in later chapters.

There are two procedures for analyzing kinetic data, the *integral* and the *differential* methods. In the integral method of analysis we guess a particular form of rate equation and, after appropriate 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 $(1/V)(dN/dt)$ from the data before attempting the fitting procedure.

There are advantages and disadvantages to each method. The integral method is easy to use and is recommended when testing specific mechanisms, or relatively simple rate expressions, or when the data are so scattered that we cannot reliably find the derivatives needed in the differential method. The differential method is useful in more complicated situations but requires more accurate or larger amounts of data. The integral method can only test this or that particular mechanism or rate form; the differential method can be used to develop or build up a rate equation to fit the data.

In general, it is suggested that integral analysis be attempted first, and, if not successful, that the differential method be tried.

3.1 CONSTANT-VOLUME BATCH REACTOR

When we mention the constant-volume batch reactor we are really referring 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

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

or for ideal gases, where $C = p/RT$,

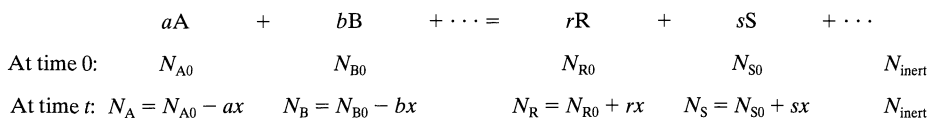
$$r_i = \frac{1}{RT} \frac{dp_i}{dt} \quad (2)$$

Thus, the rate of reaction of any component is given by the rate of change of its concentration or partial pressure; so no matter how we choose to follow the progress of the reaction, we must eventually relate this measure to the concentration or partial pressure if we are to follow the rate of reaction.

For gas reactions with changing numbers of moles, a simple way of finding the reaction rate is to follow the change in total pressure π of the system. Let us see how this is done.

Analysis of Total Pressure Data Obtained in a Constant-Volume System. For isothermal gas reactions where the number of moles of material changes during reaction, let us develop the general expression which relates the changing total pressure of the system π to the changing concentration or partial pressure of any of the reaction components.

Write the general stoichiometric equation, and under each term indicate the number of moles of that component:



Initially the total number of moles present in the system is

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

but at time t it is

$$N = N_0 + x(r + s + \cdots - a - b - \cdots) = N_0 + x \Delta n \quad (3)$$

where

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

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

$$C_A = \frac{p_A}{RT} = \frac{N_A}{V} = \frac{N_{A0} - ax}{V} \quad (4)$$

Combining Eqs. 3 and 4 we obtain

$$C_A = \frac{N_{A0}}{V} - \frac{a}{\Delta n} \frac{N - N_0}{V}$$

or

$$p_A = C_A RT = p_{A0} - \frac{a}{\Delta n} (\pi - \pi_0) \quad (5)$$

Equation 5 gives the concentration or partial pressure of reactant A as a function of the total pressure π at time t , initial partial pressure of A, p_{A0} , and initial total pressure of the system, π_0 .

Similarly, for any product R we can find

$$p_R = C_R RT = p_{R0} + \frac{r}{\Delta n} (\pi - \pi_0) \quad (6)$$

Equations 5 and 6 are the desired relationships between total pressure of the system and the partial pressure of reacting materials.

It should be emphasized that if the precise stoichiometry is not known, or if more than one stoichiometric equation is needed to represent the reaction, then the "total pressure" procedure cannot be used.

The Conversion. Let us introduce one other useful term, the fractional conversion, or the fraction of any reactant, say A, converted to something else, or the fraction of A reacted away. We call this, simply, the conversion of A, with symbol X_A .

Suppose that N_{A0} 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

$$X_A = \frac{N_{A0} - N_A}{N_{A0}} = 1 - \frac{N_A/V}{N_{A0}/V} = 1 - \frac{C_A}{C_{A0}} \quad (7)$$

and

$$dX_A = -\frac{dC_A}{C_{A0}} \quad (8)$$

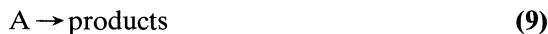
We will develop the equations in this chapter in terms of concentration of reaction components and also in terms of conversions.

Later we will relate X_A and C_A for the more general case where the volume of the system does not stay constant.

Integral Method of Analysis of Data

General Procedure. The integral method of analysis always puts a particular rate equation to the test by integrating and comparing the predicted C versus t curve with the experimental C versus t data. If the fit is unsatisfactory, another rate equation is guessed and tested. This procedure is shown and used in the cases next treated. It should be noted that the integral method is especially useful for fitting simple reaction types corresponding to elementary reactions. Let us take up these kinetic forms.

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



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

$$-r_A = -\frac{dC_A}{dt} = kC_A \quad (10)$$

for this reaction. Separating and integrating we obtain

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

or

$$-\ln \frac{C_A}{C_{A0}} = kt \quad (11)$$

In terms of conversion (see Eqs. 7 and 8), the rate equation, Eq. 10, becomes

$$\frac{dX_A}{dt} = k(1 - X_A)$$

which on rearranging and integrating gives

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

or

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

A plot of $\ln(1 - X_A)$ or $\ln(C_A/C_{A0})$ vs. t , as shown in Fig. 3.1, gives a straight line through the origin for this form of rate of equation. If the experimental data seems to be better fitted by a curve than by a straight line, try another rate form because the first-order reaction does not satisfactorily fit the data.

Caution. We should point out that equations such as

$$-\frac{dC_A}{dt} = kC_A^{0.6}C_B^{0.4}$$

are first order but are not amenable to this kind of analysis; hence, not all first-order reactions can be treated as shown above.

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

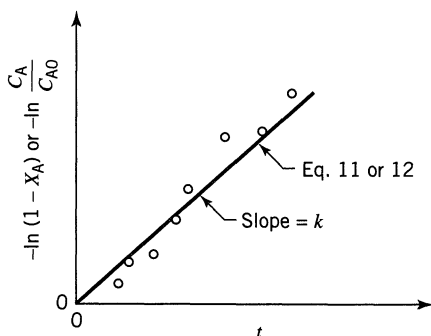
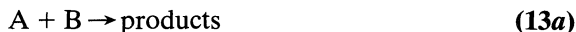


Figure 3.1 Test for the first-order rate equation, Eq. 10.

with corresponding rate equation

$$-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_A C_B \quad (13b)$$

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

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

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

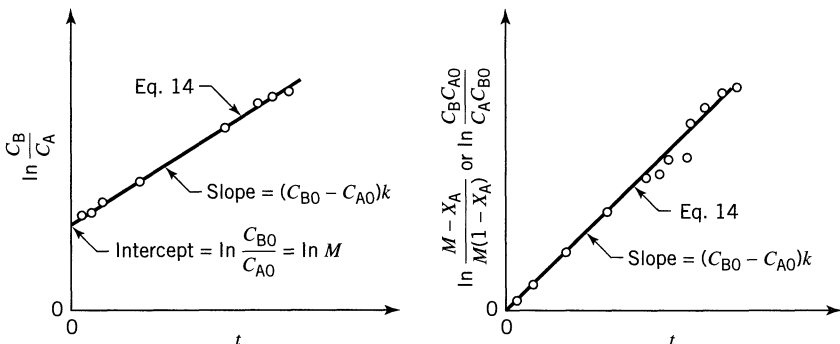


Figure 3.2 Test for the bimolecular mechanism $A + B \rightarrow R$ with $C_{A0} \neq C_{B0}$, or for the second-order reaction, Eq. 13.

If C_{B0} is much larger than C_{A0} , C_B remains approximately constant at all times, and Eq. 14 approaches Eq. 11 or 12 for the first-order reaction. Thus, the second-order reaction becomes a pseudo first-order reaction.

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



the defining second-order differential equation becomes

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

which on integration yields

$$\boxed{\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{1}{C_{A0}} \frac{X_A}{1 - X_A} = kt} \quad (16)$$

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.

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

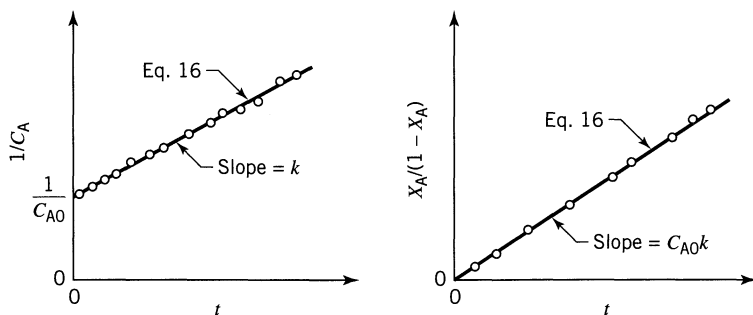


Figure 3.3 Test for the bimolecular mechanisms, $A + B \rightarrow R$ with $C_{A0} = C_{B0}$, or for the second-order reaction of Eq. 15.

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

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

The integrated form is

$$\ln \frac{C_B C_{A0}}{C_{B0} C_A} = \ln \frac{M - 2X_A}{M(1 - X_A)} = C_{A0}(M - 2)kt, \quad M \neq 2 \quad (18)$$

When a stoichiometric reactant ratio is used the integrated form is

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{1}{C_{A0}} \frac{X_A}{1 - X_A} = 2kt, \quad M = 2 \quad (19)$$

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.

Irreversible Trimolecular-Type Third-Order Reactions. For the reaction



let the rate equation be

$$-r_A = -\frac{dC_A}{dt} = kC_A C_B C_D \quad (20b)$$

or in terms of X_A

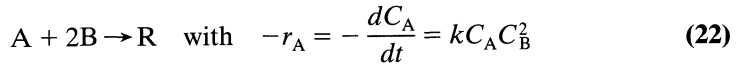
$$C_{A0} \frac{dX_A}{dt} = kC_{A0}^3 (1 - X_A) \left(\frac{C_{B0}}{C_{A0}} - X_A \right) \left(\frac{C_{D0}}{C_{A0}} - X_A \right)$$

On separation of variables, breakdown into partial fractions, and integration, we obtain after manipulation

$$\begin{aligned} \frac{1}{(C_{A0} - C_{B0})(C_{A0} - C_{D0})} \ln \frac{C_{A0}}{C_A} + \frac{1}{(C_{B0} - C_{D0})(C_{B0} - C_{A0})} \ln \frac{C_{B0}}{C_B} \\ + \frac{1}{(C_{D0} - C_{A0})(C_{D0} - C_{B0})} \ln \frac{C_{D0}}{C_D} = kt \end{aligned} \quad (21)$$

Now if C_{D0} is much larger than both C_{A0} and C_{B0} , the reaction becomes second order and Eq. 21 reduces to Eq. 14.

All trimolecular reactions found so far are of the form of Eq. 22 or 25. Thus



In terms of conversions the rate of reaction becomes

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

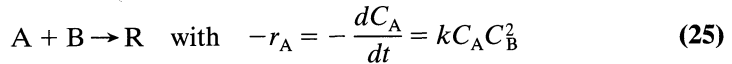
where $M = C_{B0}/C_{A0}$. On integration this gives

$$\frac{(2C_{A0} - C_{B0})(C_{B0} - C_B)}{C_{B0}C_B} + \ln \frac{C_{A0}C_B}{C_A C_{B0}} = (2C_{A0} - C_{B0})^2 kt, \quad M \neq 2 \quad (23)$$

or

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = 8kt, \quad M = 2 \quad (24)$$

Similarly, for the reaction



integration gives

$$\frac{(C_{A0} - C_{B0})(C_{B0} - C_B)}{C_{B0}C_B} + \ln \frac{C_{A0}C_B}{C_{B0}C_A} = (C_{A0} - C_{B0})^2 kt, \quad M \neq 1 \quad (26)$$

or

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = 2kt, \quad M = 1 \quad (27)$$

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

$$-r_A = -\frac{dC_A}{dt} = kC_A^n \quad (28)$$

which on separation and integration yields

$$C_A^{1-n} - C_{A0}^{1-n} = (n-1)kt, \quad n \neq 1 \quad (29)$$

The order n cannot be found explicitly from Eq. 29, so a trial-and-error solution must be made. This is not too difficult, however. Just select a value for n and calculate k . The value of n which minimizes the variation in k is the desired value of n .

One curious feature of this rate form is that reactions with order $n > 1$ can never go to completion in finite time. On the other hand, for orders $n < 1$ this rate form predicts that the reactant concentration will fall to zero and then become negative at some finite time, found from Eq. 29, so

$$C_A = 0 \quad \text{at} \quad t \geq \frac{C_{A0}^{1-n}}{(1-n)k}$$

Since the real concentration cannot fall below zero we should not carry out the integration beyond this time for $n < 1$. Also, as a consequence of this feature, in real systems the observed fractional order will shift upward to unity as reactant is depleted.

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

$$-r_A = -\frac{dC_A}{dt} = k \quad (30)$$

Integrating and noting that C_A can never become negative, we obtain directly

$$\boxed{\begin{aligned} C_{A0} - C_A = C_{A0}X_A = kt \quad \text{for} \quad t < \frac{C_{A0}}{k} \\ C_A = 0 \quad \text{for} \quad t \geq \frac{C_{A0}}{k} \end{aligned}} \quad (31)$$

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

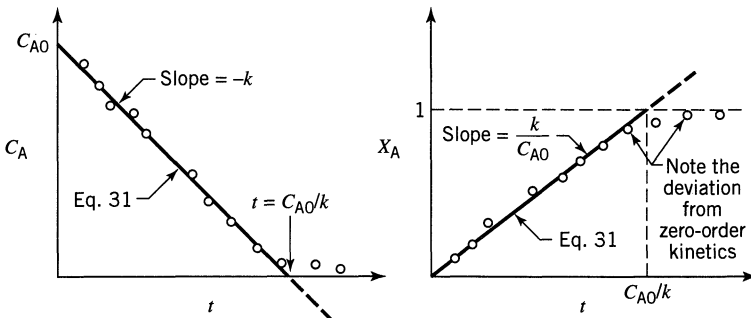


Figure 3.4 Test for a zero-order reaction, or rate equation, Eq. 30.

find that the reaction becomes concentration-dependent, in which case the order rises from zero.

In general, zero-order reactions are those whose rates are determined by some factor other than the concentration of the reacting materials, e.g., the intensity of radiation within the vat for photochemical reactions, or the surface available in certain solid catalyzed gas reactions. It is important, then, to define the rate of zero-order reactions so that this other factor is included and properly accounted for.

Overall Order of Irreversible Reactions from the Half-Life $t_{1/2}$. Sometimes, for the irreversible reaction



we may write

$$-r_A = -\frac{dC_A}{dt} = kC_A^a C_B^b \dots$$

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

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

or

$$-\frac{dC_A}{dt} = \tilde{k}C_A^n \quad (32)$$

Integrating for $n \neq 1$ gives

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

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

$$\boxed{t_{1/2} = \frac{(0.5)^{1-n} - 1}{\tilde{k}(n-1)} C_{A0}^{1-n}} \quad (33a)$$

This expression shows that a plot of $\log t_{1/2}$ vs. $\log C_{A0}$ gives a straight line of slope $1 - n$, as shown in Fig. 3.5.

The half-life method requires making a series of runs, each at a different initial concentration, and shows that the fractional conversion in a given time rises with increased concentration for orders greater than one, drops with increased

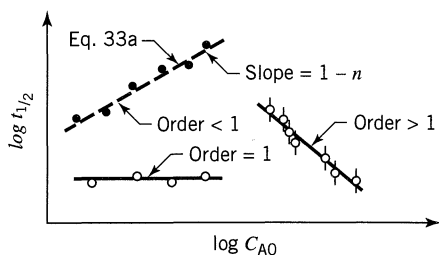


Figure 3.5 Overall order of reaction from a series of half-life experiments, each at a different initial concentration of reactant.

concentration for orders less than one, and is independent of initial concentration for reactions of first order.

Numerous variations of this procedure are possible. For instance, by having all but one component, say A in large excess, we can find the order with respect to that one component. For this situation the general expression reduces to

$$-\frac{dC_A}{dt} = \hat{k}C_A^a$$

where

$$\hat{k} = k(C_{B0}^b \cdots) \quad \text{and} \quad C_B \cong C_{B0}$$

And here is another variation of the half-life method.

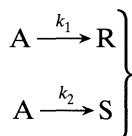
Fractional Life Method t_F . The half-life method can be extended to any fractional life method in which the concentration of reactant drops to any fractional value $F = C_A/C_{A0}$ in time t_F . The derivation is a direct extension of the half-life method giving

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

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

Example E3.1 illustrates this approach.

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



The rates of change of the three components are given by

$$-r_A = -\frac{dC_A}{dt} = k_1C_A + k_2C_A = (k_1 + k_2)C_A \quad (34)$$

$$r_R = \frac{dC_R}{dt} = k_1C_A \quad (35)$$

$$r_S = \frac{dC_S}{dt} = k_2C_A \quad (36)$$

This is the first time we have encountered multiple reactions. For these in general, if it is necessary to write N stoichiometric equations to describe what is happening, then it is necessary to follow the decomposition of N reaction components to describe the kinetics. Thus, in this system following C_A , or C_R , or C_S alone will not give both k_1 and k_2 . At least two components must be followed. Then, from the stoichiometry, noting that $C_A + C_R + C_S$ is constant, we can find the concentration of the third component.

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

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

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).

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

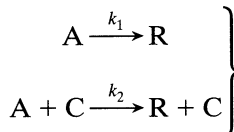
which when integrated gives simply

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

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 $C_{R0} = C_{S0} = 0$ and $k_1 > k_2$ are shown in Fig. 3.7.

Reactions in parallel are considered in detail in Chapter 7.

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



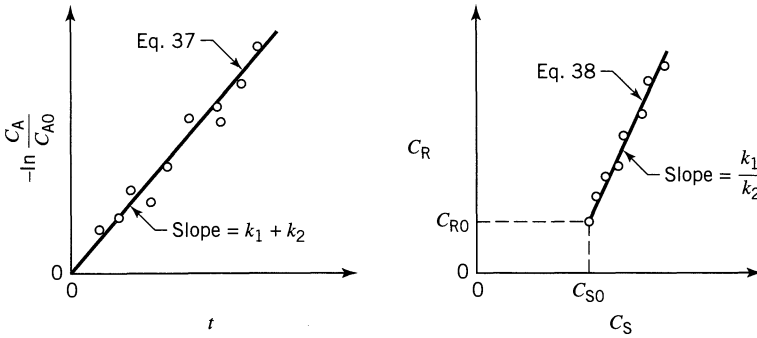
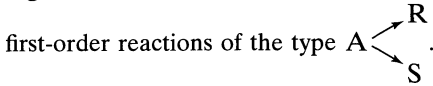


Figure 3.6 Evaluation of the rate constants for two competing elementary



with corresponding reaction rates

$$-\left(\frac{dC_A}{dt}\right)_1 = k_1 C_A$$

$$-\left(\frac{dC_A}{dt}\right)_2 = k_2 C_A C_C$$

This means that the reaction would proceed even without a catalyst present and that the rate of the catalyzed reaction is directly proportional to the catalyst concentration. The overall rate of disappearance of reactant A is then

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

On integration, noting that the catalyst concentration remains unchanged, we have

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

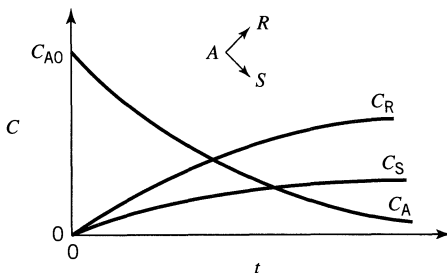


Figure 3.7 Typical concentration-time curves for competing reactions.

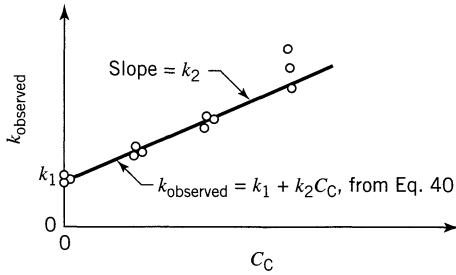


Figure 3.8 Rate constants for a homogeneous catalyzed reaction from a series of runs with different catalyst concentrations.

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



for which the rate equation is

$$-r_A = -\frac{dC_A}{dt} = kC_A C_R \quad (41b)$$

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

$$\boxed{\ln \frac{C_{A0}(C_0 - C_A)}{C_A(C_0 - C_{A0})} = \ln \frac{C_R/C_{R0}}{C_A/C_{A0}} = C_0 k t = (C_{A0} + C_{R0}) k t} \quad (42)$$

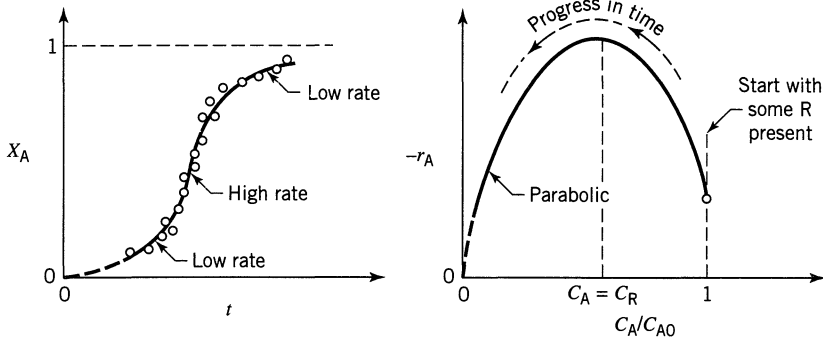


Figure 3.9 Conversion-time and rate-concentration curves for autocatalytic reaction of Eq. 41. This shape is typical for this type of reaction.

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

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

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.

Autocatalytic reactions are considered in more detail in Chapter 6.

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

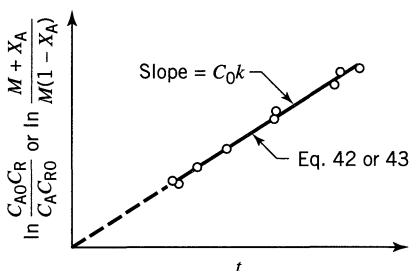
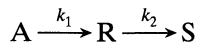


Figure 3.10 Test for the autocatalytic reaction of Eq. 41.

whose rate equations for the three components are

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

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

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

Let us start with a concentration 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

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

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

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

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

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

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

$$y e^{\int P dx} = \int Q e^{\int P dx} dx + \text{constant}$$

Applying this general procedure to the integration of Eq. 48, we find that the integrating factor is $e^{k_2 t}$. The constant of integration is found to be $-k_1 C_{A0} / (k_2 - k_1)$ from the initial conditions $C_{R0} = 0$ at $t = 0$, and the final expression for the changing concentration of R is

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

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

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

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

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

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

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

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

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

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

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

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 rises continuously, the greatest rate of increase of S occurring where R is a maximum. In particular, this figure shows that one can evaluate k_1 and k_2 by noting the maximum concentration of intermediate and the time when this maximum is reached. Chapter 8 covers series reactions in more detail.

For a longer chain of reactions, say



the treatment is similar, though more cumbersome than the two-step reaction just considered. Figure 3.12 illustrates typical concentration-time curves for this situation.

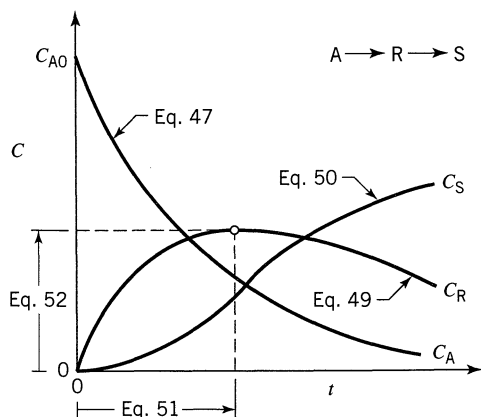
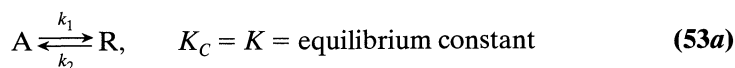


Figure 3.11 Typical concentration-time curves for consecutive first-order reactions.

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. These are the situations we have examined up to this point. Let us now consider reactions for which complete conversion cannot be assumed. The simplest case is the opposed unimolecular-type reaction



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

$$\begin{aligned} \frac{dC_R}{dt} = -\frac{dC_A}{dt} &= C_{A0} \frac{dX_A}{dt} = k_1 C_A - k_2 C_R \\ &= k_1 (C_{A0} - C_{A0} X_A) - k_2 (M C_{A0} + C_{A0} X_A) \end{aligned} \quad (53b)$$

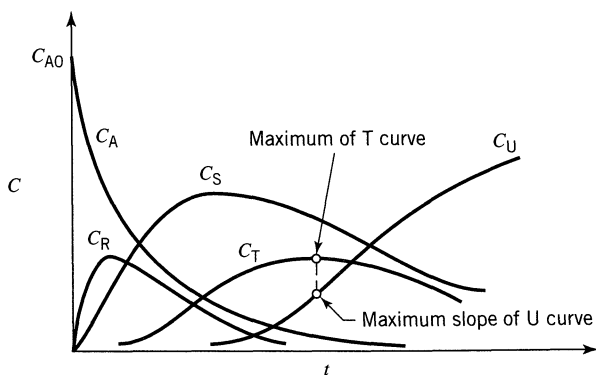


Figure 3.12 Concentration-time curves for a chain of successive first-order reactions. Only for the last two compounds do the maximum and the inflection points occur at the same time.

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

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

and the equilibrium constant to be

$$K_C = \frac{k_1}{k_2}$$

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

$$\boxed{-\ln\left(1 - \frac{X_A}{X_{Ae}}\right) = -\ln\frac{C_A - C_{Ae}}{C_{A0} - C_{Ae}} = \frac{M+1}{M+X_{Ae}}k_1t} \quad (54)$$

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

The similarity between equations for the first-order irreversible and reversible reactions can be seen by comparing Eq. 12 with Eq. 54 or by comparing Fig. 3.1 with Fig. 3.13. Thus, the irreversible reaction is simply the special case of the reversible reaction in which $C_{Ae} = 0$, or $X_{Ae} = 1$, or $K_C = \infty$.

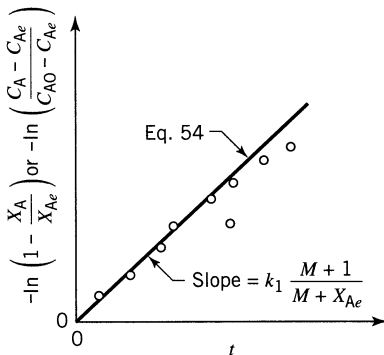


Figure 3.13 Test for the unimolecular type reversible reactions of Eq. 53.

Second-Order Reversible Reactions. For the bimolecular-type second-order reactions



with the restrictions that $C_{A0} = C_{B0}$ and $C_{R0} = C_{S0} = 0$, the integrated rate equations for A and B are all identical, as follows

$$\ln \frac{X_{Ae} - (2X_{Ae} - 1)X_A}{X_{Ae} - X_A} = 2k_1 \left(\frac{1}{X_{Ae}} - 1 \right) C_{A0}t \quad (56)$$

A plot as shown in Fig. 3.14 can then be used to test the adequacy of these kinetics.

Reversible Reactions in General. For orders other than one or two, integration of the rate equation becomes cumbersome. So if Eq. 54 or 56 is not able to fit the data, then the search for an adequate rate equation is best done by the differential method.

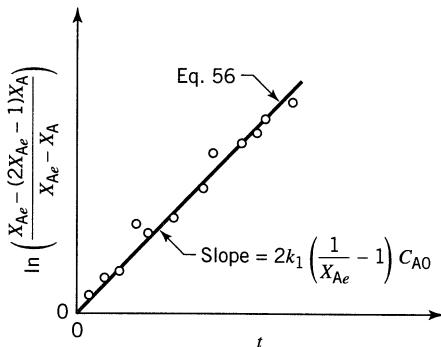


Figure 3.14 Test for the reversible bimolecular reactions of Eq. 55.

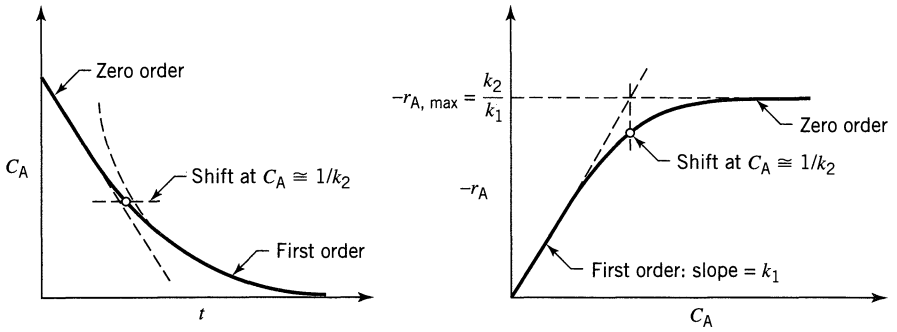
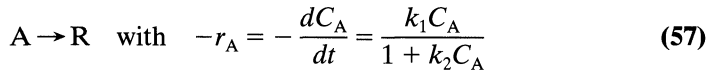


Figure 3.15 Behavior of a reaction that follows Eq. 57.

Reactions of Shifting Order. In searching for a kinetic equation it may be found that the data are well fitted by one reaction order at high concentrations but by another order at low concentrations. Consider the reaction



From this rate equation we see

At high C_A —the reaction is of zero order with rate constant k_1/k_2
(or $k_2 C_A \gg 1$)

At low C_A —the reaction is of first order with rate constant k_1
(or $k_2 C_A \ll 1$)

This behavior is shown in Fig. 3.15.

To apply the integral method, separate variables and integrate Eq. 57. This gives

$$\ln \frac{C_{A0}}{C_A} + k_2 (C_{A0} - C_A) = k_1 t \quad (58a)$$

To linearize, rearrange Eq. 58a to give

$$\frac{C_{A0} - C_A}{\ln (C_{A0}/C_A)} = -\frac{1}{k_2} + \frac{k_1}{k_2} \left(\frac{t}{\ln (C_{A0}/C_A)} \right) \quad (58b)$$

or

$$\frac{\ln (C_{A0}/C_A)}{C_{A0} - C_A} = -k_2 + \frac{k_1 t}{C_{A0} - C_A} \quad (58c)$$

Two ways to test this rate form are then shown in Fig. 3.16.

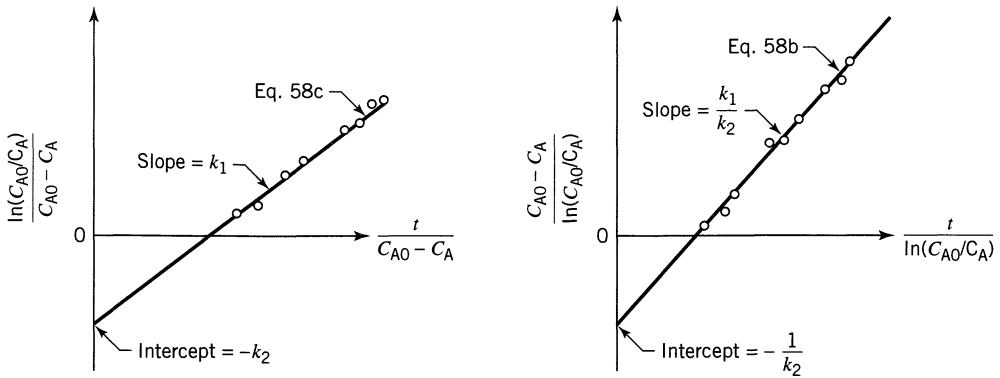


Figure 3.16 Test of the rate equation, Eq. 57, by integral analysis.

By similar reasoning to the above we can show that the general rate form

$$-r_A = -\frac{dC_A}{dt} = \frac{k_1 C_A^m}{1 + k_2 C_A^n} \quad (59)$$

shifts from order $m - n$ at high concentration to order m at low concentration, the transition taking place where $k_2 C_A^n \cong 1$. This type of equation can then be used to fit data of any two orders.

Another form which can account for this shift is

$$-r_A = -\frac{dC_A}{dt} = \frac{k_1 C_A^m}{(1 + k_2 C_A)^n} \quad (60)$$

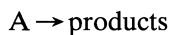
Mechanism studies may suggest which form to use. In any case, if one of these equation forms will fit the data, so will the other.

The rate form of Eq. 57 and some of its generalizations are used to represent a number of widely different kinds of reactions. For example, in homogeneous systems this form is used for enzyme-catalyzed reactions where it is suggested by mechanistic studies (see the Michaelis-Menten mechanism in Chap. 2 and in Chap. 27). It is also used to represent the kinetics of surface-catalyzed reactions.

In mechanistic studies, this form of equation appears whenever the rate-controlling step of a reaction is viewed to involve the association of reactant with some quantity that is present in limited but fixed amounts; for example, the association of reactant with enzyme to form a complex, or the association of gaseous reactant with an active site on the catalytic surface.

EXAMPLE 3.1 FIND A RATE EQUATION USING THE INTEGRAL METHOD

Reactant A decomposes in a batch reactor



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 $C_A, \text{mol/liter}$	$\ln \frac{C_{A0}}{C_A}$	$\frac{1}{C_A}$
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. E3.1a 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.

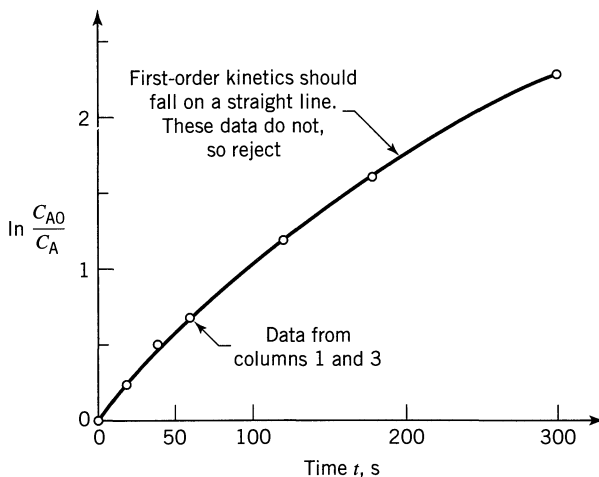


Figure E3.1a

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. E3.1b. Again, this does not give a straight line, so a second-order kinetic form is rejected.

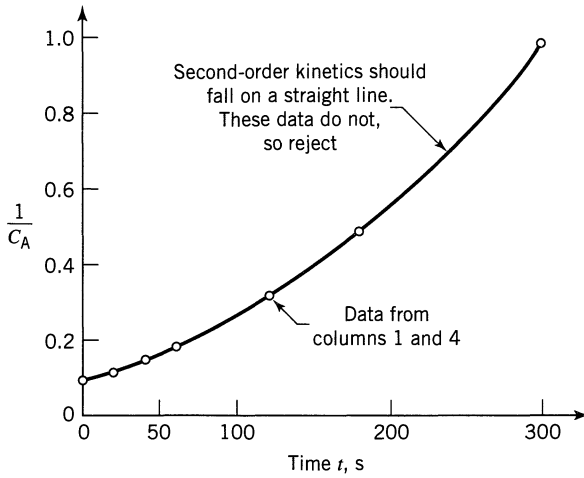


Figure E3.1b

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

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

Next take logarithms

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

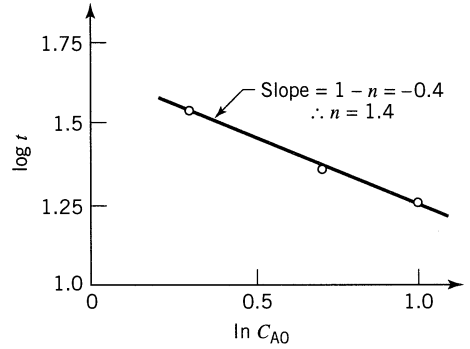
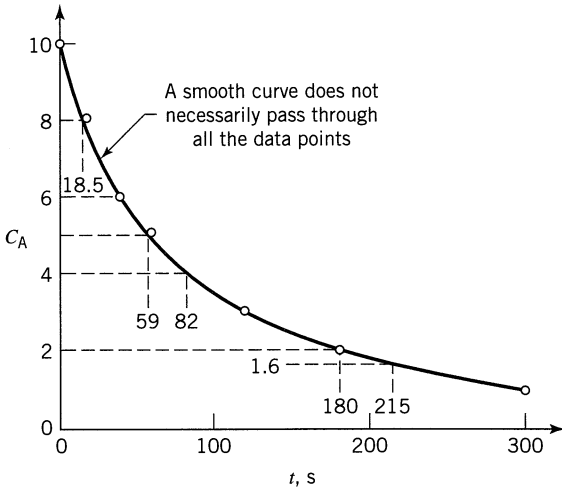
$\frac{\log t_F}{y} = \frac{\log \left(\frac{0.8^{1-n} - 1}{k(n-1)} \right)}{a} + \frac{(1-n) \log C_{A0}}{bx}$

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}	$C_{A \text{ end}}$ ($= 0.8C_{A0}$)	Time needed t_F, s	$\log t_F$	$\log C_{A0}$
10	8	$0 \rightarrow 18.5 = 18.5$	$\log 18.5 = 1.27$	1.00
5	4	$59 \rightarrow 82 = 23$	1.36	0.70
2	1.6	$180 \rightarrow 215 = 35$	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 E3.1c 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

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

Differential Method of Analysis of Data

The differential method of analysis deals directly with the differential rate equation to be tested, evaluating all terms in the equation including the derivative dC_i/dt , and testing the goodness of fit of the equation with experiment.

The procedure is as follows.

1. Plot the C_A vs. t data, and then by eye carefully draw a smooth curve to represent the data. This curve most likely will not pass through all the experimental points.
2. Determine the slope of this curve at suitably selected concentration values. These slopes $dC_A/dt = r_A$ are the rates of reaction at these compositions.

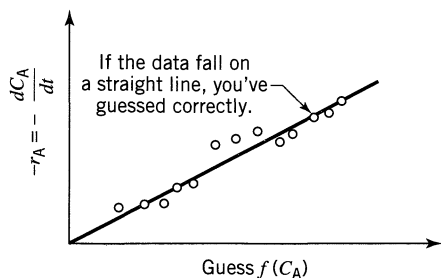


Figure 3.17 Test for the particular rate form $-r_A = kf(C_A)$ by the differential method.

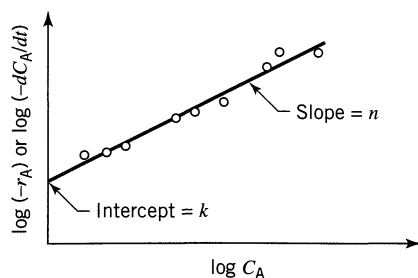


Figure 3.18 Test for an n th-order rate form by the differential method.

3. Now search for a rate expression to represent this r_A vs. C_A data, either by
- (a) picking and testing a particular rate form, $-r_A = kf(C_A)$, see Fig. 17, or
 - (b) testing an n th-order form $-r_A = kC_A^n$ by taking logarithms of the rate equation (see Fig. 3.18).

With certain simpler rate equations, however, mathematical manipulation may be able to yield an expression suitable for graphical testing. As an example, consider a set of C_A vs. t data to which we want to fit the M–M equation

$$-r_A = -\frac{dC_A}{dt} = \frac{k_1 C_A}{1 + k_2 C_A} \quad (57)$$

which has already been treated by the integral method of analysis. By the differential method we can obtain $-r_A$ vs. C_A . However, how do we make a straight-line plot to evaluate k_1 and k_2 ? As suggested, let us manipulate Eq. 57 to obtain a more useful expression. Thus, taking reciprocals we obtain

$$\frac{1}{(-r_A)} = \frac{1}{k_1 C_A} + \frac{k_2}{k_1} \quad (61)$$

and a plot of $1/(-r_A)$ vs. $1/C_A$ is linear, as shown in Fig. 3.19.

Alternatively, a different manipulation (multiply Eq. 61 by $k_1(-r_A)/k_2$) yields another form, also suitable for testing, thus

$$(-r_A) = \frac{k_1}{k_2} - \frac{1}{k_2} \left[\frac{(-r_A)}{C_A} \right] \quad (62)$$

A plot of $-r_A$ vs. $(-r_A)/C_A$ is linear, as shown in Fig. 3.19.

Whenever a rate equation can be manipulated to give a linear plot, this becomes a simple way of testing the equation. So, with any given problem we must use good judgment in planning our experimental program.

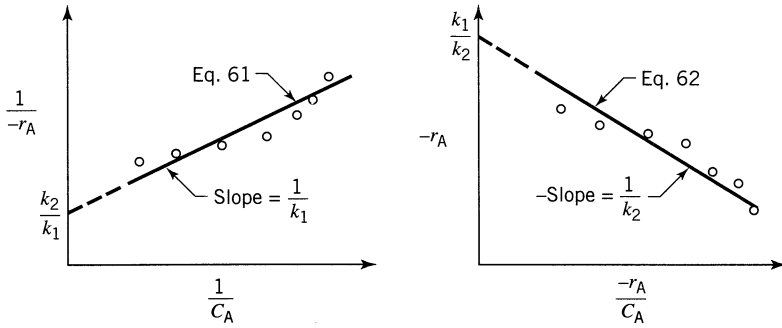


Figure 3.19 Two ways of testing the rate equation $-r_A = k_1 C_A / (1 + k_2 C_A)$ by differential analysis.

EXAMPLE 3.2 FIND A RATE EQUATION TO FIT A SET OF DATA USING THE DIFFERENTIAL METHOD

Try to fit an n th-order rate equation to the concentration vs. time data of Example 3.1.

SOLUTION

The data are tabulated in the following columns 1 and 2 and are plotted in Fig. E3.2a.

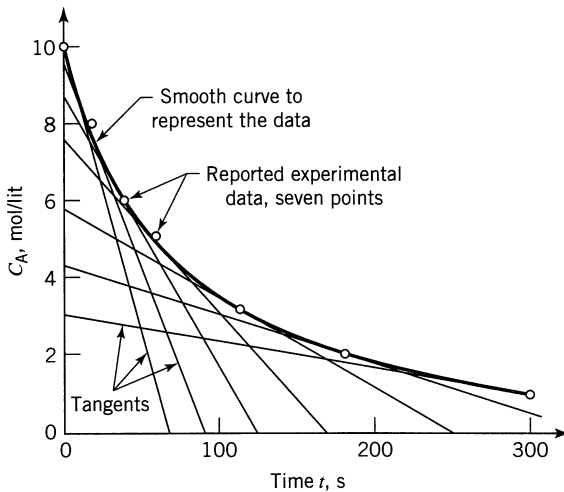


Figure E3.2a

Column 1	Column 2	Column 3	Column 4	Column 5
Time t, s	Concentration $C_A, \text{mol/liter}$	Slope, from Fig. E3.2a (dC_A/dt)	$\log_{10}(-dC_A/dt)$	$\log_{10} C_A$
0	10	$(10 - 0)/(0 - 75) = -0.1333$	-0.875	1.000
20	8	$(10 - 0)/(-3 - 94) = -0.1031$	-0.987	0.903
40	6	$(10 - 0)/(-21 - 131) = -0.0658$	-1.182	0.778
60	5	$(8 - 0)/(-15 - 180) = -0.0410$	-1.387	0.699
120	3	$(6 - 0)/(-10 - 252) = -0.0238$	-1.623	0.477
180	2	$(4 - 1)/(24 - 255) = -0.0108$	-1.967	0.301
300	1	$(3 - 1)/(-10 - 300) = -0.0065$	-2.187	0.000

Now carefully draw a smooth curve to represent the data and at $C_A = 10, 8, 6, 5, 3, 2, 1$, draw tangents to the curve, and evaluate them (see column 3).

Next, to fit an n th-order rate equation to this data, or

$$-r_A = -\frac{dC_A}{dt} = kC_A^n$$

take logarithms of both sides (see columns 3 and 4), or

$$\log_{10}\left(\frac{dC_A}{dt}\right) = \log_{10}k + n\log_{10}C_A$$

y

x

intercept
slope

and plot as in Fig. E3.2b. The slope and intercept of the best line gives n and k (see Fig. E3.2b). So the rate equation is

$$\underline{\underline{-r_A = -\frac{dC_A}{dt} = \left(0.005 \frac{\text{liter}^{0.43}}{\text{mol}^{0.43} \cdot \text{s}}\right) C_A^{1.43}, \frac{\text{mol}}{\text{liter} \cdot \text{s}}}}$$

Warning. In step 1, if you use a computer to fit a polynomial to the data it could lead to disaster. For example, consider fitting a sixth-degree polynomial to the seven data points, or an $(n - 1)$ degree polynomial to n points.

Fitting by eye you'd get a smooth curve, as shown in Fig. E3.2c. But if a computer is used to obtain a polynomial that would pass through all the points the result would very well be as shown in Fig. E3.2d.

Now, which of these curves makes more sense and which would you use? This is why we say "draw a smooth curve by eye to represent the data." But beware, to draw such a curve is not that simple. Take care.

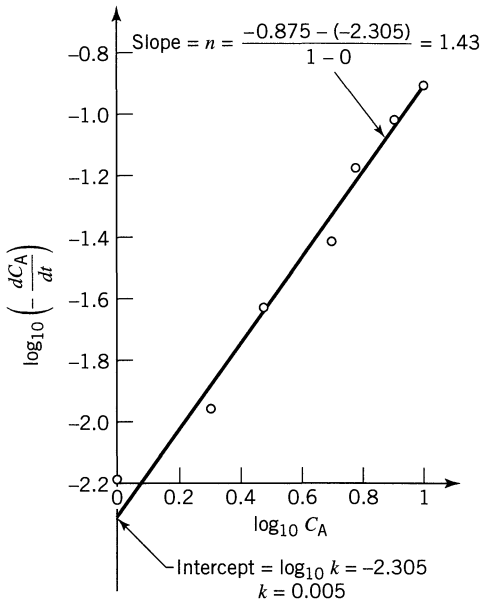


Figure E3.2b

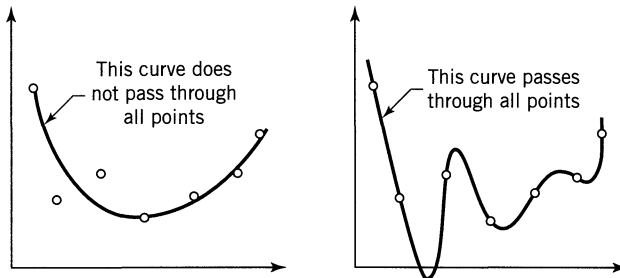


Figure E3.2c, d The same seven points fitted by curves two different ways.

3.2 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 .

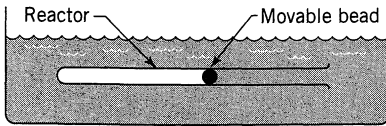


Figure 3.20 A varying-volume batch reactor.

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

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

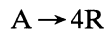
or

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

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

$$\varepsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}} \quad (64)$$

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



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

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

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

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

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. 63a 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

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

Differential Method of Analysis

The procedure for differential analysis of isothermal varying volume data is the same as for the constant-volume situation except that we replace

$$\frac{dC_A}{dt} \quad \text{with} \quad \frac{C_{A0}}{V\varepsilon_A} \frac{dV}{dt} \quad \text{or} \quad \frac{C_{A0}}{\varepsilon_A} \frac{d(\ln V)}{dt} \quad (68)$$

This means plot $\ln V$ vs. t and take slopes.

Integral Method of Analysis

Unfortunately, only a few of the simpler rate forms integrate to give manageable V vs. t expressions. Let us look at these.

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

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

Integrating gives

$$\boxed{\frac{C_{A0}}{\varepsilon_A} \ln \frac{V}{V_0} = kt} \quad (70)$$

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

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

Replacing X_A by V from Eqs. 63 and integrating gives

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

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

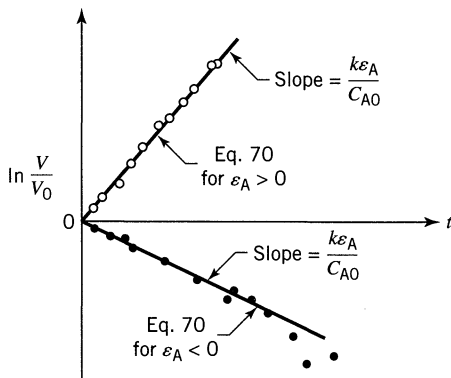
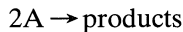


Figure 3.21 Test for a homogeneous zero-order reaction, Eq. 69, in a constant-pressure, varying volume reactor.

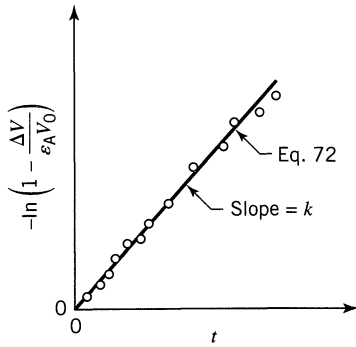
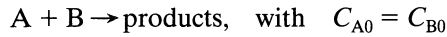


Figure 3.22 Test for a first-order reaction, Eq. 71, in a constant-pressure, varying-volume reactor.

or



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,

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

Figure 3.23 shows how to test for those kinetics.

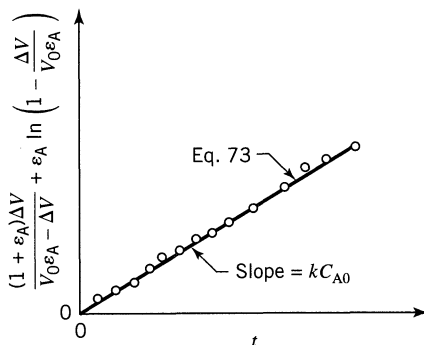


Figure 3.23 Test for the second-order reaction, Eq. 73, in a constant-pressure, varying-volume reactor.

***n*th-Order and Other Reactions.** For all rate forms other than zero-, first-, and second-order the integral method of analysis is not useful.

3.3 TEMPERATURE AND REACTION RATE

So far we have examined the effect of concentration of reactants and products on the rate of reaction, all at a given temperature level. To obtain the complete rate equation, we also need to know the role of temperature on reaction rate. Now in a typical rate equation we have

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt} = kf(C)$$

and it is the reaction rate constant, the concentration-independent term, which is affected by the temperature, whereas the concentration-dependent terms $f(C)$ usually remain unchanged at different temperatures.

Chemical theory predicts that the rate constant should be temperature-dependent in the following manner:

$$k \propto T^m e^{-E/RT}$$

However, since the exponential term is much more temperature-sensitive than the power term, we can reasonably consider the rate constants to vary approximately as $e^{-E/RT}$.

Thus, after finding the concentration dependency of the reaction rate, we can then examine for the variation of the rate constant with temperature by an Arrhenius-type relationship

$$k = k_0 e^{-E/RT}, \quad E = \left[\frac{\text{J}}{\text{mol}} \right] \quad (2.34) \text{ or } (74)$$

This is conveniently determined by plotting $\ln k$ versus $1/T$, as shown in Fig. 3.24.

If the rate constant is found at two different temperatures we have from Chap. 2,

$$\ln \frac{k_2}{k_1} = \frac{E}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad \text{or} \quad E = \frac{RT_1 T_2}{T_2 - T_1} \ln \frac{k_2}{k_1} \quad (2.35) \text{ or } (75)$$

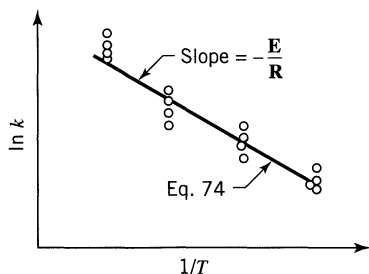


Figure 3.24 Temperature dependency of a reaction according to Arrhenius' law.

Finally, as mentioned in Chap. 2, a shift in E with temperature reflects a change in controlling mechanism of reaction. Since this is likely to be accompanied by a change in concentration dependency, this possibility should also be examined.

Warning on Using Pressure Measures. When dealing with gases, engineers and chemists often measure compositions in terms of partial and total pressures, and then develop their rate equations in terms of pressures, without realizing that this can lead to problems. The reason is that the activation energy calculated when using these units is incorrect. Let us illustrate.

EXAMPLE 3.4 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:

$$\begin{array}{l} \text{at 400 K} \quad -r_A = 2.3 p_A^2 \\ \text{at 500 K} \quad -r_A = 2.3 p_A^2 \end{array} \quad \text{where} \quad \begin{cases} -r_A = \left[\frac{\text{mol}}{\text{m}^3 \cdot \text{s}} \right] \\ p_A = [\text{atm}] \end{cases}$$

- Evaluate the activation using these units
- 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

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

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

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

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

- 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

$$\begin{aligned} -r_{A1} &= 2.3 \frac{\text{mol}}{\text{m}^3 \cdot \text{s} \cdot \text{atm}^2} \cdot C_A^2 \left(82.06 \times 10^{-6} \frac{\text{m}^3 \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right)^2 (400 \text{ K})^2 \\ &= 0.0025 C_A^2 \quad \text{where} \quad k_1 = 0.0025 \frac{\text{m}^3}{\text{mol} \cdot \text{s}} \end{aligned}$$

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 \mathbf{E} values differ when either p or C used to measure concentrations of materials. ■

Final Notes

1. Chemistry (collision theory or transition state theory) has developed the equations for reaction rates and activation energies in terms of concentration.
2. Literature tabulations for \mathbf{E} and $-r_A$ for homogeneous reactions are normally based on concentrations. The clue to this is that the units for the rate constant are often s^{-1} , $\text{liter/mol} \cdot \text{s}$, etc., without pressure appearing in the units.

3. It is a good idea when making runs at different temperatures first to change all p values to C values by using the relationships

$$p_A = C_A \mathbf{R}T \quad \text{for ideal gases}$$

$$p_A = zC_A \mathbf{R}T \quad \text{for nonideal gases, where } z = \text{compressibility factor}$$

and then proceed to solve the problem. This will avoid confusion on units later on, especially if the reaction is reversible or involves liquids and/or solids as well as gases.

3.4 THE SEARCH FOR A RATE EQUATION

In searching for a rate equation and mechanism to fit a set of experimental data, we would like answers to two questions:

1. Have we the correct mechanism and corresponding type of rate equation?
2. Once we have the right form of rate equation, do we have the best values for the rate constants in the equation?

The difficult question to answer is the first of the preceding two questions. Let us see why this is so.

Suppose we have a set of data and we wish to find out whether any one of the families of curves—parabolas, cubics, hyperbolas, exponentials, etc., each representing a different rate family—really fits these data better than any other. This question cannot be answered simply; neither can high-powered mathematical or statistical methods help in deciding for us. The one exception to this conclusion occurs when one of the families being compared is a straight line. For this situation we can simply, consistently, and fairly reliably tell whether the straight line does not reasonably fit the data. Thus, we have what is essentially a negative test, one that allows us to reject a straight line family when there is sufficient evidence against it.

All the rate equations in this chapter were manipulated mathematically into a linearized form because of this particular property of the family of straight lines that allows it to be tested and rejected.

Three methods are commonly used to test for the linearity of a set of points. These are as follows:

Calculation of k from Individual Data Points. With a rate equation at hand, the rate constant can be found for each experimental point by either the integral or differential method. If no trend in k values is discernible, the rate equation is considered to be satisfactory and the k values are averaged.

Now the k values calculated this way are the slopes of lines joining the individual points to the origin. So for the same magnitude of scatter on the graph the k values calculated for points near the origin (low conversion) will vary widely, whereas those calculated for points far from the origin will show little variation (Fig. 3.25). This fact can make it difficult to decide whether k is constant and, if so, what is its best mean value.

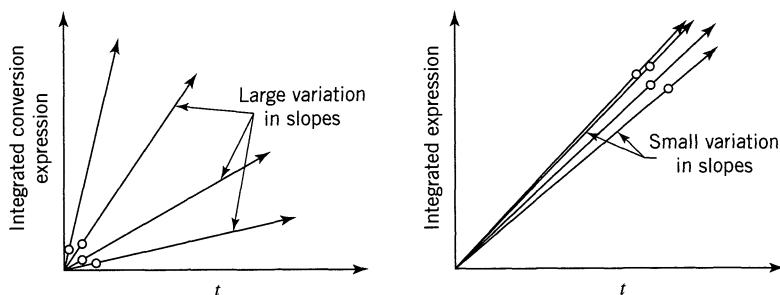


Figure 3.25 How the location of the experimental points influences the scatter in calculated k values.

Calculation of k from Pairs of Data Points. k values can be calculated from successive pairs of experimental points. For large data scatter, however, or for points close together, this procedure will give widely different k values from which k_{mean} will be difficult to determine. In fact, finding k_{mean} by this procedure for points located at equal intervals on the x -axis is equivalent to considering only the two extreme data points while ignoring all the data points in between. This fact can easily be verified. Figure 3.26 illustrates this procedure.

This is a poor method in all respects and is not recommended for testing the linearity of data or for finding mean values of rate constants.

Graphical Method of Fitting Data. Actually, the preceding methods do not require making a plot of the data to obtain k values. With the graphical method the data are plotted and then examined for deviations from linearity. The decision whether a straight line gives a satisfactory fit is usually made intuitively by using good judgment when looking at the data. When in doubt we should take more data.

The graphical procedure is probably the safest, soundest, and most reliable method for evaluating the fit of rate equations to the data, and should be used whenever possible. For this reason we stress this method here.

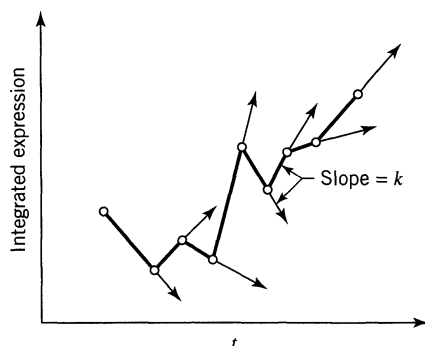


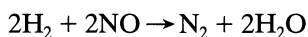
Figure 3.26 Calculated k values from successive experimental points are likely to fluctuate widely.

RELATED READINGS

- Frost, A. A., and Pearson, R. G., *Kinetics and Mechanism*, 2nd ed., John Wiley & Sons, New York, 1961.
- Laidler, K. J., *Chemical Kinetics*, 2nd ed., McGraw-Hill, New York, 1965.

PROBLEMS

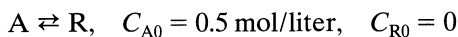
- 3.1. If $-r_A = -(dC_A/dt) = 0.2$ mol/liter·sec when $C_A = 1$ mol/liter, what is the rate of reaction when $C_A = 10$ mol/liter?
Note: the order of reaction is not known.
- 3.2. Liquid A decomposes by first-order kinetics, and in a batch reactor 50% of A is converted in a 5-minute run. How much longer would it take to reach 75% conversion?
- 3.3. Repeat the previous problem for second-order kinetics.
- 3.4. A 10-minute experimental run shows that 75% of liquid reactant is converted to product by a $\frac{1}{2}$ -order rate. What would be the fraction converted in a half-hour run?
- 3.5. 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?
- 3.6. 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.
- 3.7. Snake-Eyes Magoo is a man of habit. For instance, his Friday evenings are all alike—into the joint with his week's salary of \$180, steady gambling at "2-up" for two hours, then home to his family leaving \$45 behind. Snake Eyes's betting pattern is predictable. He always bets in amounts proportional to his cash at hand, and his losses are also predictable—at a rate proportional to his cash at hand. This week Snake-Eyes received a raise in salary, so he played for three hours, but as usual went home with \$135. How much was his raise?
- 3.8. Find the overall order of the irreversible reaction



from the following constant-volume data using equimolar amounts of hydrogen and nitric oxide:

Total pressure, mm Hg	200	240	280	320	360
Half-life, sec	265	186	115	104	67

3.9. The first-order reversible liquid reaction



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.

3.10. 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.

3.11. Aqueous A at a concentration $C_{A0} = 1$ mol/liter is introduced into a batch reactor where it reacts away to form product R according to stoichiometry $A \rightarrow R$. The concentration of A in the reactor is monitored at various times, as shown below:

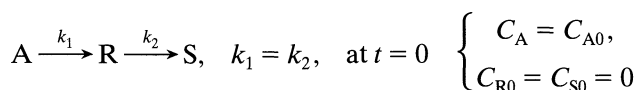
$t, \text{ min}$	0	100	200	300	400
$C_A, \text{ mol/m}^3$	1000	500	333	250	200

For $C_{A0} = 500$ mol/m³ find the conversion of reactant after 5 hours in the batch reactor.

3.12. Find the rate for the reaction of Problem 11.

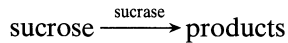
3.13. Betahundert Bashby likes to play the gaming tables for relaxation. He does not expect to win, and he doesn't, so he picks games in which losses are a given small fraction of the money bet. He plays steadily without a break, and the sizes of his bets are proportional to the money he has. If at "galloping dominoes" it takes him 4 hours to lose half of his money and it takes him 2 hours to lose half of his money at "chuk-a-luck," how long can he play both games simultaneously if he starts with \$1000 and quits when he has \$10 left, which is just enough for a quick nip and carfare home?

3.14. For the elementary reactions in series



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

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



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):

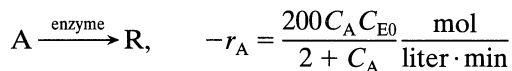
C_A , millimol/liter	0.84	0.68	0.53	0.38	0.27	0.16	0.09	0.04	0.018	0.006	0.0025
t , hr	1	2	3	4	5	6	7	8	9	10	11

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

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

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

- 3.16.** Repeat the above problem, except this time solve by the differential method.
- 3.17.** 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.
- 3.18.** Enzyme E catalyzes the transformation of reactant A to product R as follows:



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.

- 3.19.** Find the conversion after 1 hour in a batch reactor for

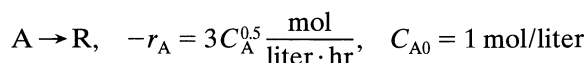


Table P3.20

t , min	$\text{C}_2\text{H}_5\text{SO}_4\text{H}$, mol/liter	t , min	$\text{C}_2\text{H}_5\text{SO}_4\text{H}$, 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)

- 3.20.** M. Hellin and J. C. Jungers, *Bull. soc. chim. France*, **386** (1957), present the data in Table P3.20 on the reaction of sulfuric acid with diethylsulfate in aqueous solution at 22.9°C:



Initial concentrations of H_2SO_4 and $(\text{C}_2\text{H}_5)_2\text{SO}_4$ are each 5.5 mol/liter. Find a rate equation for this reaction.

- 3.21.** 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 P3.21 are obtained. The stoichiometry of the reaction is $2\text{A} \rightarrow \text{B}$, 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.

Table P3.21

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

- 3.22. For the reaction $A \rightarrow R$, 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?
- 3.23. For the decomposition $A \rightarrow R$, $C_{A0} = 1$ 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.
- 3.24. 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

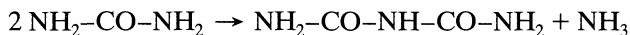
We plan to run this reaction in a batch reactor at the same catalyst concentration as used in getting the above data. Find the time needed to lower the concentration of A from $C_{A0} = 10$ mol/liter to $C_{Af} = 2$ mol/liter.

- 3.25. 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 $A \rightarrow 2.5R$. Find a rate equation which satisfactorily represents this decomposition.

- 3.26. Example 3.1c showed how to find a rate equation by using the fractional life method where $F = 80\%$. Take the data from that example and find the rate equation by using the half-life method. As a suggestion, why not take $C_{A0} = 10, 6,$ and 2 ?
- 3.27. When a concentrated urea solution is stored it slowly condenses to biuret by the following elementary reaction:



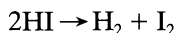
To study the rate of condensation a sample of urea ($C = 20$ mol/liter) is stored at 100°C and after 7 hr 40 min we find that 1 mol% has turned into biuret. Find the rate equation for this condensation reaction. [Data from W. M. Butt, *Pak. I. Ch. E.*, **1**, 99 (1973).]

- 3.28. The presence of substance C seems to increase the rate of reaction of A and B, $A + B \rightarrow AB$. We suspect that C acts catalytically by combining with one of the reactants to form an intermediate, which then reacts further. From the rate data in Table P3.28 suggest a mechanism and rate equation for this reaction.

Table P3.28

[A]	[B]	[C]	r_{AB}
1	3	0.02	9
3	1	0.02	5
4	4	0.04	32
2	2	0.01	6
2	4	0.03	20
1	2	0.05	12

- 3.29.** Find the first-order rate constant for the disappearance of A in the gas reaction $2A \rightarrow R$ if, on holding the pressure constant, the volume of the reaction mixture, starting with 80% A, decreases by 20% in 3 min.
- 3.30.** Find the first-order rate constant for the disappearance of A in the gas reaction $A \rightarrow 1.6R$ if the volume of the reaction mixture, starting with pure A increases by 50% in 4 min. The total pressure within the system stays constant at 1.2 atm, and the temperature is 25°C.
- 3.31.** The thermal decomposition of hydrogen iodide



is reported by M. Bodenstein [*Z. phys. chem.*, **29**, 295 (1899)] as follows:

$T, ^\circ\text{C}$	508	427	393	356	283
$k, \text{cm}^3/\text{mol} \cdot \text{s}$	0.1059	0.003 10	0.000 588	80.9×10^{-6}	0.942×10^{-6}

Find the complete rate equation for this reaction. Use units of joules, moles, cm^3 , and seconds.

Chapter 4

Introduction to Reactor Design

4.1 GENERAL DISCUSSION

So far we have considered the mathematical expression called the *rate equation* which describes the progress of a homogeneous reaction. The rate equation for a reacting component i is an intensive measure, and it tells how rapidly component i forms or disappears in a given environment as a function of the conditions there, or

$$r_i = \frac{1}{V} \left(\frac{dN_i}{dt} \right)_{\text{by reaction}} = f(\text{conditions within the region of volume } V)$$

This is a differential expression.

In reactor design we want to know what size and type of reactor and method of operation are best for a given job. Because this may require that the conditions in the reactor vary with position as well as time, this question can only be answered by a proper integration of the rate equation for the operation. This may pose difficulties because the temperature and composition of the reacting fluid may vary from point to point within the reactor, depending on the endothermic or exothermic character of the reaction, the rate of heat addition or removal from the system, and the flow pattern of fluid through the vessel. In effect, then, many factors must be accounted for in predicting the performance of a reactor. How best to treat these factors is the main problem of reactor design.

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.

Let us briefly indicate the particular features and the main areas of application of these reactor types. Naturally these remarks will be amplified further along in the text. The batch reactor is simple, needs little supporting equipment, and is therefore ideal for small-scale experimental studies on reaction kinetics. Industrially it is used when relatively small amounts of material are to be treated. The steady-state flow reactor is ideal for industrial purposes when large quantities of material are to be processed and when the rate of reaction is fairly high to extremely high. Supporting equipment needs are great; however, extremely good

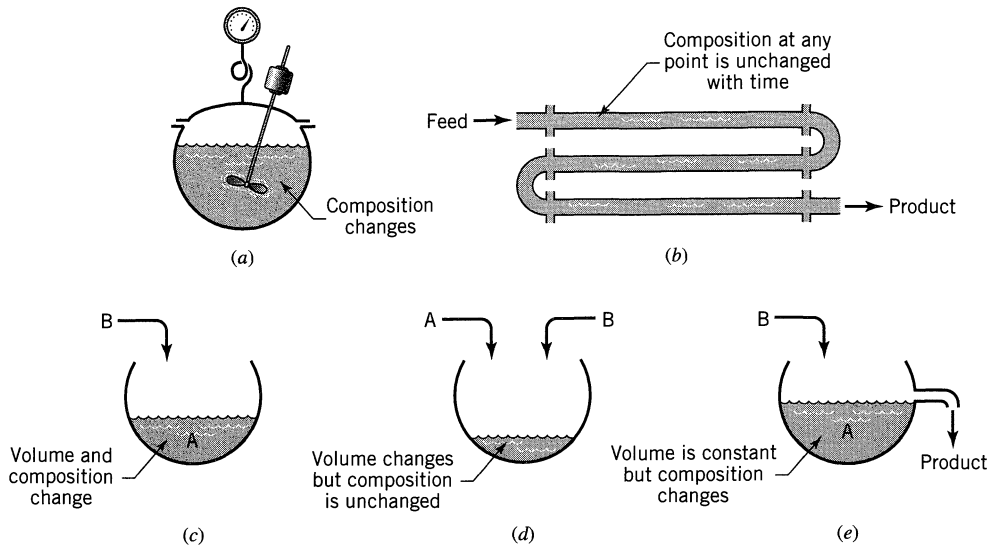


Figure 4.1 Broad classification of reactor types. (a) The batch reactor. (b) The steady-state flow reactor. (c), (d), and (e) Various forms of the semibatch reactor.

product quality control can be obtained. As may be expected, this is the reactor that is widely used in the oil industry. The semibatch reactor is a flexible system but is more difficult to analyze than the other reactor types. It offers good control of reaction speed because the reaction proceeds as reactants are added. Such reactors are used in a variety of applications from the calorimetric titrations in the laboratory to the large open hearth furnaces for steel production.

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

$$\left(\begin{array}{c} \text{rate of} \\ \text{reactant} \\ \text{flow into} \\ \text{element} \\ \text{of volume} \end{array} \right) = \left(\begin{array}{c} \text{rate of} \\ \text{reactant} \\ \text{flow out} \\ \text{of element} \\ \text{of volume} \end{array} \right) + \left(\begin{array}{c} \text{rate of reactant} \\ \text{loss due to} \\ \text{chemical reaction} \\ \text{within the element} \\ \text{of volume} \end{array} \right) + \left(\begin{array}{c} \text{rate of} \\ \text{accumulation} \\ \text{of reactant} \\ \text{in element} \\ \text{of volume} \end{array} \right) \quad (1)$$

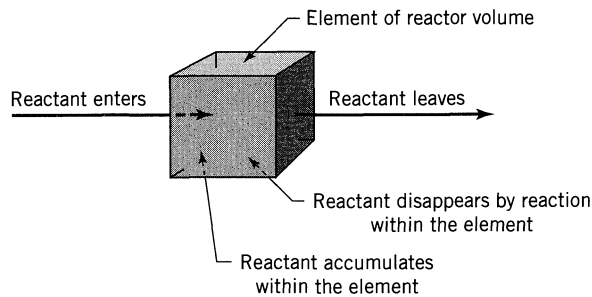


Figure 4.2 Material balance for an element of volume of the reactor.

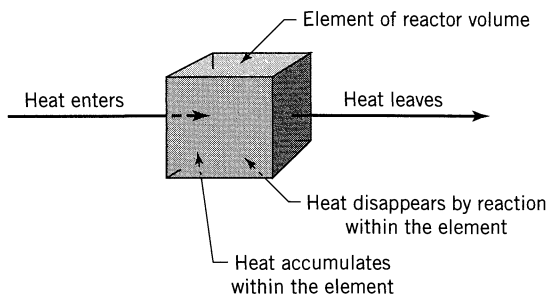


Figure 4.3 Energy balance for an element of volume of the reactor.

Where the composition within the reactor is uniform (independent of position), the accounting may be made over the whole reactor. Where the composition is not uniform, it must be made over a differential element of volume and then integrated across the whole reactor for the appropriate flow and concentration conditions. For the various reactor types this equation simplifies one way or another, and the resultant expression when integrated gives the basic *performance equation* for that type of unit. Thus, in the batch reactor the first two terms are zero; in the steady-state flow reactor the fourth term disappears; for the semibatch reactor all four terms may have to be considered.

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

$$\left(\begin{array}{c} \text{rate of heat} \\ \text{flow into} \\ \text{element of} \\ \text{volume} \end{array} \right) = \left(\begin{array}{c} \text{rate of heat} \\ \text{flow out of} \\ \text{element of} \\ \text{volume} \end{array} \right) + \left(\begin{array}{c} \text{rate of} \\ \text{disappearance} \\ \text{of heat by} \\ \text{reaction within} \\ \text{element of} \\ \text{volume} \end{array} \right) + \left(\begin{array}{c} \text{rate of} \\ \text{accumulation} \\ \text{of heat within} \\ \text{element of} \\ \text{volume} \end{array} \right) \quad (2)$$

Again, depending on circumstances, this accounting may be made either about a differential element of reactor or about the reactor as a whole.

The material balance of Eq. 1 and the energy balance of Eq. 2 are tied together by their third terms because the heat effect is produced by the reaction itself.

Since Eqs. 1 and 2 are the starting points for all design, we consider their integration for a variety of situations of increasing complexity in the chapters to follow.

When we can predict the response of the reacting system to changes in operating conditions (how rates and equilibrium conversion change with temperature and pressure), when we are able to compare yields for alternative designs (adiabatic versus isothermal operations, single versus multiple reactor units, flow versus batch system), and when we can estimate the economics of these various alternatives, then and only then will we feel sure that we can arrive at the design well fitted for the purpose at hand. Unfortunately, real situations are rarely simple.

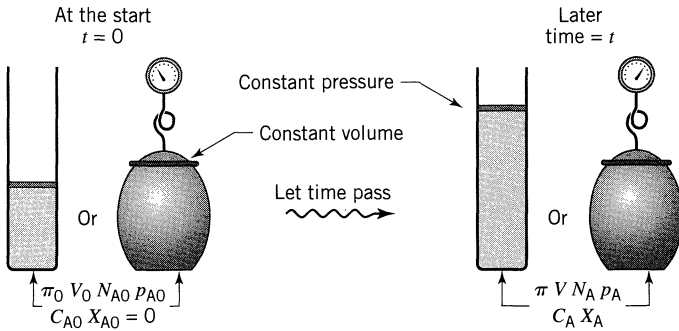


Figure 4.4 Symbols used for batch reactors.

Should we explore all reasonable design alternatives? How sophisticated should our analysis be? What simplifying assumptions should we make? What shortcuts should we take? Which factors should we ignore and which should we consider? And how should the reliability and completeness of the data at hand influence our decisions? Good engineering judgment, which only comes with experience, will suggest the appropriate course of action.

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:

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

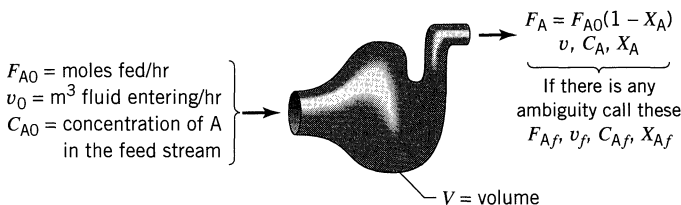


Figure 4.5 Symbols used for flow reactors.

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

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

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 $V = V_0(1 + \varepsilon_A X_A)$.

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

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

To follow changes in the other components we have

$$\text{between} \begin{cases} \varepsilon_A X_A = \varepsilon_B X_B \\ \frac{a\varepsilon_A}{C_{A0}} = \frac{b\varepsilon_B}{C_{B0}} \end{cases} \quad \text{for products} \begin{cases} \frac{C_R}{C_{A0}} = \frac{(r/a)X_A + C_{R0}/C_{A0}}{1 + \varepsilon_A X_A} \\ \frac{C_I}{C_{I0}} = \frac{1}{1 + \varepsilon_A X_A} \end{cases} \quad (6)$$

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



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,

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

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

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

For high-pressure nonideal gas behavior replace $\left(\frac{T_0\pi}{\tau_0\pi_0}\right)$ by $\left(\frac{z_0T_0\pi}{zT\pi}\right)$, 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



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).

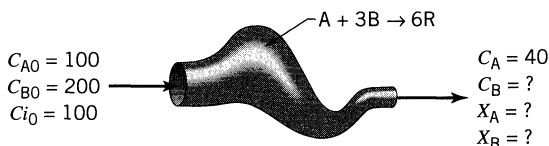


Figure E4.1

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

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

Then from the equations in the text

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

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

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

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

PROBLEMS

The following four problems consider an isothermal single-phase flow reactor operating at steady-state and constant pressure.

- 4.1. Given a gaseous feed, $C_{A0} = 100$, $C_{B0} = 200$, $A + B \rightarrow R + S$, $X_A = 0.8$. Find X_B , C_A , C_B .
- 4.2. Given a dilute aqueous feed, $C_{A0} = C_{B0} = 100$, $A + 2B \rightarrow R + S$, $C_A = 20$. Find X_A , X_B , C_B .
- 4.3. Given a gaseous feed, $C_{A0} = 200$, $C_{B0} = 100$, $A + B \rightarrow R$, $C_A = 50$. Find X_A , X_B , C_B .
- 4.4. Given a gaseous feed, $C_{A0} = C_{B0} = 100$, $A + 2B \rightarrow R$, $C_B = 20$. Find X_A , X_B , C_A .

In the following two problems a continuous stream of fluid enters a vessel at temperature T_0 and pressure π_0 , reacts there, and leaves at T and π .

- 4.5. Given a gaseous feed, $T_0 = 400$ K, $\pi_0 = 4$ atm, $C_{A0} = 100$, $C_{B0} = 200$, $A + B \rightarrow 2R$, $T = 300$ K, $\pi = 3$ atm, $C_A = 20$. Find X_A , X_B , C_B .
- 4.6. Given a gaseous feed, $T_0 = 1000$ K, $\pi_0 = 5$ atm, $C_{A0} = 100$, $C_{B0} = 200$, $A + B \rightarrow 5R$, $T = 400$ K, $\pi = 4$ atm, $C_A = 20$. Find X_A , X_B , C_B .
- 4.7. *A Commercial Popcorn Popping Popcorn Popper.* We are constructing a 1-liter popcorn popper to be operated in steady flow. First tests in this unit show that 1 liter/min of raw corn feed stream produces 28 liter/min of mixed exit stream. Independent tests show that when raw corn pops its volume goes from 1 to 31. With this information determine what fraction of raw corn is popped in the unit.

Chapter 5

Ideal Reactors for a Single Reaction

In this chapter we develop the performance equations for a single fluid reacting in the three ideal reactors shown in Fig. 5.1. We call these *homogeneous reactions*. Applications and extensions of these equations to various isothermal and nonisothermal operations are considered in the following four chapters.

In the *batch reactor*, or BR, of Fig. 5.1a the reactants are initially charged into a container, are well mixed, and are left to react for a certain period. The resultant mixture is then discharged. This is an unsteady-state operation where composition changes with time; however, at any instant the composition throughout the reactor is uniform.

The first of the two ideal steady-state flow reactors is variously known as the plug flow, slug flow, piston flow, ideal tubular, and unmixed flow reactor, and it is shown in Fig. 5.1b. We refer to it as the *plug flow reactor*, or PFR, and to this pattern of flow as *plug flow*. It is characterized by the fact that the flow of fluid through the reactor is orderly with no element of fluid overtaking or mixing with any other element ahead or behind. Actually, there may be lateral mixing of fluid in a plug flow reactor; however, there must be no mixing or diffusion along

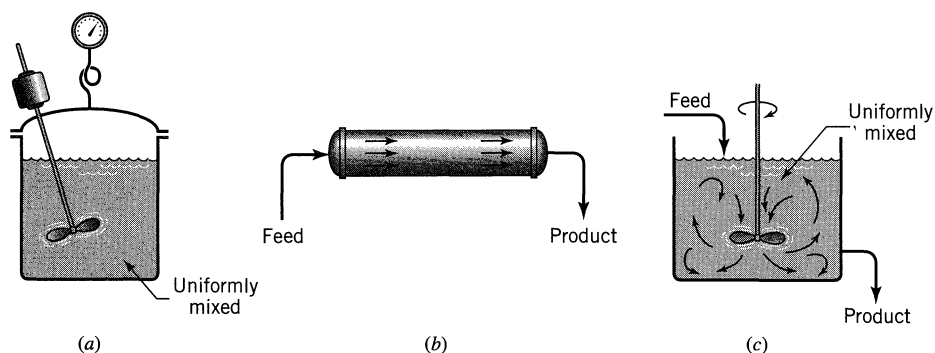


Figure 5.1 The three types of ideal reactors: (a) batch reactor, or BR; (b) plug flow reactor, or PFR; and (c) mixed flow reactor, or MFR.

the flow path. The necessary and sufficient condition for plug flow is for the residence time in the reactor to be the same for all elements of fluid.*

The other ideal steady-state flow reactor is called the mixed reactor, the backmix reactor, the ideal stirred tank reactor, the C* (meaning C-star), CSTR, or the CFSTR (constant flow stirred tank reactor), and, as its names suggest, it is a reactor in which the contents are well stirred and uniform throughout. Thus, the exit stream from this reactor has the same composition as the fluid within the reactor. We refer to this type of flow as *mixed flow*, and the corresponding reactor the *mixed flow reactor*, or MFR.

These three ideals are relatively easy to treat. In addition, one or other usually represents the best way of contacting the reactants—no matter what the operation. For these reasons, we often try to design real reactors so that their flows approach these ideals, and much of the development in this book centers about them.

In the treatment to follow it should be understood that the term V , called the reactor volume, really refers to the volume of fluid in the reactor. When this differs from the internal volume of reactor, then V_r designates the internal volume of reactor while V designates the volume of reacting fluid. For example, in solid catalyzed reactors with voidage ε we have

$$V = \varepsilon V_r$$

For homogeneous systems, however, we usually use the term V alone.

5.1 IDEAL BATCH REACTOR

Make a material balance for any component A. For such an accounting we usually select the limiting component. In a batch reactor, since the composition is uniform throughout at any instant of time, we may make the accounting about the whole reactor. Noting that no fluid enters or leaves the reaction mixture during reaction, Eq. 4.1, which was written for component A, becomes

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

or

$$+ \left(\begin{array}{c} \text{rate of loss of reactant A} \\ \text{within reactor due to} \\ \text{chemical reaction} \end{array} \right) = - \left(\begin{array}{c} \text{rate of accumulation} \\ \text{of reactant A} \\ \text{within the reactor} \end{array} \right) \quad (1)$$

Evaluating the terms of Eq. 1, we find

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

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

* The necessary condition follows directly from the definition of plug flow. However, the sufficient condition—that the same residence times implies plug flow—can be established only from the second law of thermodynamics.

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

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

Rearranging and integrating then gives

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

This is the general equation showing the time required to achieve a conversion X_A for either isothermal or nonisothermal operation. The volume of reacting fluid and the reaction rate remain under the integral sign, for in general they both change as reaction proceeds.

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

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

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

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

In one form or another, Eqs. 2 to 5 have all been encountered in Chapter 3. They are applicable to both isothermal and nonisothermal operations. For the latter the variation of rate with temperature, and the variation of temperature with conversion, must be known before solution is possible. Figure 5.2 is a graphical representation of two of these equations.

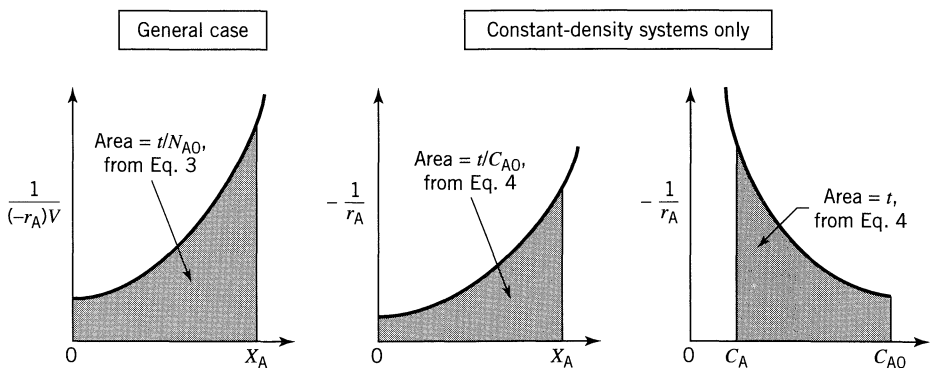


Figure 5.2 Graphical representation of the performance equations for batch reactors, isothermal or nonisothermal.

Space-Time and Space-Velocity

Just as the reaction time t is the natural performance measure for a batch reactor, so are the space-time and space-velocity the proper performance measures of flow reactors. These terms are defined as follows:

Space-time:

$$\tau = \frac{1}{s} = \left(\frac{\text{time required to process one reactor volume of feed measured at specified conditions}}{\text{reactor volume of feed measured at specified conditions}} \right) = [\text{time}] \quad (6)$$

Space-velocity:

$$s = \frac{1}{\tau} = \left(\frac{\text{number of reactor volumes of feed at specified conditions which can be treated in unit time}}{\text{reactor volume of feed measured at specified conditions}} \right) = [\text{time}^{-1}] \quad (7)$$

Thus, a space-velocity of 5 hr^{-1} means that five reactor volumes of feed at specified conditions are being fed into the reactor per hour. A space-time of 2 min means that every 2 min one reactor volume of feed at specified conditions is being treated by the reactor.

Now we may arbitrarily select the temperature, pressure, and state (gas, liquid, or solid) at which we choose to measure the volume of material being fed to the reactor. Certainly, then, the value for space-velocity or space-time depends on the conditions selected. If they are of the stream entering the reactor, the relation between s and τ and the other pertinent variables is

$$\begin{aligned} \tau &= \frac{1}{s} = \frac{C_{A0}V}{F_{A0}} = \frac{\left(\frac{\text{moles A entering}}{\text{volume of feed}} \right) (\text{volume of reactor})}{\left(\frac{\text{moles A entering}}{\text{time}} \right)} \\ &= \frac{V}{v_0} = \frac{(\text{reactor volume})}{(\text{volumetric feed rate})} \end{aligned} \quad (8)$$

It may be more convenient to measure the volumetric feed rate at some standard state, especially when the reactor is to operate at a number of temperatures. If, for example, the material is gaseous when fed to the reactor at high temperature but is liquid at the standard state, care must be taken to specify precisely what state has been chosen. The relation between the space-velocity and space-time for actual feed conditions (unprimed symbols) and at standard conditions (designated by primes) is given by

$$\tau' = \frac{1}{s'} = \frac{C'_{A0}V}{F_{A0}} = \tau \frac{C'_{A0}}{C_{A0}} = \frac{1}{s} \frac{C'_{A0}}{C_{A0}} \quad (9)$$

In most of what follows, we deal with the space-velocity and space-time based on feed at actual entering conditions; however, the change to any other basis is easily made.

5.2 STEADY-STATE MIXED FLOW REACTOR

The performance equation for the mixed flow reactor is obtained from Eq. 4.1, which makes an accounting of a given component within an element of volume of the system. But since the composition is uniform throughout, the accounting may be made about the reactor as a whole. By selecting reactant A for consideration, Eq. 4.1 becomes

$$\text{input} = \text{output} + \text{disappearance by reaction} + \text{accumulation} = 0 \quad (10)$$

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

$$\begin{aligned} \text{input of A, moles/time} &= F_{A0}(1 - X_{A0}) = F_{A0} \\ \text{output of A, moles/time} &= F_A = F_{A0}(1 - X_A) \\ \text{disappearance of A} & \\ \text{by reaction,} & \\ \text{moles/time} &= (-r_A)V = \left(\frac{\text{moles A reacting}}{(\text{time})(\text{volume of fluid})} \right) \left(\text{volume of reactor} \right) \end{aligned}$$

Introducing these three terms into Eq. 10, we obtain

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

which on rearrangement becomes

OR

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

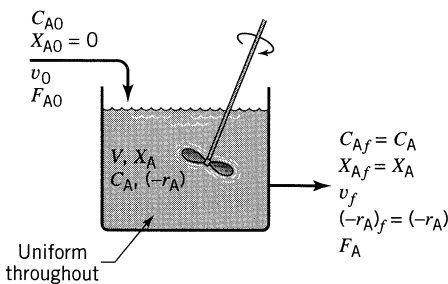


Figure 5.3 Notation for a mixed reactor.

where X_A and r_A are measured at exit stream conditions, which are the same as the conditions within the reactor.

More generally, if the feed on which conversion is based, subscript 0, enters the reactor partially converted, subscript i , and leaves at conditions given by subscript f , we have

$$\frac{V}{F_{A0}} = \frac{\Delta X_A}{(-r_A)_f} = \frac{X_{Af} - X_{Ai}}{(-r_A)_f}$$

or (12)

$$\tau = \frac{VC_{A0}}{F_{A0}} = \frac{C_{A0}(X_{Af} - X_{Ai})}{(-r_A)_f}$$

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

$$\frac{V}{F_{A0}} = \frac{X_A}{-r_A} = \frac{C_{A0} - C_A}{C_{A0}(-r_A)}$$

or $\varepsilon_A = 0$ (13)

$$\tau = \frac{V}{v} = \frac{C_{A0}X_A}{-r_A} = \frac{C_{A0} - C_A}{-r_A}$$

These expressions relate in a simple way the four terms X_A , $-r_A$, V , F_{A0} ; thus, knowing any three allows the fourth to be found directly. In design, then, the size of reactor needed for a given duty or the extent of conversion in a reactor of given size is found directly. In kinetic studies each steady-state run gives, without integration, the reaction rate for the conditions within the reactor. The ease of interpretation of data from a mixed flow reactor makes its use very attractive in kinetic studies, in particular with messy reactions (e.g., multiple reactions and solid catalyzed reactions).

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.

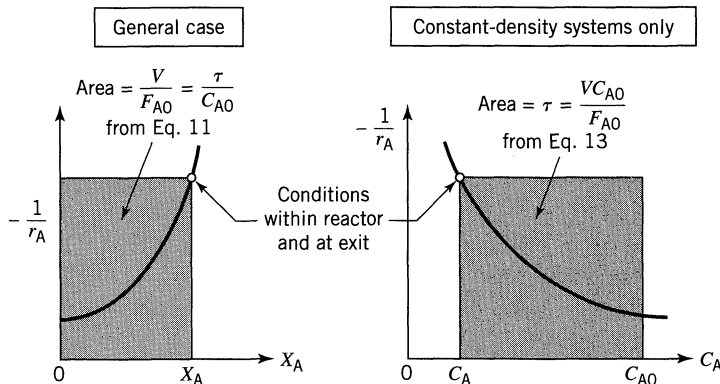


Figure 5.4 Graphical representation of the design equations for mixed flow reactor.

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

$$k\tau = \frac{X_A}{1 - X_A} = \frac{C_{A0} - C_A}{C_A} \quad \text{for } \varepsilon_A = 0 \quad (14a)$$

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

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

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

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

Similar expressions can be written for any other form of rate equation. These expressions can be written either in terms of concentrations or conversions. Using conversions is simpler for systems of changing density, while either form can be used for systems of constant density.

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.

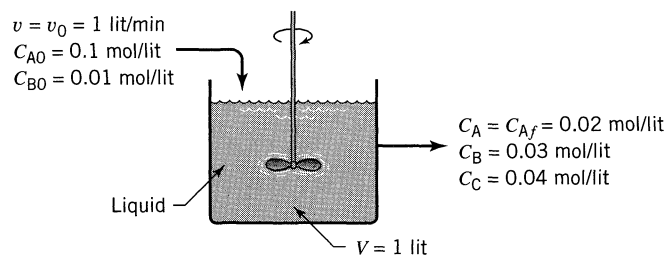


Figure E5.1

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

Run	Given		Calculated			
	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

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

These values are tabulated in column 5 of Table E5.2.

Having paired values of r_A and C_A (see Table E5.2) we are ready to test various kinetic expressions. Instead of separately testing for first-order (plot r_A vs. C_A), second-order (plot r_A vs. C_A^2), etc., let us test directly for n th-order kinetics. For this take logarithms of $-r_A = kC_A^n$, giving

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

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

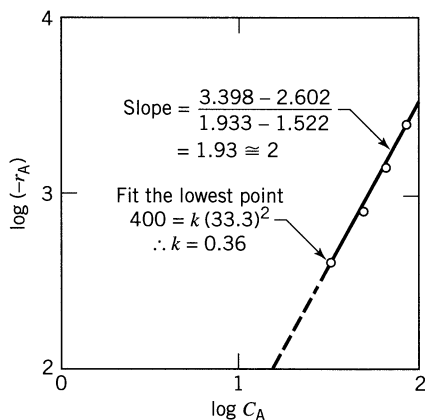


Figure E5.2

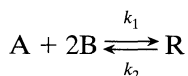
four data points are reasonably represented by a straight line of slope 2, so the rate equation for this dimerization is

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

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



with rate equation

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

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.

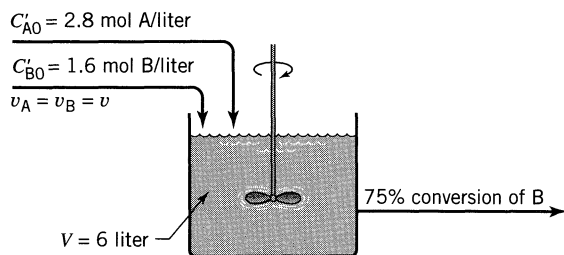


Figure E5.3

SOLUTION

The concentration of components in the mixed feed stream is

$$C_{A0} = 1.4 \text{ mol/liter}$$

$$C_{B0} = 0.8 \text{ mol/liter}$$

$$C_{R0} = 0$$

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

$$C_A = 1.4 - 0.6/2 = 1.1 \text{ mol/liter}$$

$$C_B = 0.8 - 0.6 = 0.2 \text{ mol/liter} \quad \text{or} \quad 75\% \text{ conversion}$$

$$C_R = 0.3 \text{ mol/liter}$$

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

$$\begin{aligned} -r_B &= 2(-r_A) = (2 \times 12.5)C_A C_B^2 - (2 \times 1.5)C_R \\ &= \left(25 \frac{\text{liter}^2}{\text{mol}^2 \cdot \text{min}}\right) \left(1.1 \frac{\text{mol}}{\text{liter}}\right) \left(0.2 \frac{\text{mol}}{\text{liter}}\right)^2 - (3 \text{ min}^{-1}) \left(0.3 \frac{\text{mol}}{\text{liter}}\right) \\ &= (1.1 - 0.9) \frac{\text{mol}}{\text{liter} \cdot \text{min}} = 0.2 \frac{\text{mol}}{\text{liter} \cdot \text{min}} \end{aligned}$$

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

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

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

$$\begin{aligned} v &= \frac{V(-r_B)}{C_{B0} - C_B} \\ &= \frac{(6 \text{ liter})(0.2 \text{ mol/liter} \cdot \text{min})}{(0.8 - 0.6) \text{ mol/liter}} = \underline{\underline{6 \text{ liter/min}}} \end{aligned}$$

or

3 liter/min of each of the two feed streams

5.3 STEADY-STATE PLUG FLOW REACTOR

In a plug flow reactor the composition of the fluid varies from point to point along a flow path; consequently, the material balance for a reaction component must be made for a differential element of volume dV . Thus for reactant A, Eq. 4.1 becomes

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

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

$$\text{input of A, moles/time} = F_A$$

$$\text{output of A, moles/time} = F_A + dF_A$$

disappearance of A by

$$\text{reaction, moles/time} = (-r_A)dV$$

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

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

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

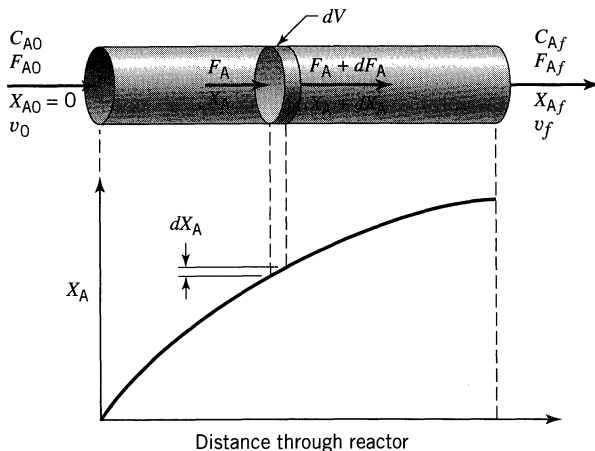


Figure 5.5 Notation for a plug flow reactor.

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

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

Equation 17 allows the determination of reactor size for a given feed rate and required conversion. Compare Eqs. 11 and 17. The difference is that in plug flow r_A varies, whereas in mixed flow r_A is constant.

As a more general expression for plug flow reactors, if the feed on which conversion is based, subscript 0, enters the reactor partially converted, subscript i , and leaves at a conversion designated by subscript f , we have

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

or

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

(18)

For the special case of *constant-density systems*

$$X_A = 1 - \frac{C_A}{C_{A0}} \quad \text{and} \quad dX_A = -\frac{dC_A}{C_{A0}}$$

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

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

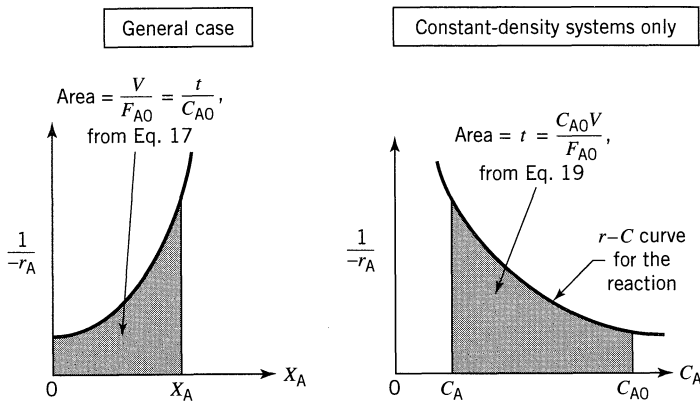


Figure 5.6 Graphical representation of the performance equations for plug flow reactors.

These performance equations, Eqs. 17 to 19, can be written either in terms of concentrations or conversions. For systems of changing density it is more convenient to use conversions; however, there is no particular preference for constant density systems. Whatever its form, the performance equations interrelate the *rate of reaction*, the *extent of reaction*, the *reactor volume*, and the *feed rate*, and if any one of these quantities is unknown it can be found from the other three.

Figure 5.6 displays these performance equations and shows that the space-time needed for any particular duty can always be found by numerical or graphical integration. However, for certain simple kinetic forms analytic integration is possible—and convenient. 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

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

First-order irreversible reaction, $A \rightarrow$ products, any constant ε_A ,

$$k\tau = -(1 + \varepsilon_A) \ln(1 - X_A) - \varepsilon_A X_A \quad (21)$$

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

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

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

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

Where the density is constant, put $\varepsilon_A = 0$ to obtain the simplified performance equation.

By comparing the batch expressions of Chapter 3 with these plug flow expressions we find:

- (1) For systems of constant density (constant-volume batch and constant-density plug flow) the performance equations are identical, τ for plug flow is equivalent to t for the batch reactor, and the equations can be used interchangeably.
- (2) For systems of changing density there is no direct correspondence between the batch and the plug flow equations and the correct equation must be used for each particular situation. In this case the performance equations cannot be used interchangeably.

The following illustrative examples show how to use these expressions.

EXAMPLE 5.4 PLUG FLOW REACTOR PERFORMANCE

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

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

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).

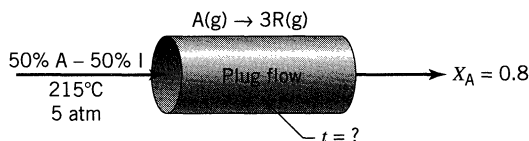


Figure E5.4a

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

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

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. E5.4b).

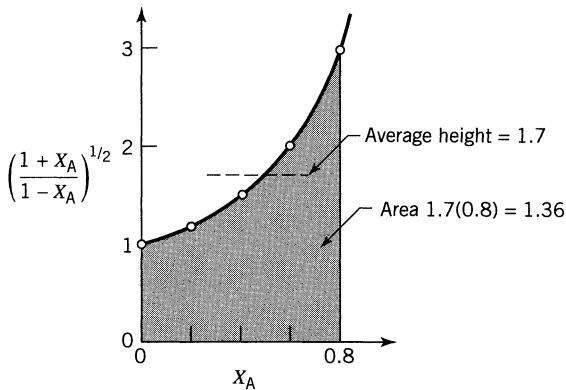


Figure E5.4b

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,

$$\begin{aligned} \int_0^{0.8} \left(\frac{1 + X_A}{1 - X_A}\right)^{1/2} dX_A &= (\text{average height})(\text{total width}) \\ &= \left[\frac{1(1) + 4(1.227) + 2(1.528) + 4(2) + 1(3)}{12} \right] (0.8) \\ &= \underline{\underline{1.331}} \end{aligned}$$

Analytical Integration. From a table of integrals

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

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

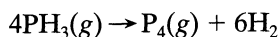
The method of integration recommended depends on the situation. In this problem probably the numerical method is the quickest and simplest and gives a good enough answer for most purposes.

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

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

EXAMPLE 5.5 PLUG FLOW REACTOR VOLUME

The homogeneous gas decomposition of phosphine



proceeds at 649°C with the first-order rate

$$-r_{\text{PH}_3} = (10/\text{hr}) C_{\text{PH}_3}$$

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?

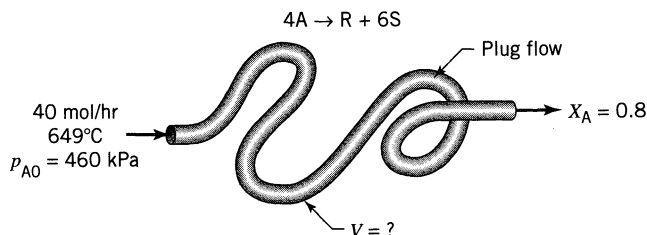


Figure E5.5

SOLUTION

Let $A = \text{PH}_3$, $R = \text{P}_4$, $S = \text{H}_2$. Then the reaction becomes



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

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

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

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

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

$$X_A = 0.8$$

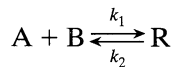
hence the volume of reactor

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

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

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



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

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

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

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

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

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

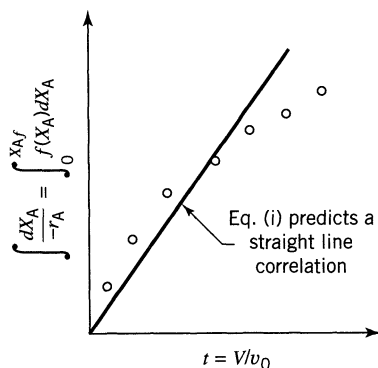


Figure E5.6

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:

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

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

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.

As a simple illustration of the difference between \bar{t} and τ , consider two cases of the steady-flow popcorn popper of Problem 4.7 which takes in 1 liter/min of raw corn and produces 28 liters/min of product popcorn.

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

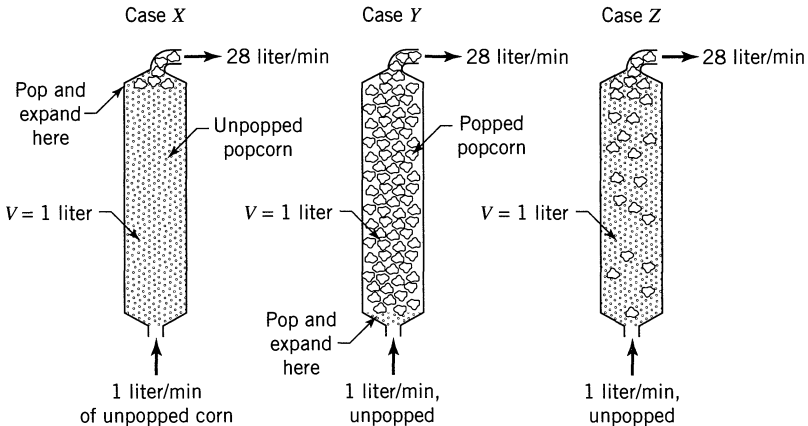


Figure 5.7 For the same τ value the \bar{t} values differ in these three cases.

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

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

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

Note that the value of \bar{t} depends on what happens in the reactor, while the value of τ is independent of what happens in the reactor.

This example shows that \bar{t} and τ are not, in general, identical. Now which is the natural performance measure for reactors? For batch systems Chapter 3 shows that it is the time of reaction; however, holding time does not appear anywhere in the performance equations for flow systems developed in this chapter, Eqs. 13 to 19, while it is seen that space-time or V/F_{A0} does naturally appear. Hence, τ or V/F_{A0} is the proper performance measure for flow systems.

The above simple example shows that in the special case of constant fluid density the space-time is equivalent to the holding time; hence, these terms can be used interchangeably. This special case includes practically all liquid phase reactions. However, for fluids of changing density, e.g., nonisothermal gas reactions or gas reactions with changing number of moles, a distinction should be made between τ and \bar{t} and the correct measure should be used in each situation.

Summary of Performance Equations

Tables 5.1 and 5.2 present the integrated performance equations for single ideal reactors.

REFERENCES

- Corcoran, W. H., and Lacey, W. N., *Introduction to Chemical Engineering Problems*, McGraw Hill, New York, 1970, p. 103.
 Pease, R. N., *J. Am. Chem. Soc.*, **51**, 3470 (1929).

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

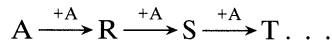
	Plug Flow or Batch	Mixed Flow
$n = 0$ $-r_A = k$	$\frac{k\tau}{C_{A0}} = \frac{C_{A0} - C_A}{C_{A0}} = X_A$ (20)	$\frac{k\tau}{C_{A0}} = \frac{C_{A0} - C_A}{C_{A0}} = X_A$
$n = 1$ $-r_A = kC_A$	$k\tau = \ln \frac{C_{A0}}{C_A} = \ln \frac{1}{1 - X_A}$ (3.12)	$k\tau = \frac{C_{A0} - C_A}{C_A} = \frac{X_A}{1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

Table 5.2 Performance Equations for n th-order Kinetics and $\varepsilon_A \neq 0$

	Plug Flow	Mixed Flow
$n = 0$ $-r_A = k$	$\frac{k\tau}{C_{A0}} = X_A$ (20)	$\frac{k\tau}{C_{A0}} = X_A$
$n = 1$ $-r_A = kC_A$	$k\tau = (1 + \varepsilon_A) \ln \frac{1}{1 - X_A} - \varepsilon_A X_A$ (21)	$k\tau = \frac{X_A(1 + \varepsilon_A X_A)}{1 - X_A}$ (14b)
$n = 2$ $-r_A = kC_A^2$	$k\tau C_{A0} = 2\varepsilon_A(1 + \varepsilon_A) \ln(1 - X_A) + \varepsilon_A^2 X_A + (\varepsilon_A + 1)^2 \cdot \frac{X_A}{1 - X_A}$ (23)	$k\tau C_{A0} = \frac{X_A(1 + \varepsilon_A X_A)^2}{(1 - X_A)^2}$ (15)
any n $-r_A = kC_A^n$		$k\tau C_{A0}^{n-1} = \frac{X_A(1 + \varepsilon_A X_A)^n}{(1 - X_A)^n}$
$n = 1$ $A \xrightarrow[\frac{2}{r}]{1} rR$ $C_{R0} = 0$	$\frac{k\tau}{X_{Ae}} = (1 + \varepsilon_A X_{Ae}) \ln \frac{X_{Ae}}{X_{Ae} - X_A} - \varepsilon_A X_A$ (22)	$\frac{k\tau}{X_{Ae}} = \frac{X_A(1 + \varepsilon_A X_A)}{X_{Ae} - X_A}$
General expression	$\tau = C_{A0} \int_0^{X_A} \frac{dX_A}{-r_A}$ (17)	$\tau = \frac{C_{A0} X_A}{-r_A}$ (11)

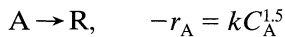
PROBLEMS

- 5.1. Consider a gas-phase reaction $2A \rightarrow R + 2S$ with unknown kinetics. If a space velocity of 1/min is needed for 90% conversion of A in a plug flow reactor, find the corresponding space-time and mean residence time or holding time of fluid in the plug flow reactor.
- 5.2. 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?
- 5.3. A stream of aqueous monomer A (1 mol/liter, 4 liter/min) enters a 2-liter mixed flow reactor, is radiated therein, and polymerizes as follows:



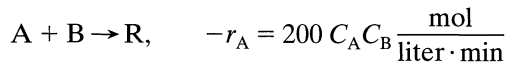
In the exit stream $C_A = 0.01$ mol/liter, and for a particular reaction product W, $C_W = 0.0002$ mol/liter. Find the rate of reaction of A and the rate of formation of W.

- 5.4. 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



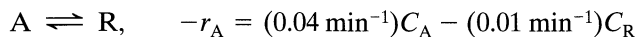
and present conversion is 70%.

- 5.5. 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



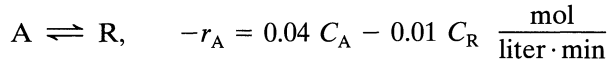
Find the volume of reactor needed for 99.9% conversion of A to product.

- 5.6. 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



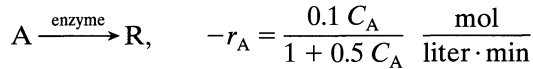
First find the equilibrium conversion and then find the actual conversion of A in the reactor.

- 5.7. 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.
- 5.8. A mixed flow reactor (2 m^3) processes an aqueous feed (100 liter/min) containing reactant A ($C_{A0} = 100 \text{ mmol/liter}$). The reaction is reversible and represented by



What is the equilibrium conversion and the actual conversion in the reactor?

- 5.9. 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 ($C_{A0} = 2 \text{ mol/liter}$). The kinetics of the fermentation at this enzyme concentration is given by

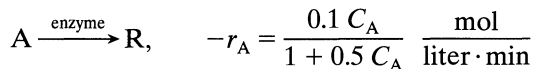


- 5.10. A gaseous feed of pure A (2 mol/liter, 100 mol/min) decomposes to give a variety of products in a plug flow reactor. The kinetics of the conversion is represented by



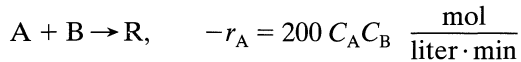
Find the expected conversion in a 22-liter reactor.

- 5.11. Enzyme E catalyses the fermentation of substrate A (the reactant) to product R. Find the size of mixed flow reactor needed for 95% conversion of reactant in a feed stream (25 liter/min) of reactant (2 mol/liter) and enzyme. The kinetics of the fermentation at this enzyme concentration are given by



- 5.12. 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 mixed flow reactor. The kinetics

of the reaction are represented by



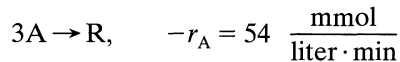
Find the volume of reactor needed for 99.9% conversion of A to product.

5.13. At 650°C phosphine vapor decomposes as follows:



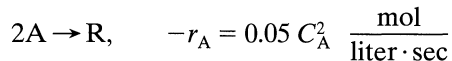
What size of plug flow reactor operating at 649°C and 11.4 atm is needed for 75% conversion of 10 mol/hr of phosphine in a 2/3 phosphine–1/3 inert feed?

5.14. 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



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

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



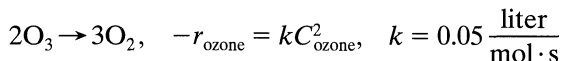
Find what feed rate (liter/min) will give an outlet concentration $C_A = 0.5$ mol/liter.

5.16. Gaseous reactant A decomposes as follows:



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 m³ mixed flow reactor.

5.17. 1 liter/s of a 20% ozone–80% air mixture at 1.5 atm and 93°C passes through a plug flow reactor. Under these conditions ozone decomposes by homogeneous reaction



What size reactor is needed for 50% decomposition of ozone? This problem is a modification of a problem given by Corcoran and Lacey (1970).

- 5.18.** 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 \cdot s). Find the outlet concentration of A for a feed rate of 0.5 liter/min.
- 5.19.** Pure gaseous A at about 3 atm and 30°C (120 mmol/liter) is fed into a 1-liter mixed flow reactor at various flow rates. There it decomposes, and the exit concentration of A is measured for each flow rate. From the following data find a rate equation to represent the kinetics of the decomposition of A. Assume that reactant A alone affects the rate.

v_0 , liter/min	0.06	0.48	1.5	8.1	$A \rightarrow 3R$
C_A , mmol/liter	30	60	80	105	

- 5.20.** 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

- 5.21.** 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 P5.21. 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?

Table P5.21

C_A , mol/liter	$-r_A$, mol/liter \cdot 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

- 5.22.** For the reaction of Problem 5.21, 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?

- 5.23. (a)** For the reaction of Problem 5.21, 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.
- 5.24.** 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.

- 5.25.** The aqueous decomposition of A is studied in an experimental mixed flow reactor. The results in Table P5.25 are obtained in steady-state runs. To obtain 75% conversion of reactant in a feed, $C_{A0} = 0.8$ mol/liter, what holding time is needed in a plug flow reactor?

Table P5.25

Concentration of A, mol/liter		Holding Time, sec
In Feed	In Exit Stream	
2.00	0.65	300
2.00	0.92	240
2.00	1.00	250
1.00	0.56	110
1.00	0.37	360
0.48	0.42	24
0.48	0.28	200
0.48	0.20	560

- 5.26.** Repeat the previous problem but for a mixed flow reactor.
- 5.27.** HOLMES: You say he was last seen tending this vat
 SIR BOSS: You mean "overflow stirred tank reactor," Mr. Holmes.
 HOLMES: You must excuse my ignorance of your particular technical jargon, Sir Boss.
 SIR BOSS: That's all right; however, you must find him, Mr. Holmes.

Imbibit was a queer chap; always staring into the reactor, taking deep breaths, and licking his lips, but he was our very best operator. Why, since he left, our conversion of googliox has dropped from 80% to 75%. HOLMES (*tapping the side of the vat idly*): By the way, what goes on in the vat?

SIR BOSS: Just an elementary second-order reaction, between ethanol and googliox, if you know what I mean. Of course, we maintain a large excess of alcohol, about 100 to 1 and . . .

HOLMES (*interrupting*): Intriguing, we checked every possible lead in town and found not a single clue.

SIR BOSS (*wiping away the tears*): We'll give the old chap a raise—about twopence per week—if only he'll come back.

DR. WATSON: Pardon me, but may I ask a question?

HOLMES: Why certainly, Watson.

WATSON: What is the capacity of this vat, Sir Boss?

SIR BOSS: A hundred Imperial gallons, and we always keep it filled to the brim. That is why we call it an overflow reactor. You see we are running at full capacity—profitable operation you know.

HOLMES: Well, my dear Watson, we must admit that we're stumped, for without clues deductive powers are of no avail.

WATSON: Ahh, but there is where you are wrong, Holmes. (*Then, turning to the manager*): Imbibit was a largish fellow—say about 18 stone—was he not?

SIR BOSS: Why yes, how did you know?

HOLMES (*with awe*): Amazing, my dear Watson!

WATSON (*modestly*): Why it's quite elementary, Holmes. We have all the clues necessary to deduce what happened to the happy fellow. But first of all, would someone fetch me some dill?

With Sherlock Holmes and Sir Boss impatiently waiting, Dr. Watson casually leaned against the vat, slowly and carefully filled his pipe, and—with the keen sense of the dramatic—lit it. There our story ends.

(a) What momentous revelation was Dr. Watson planning to make, and how did he arrive at this conclusion?

(b) Why did he never make it?

5.28. The data in Table P5.28 have been obtained on the decomposition of gaseous reactant A in a constant volume batch reactor at 100°C. The

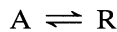
Table P5.28

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% conversion of A?

5.29. Repeat the previous problem for a mixed flow reactor.

5.30. The aqueous decomposition of A produces R as follows:



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

Chapter 6

Design for Single Reactions

There are many ways of processing a fluid: in a single batch or flow reactor, in a chain of reactors possibly with interstage feed injection or heating, in a reactor with recycle of the product stream using various feed ratios and conditions, and so on. Which scheme should we use? Unfortunately, numerous factors may have to be considered in answering this question; for example, the reaction type, planned scale of production, cost of equipment and operations, safety, stability and flexibility of operation, equipment life expectancy, length of time that the product is expected to be manufactured, ease of convertibility of the equipment to modified operating conditions or to new and different processes. With the wide choice of systems available and with the many factors to be considered, no neat formula can be expected to give the optimum setup. Experience, engineering judgment, and a sound knowledge of the characteristics of the various reactor systems are all needed in selecting a reasonably good design and, needless to say, the choice in the last analysis will be dictated by the economics of the overall process.

The reactor system selected will influence the economics of the process by dictating the size of the units needed and by fixing the ratio of products formed. The first factor, reactor size, may well vary a hundredfold among competing designs while the second factor, product distribution, is usually of prime consideration where it can be varied and controlled.

In this chapter we deal with *single reactions*. These are reactions whose progress can be described and followed adequately by using one and only one rate expression coupled with the necessary stoichiometric and equilibrium expressions. For such reactions product distribution is fixed; hence, the important factor in comparing designs is the reactor size. We consider in turn the size comparison of various single and multiple ideal reactor systems. Then we introduce the recycle reactor and develop its performance equations. Finally, we treat a rather unique type of reaction, the autocatalytic reaction, and show how to apply our findings to it.

Design for multiple reactions, for which the primary consideration is product distribution, is treated in the next two chapters.

6.1 SIZE COMPARISON OF SINGLE REACTORS

Batch Reactor

First of all, before we compare flow reactors, let us mention the batch reactor briefly. The batch reactor has the advantage of small instrumentation cost and flexibility of operation (may be shut down easily and quickly). It has the disadvantage of high labor and handling cost, often considerable shutdown time to empty, clean out, and refill, and poorer quality control of the product. Hence we may generalize to state that the batch reactor is well suited to produce small amounts of material and to produce many different products from one piece of equipment. On the other hand, for the chemical treatment of materials in large amounts the continuous process is nearly always found to be more economical.

Regarding reactor sizes, a comparison of Eqs. 5.4 and 5.19 for a given duty and for $\varepsilon = 0$ shows that an element of fluid reacts for the same length of time in the batch and in the plug flow reactor. Thus, the same volume of these reactors is needed to do a given job. Of course, on a long-term production basis we must correct the size requirement estimate to account for the shutdown time between batches. Still, it is easy to relate the performance capabilities of the batch reactor with the plug flow reactor.

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

For a given duty 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 n th-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

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

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

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

or

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

(2)

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

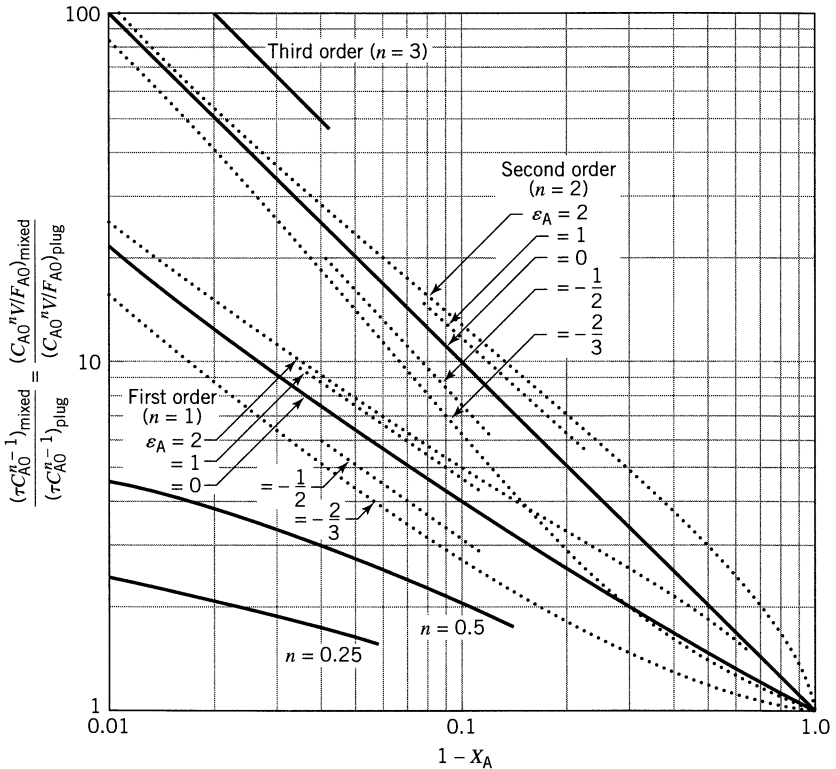
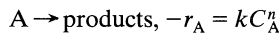


Figure 6.1 Comparison of performance of single mixed flow and plug flow reactors for the n th-order reactions



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.

Figures 6.5 and 6.6 show the same first- and second-order curves for $\varepsilon = 0$ but also include dashed lines which represent fixed values of the dimensionless reaction rate group, defined as

$k\tau$ for first-order reaction

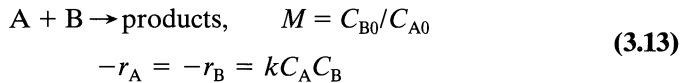
$kC_{A0}\tau$ for second-order reaction

With these lines we can compare different reactor types, reactor sizes, and conversion levels.

Example 6.1 illustrates the use of these charts.

Variation of Reactant Ratio for Second-Order Reactions

Second-order reactions of two components and of the type



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

$$-r_A = kC_A C_B = kC_A^2 \quad \text{when } M = 1 \quad (3)$$

On the other hand, 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

$$-r_A = kC_A C_B = (kC_{B0})C_A = k'C_A \quad \text{when } M \gg 1 \quad (4)$$

Thus in Fig. 6.1, and in terms of the limiting component A, the size ratio of mixed to plug flow reactors is represented by the region between the first-order and the second-order curves.

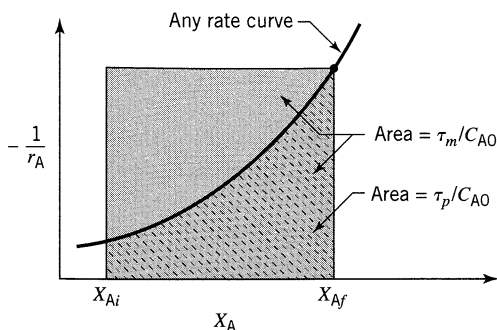


Figure 6.2 Comparison of performance of mixed flow and plug flow reactors for any reaction kinetics.

General Graphical Comparison

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, \dots, X_N be the fractional conversion of component A leaving reactor 1, 2, \dots , N . Basing the material balance on the feed rate of A to the first reactor, we find for the i th 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

$$\begin{aligned} \frac{V}{F_0} &= \sum_{i=1}^N \frac{V_i}{F_0} = \frac{V_1 + V_2 + \dots + V_N}{F_0} \\ &= \int_{X_0=0}^{X_1} \frac{dX}{-r} + \int_{X_1}^{X_2} \frac{dX}{-r} + \dots + \int_{X_{N-1}}^{X_N} \frac{dX}{-r} = \int_0^{X_N} \frac{dX}{-r} \end{aligned}$$

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 .

For the optimum hook up of plug flow reactors connected in parallel or in any parallel-series combination, we can treat the whole system as a single plug flow reactor of volume equal to the total volume of the individual units if the feed is distributed in such a manner that fluid streams that meet have the same composition. Thus, for reactors in parallel V/F or τ must be the same for each parallel line. Any other way of feeding is less efficient.

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?

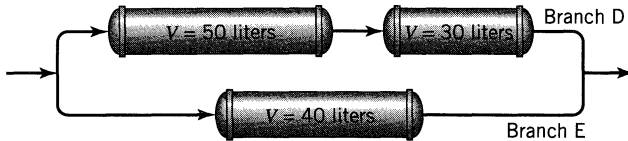


Figure E6.1

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,

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

or

$$\frac{F_D}{F_E} = \frac{V_D}{V_E} = \frac{80}{40} = 2$$

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

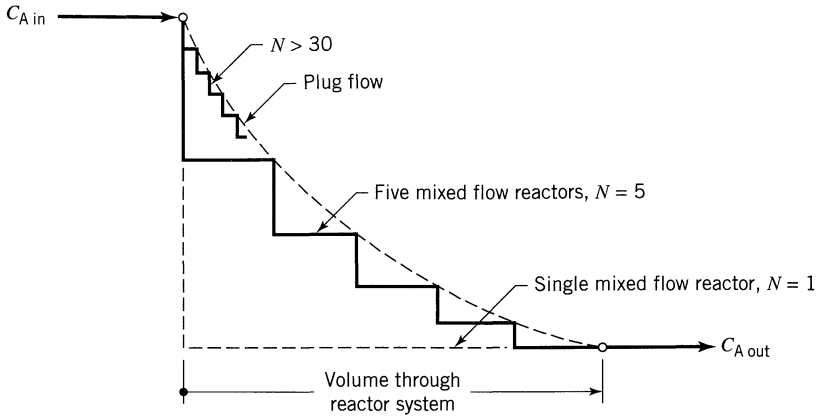


Figure 6.3 Concentration profile through an N -stage mixed flow reactor system compared with single flow reactors.

Equal-Size Mixed Flow Reactors in Series

In plug flow, the concentration of reactant decreases progressively through the system; in mixed flow, the concentration drops immediately to a low value. Because of this fact, a plug flow reactor is more efficient than a mixed flow reactor for reactions whose rates increase with reactant concentration, such as n th-order irreversible reactions, $n > 0$.

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.

Let us now quantitatively evaluate the behavior of a series of N equal-size mixed flow reactors. Density changes will be assumed to be negligible; hence $\varepsilon = 0$ and $t = \tau$. As a rule, with mixed flow reactors it is more convenient to develop the necessary equations in terms of concentrations rather than fractional conversions; therefore, we use this approach. The nomenclature used is shown in Fig. 6.4 with subscript i referring to the i th vessel.

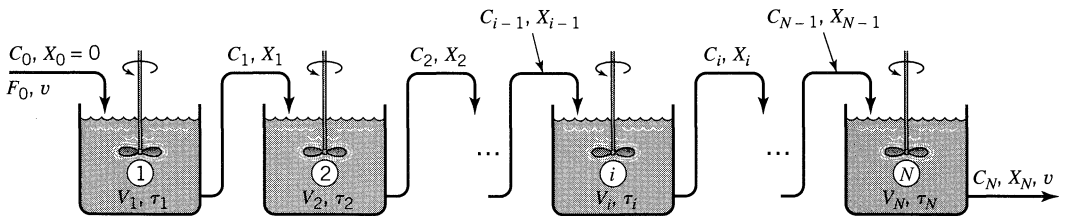


Figure 6.4 Notation for a system of N equal-size mixed reactors in series.

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

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

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

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

Rearranging, we find for the system as a whole

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

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

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

With Eqs. 6b and 7 we can 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.

Second-Order Reactions. We may evaluate 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. Thus, for

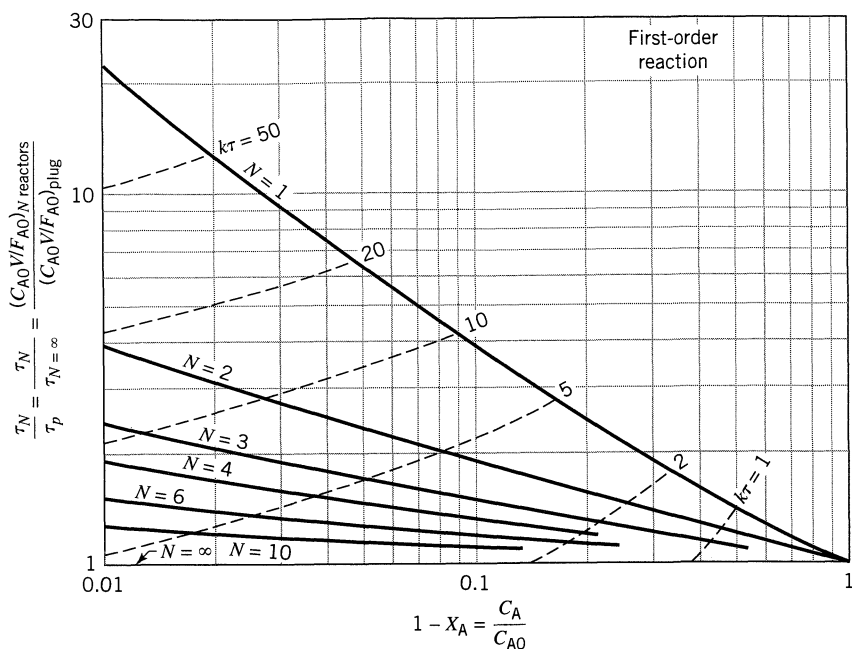
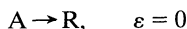


Figure 6.5 Comparison of performance of a series of N equal-size mixed flow reactors with a plug flow reactor for the first-order reaction



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

$$C_N = \frac{1}{4k\tau_i} \left(-2 + 2 \sqrt{-1 \dots + 2 \sqrt{-1 + 2 \sqrt{1 + 4C_0 k\tau_i}}} \right) \quad (8a)$$

whereas for plug flow

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

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

Figures 6.5 and 6.6 support our intuition by showing that the volume of system required for a given conversion decreases to plug flow volume as the number of reactors in series is increased, the greatest change taking place with the addition of a second vessel to a one-vessel system.

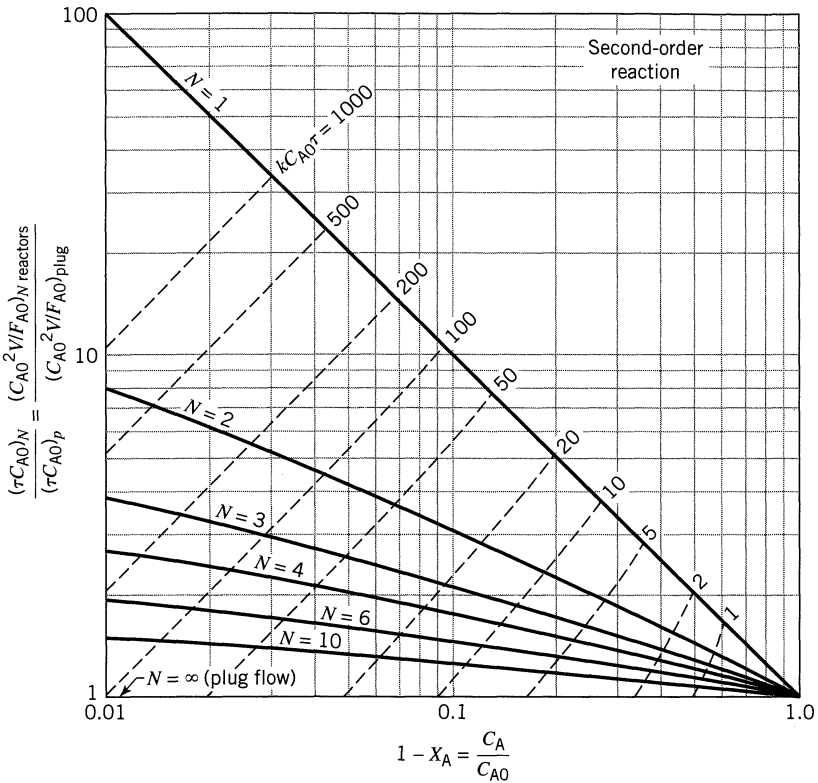
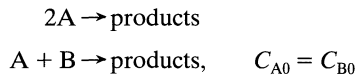


Figure 6.6 Comparison of performance of a series of N equal-size mixed flow reactors with a plug flow reactor for elementary second-order reactions



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.

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.

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

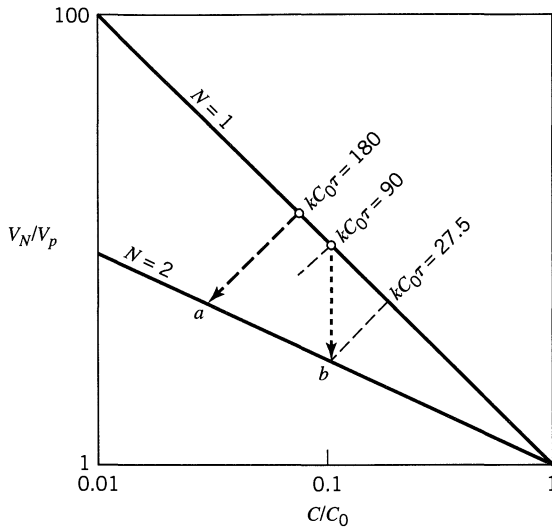


Figure E6.2

(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 $X = 97.4\%$, point *a*.

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

$$kC_0\tau = 27.5, \quad \text{point } b$$

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: how to find the outlet conversion from a given reactor system, and the inverse question, how to find the best setup to achieve a given conversion. Different procedures are used for these two problems. We treat them in turn.

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.

Let us illustrate the use of this method by considering three mixed flow reactors in series with volumes, feed rates, concentrations, space-times (equal to residence times because $\varepsilon = 0$), and volumetric flow rates as shown in Fig. 6.7. Now from Eq. 5.11, noting that $\varepsilon = 0$, we may write for component A in the first reactor

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

or

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

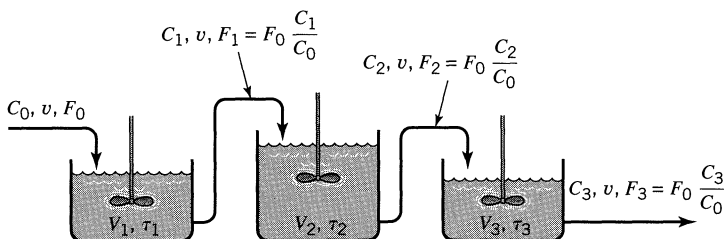


Figure 6.7 Notation for a series of unequal-size mixed flow reactors.

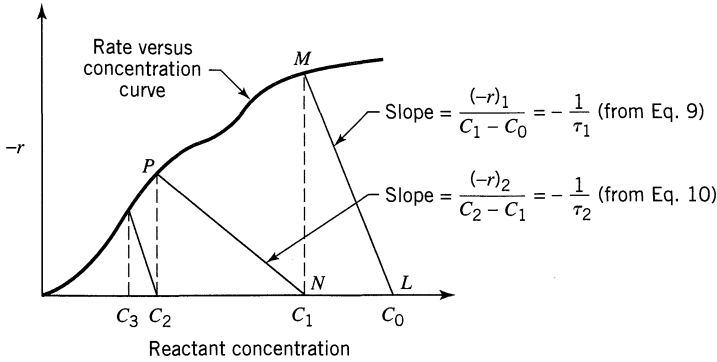


Figure 6.8 Graphical procedure for finding compositions in a series of mixed flow reactors.

Similarly, from Eq. 5.12 for the i th reactor we may write

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

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.

With slight modification this graphical method can be extended to reactions in which density changes are appreciable.

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

$$\tau_1 = \frac{X_1}{(-r)_1} \quad (11)$$

and for the second reactor

$$\tau_2 = \frac{X_2 - X_1}{(-r)_2} \quad (12)$$

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

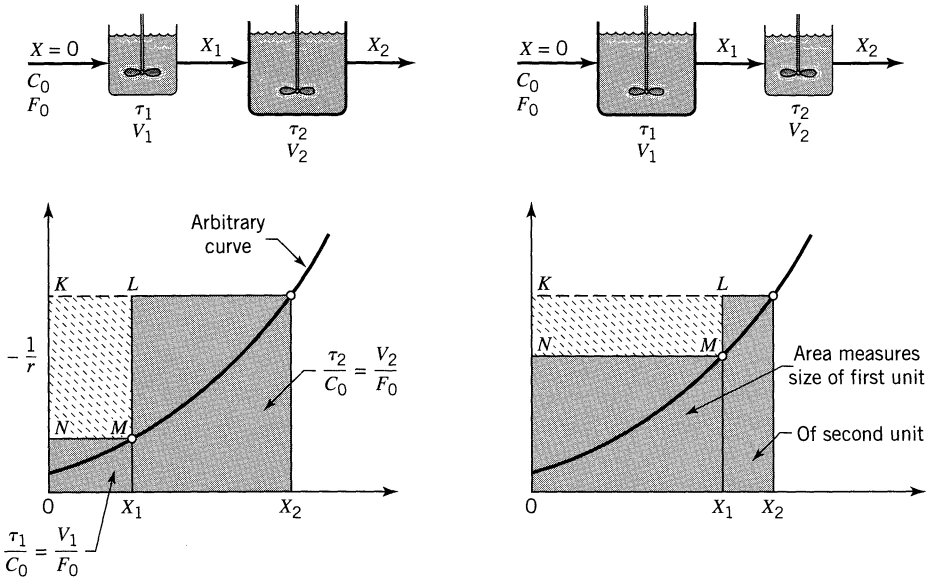


Figure 6.9 Graphical representation of the variables for two mixed flow reactors in series.

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

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

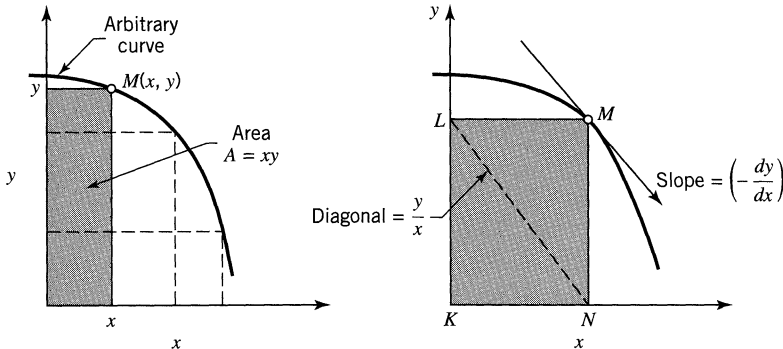


Figure 6.10 Graphical procedure for maximizing the area of a rectangle.

This area is maximized when

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

or when

$$-\frac{dy}{dx} = \frac{y}{x} \quad (14)$$

In words, 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 n th-order kinetics, $n > 0$, there always is just one “best” point.

We will use this method of maximizing a rectangle in later chapters. But let us return to our problem.

The optimum size ratio of the two reactors is achieved where the slope of the rate curve at M equals the diagonal NL . The best value of M is shown in Fig. 6.11, and this determines the intermediate conversion X_1 as well as the size of units needed.

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. For the special case of first-order reactions equal-size reactors are best; for reaction orders $n > 1$ the smaller reactor should come first; for $n < 1$ the larger should come first (see Problem 6.3). However, Szepe and Levenspiel (1964) show that the advantage of the minimum size system over the equal-size system is quite small, only a few percent at most. Hence, overall economic consideration would nearly always recommend using equal-size units.

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.

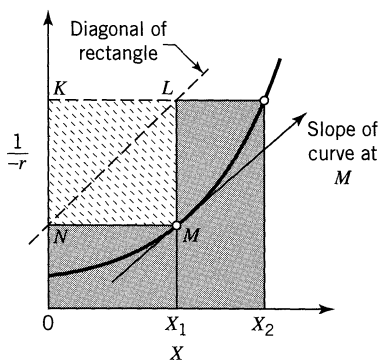


Figure 6.11 Maximization of rectangles applied to find the optimum intermediate conversion and optimum sizes of two mixed flow reactors in series.

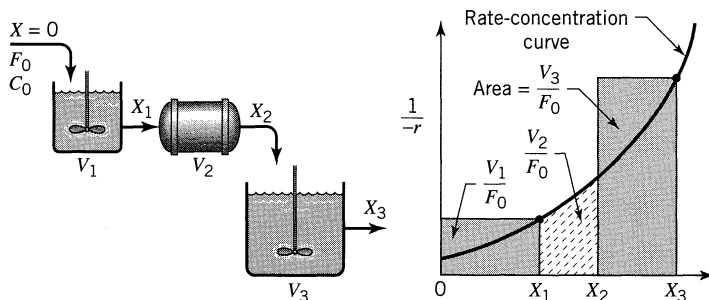


Figure 6.12 Graphical design procedure for reactors in series.

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. This allows us to predict the overall conversions for such systems, or conversions at intermediate points between the individual reactors. These intermediate conversions may be needed to determine the duty of interstage heat exchangers.

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 n th-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.

The problems at the end of this chapter illustrate these findings.

6.3 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* R be defined as

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

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 ($R = 0$) to mixed flow ($R = \infty$). 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

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

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. Let us now do this.

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

$$\begin{aligned} F'_{A0} &= \left(\begin{array}{l} \text{A which would enter in an} \\ \text{unconverted recycle stream} \end{array} \right) + \left(\begin{array}{l} \text{A entering in} \\ \text{fresh feed} \end{array} \right) \\ &= RF_{A0} + F_{A0} = (R + 1)F_{A0} \end{aligned} \quad (17)$$

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

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

Because the pressure is taken to be constant, the streams meeting at point K may be added directly. This gives

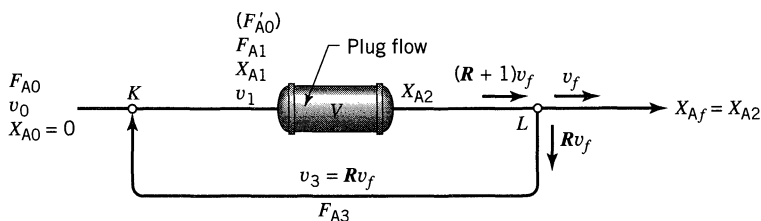


Figure 6.13 Nomenclature for the recycle reactor.

$$C_{A1} = \frac{F_{A1}}{v_1} = \frac{F_{A0} + F_{A3}}{v_0 + Rv_f} = \frac{F_{A0} + RF_{A0}(1 - X_{Af})}{v_0 + Rv_0(1 + \varepsilon_A X_{Af})} = C_{A0} \left(\frac{1 + R - RX_{Af}}{1 + R + R\varepsilon_A X_{Af}} \right) \quad (19)$$

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

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

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 $X_{A0} = 0$.

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

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

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

These expressions are represented graphically in Fig. 6.14.

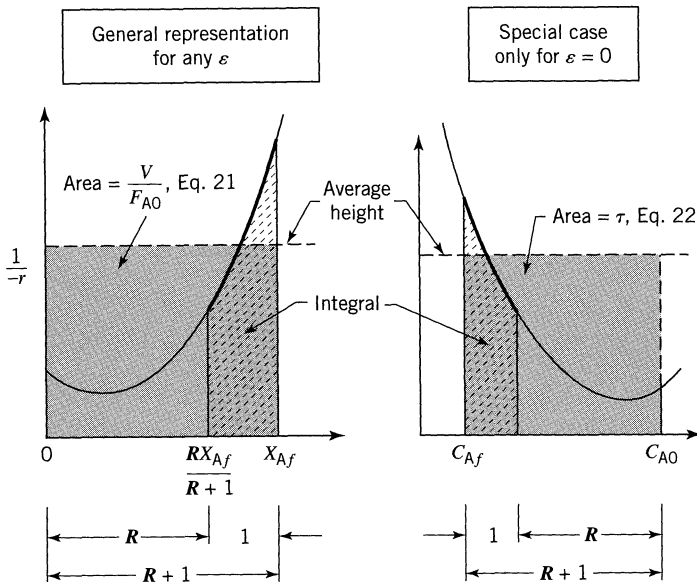


Figure 6.14 Representation of the performance equation for recycle reactors.

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

$$\frac{V}{F_{A0}} = (R + 1) \int_{\frac{R}{R+1} X_{Af}}^{X_{Af}} \frac{dX_A}{-r_A}$$

$R = 0$
 \downarrow
 $\frac{V}{F_{A0}} = \int_A^{X_{Af}} \frac{dX_A}{-r_A}$

 plug flow

$R = \infty$
 \downarrow
 $\frac{V}{F_{A0}} = \frac{X_{Af}}{-r_{Af}}$

 mixed flow

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

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

$$\frac{k\tau}{R + 1} = \ln \left[\frac{C_{A0} + RC_{Af}}{(R + 1)C_{Af}} \right] \quad (23)$$

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

$$\frac{kC_{A0}\tau}{R + 1} = \frac{C_{A0}(C_{A0} - C_{Af})}{C_{Af}(C_{A0} + RC_{Af})} \quad (24)$$

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

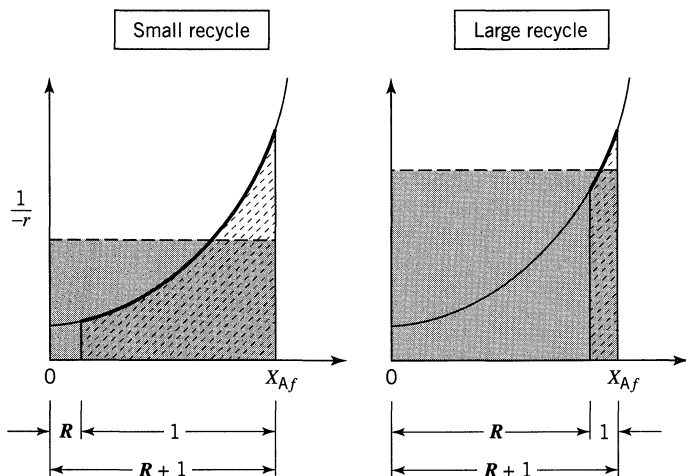


Figure 6.15 The recycle extremes approach plug flow ($R \rightarrow 0$) and mixed flow ($R \rightarrow \infty$).

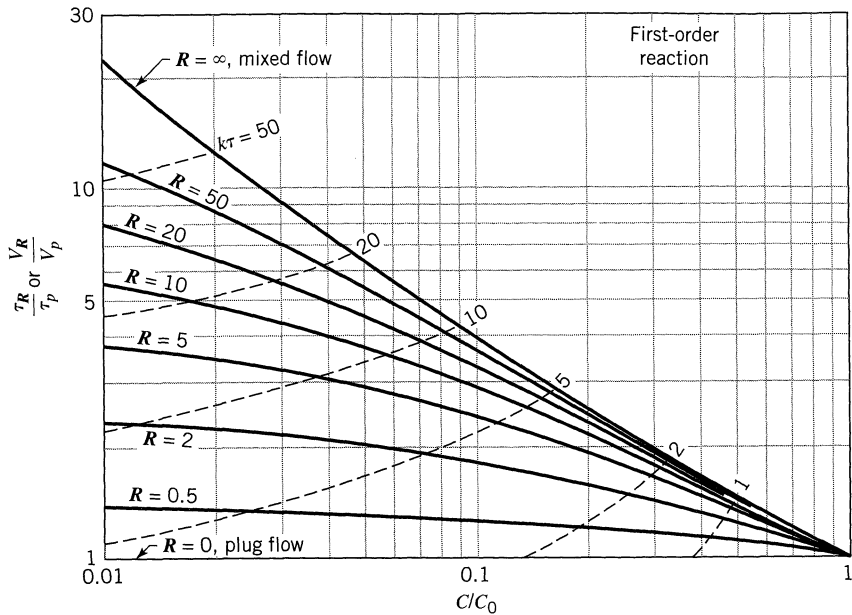
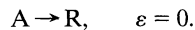


Figure 6.16 Comparison of performance of recycle and plug flow for first-order reactions



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) gives the following rough comparison for equal performance:

No. of tanks	R for first-order reaction			R for second-order reaction		
	at $X_A = 0.5$	0.90	0.99	at $X_A = 0.5$	0.90	0.99
1	∞	∞	∞	∞	∞	∞
2	1.0	2.2	5.4	1.0	2.8	7.5
3	0.5	1.1	2.1	0.5	1.4	2.9
4	0.33	0.68	1.3	0.33	0.90	1.7
10	0.11	0.22	0.36	0.11	0.29	0.5
∞	0	0	0	0	0	0

The recycle reactor is a convenient way for approaching mixed flow with what is essentially a plug flow device. Its particular usefulness is with solid catalyzed reactions with their fixed bed contactors. We meet this and other applications of recycle reactors in later chapters.

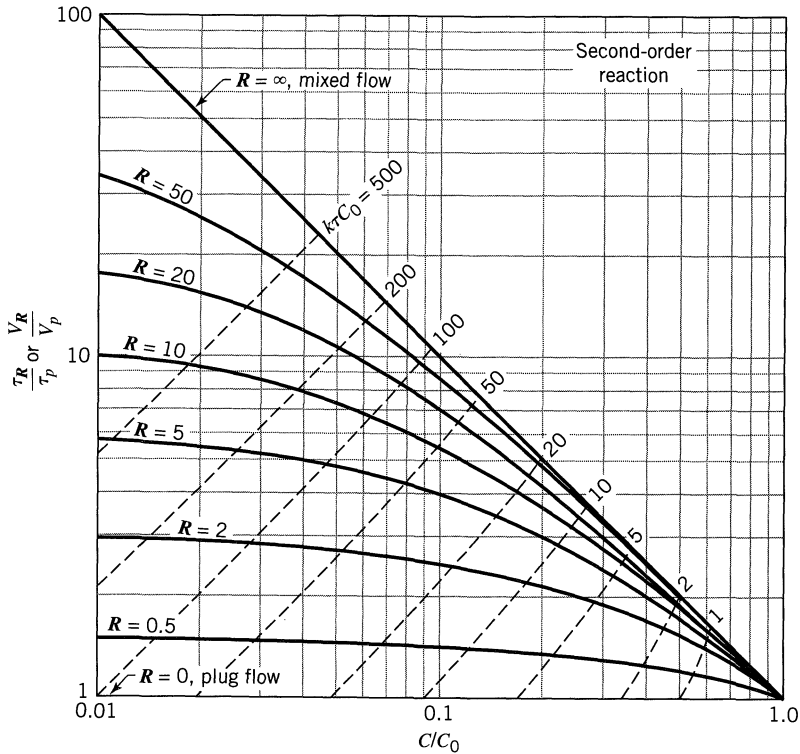
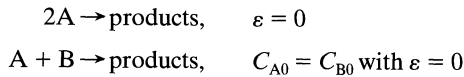


Figure 6.17 Comparison of performance of recycle reactors with plug flow reactors for elementary second-order reactions (Personal communication, from T. J. Fitzgerald and P. Filleli):



6.4 AUTOCATALYTIC REACTIONS

When a material reacts away by any n th order rate ($n > 0$) in a batch reactor, its rate of disappearance is rapid at the start when the concentration of reactant is high. This rate then slows progressively as reactant is consumed. In an autocatalytic reaction, however, the rate at the start is low because little product is present; it increases to a maximum as product is formed and then drops again to a low value as reactant is consumed. Figure 6.18 shows a typical situation.

Reactions with such rate-concentration curves lead to interesting optimization problems. In addition, they provide a good illustration of the general design method presented in this chapter. For these reasons let us examine these reactions in some detail. 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.

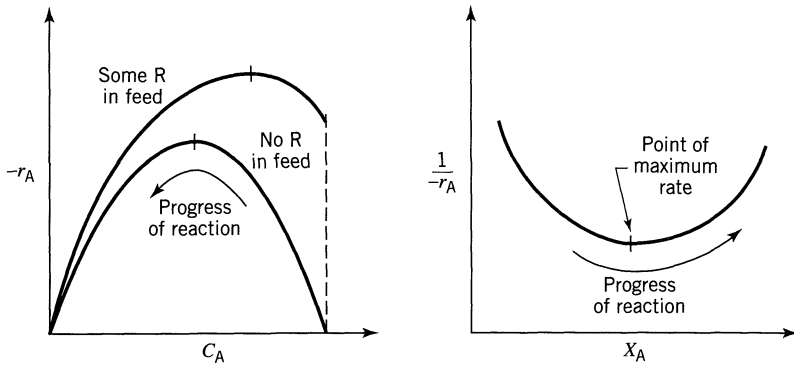
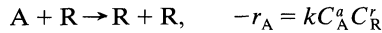


Figure 6.18 Typical rate-concentration curve for autocatalytic reactions, for example:



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.

These findings differ from ordinary n th-order reactions ($n > 0$) where the plug flow reactor is always more efficient than the mixed flow reactor. In addition, we should note 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.

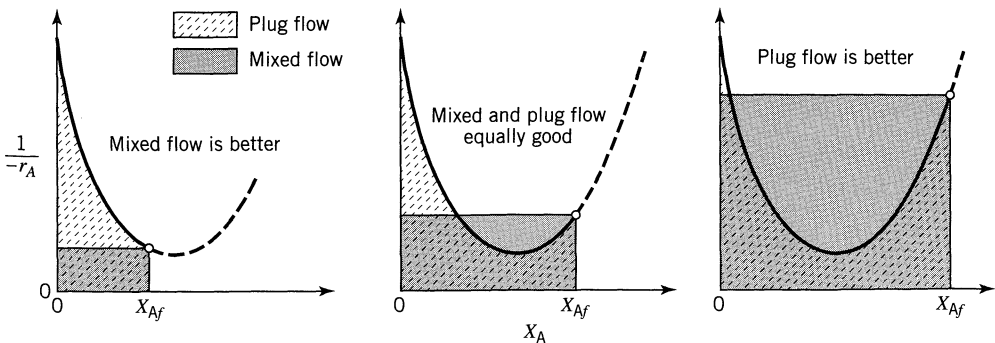


Figure 6.19 For autocatalytic reactions mixed flow is more efficient at low conversions, plug flow is more efficient at high conversions.

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 R .

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

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

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

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

then

$$\frac{dF}{dR} = \int_{a(R)}^{b(R)} \frac{\partial f(x, R)}{\partial R} dx + f(b, R) \frac{db}{dR} - f(a, R) \frac{da}{dR} \quad (27)$$

For our case, Eq. 25, we then find

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

where

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

Combining and rearranging then gives for the optimum

$$\boxed{\frac{1}{-r_A} \Big|_{X_{Ai}} = \frac{\int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{-r_A}}{(X_{Af} - X_{Ai})}} \quad (28)$$

In words, the optimum recycle ratio introduces to the reactor a feed whose $1/(-r_A)$ value (KL in Fig. 6.20) equals the average $1/(-r_A)$ value in the reactor as a whole (PQ in Fig. 6.20). Figure 6.20 compares this optimum with conditions where the recycle is either too high or too low.

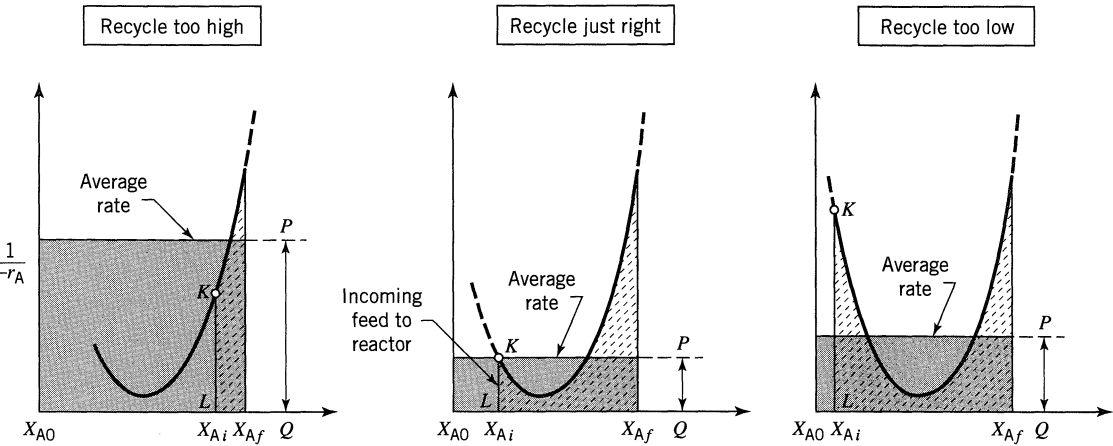


Figure 6.20 Correct recycle ratio for an autocatalytic reaction compared with recycle ratios which are too high and too low.

Occurrence of Autocatalytic Reactions. The most important examples of autocatalytic reactions are the broad class of fermentation reactions which result from the reaction of microorganism on an organic feed. When they can be treated as single reactions, the methods of this chapter can be applied directly. Another type of reaction which has autocatalytic behavior is the exothermic reaction (say, the combustion of fuel gas) proceeding in an adiabatic manner with cool reactants entering the system. In such a reaction, called *autothermal*, heat may be considered to be the product which sustains the reaction. Thus, with plug flow the reaction will die. With backmixing the reaction will be self-sustaining because the heat generated by the reaction can raise fresh reactants to a temperature at which they will react. Autothermal reactions are of great importance in solid catalyzed gas-phase systems and are treated later in the book.

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. 6.21b).

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.

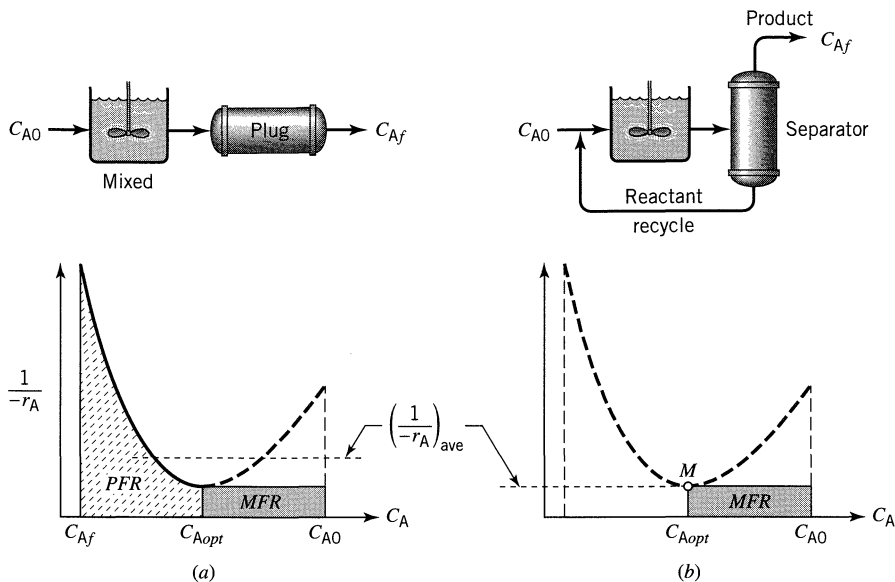


Figure 6.21 (a) The best multiple reactor scheme. (b) The best scheme when unconverted reactant can be separated and recycled.

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 .

- 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.
- 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?
- 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. E6.3a, b, c) so we must prepare to deal with an autocatalytic type reacting system.

Table E6.3

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
$\frac{1}{-r_A} = \frac{\tau}{C_{A0} - C_A}$, $\frac{\text{m}^3 \cdot \text{min}}{\text{mmol}}$	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. E6.3a we find

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

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

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

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

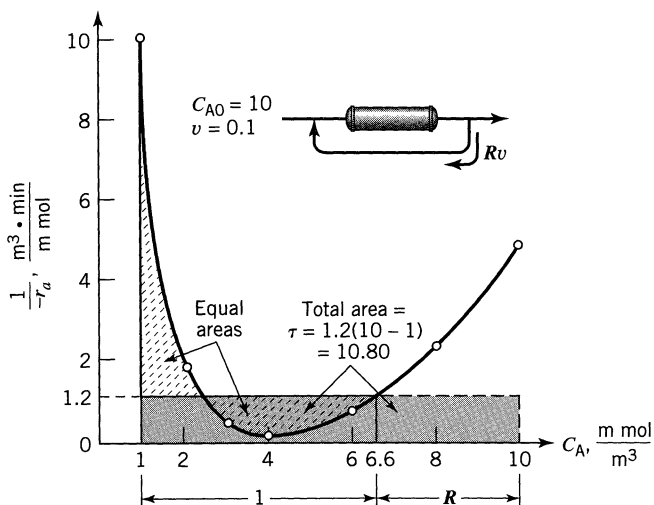


Figure E6.3a Plug flow with recycle.

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

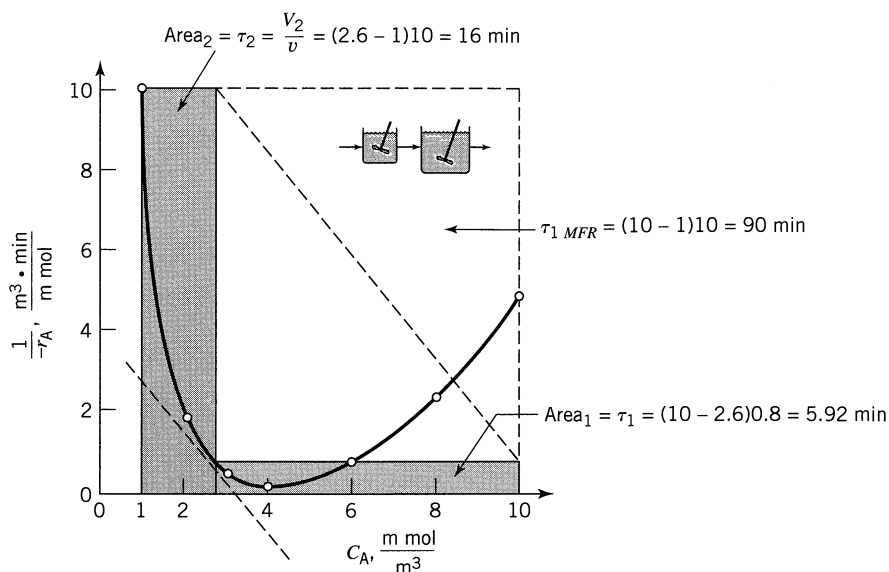


Figure E6.3b One and two mixed flow reactors in series.

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

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

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. E6.3c we find

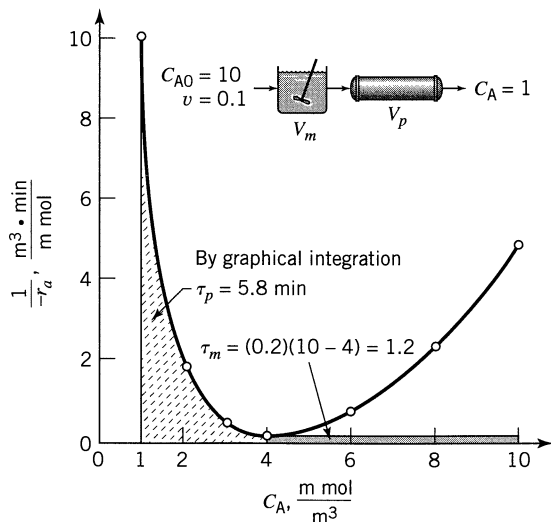


Figure E6.3c Arrangement with smallest volume.

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

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

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- Jones, R. W., *Chem. Eng. Progr.*, **47**, 46 (1951).
 Szepe, S., and O. Levenspiel, *Ind. Eng. Chem. Process Design Develop.*, **3**, 214 (1964).

PROBLEMS

- 6.1.** A liquid reactant stream (1 mol/liter) passes through two mixed flow reactors in a series. The concentration of A in the exit of the first reactor is 0.5 mol/liter. Find the concentration in the exit stream of the second reactor. The reaction is second-order with respect to A and $V_2/V_1 = 2$.
- 6.2.** Water containing a short-lived radioactive species flows continuously through a well-mixed holdup tank. This gives time for the radioactive material to decay into harmless waste. As it now operates, the activity of the exit stream is 1/7 of the feed stream. This is not bad, but we'd like to lower it still more.
 One of our office secretaries suggests that we insert a baffle down the middle of the tank so that the holdup tank acts as two well-mixed tanks in series. Do you think this would help? If not, tell why; if so, calculate the expected activity of the exit stream compared to the entering stream.
- 6.3.** An aqueous reactant stream (4 mol A/liter) passes through a mixed flow reactor followed by a plug flow reactor. Find the concentration at the exit of the plug flow reactor if in the mixed flow reactor $C_A = 1$ mol/liter. The reaction is second-order with respect to A, and the volume of the plug flow unit is three times that of the mixed flow unit.
- 6.4.** Reactant A ($A \rightarrow R$, $C_{A0} = 26$ mol/m³) passes in steady flow through four equal-size mixed flow reactors in series ($\tau_{\text{total}} = 2$ min). When steady state is achieved the concentration of A is found to be 11, 5, 2, 1 mol/m³ in the four units. For this reaction, what must be τ_{plug} so as to reduce C_A from $C_{A0} = 26$ to $C_{Af} = 1$ mol/m³?
- 6.5.** Originally we had planned to lower the activity of a gas stream containing radioactive Xe-138 (half-life = 14 min) by having it pass through two holdup tanks in series, both well mixed and of such size that the mean residence time of gas is 2 weeks in each tank. It has been suggested that we replace the two tanks with a long tube (assume plug flow). What must be the size of this tube compared to the two original stirred tanks, and

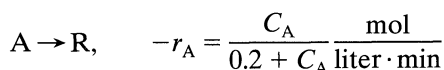
what should be the mean residence time of gas in this tube for the same extent of radioactive decay?

- 6.6. At 100°C pure gaseous A reacts away with stoichiometry $2A \rightarrow R + S$ in a constant volume batch reactor as follows:

$t, \text{ sec}$	0	20	40	60	80	100	120	140	160
$p_A, \text{ atm}$	1.00	0.96	0.80	0.56	0.32	0.18	0.08	0.04	0.02

What size of plug flow reactor operating at 100°C and 1 atm can treat 100 moles A/hr in a feed consisting of 20% inerts to obtain 95% conversion of A?

- 6.7. We wish to treat 10 liters/min of liquid feed containing 1 mol A/liter to 99% conversion. The stoichiometry and kinetics of the reaction are given by



Suggest a good arrangement for doing this using two mixed flow reactors, and find the size of the two units needed. Sketch the final design chosen.

- 6.8. From steady-state kinetics runs in a mixed flow reactor, we obtain the following data on the reaction $A \rightarrow R$.

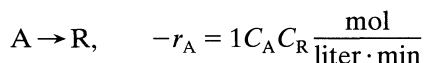
$\tau, \text{ sec}$	$C_{A0}, \text{ mmol/liter}$	$C_A, \text{ mmol/liter}$
60	50	20
35	100	40
11	100	60
20	200	80
11	200	100

Find the space time needed to treat a feed of $C_{A0} = 100 \text{ mmol/liter}$ to 80% conversion

- (a) in a plug flow reactor.
(b) in a mixed flow reactor.

- 6.9. At present we have 90% conversion of a liquid feed ($n = 1, C_{A0} = 10 \text{ mol/liter}$) to our plug flow reactor with recycle of product ($R = 2$). If we shut off the recycle stream, by how much will this lower the processing rate of our feed to the same 90% conversion?

- 6.10. Aqueous feed containing reactant A ($C_{A0} = 2 \text{ mol/liter}$) enters a plug flow reactor (10 liter) which has a provision for recycling a portion of the flowing stream. The reaction kinetics and stoichiometry are

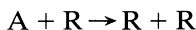


and we wish to get 96% conversion. Should we use the recycle stream? If so, at what value should we set the recycle flow rate so as to obtain the highest production rate, and what volumetric feed rate can we process to this conversion in the reactor?

- 6.11.** Consider the autocatalytic reaction $A \rightarrow R$, with $-r_A = 0.001 C_A C_R$ mol/liter \cdot s. We wish to process 1.5 liters/s of a $C_{A0} = 10$ mol/liter feed to the highest conversion possible in the reactor system consisting of four 100-liter mixed flow reactors connected as you wish and any feed arrangement. Sketch your recommended design and feed arrangement and determine C_{Af} from this system.
- 6.12.** A first-order liquid-phase reaction, 92% conversion, is taking place in a mixed flow reactor. It has been suggested that a fraction of the product stream, with no additional treatment, be recycled. If the feed rate remains unchanged, in what way would this affect conversion?
- 6.13.** 100 liters/hr of radioactive fluid having a half-life of 20 hr is to be treated by passing it through two ideal stirred tanks in series, $V = 40\,000$ liters each. In passing through this system, how much will the activity decay?
- 6.14.** At present the elementary liquid-phase reaction $A + B \rightarrow R + S$ takes place in a plug flow reactor using equimolar quantities of A and B. Conversion is 96%, $C_{A0} = C_{B0} = 1$ mol/liter. If a mixed flow reactor ten times as large as the plug flow reactor were hooked up in series with the existing unit, which unit should come first and by what fraction could production be increased for that setup?
- 6.15.** The kinetics of the aqueous-phase decomposition of A is investigated in two mixed flow reactors in series, the second having twice the volume of the first reactor. At steady state with a feed concentration of 1 mol A/liter and mean residence time of 96 sec in the first reactor, the concentration in the first reactor is 0.5 mol A/liter and in the second is 0.25 mol A/liter. Find the kinetic equation for the decomposition.
- 6.16.** Using a color indicator which shows when the concentration of A falls below 0.1 mol/liter, the following scheme is devised to explore the kinetics of the decomposition of A. A feed of 0.6 mol A/liter is introduced into the first of the two mixed flow reactors in series, each having a volume of 400 cm³. The color change occurs in the first reactor for a steady-state feed rate of 10 cm³/min, and in the second reactor for a steady-state feed rate of 50 cm³/min. Find the rate equation for the decomposition of A from this information.
- 6.17.** The elementary irreversible aqueous-phase reaction $A + B \rightarrow R + S$ is carried out isothermally as follows. Equal volumetric flow rates of two liquid streams are introduced into a 4-liter mixing tank. One stream contains 0.020 mol A/liter, the other 1.400 mol B/liter. The mixed stream is then

passed through a 16-liter plug flow reactor. We find that some R is formed in the mixing tank, its concentration being 0.002 mol/liter. Assuming that the mixing tank acts as a mixed flow reactor, find the concentration of R at the exit of the plug flow reactor as well as the fraction of initial A that has been converted in the system.

- 6.18.** At present conversion is $2/3$ for our elementary second-order liquid reaction $2A \rightarrow 2R$ when operating in an isothermal plug flow reactor with a recycle ratio of unity. What will be the conversion if the recycle stream is shut off?
- 6.19.** We wish to explore various reactor setups for the transformation of A into R. The feed contains 99% A, 1% R; the desired product is to consist of 10% A, 90% R. The transformation takes place by means of the elementary reaction



with rate constant $k = 1$ liter/mol \cdot min. The concentration of active materials is

$$C_{A0} + C_{R0} = C_A + C_R = C_0 = 1 \text{ mol/liter}$$

throughout.

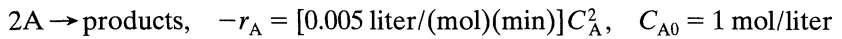
What reactor holding time will yield a product in which $C_R = 0.9$ mol/liter (a) in a plug flow reactor, (b) in a mixed flow reactor, and (c) in a minimum-size setup without recycle?

- 6.20.** Reactant A decomposes with stoichiometry $A \rightarrow R$ and with rate dependent only on C_A . The following data on this aqueous decomposition are obtained in a mixed flow reactor:

τ , sec	C_{A0}	C_A
14	200	100
25	190	90
29	180	80
30	170	70
29	160	60
27	150	50
24	140	40
19	130	30
15	120	20
12	110	10
20	101	1

Determine which setup, plug flow, mixed flow, or any two-reactor combination gives minimum τ for 90% conversion of a feed consisting of $C_{A0} = 100$. Also find this τ minimum. If a two-reactor scheme is found to be optimum, give C_A between stages and τ for each stage.

- 6.21.** For an irreversible first-order liquid-phase reaction ($C_{A0} = 10$ mol/liter) conversion is 90% in a plug flow reactor. If two-thirds of the stream leaving the reactor is recycled to the reactor entrance, and if the throughput to the whole reactor-recycle system is kept unchanged, what does this do to the concentration of reactant leaving the system?
- 6.22.** At room temperature the second-order irreversible liquid-phase reaction proceeds as follows:



A batch reactor takes 18 min to fill and empty. What percent conversion and reaction time should we use so as to maximize the daily output of product R?

Chapter 7

Design for Parallel Reactions

Introduction to Multiple Reactions

The preceding chapter on single reactions showed that the performance (size) of a reactor was influenced by the pattern of flow within the vessel. In this and the next chapter, we extend the discussion to multiple reactions and show that for these, both the size requirement and the distribution of reaction products are affected by the pattern of flow within the vessel. We may recall at this point that the distinction between a *single* reaction and *multiple* reactions is that the single reaction requires only one rate expression to describe its kinetic behavior whereas multiple reactions require more than one rate expression.

Since multiple reactions are so varied in type and seem to have so little in common, we may despair of finding general guiding principles for design. Fortunately, this is not so because many multiple reactions can be considered to be combinations of two primary types: *parallel* reactions and *series* reactions.

In this chapter we treat parallel reactions. In the next chapter we treat series reactions as well as all sorts of series-parallel combinations.

Let us consider the general approach and nomenclature. First of all, we find it more convenient to deal with concentrations rather than conversions. Second, in examining product distribution the procedure is to eliminate the time variable by dividing one rate equation by another. We end up then with equations relating the rates of change of certain components with respect to other components of the systems. Such relationships are relatively easy to treat. Thus, we use two distinct analyses, one for determination of reactor size and the other for the study of product distribution.

The two requirements, small reactor size and maximization of desired product, may run counter to each other. In such a situation an economic analysis will yield the best compromise. In general, however, product distribution controls; consequently, this chapter concerns primarily optimization with respect to product distribution, a factor which plays no role in single reactions.

Finally, we ignore expansion effects in this chapter; thus, we take $\varepsilon = 0$ throughout. This means that we may use the terms mean residence time, reactor holding time, space time, and reciprocal space velocity interchangeably.

Qualitative Discussion About Product Distribution. Consider the decomposition of A by either one of two paths:



with corresponding rate equations

$$r_R = \frac{dC_R}{dt} = k_1 C_A^{a_1} \quad (2a)$$

$$r_S = \frac{dC_S}{dt} = k_2 C_A^{a_2} \quad (2b)$$

Dividing Eq. 2a by Eq. 2b gives a measure of the relative rates of formation of R and S. Thus

$$\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_2}{k_1} C_A^{a_1 - a_2} \quad (3)$$

and we wish this ratio to be as large as possible.

Now C_A is the only factor in this equation which we can adjust and control (k_1 , k_2 , a_1 , and a_2 are all constant for a specific system at a given temperature) and we can keep C_A low throughout the reactor by any of the following means: by using a mixed flow reactor, maintaining high conversions, increasing inerts in the feed, or decreasing the pressure in gas-phase systems. On the other hand, we can keep C_A high by using a batch or plug flow reactor, maintaining low conversions, removing inerts from the feed, or increasing the pressure in gas-phase systems.

For the reactions of Eq. 1 let us see whether the concentration of A should be kept high or low.

If $a_1 > a_2$, or the desired reaction is of higher order than the unwanted reaction, Eq. 3 shows that a high reactant concentration is desirable since it increases the R/S ratio. As a result, a batch or plug flow reactor would favor formation of product R and would require a minimum reactor size.

If $a_1 < a_2$, or the desired reaction is of lower order than the unwanted reaction, we need a low reactant concentration to favor formation of R. But this would also require large mixed flow reactor.

If $a_1 = a_2$, or the two reactions are of the same order, Eq. 3 becomes

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

Hence, product distribution is fixed by k_2/k_1 alone and is unaffected by type of reactor used.

We also may control product distribution by varying k_2/k_1 . This can be done in two ways:

1. By changing the temperature level of operation. If the activation energies of the two reactions are different, k_1/k_2 can be made to vary. Chapter 9 considers this problem.
2. By using a catalyst. One of the most important features of a catalyst is its selectivity in depressing or accelerating specific reactions. This may be a much more effective way of controlling product distribution than any of the methods discussed so far.

We summarize our qualitative findings as follows:

For reactions in parallel, the concentration level of reactants is the key to proper control of product distribution. A high reactant concentration favors the reaction of higher order, a low concentration favors the reaction of lower order, while the concentration level has no effect on the product distribution for reactions of the same order.

(4)

When you have two or more reactants, combinations of high and low reactant concentrations can be obtained by controlling the concentration of feed materials, by having certain components in excess, and by using the correct contacting pattern of reacting fluids. Figures 7.1 and 7.2 illustrate methods of contacting two reacting fluids in continuous and noncontinuous operations that keep the concentrations of these components both high, both low, or one high and the other low. In general, the number of reacting fluids involved, the possibility of recycle, and the cost of possible alternative setups must all be considered before the most desirable contacting pattern can be achieved.

In any case, the use of the proper contacting pattern is the critical factor in obtaining a favorable distribution of products for multiple reactions.

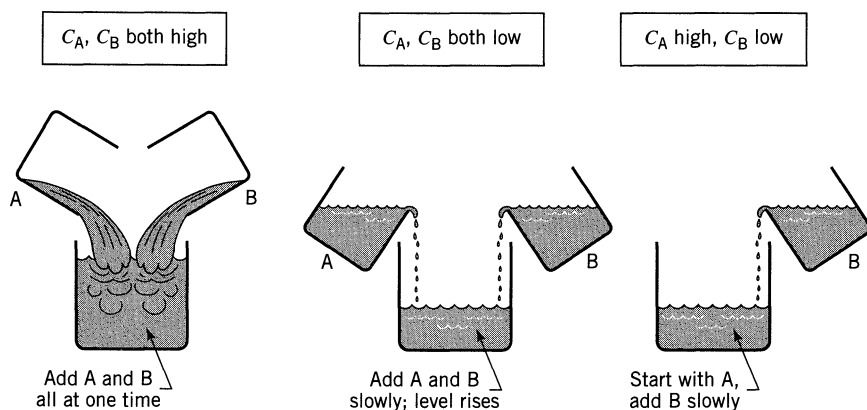


Figure 7.1 Contacting patterns for various combinations of high and low concentration of reactants in noncontinuous operations.

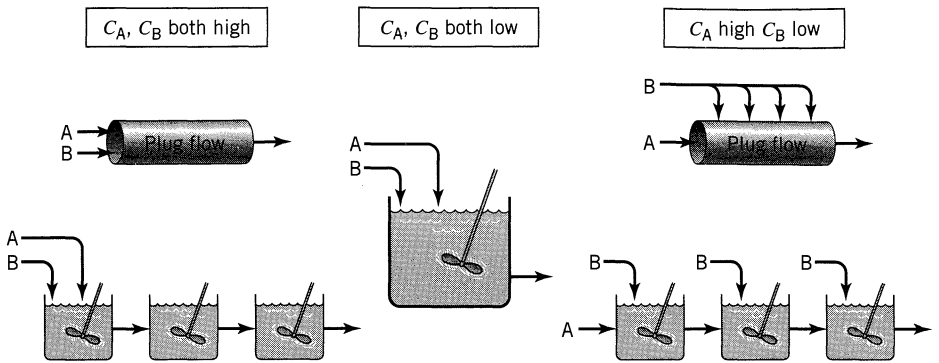
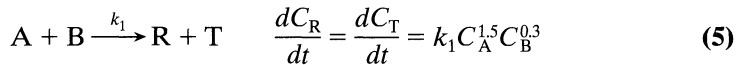


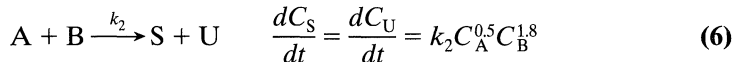
Figure 7.2 Contacting patterns for various combinations of high and low concentration of reactants in continuous flow operations.

EXAMPLE 7.1 CONTACTING PATTERNS FOR REACTIONS IN PARALLEL

The desired liquid-phase reaction



is accompanied by the unwanted side reaction



From the standpoint of favorable product distribution, order the contacting schemes of Fig. 7.2, from the most desirable to the least desirable.

SOLUTION

Dividing Eq. (5) by Eq. (6) gives the ratio

$$\frac{r_R}{r_S} = \frac{k_1}{k_2} C_A C_B^{-1.5}$$

which is to be kept as large as possible. According to the rule for reactions in parallel, we want to keep C_A high, C_B low, and since the concentration dependency of B is more pronounced than of A, it is more important to have low C_B than high C_A . The contacting schemes are therefore ordered as shown in Fig. E7.1.

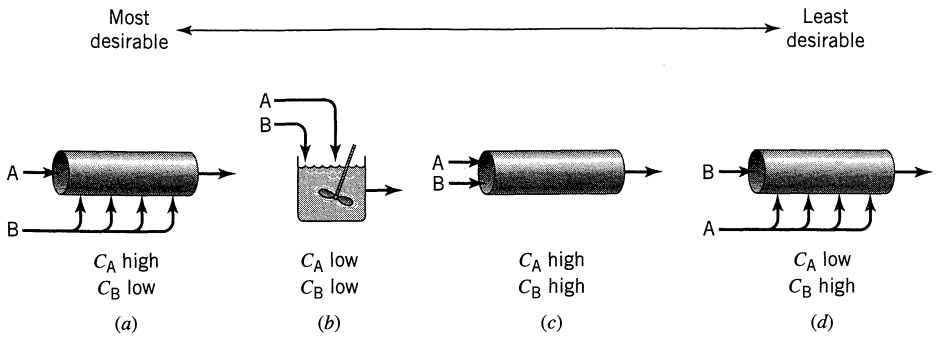


Figure E7.1

Comment. Example 7.2 verifies these qualitative findings. We should also note that there are still other contacting schemes which are superior to the best found in this example. For example, if we can use an excess of a reactant, or if it is practical to separate and recycle unconverted reactant, then vastly improved product distribution is possible.

Quantitative Treatment of Product Distribution and of Reactor Size. If rate equations are known for the individual reactions, we can quantitatively determine product distribution and reactor-size requirements. For convenience in evaluating product distribution we introduce two terms, φ and Φ . First, consider the decomposition of reactant A, and let φ be the fraction of A disappearing at any instant which is transformed into desired product R. We call this the *instantaneous fractional yield of R*. Thus at any C_A

$$\varphi = \left(\frac{\text{moles R formed}}{\text{moles A reacted}} \right) = \frac{dC_R}{-dC_A} \quad (7)$$

For any particular set of reactions and rate equations φ is a function of C_A , and since C_A in general varies through the reactor, φ will also change with position in the reactor. So let us define Φ as the fraction of all the reacted A that has been converted into R, and let us call this the *overall fractional yield of R*. The overall fractional yield is then the mean of the instantaneous fractional yields at all points within the reactor; thus we may write

$$\Phi = \left(\frac{\text{all R formed}}{\text{all A reacted}} \right) = \frac{C_{R_f}}{C_{A0} - C_{A_f}} = \frac{C_{R_f}}{(-\Delta C_A)} = \bar{\varphi}_{\text{in reactor}} \quad (8)$$

It is the overall fractional yield that really concerns us for it represents the product distribution at the reactor outlet. Now the proper averaging for φ depends

on the type of flow within the reactor. Thus for *plug flow*, where C_A changes progressively through the reactor, we have from Eq. 7:

$$\text{For PFR: } \Phi_p = \frac{-1}{C_{A0} - C_{Af}} \int_{C_{A0}}^{C_{Af}} \varphi dC_A = \frac{1}{\Delta C_A} \int_{C_{A0}}^{C_{Af}} \varphi dC_A \quad (9)$$

For *mixed flow*, the composition is C_{Af} everywhere, so φ is likewise constant throughout the reactor, and we have

$$\text{For MFR: } \Phi_m = \varphi_{\text{evaluated at } C_{Af}} \quad (10)$$

The over-all fractional yields from mixed and plug flow reactors processing A from C_{A0} to C_{Af} are related by

$$\Phi_m = \left(\frac{d\Phi_p}{dC_A} \right)_{\text{at } C_{Af}} \quad \text{and} \quad \Phi_p = \frac{1}{\Delta C_A} \int_{C_{A0}}^{C_{Af}} \Phi_m dC_A \quad (11)$$

These expressions allow us to predict the yields from one type of reactor given the yields from the other.

For a series of 1, 2, ..., N mixed flow reactors in which the concentration of A is C_{A1} , C_{A2} , ..., C_{AN} , the overall fractional yield is obtained by summing the fractional yields in each of the N vessels and weighting these values by the amount of reaction occurring in each vessel. Thus

$$\varphi_1(C_{A0} - C_{A1}) + \cdots + \varphi_N(C_{A,N-1} - C_{AN}) = \Phi_{N \text{ mixed}} (C_{A0} - C_{AN})$$

from which

$$\Phi_{N \text{ mixed}} = \frac{\varphi_1(C_{A0} - C_{A1}) + \varphi_2(C_{A1} - C_{A2}) + \cdots + \varphi_N(C_{A,N-1} - C_{AN})}{C_{A0} - C_{AN}} \quad (12)$$

For any reactor type the exit concentration of R is obtained directly from Eq. 8. Thus

$$C_{Rf} = \Phi(C_{A0} - C_{Af}) \quad (13)$$

and Fig. 7.3 shows how C_R is found for different types of reactors. For mixed flow reactors, or mixed flow reactors in series, the best outlet concentration to use, that which maximizes C_R , may have to be found by maximization of rectangles (see Chapter 6).

Now the shape of the φ versus C_A curve determines which type of flow gives the best product distribution, and Fig. 7.4 shows typical shapes of these curves for which plug flow, mixed flow, and mixed followed by plug flow are best.

These fractional yield expressions allow us to relate the product distribution from different types of reactors and to search for the best contacting scheme. However, one condition must be satisfied before we can safely use these relationships: We must truly have parallel reactions in which no product influences the

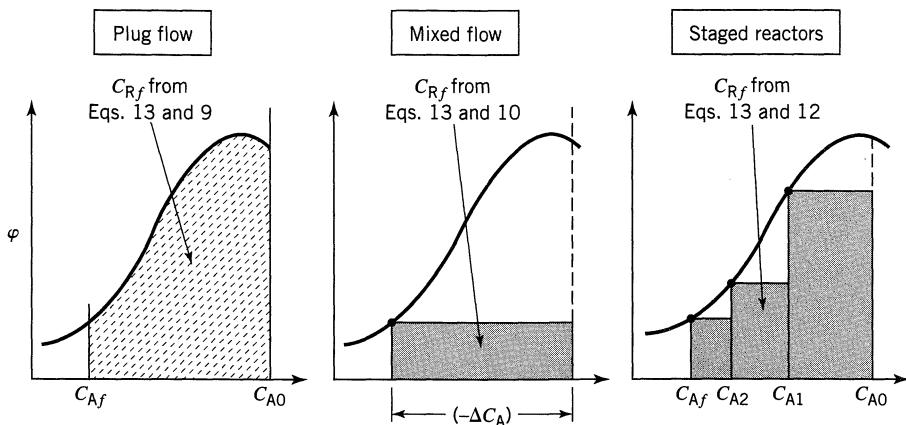


Figure 7.3 Shaded and dashed area gives total R formed.

rate to change the product distribution. The easiest way to test this is to add products to the feed and verify that the product distribution is in no way altered.

So far, the fractional yield of R has been taken as a function of C_A alone and has been defined on the basis of the amount of this component consumed. More generally, when there are two or more reactants involved, the fractional yield can be based on one of the reactants consumed, on all reactants consumed, or on products formed. It is simply a matter of convenience which definition is used. Thus, in general, we define $\varphi(M/N)$ as the instantaneous fractional yield of M, based on the disappearance or formation of N.

The use of fractional yields to determine the product distribution for parallel reactions was developed by Denbigh (1944, 1961).

The Selectivity. Another term, the selectivity, is often used in place of fractional yield. It is usually defined as follows:

$$\text{selectivity} = \left(\frac{\text{moles of desired product formed}}{\text{moles of undesired material formed}} \right)$$

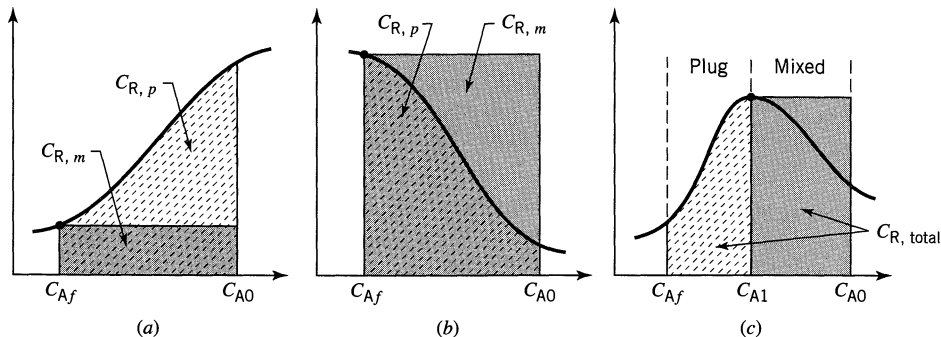
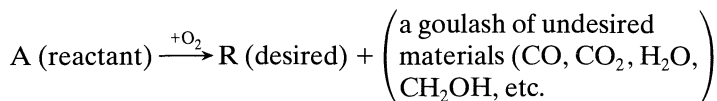


Figure 7.4 The contacting pattern with the largest area produces most R: (a) plug flow is best, (b) mixed flow is best, (c) mixed flow up to C_{A1} followed by plug flow is best.

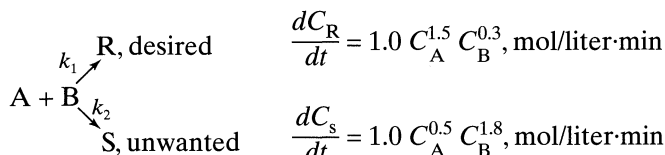
This definition may lead to difficulties. For example, if the reaction is the partial oxidation of a hydrocarbon, as follows:



Here the selectivity is hard to evaluate, and not very useful. Thus, we stay away from selectivity and use the clearly defined and useful fractional yield, $\varphi(R/A)$.

EXAMPLE 7.2. PRODUCT DISTRIBUTION FOR PARALLEL REACTIONS

Consider the aqueous reactions



For 90% conversion of A find the concentration of R in the product stream. Equal volumetric flow rates of the A and of B streams are fed to the reactor, and each stream has a concentration of 20 mol/liter of reactant.

The flow in the reactor follows.

- Plug flow
- Mixed flow
- The best of the four plug-mixed contacting schemes of Example 7.1.

SOLUTION

As a warning, be careful to get the concentrations right when you mix streams. We show this in the three sketches for this problem. Also, the instantaneous fractional yield of the desired compound is

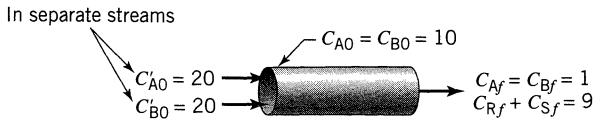
$$\varphi \left(\frac{R}{A} \right) = \frac{dC_R}{dC_R + dC_S} = \frac{k_1 C_A^{1.5} C_B^{0.3}}{k_1 C_A^{1.5} C_B^{0.3} + k_2 C_A^{0.5} C_B^{1.8}} = \frac{C_A}{C_A + C_B^{1.5}}$$

Now let us proceed.

(a) Plug Flow

Referring to Fig. E7.2a, noting that the starting concentration of each reactant in the combined feed is $C_{A0} = C_{B0} = 10$ mol/liter and that $C_A = C_B$ everywhere, we find from Eq. 9 that

$$\Phi_p = \frac{-1}{C_{A0} - C_{Af}} \int \varphi dC_A = \frac{-1}{10 - 1} \int_{10}^1 \frac{C_A dC_A}{C_A + C_A^{1.5}} = \frac{1}{9} \int_1^{10} \frac{dC_A}{1 + C_A^{0.5}}$$


Figure E7.2a

Let $C_A^{0.5} = x$, then $C_A = x^2$ and $dC_A = 2xdx$. Replacing C_A by x in the above expression gives

$$\Phi_p = \frac{1}{9} \int_1^{\sqrt{10}} \frac{2xdx}{1+x} = \frac{2}{9} \left[\int_1^{\sqrt{10}} dx - \int_1^{\sqrt{10}} \frac{dx}{1+x} \right]$$

$$= 0.32$$

$$\therefore C_{Rf} = 9(0.32) = \underline{\underline{2.86}}$$

$$C_{Sf} = 9(1 - 0.32) = \underline{\underline{6.14}}$$

(b) Mixed Flow

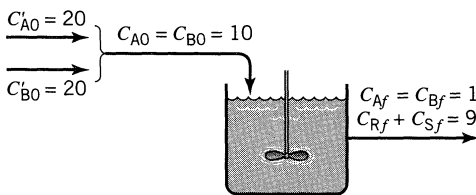
Referring to Fig. E7.2b, we have from Eq. 10, for $C_A = C_B$

$$\Phi_m \left(\frac{R}{A} \right) = \varphi_{\text{at exit}} = \frac{1}{1 + C_A^{0.5}} = 0.5$$

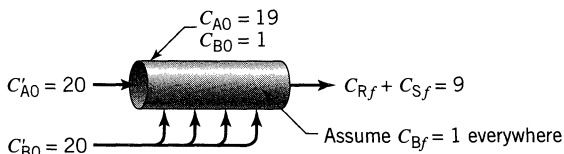
Therefore Eq. 13 gives

$$C_{Rf} = 9(0.5) = \underline{\underline{4.5 \text{ mol/liter}}}$$

$$C_{Sf} = 9(1 - 0.5) = \underline{\underline{4.5 \text{ mol/liter}}}$$


Figure E7.2b
(c) Plug Flow A—Mixed Flow B

Assuming that B is introduced into the reactor in such a way that $C_B = 1$ mol/liter throughout, we find concentrations as shown in Fig. E7.2c. Then accounting


Figure E7.2c

for the changing C_A in the reactor, we find

$$\begin{aligned}\Phi\left(\frac{R}{A}\right) &= \frac{-1}{C_{A0} - C_{Af}} \int_{C_{A0}}^{C_{Af}} \varphi dC_A = \frac{-1}{19 - 1} \int_{19}^1 \frac{C_A dC_A}{C_A + (1)^{1.5}} \\ &= \frac{1}{18} \left[\int_1^{19} dC_A - \int_1^{19} \frac{dC_A}{C_A + 1} \right] = \frac{1}{18} \left[(19 - 1) - \ln \frac{20}{2} \right] = 0.87\end{aligned}$$

Therefore

$$C_{Rf} = 9(0.87) = \underline{7.85 \text{ mol/liter}}$$

$$C_{Sf} = 9(1 - 0.87) = \underline{1.15 \text{ mol/liter}}$$

To summarize

$$\text{For plug flow: } \Phi\left(\frac{R}{A}\right) = 0.32 \quad \text{and} \quad C_{Rf} = 2.86 \text{ mol/liter}$$

$$\text{For mixed flow: } \Phi\left(\frac{R}{A}\right) = 0.50 \quad \text{and} \quad C_{Rf} = 4.5 \text{ mol/liter}$$

$$\text{For the optimum: } \Phi\left(\frac{R}{A}\right) = 0.87 \quad \text{and} \quad C_{Rf} = 7.85 \text{ mol/liter}$$

Note. These results verify the qualitative findings of Example 7.1.

The Side Entry Reactor

To evaluate how best to distribute the side entry feed and how to calculate the corresponding conversion equation is a rather complex problem. For this type of contacting in general see Westerterp et al. (1984).

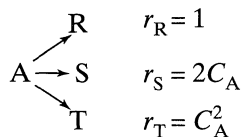
To actually build a commercial-sized side entry reactor is another problem. *Chem. Eng. News* (1997) reports on how this was cleverly done by using a reactor somewhat like a shell-and-tube heat exchanger which used porous walled tubes.

Reactant A flowed through the tubes which contained baffles to encourage lateral mixing of fluid and approach to plug flow. Reactant B, to be kept at a close-to-constant low concentration in the tubes, enters the exchanger through the shell side at a somewhat higher pressure than that in the tubes. Thus, B diffused into the tubes along the whole length of the tubes.

EXAMPLE 7.3 GOOD OPERATING CONDITIONS FOR PARALLEL REACTIONS

Often a desired reaction is accompanied by a variety of undesired side reactions, some of higher order, some of lower order. To see which type of single reactor gives the best product distribution, consider the simplest typical case, the parallel

decompositions of A, $C_{A0} = 2$,



Find the maximum expected C_{S} for isothermal operations

- in a mixed flow reactor
- in a plug flow reactor
- in a reactor of your choice if unreacted A can be separated from the product stream and returned to the feed at $C_{A0} = 2$.

SOLUTION

Since S is the desired product, let us write fractional yields in terms of S. Thus

$$\varphi(\text{S/A}) = \frac{dC_{\text{S}}}{dC_{\text{R}} + dC_{\text{S}} + dC_{\text{T}}} = \frac{2C_{\text{A}}}{1 + 2C_{\text{A}} + C_{\text{A}}^2} = \frac{2C_{\text{A}}}{(1 + C_{\text{A}})^2}$$

Plotting this function we find the curve of Fig. E7.3 whose maximum occurs where

$$\frac{d\varphi}{dC_{\text{A}}} = \frac{d}{dC_{\text{A}}} \left[\frac{2C_{\text{A}}}{(1 + C_{\text{A}})^2} \right] = 0$$

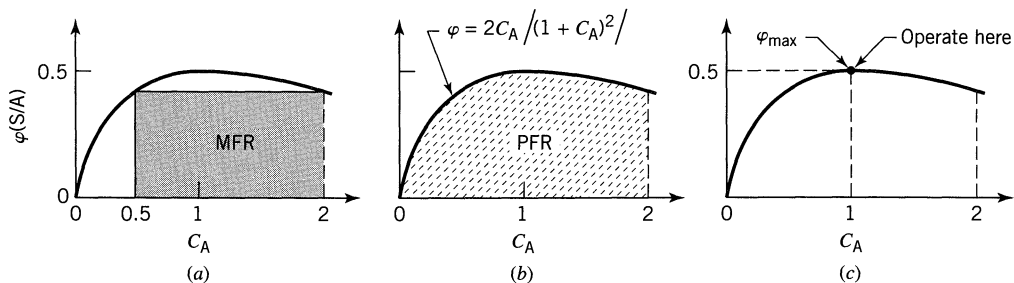


Figure E7.3a, b, c

Solving we find

$$\varphi = 0.5 \quad \text{at} \quad C_{\text{A}} = 1.0$$

(a) Mixed Reactor. Most S is formed when the rectangle under the φ versus C_{A} curve has the largest area. The required conditions can be found either by graphical maximization of rectangles or analytically. Since simple explicit expressions are available in this problem, let us use the latter approach. Then from Eqs. 10 and 13 we find for the area of the rectangle

$$C_{\text{Sf}} = \varphi(\text{S/A}) \cdot (-\Delta C_{\text{A}}) = \frac{2C_{\text{A}}}{(1 + C_{\text{A}})^2} (C_{\text{A}0} - C_{\text{A}})$$

Differentiating and setting to zero to find the conditions at which most S is formed

$$\frac{dC_{Sf}}{dC_A} = \frac{d}{dC_A} \left[\frac{2C_A}{(1 + C_A)^2} (2 - C_A) \right] = 0$$

Evaluating this quantity gives the optimum operating conditions of a mixed reactor as

$$\underline{\underline{C_{Sf} = \frac{2}{3}}} \quad \text{at} \quad C_{Af} = \frac{1}{2}$$

(b) Plug Flow Reactor. The production of S is maximum when the area under the φ versus C_A curve is maximum. This occurs at 100% conversion of A, as seen in Fig. E7.3b. Thus, from Eqs. 9 and 13

$$C_{Sf} = - \int_{C_{A0}}^{C_{Af}} \varphi(S/A) dC_A = \int_0^2 \frac{2C_A}{(1 + C_A)^2} dC_A$$

Evaluating this integral gives, for the plug flow optimum,

$$\underline{\underline{C_{Sf} = 0.867}} \quad \text{at} \quad C_{Af} = 0$$

(c) Any Reactor with Separation and Recycle of Unused Reactant. Since no reactant leaves the system unconverted, what is important is to operate at conditions of highest fractional yield. This is at $C_A = 1$, where $\varphi(S/A) = 0.5$, as shown in Fig. E7.3c. Thus, we should use a mixed flow reactor operating at $C_A = 1$. We would then have 50% of reactant A forming product S.

Comment. Summarizing, we find

$$\begin{aligned} \left(\frac{\text{moles S formed}}{\text{moles A fed}} \right) &= 0.33 \text{ for MFR} \\ &= 0.43 \text{ for a PFR} \\ &= 0.50 \text{ for an MFR with separation and recycle} \end{aligned}$$

Thus, a mixed flow reactor operating at conditions of highest φ with separation and recycle of unused reactant gives the best product distribution. This result is quite general for a set of parallel reactions of different order.

EXAMPLE 7.4 BEST OPERATING CONDITIONS FOR PARALLEL REACTIONS

For the reaction of Example 7.3 determine the arrangement of reactors which would produce most S in a flow system where recycle and reconcentration of unreacted feed is not possible. Find $C_{S,\text{total}}$ for this arrangement of reactors.

SOLUTION

From Fig. E7.4 we see that mixed flow followed by plug flow would be best.

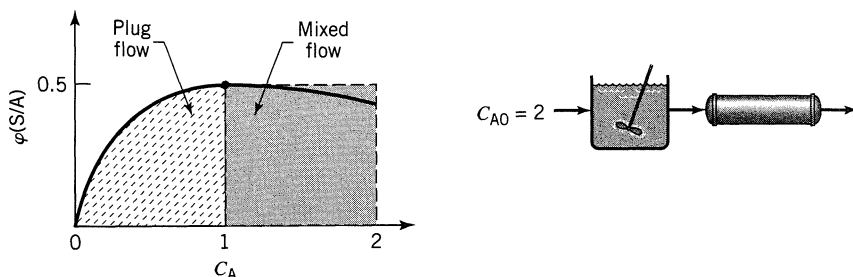


Figure E7.4

Thus, for mixed flow, from Example 7.3

$$C_A = 1, \varphi = 0.5, \quad \text{thus} \quad C_S = \varphi(\Delta C_A) = 0.5(2 - 1) = 0.5 \text{ mol/liter}$$

For plug flow, from Example 7.3

$$C_S = - \int_1^0 \varphi dC_A = \int_0^1 \frac{2C_A}{(1 + C_A)^2} dC_A = 0.386 \text{ mol/liter}$$

Therefore, the total amount of C_S formed is

$$C_{S, \text{total}} = 0.5 + 0.386 = \underline{\underline{0.886 \text{ mol/liter}}}$$

This is only slightly better than for plug flow alone, calculated in Example 7.3.

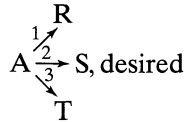
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 Denbigh, K. G., *Chem. Eng. Sci.*, **14**, 25 (1961).
 Westerterp, K. R., van Swaaij, W. P. M., and Beenackers, A. A. C. M., *Chemical Reactor Design and Operation*, Wiley, New York, 1984.

PROBLEMS

- 7.1.** For a given feed stream having C_{A0} should we use a PFR or a MFR and should we use a high or low or some intermediate conversion level for the

exit stream if we wish to maximize $\phi(S/A)$? The reaction system is



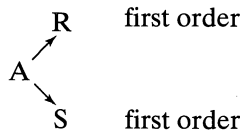
where $n_1, n_2,$ and n_3 are the reaction orders of reactions 1, 2, and 3.

- (a) $n_1 = 1, n_2 = 2, n_3 = 3$
- (b) $n_1 = 2, n_2 = 3, n_3 = 1$
- (c) $n_1 = 3, n_2 = 1, n_3 = 2$

Using separate feeds of A and B sketch the contacting pattern and reactor conditions which would best promote the formation of product R for the following systems of elementary reactions.

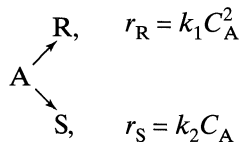
- | | |
|--|---|
| <p>7.2. $\left. \begin{array}{l} \text{A} + \text{B} \rightarrow \text{R} \\ \text{A} \rightarrow \text{S} \end{array} \right\}$ Flow system</p> | <p>7.3. $\left. \begin{array}{l} \text{A} + \text{B} \rightarrow \text{R} \\ 2\text{A} \rightarrow \text{S} \\ 2\text{B} \rightarrow \text{T} \end{array} \right\}$ Batch system</p> |
| <p>7.4. $\left. \begin{array}{l} \text{A} + \text{B} \rightarrow \text{R} \\ \text{A} \rightarrow \text{S} \end{array} \right\}$ Batch system</p> | <p>7.5. $\left. \begin{array}{l} \text{A} + \text{B} \rightarrow \text{R} \\ 2\text{A} \rightarrow \text{S} \end{array} \right\}$ Flow system</p> |

7.6. Substance A in a liquid reacts to produce R and S as follows:



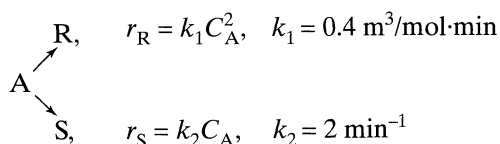
A feed ($C_{A0} = 1, C_{R0} = 0, C_{S0} = 0$) enters two mixed flow reactors in series, ($\tau_1 = 2.5$ min, $\tau_2 = 5$ min). Knowing the composition in the first reactor ($C_{A1} = 0.4, C_{R1} = 0.4, C_{S1} = 0.2$), find the composition leaving the second reactor.

7.7. Substance A in the liquid phase produces R and S by the following reactions:



The feed ($C_{A0} = 1.0, C_{R0} = 0, C_{S0} = 0.3$) enters two mixed flow reactors in series ($\tau_1 = 2.5$ min, $\tau_2 = 10$ min). Knowing the composition in the first reactor ($C_{A1} = 0.4, C_{R1} = 0.2, C_{S1} = 0.7$), find the composition leaving the second reactor.

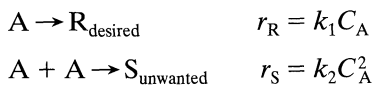
Liquid reactant A decomposes as follows:



A feed of aqueous A ($C_{\text{A}0} = 40 \text{ mol/m}^3$) enters a reactor, decomposes, and a mixture of A, R, and S leaves.

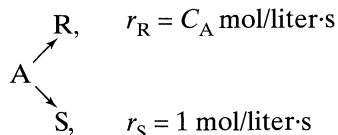
- 7.8.** Find C_{R} , and C_{S} and τ for $X_{\text{A}} = 0.9$ in a mixed flow reactor.
- 7.9.** Find C_{R} , and C_{S} and τ for $X_{\text{A}} = 0.9$ in a plug flow reactor.
- 7.10.** Find the operating condition (X_{A} , τ , and C_{S}) which maximizes C_{S} in a mixed flow reactor.
- 7.11.** Find the operating condition (X_{A} , τ , and C_{R}) which maximizes C_{R} in a mixed flow reactor.

7.12. Reactant A in a liquid either isomerizes or dimerizes as follows:



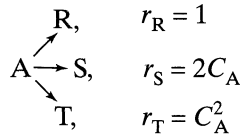
- (a) Write $\varphi(\text{R}/\text{A})$ and $\varphi[\text{R}/(\text{R} + \text{S})]$.
 With a feed stream of concentration $C_{\text{A}0}$ find $C_{\text{R,max}}$ which can be formed
- (b) in a plug flow reactor,
 (c) in a mixed flow reactor.
- A quantity of A of initial concentration $C_{\text{A}0} = 1 \text{ mol/liter}$ is dumped into a batch reactor and is reacted to completion.
- (d) If $C_{\text{S}} = 0.18 \text{ mol/liter}$ in the resultant mixture, what does this tell of the kinetics of the reaction?

7.13. In a reactive environment, chemical A decomposes as follows



For a feed stream $C_{\text{A}0} = 4 \text{ mol/liter}$ what size ratio of two mixed flow reactors will maximize the production rate of R? Also give the composition of A and R leaving these two reactors.

Consider the parallel decomposition of A of different orders

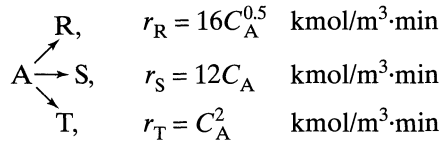


Determine the maximum concentration of desired product obtainable in

- (a) plug flow,
- (b) mixed flow.

- 7.14. R is the desired product and $C_{A0} = 2$.
- 7.15. S is the desired product and $C_{A0} = 4$.
- 7.16. T is the desired product and $C_{A0} = 5$.

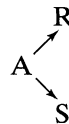
Under ultraviolet radiation, reactant A of $C_{A0} = 10 \text{ kmol/m}^3$ in a process stream ($v = 1 \text{ m}^3/\text{min}$) decomposes as follows.



We wish to design a reactor setup for a specific duty. Sketch the scheme selected, and calculate the fraction of feed transformed into desired product as well as the volume of reactor needed.

- 7.17. Product R is the desired material.
- 7.18. Product S is the desired material.
- 7.19. Product T is the desired material.

The stoichiometry of a liquid-phase decomposition is known to be



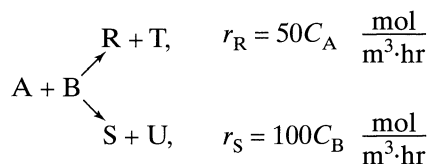
In a series of steady-state flow experiments ($C_{A0} = 100, C_{R0} = C_{S0} = 0$) in a laboratory mixed flow reactor the following results are obtained:

C_A	90	80	70	60	50	40	30	20	10	0
C_R	7	13	18	22	25	27	28	28	27	25

Further experiments indicate that the level of C_R and C_S have no effect on the progress of the reaction.

- 7.20.** With a feed $C_{A0} = 100$ and exit concentration $C_{Af} = 20$, find C_R at the exit from a plug flow reactor.
- 7.21.** With $C_{A0} = 200$ and $C_{Af} = 20$, find C_R at the exit from a mixed flow reactor.
- 7.22.** How should we operate a mixed flow reactor so as to maximize the production of R? Separation and recycle of unused reactant is not practical.

When aqueous A and aqueous B ($C_{A0} = C_{B0}$) are brought together they react in two possible ways:



to give a mixture whose concentration of active components (A, B, R, S, T, U) is $C_{\text{total}} = C_{A0} + C_{B0} = 60 \text{ mol/m}^3$. Find the size of reactor needed and the R/S ratio produced for 90% conversion of an equimolar feed of $F_{A0} = F_{B0} = 300 \text{ mol/hr}$:

- 7.23.** in a mixed flow reactor;
- 7.24.** in a plug flow reactor;
- 7.25.** in a reactor that gives highest C_R . Chapter 6 tells that this should be plug flow for A and side entry for B. In such a reactor introduce B in such a way that C_B is constant throughout the reactor.

- 7.26.** Reactant A decomposes in an isothermal batch reactor ($C_{A0} = 100$) to produce wanted R and unwanted S, and the following progressive concentration readings are recorded:

C_A	(100)	90	80	70	60	50	40	30	20	10	(0)
C_R	(0)	1	4	9	16	25	35	45	55	64	(71)

Additional runs show that adding R or S does not affect the distribution of products formed and that only A does. Also, it is noted that the total number of moles of A, R, and S is constant.

- (a)** Find the φ versus C_A curve for this reaction.
 With a feed of $C_{A0} = 100$ and $C_{Af} = 10$, find C_R
- (b)** from a mixed flow reactor,
(c) from a plug flow reactor,
(d) and **(e)**: Repeat parts (b) and (c) with the modification that $C_{A0} = 70$.

- 7.27.** The great naval battle, to be known to history as the Battle of Trafalgar (1805), was soon to be joined. Admiral Villeneuve proudly surveyed his powerful fleet of 33 ships stately sailing in single file in the light breeze.

The British fleet under Lord Nelson was now in sight, 27 ships strong. Estimating that it would still be 2 hours before battle, Villeneuve popped open another bottle of burgundy and point by point reviewed his carefully thought-out battle strategy. As was the custom of naval battles at that time, the two fleets would sail in single file parallel to each other and in the same direction, firing their cannons madly. Now, by long experience in battles of this kind, it was a well-known fact that the rate of destruction of a fleet is proportional to the fire power of the opposing fleet. Considering his ships to be on a par, one for one, with the British, Villeneuve was confident of victory. Looking at his sundial, Villeneuve sighed and cursed the light wind—he'd never get it over with in time for his afternoon snooze. "Oh well," he sighed, "c'est la vie." He could see the headlines next morning: "British fleet annihilated, Villeneuve's losses are . . ." Villeneuve stopped short. How many ships would he lose? Villeneuve called over his chief bottle-cork popper, Monsieur Dubois, and asked this question. What answer does he get?

At this very moment, Nelson, who was enjoying the air on the poop deck of the *Victory*, was stuck with the realization that all was ready except for one detail—he had forgotten to formulate his battle plan. Commodore Archibald Forsythe-Smythe, his trusty trusty, was hurriedly called over for a conference. Being familiar with the firepower law, Nelson was loathe to fight the whole French fleet (he could see the headlines too). Now certainly it was no disgrace for Nelson to be defeated in battle by superior forces, so long as he did his best and played the game; however, he had a sneaking suspicion that maybe he could pull a fast one. With a nagging conscience as to whether it was cricket or not, he proceeded to investigate this possibility.

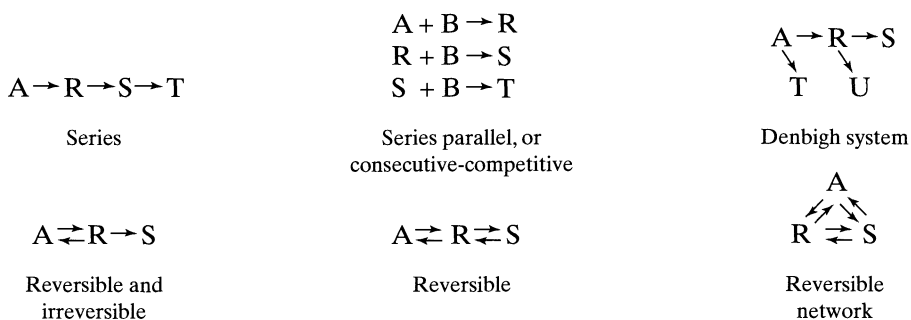
It was possible to "break the line"—that is, to start parallel to the French fleet, and then cut in and divide the enemy fleet into two sections. The rear section could be engaged and disposed of before the front section could turn around and rejoin the fray. Now to the question. Should he split the French fleet and if so, then where? Commodore Forsythe-Smythe, who was so rudely taken from his grog, grumpily agreed to consider this question and to advise Nelson at what point to split the French fleet so as to maximize their chance for success. He also agreed to predict the outcome of the battle using this strategy. What did he come up with?

- 7.28** Find the size of the two reactors needed in Example 7.4 (see Figure E7.4) for a feed flow rate of 100 liter/s, and for reaction rates given in units of mol/liter · s.

Chapter 8

Potpourri of Multiple Reactions

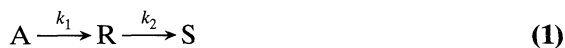
Chapter 7 considered reactions in parallel. These are reactions where the product does not react further. This chapter considers all sorts of reactions where the product formed may react further. Here are some examples:



We develop or present the performance equations of some of the simpler systems and point out their special features such as maxima of intermediates.

8.1 IRREVERSIBLE FIRST-ORDER REACTIONS IN SERIES

For easy visualization consider that the reactions



proceed only in the presence of light, that they stop the instant the light is turned off, and that for a given intensity of radiation, the rate equations are

$$r_A = -k_1 C_A \quad (2)$$

$$r_R = k_1 C_A - k_2 C_R \quad (3)$$

$$r_S = k_2 C_R \quad (4)$$

Our discussion centers about these reactions.

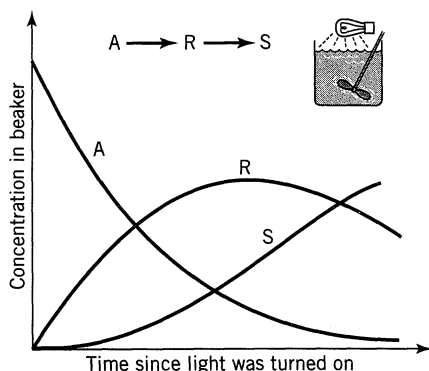


Figure 8.1 Concentration-time curves if the contents of the beaker are irradiated uniformly.

Qualitative Discussion About Product Distribution. Consider the following two ways of treating a beaker containing A: First, the contents are uniformly irradiated; second, a small stream is continuously withdrawn from the beaker, irradiated, and returned to the beaker; and the rate of absorption of radiant energy is the same in the two cases. The two schemes are shown in Figs. 8.1 and 8.2. During this process A disappears and products are formed. Is the product distribution of R and S different in the two beakers? Let us see whether we can answer this question qualitatively for all values of the rate constants.

In the first beaker, when the contents are being irradiated all at the same time, the first bit of light will attack A alone because only A is present at the start. The result is that R is formed. With the next bit of light both A and R will compete; however, A is in very large excess so it will preferentially absorb the radiant energy to decompose and form more R. Thus, the concentration of R will rise while the concentration of A will fall. This process will continue until R is present in high enough concentration so that it can compete favorably with A for the radiant energy. When this happens, a maximum R concentration is reached. After this the decomposition of R becomes more rapid than its rate of

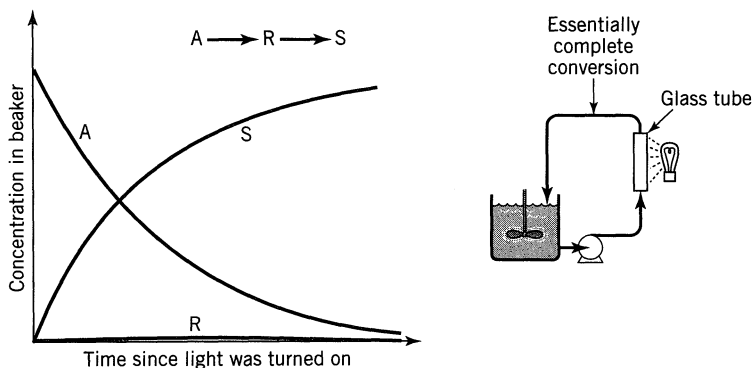


Figure 8.2 Concentration-time curves for the contents of the beaker if only a small portion of the fluid is irradiated at any instant.

formation and its concentration drops. A typical concentration time curve is shown in Fig. 8.1.

In the alternative way of treating A, a small fraction of the beaker's contents is continuously removed, irradiated, and returned to the beaker. Although the total absorption rate is the same in the two cases, the intensity of radiation received by the removed fluid is greater, and it could well be, if the flow rate is not too high, that the fluid being irradiated reacts essentially to completion. In this case, then, A is removed and S is returned to the beaker. So, as time passes the concentration of A slowly decreases in the beaker, S rises, while R is absent. This progressive change is shown in Fig. 8.2.

These two methods of reacting the contents of the beaker yield different product distributions and represent the two extremes in possible operations, one with a maximum possible formation of R and the other with a minimum, or no formation, of R. How can we best characterize this behavior? We note in the first method that the contents of the beaker remain homogeneous throughout, all changing slowly with time, whereas in the second a stream of highly reacted fluid is continually being mixed with fresh fluid. In other words, we are mixing two streams of different compositions. This discussion suggests the following rule governing product distribution for reactions in series.

For irreversible reactions in series the mixing of fluid of different composition is the key to the formation of intermediate. The maximum possible amount of any and all intermediates is obtained if fluids of different compositions and at different stages of conversion are not allowed to mix.

(5)

As the intermediate is frequently the desired reaction product, this rule allows us to evaluate the effectiveness of various reactor systems. For example, plug flow and batch operations should both give a maximum R yield because here there is no mixing of fluid streams of different compositions. On the other hand, the mixed reactor should not give as high a yield of R as possible because a fresh stream of pure A is being mixed continually with an already reacted fluid in the reactor.

The following examples illustrate the point just made. We then give a quantitative treatment which will verify these qualitative findings.

EXAMPLE 8.1

FAVORABLE CONTACTING PATTERNS FOR ANY SET OF IRREVERSIBLE REACTIONS IN SERIES, NOT JUST $A \rightarrow R \rightarrow S$

Which contacting pattern of Figs. E8.1, when properly operated, can give a higher concentration of any intermediate, the contacting pattern on the left or the one on the right?

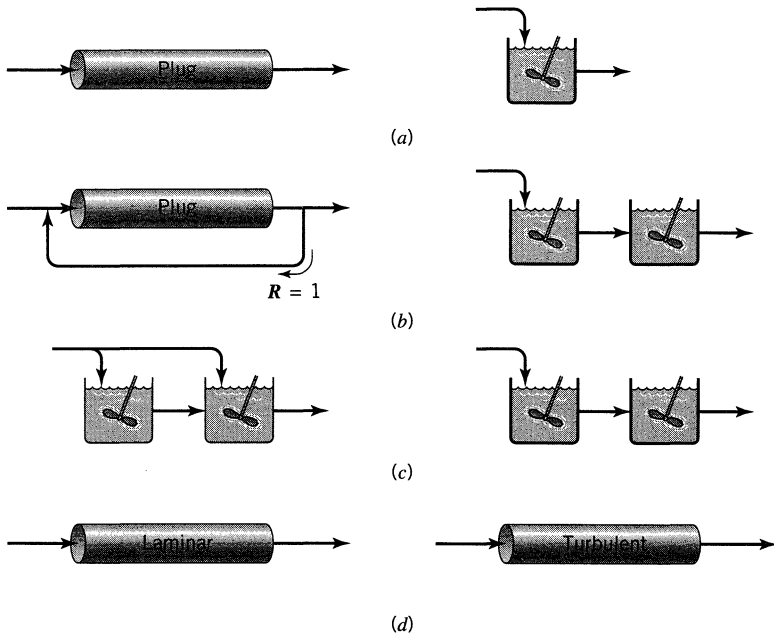


Figure E8.1a, b, c, d

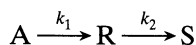
SOLUTION

Focusing on the mixing rule for reactions in series, that the extent of mixing of streams of different composition should be minimized, we reason

- for part (a): The left pattern is better; in fact it is the best possible flow scheme.
- for part (b): Looking at Figs. 6.5, 6.6, and 6.16, 6.17 of Chapter 6 we see that the left is closer to plug flow for both first- and for second-order reactions. So we generalize this to any positive order reaction.
- for part (c): The right pattern is better because it is closer to plug flow.
- for part (d): Turbulent flow has less intermixing of fluids of different ages, less bypassing; hence, the right scheme is better.

Note. In the quantitative analysis that follows we verify this general and important rule. ■

Quantitative Treatment, Plug Flow or Batch Reactor. In Chapter 3 we developed the equations relating concentration with time for all components of the unimolecular-type reactions



in batch reactors. The derivations assumed that the feed contained no reaction products R or S. If we replace reaction time by the space time, these equations apply equally well for plug flow reactors, thus

$$\frac{C_A}{C_{A0}} = e^{-k_1\tau} \quad (3.47) \text{ or } (6)$$

$$\frac{C_R}{C_{A0}} = \frac{k_1}{k_2 - k_1} (e^{-k_1\tau} - e^{-k_2\tau}) \quad (3.49) \text{ or } (7)$$

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

The maximum concentration of intermediate and the time at which it occurs is given by

$$\frac{C_{R,\max}}{C_{A0}} = \left(\frac{k_1}{k_2}\right)^{k_2/(k_2-k_1)} \quad (3.52) \text{ or } (8)$$

$$\tau_{p,\text{opt}} = \frac{1}{k_{\log \text{ mean}}} = \frac{\ln(k_2/k_1)}{k_2 - k_1} \quad (3.51) \text{ or } (9)$$

This is also the point at which the rate of formation of S is most rapid.

Figure 8.3a, prepared for various k_2/k_1 values, illustrates how this ratio governs

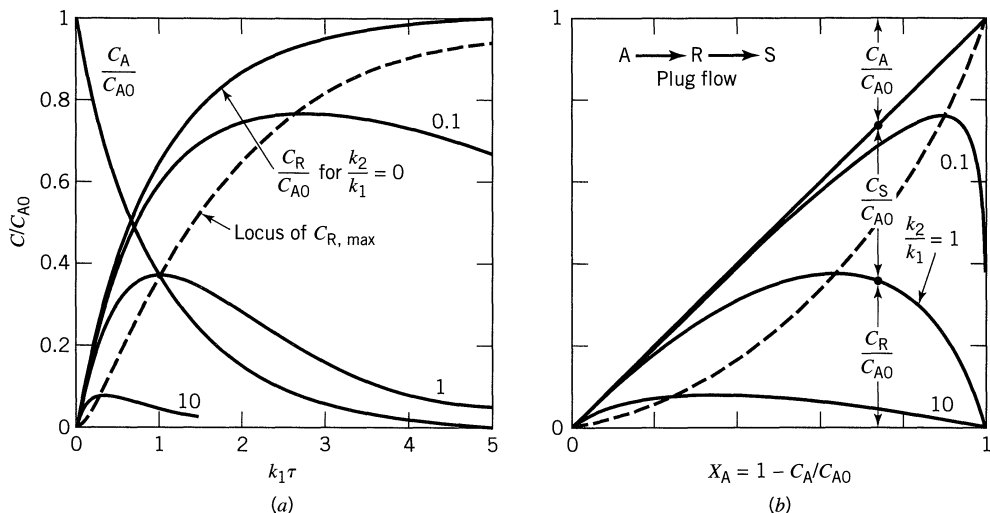
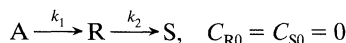


Figure 8.3a, b Behavior of unimolecular-type reactions



in a plug flow reactor: (a) concentration-time curves, and (b) relative concentration of the reaction components. See Fig. 8.13 for a more detailed figure.

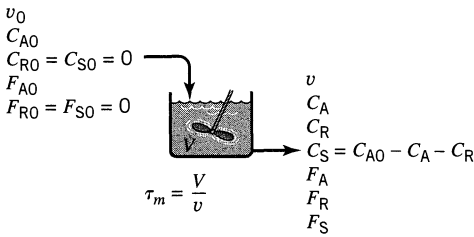


Figure 8.4 Variables for reactions in series (no R or S in the feed) occurring in a mixed flow reactor.

the concentration-time curves of the intermediate R. Figure 8.3*b*, a time-independent plot, relates the concentration of all reaction components; also see Eq. 37.

Quantitative Treatment, Mixed Flow Reactor. Let us develop the concentration-time curves for this reaction when it takes place in a mixed flow reactor. This may be done by referring to Fig. 8.4. Again, the derivation will be limited to a feed which contains no reaction product R or S.

By the steady-state material balance we obtain for any component

$$\text{input} = \text{output} + \text{disappearance by reaction} \quad (4.1) \text{ or } (10)$$

which for reactant A becomes

$$F_{A0} = F_A + (-r_A)V$$

or

$$vC_{A0} = vC_A + k_1C_AV$$

Noting that

$$\frac{V}{v} = \tau_m = \bar{t} \quad (11)$$

we obtain for A, on rearranging,

$$\frac{C_A}{C_{A0}} = \frac{1}{1 + k_1\tau_m} \quad (12)$$

For component R the material balance, Eq. 10, becomes

$$vC_{R0} = vC_R + (-r_R)V$$

or

$$0 = vC_R + (-k_1C_A + k_2C_R)V$$

With Eqs. 11 and 12 we obtain, on rearranging,

$$\frac{C_R}{C_{A0}} = \frac{k_1 \tau_m}{(1 + k_1 \tau_m)(1 + k_2 \tau_m)} \quad (13)$$

C_S is found by simply noting that at any time

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

hence

$$\frac{C_S}{C_{A0}} = \frac{k_1 k_2 \tau_m^2}{(1 + k_1 \tau_m)(1 + k_2 \tau_m)} \quad (14)$$

The location and maximum concentration of R are found by determining $dC_R/d\tau_m = 0$. Thus

$$\frac{dC_R}{d\tau_m} = 0 = \frac{C_{A0} k_1 (1 + k_1 \tau_m)(1 + k_2 \tau_m) - C_{A0} k_1 \tau_m [k_1 (1 + k_2 \tau_m) + (1 + k_1 \tau_m) k_2]}{(1 + k_1 \tau_m)^2 (1 + k_2 \tau_m)^2}$$

which simplifies neatly to give

$$\tau_{m,\text{opt}} = \frac{1}{\sqrt{k_1 k_2}} \quad (15)$$

The corresponding concentration of R is given by replacing Eq. 15 in Eq. 13. On rearranging, this becomes

$$\frac{C_{R,\text{max}}}{C_{A0}} = \frac{1}{[(k_2/k_1)^{1/2} + 1]^2} \quad (16)$$

Typical concentration-time curves for various k_2/k_1 values are shown in Fig. 8.5a. A time-independent plot, Fig. 8.5b, relates the concentrations of reactant and products.

Remarks on Performance Characteristics, Kinetic Studies, and Design. Figures 8.3a and 8.5a show the general time-concentration behavior for plug and mixed flow reactors and are an aid in visualizing the actual progress of the reaction. Comparison of these figures shows that except when $k_1 = k_2$ the plug flow reactor always requires a smaller time than does the mixed reactor to achieve the maximum concentration of R, the difference in times becoming progressively

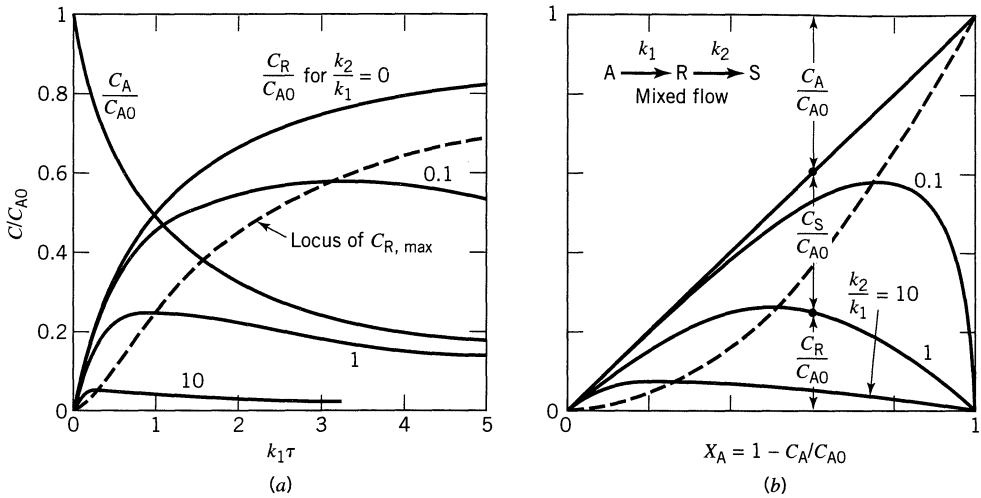
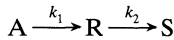


Figure 8.5a, b Behavior of unimolecular-type reactions



in a mixed flow reactor: (a) concentration-time curves, and (b) relative concentration of the reaction components. See Fig. 8.14 for a more detailed figure.

larger as k_2/k_1 departs from unity (see Eqs. 15 and 9). In addition, for any reaction the maximum obtainable concentration of R in a plug flow reactor is always higher than the maximum obtainable in a mixed reactor (see Eqs. 16 and 8). This verifies the conclusions arrived at by qualitative reasoning.

Figures 8.3b and 8.5b, time-independent plots, show the distribution of materials during reaction. Such plots find most use in kinetic studies because they allow the determination of k_2/k_1 by matching the experimental points with one of the family of curves on the appropriate graph. Figures 8.13 and 8.14 are more detailed representations of these two figures. Though not shown in the figures, C_S can be found by difference between C_{A0} and $C_A + C_R$.

Figure 8.6 presents the fractional yield curves for intermediate R as a function of the conversion level and the rate constant ratio. These curves clearly show that the fractional yield of R is always higher for plug flow than for mixed flow for any conversion level. A second important observation in this figure concerns the extent of conversion of A we should plan for. If for the reaction considered k_2/k_1 is much smaller than unity, we should design for a high conversion of A and probably dispense with recycle of unused reactant. However, if k_2/k_1 is greater than unity, the fractional yield drops very sharply even at low conversion. Hence, to avoid obtaining unwanted S instead of R we must design for a very small conversion of A per pass, separation of R, and recycle of unused reactant. In such a case large quantities of material will have to be treated in the A-R separator and recycled, and this part of the process will figure prominently in cost considerations.

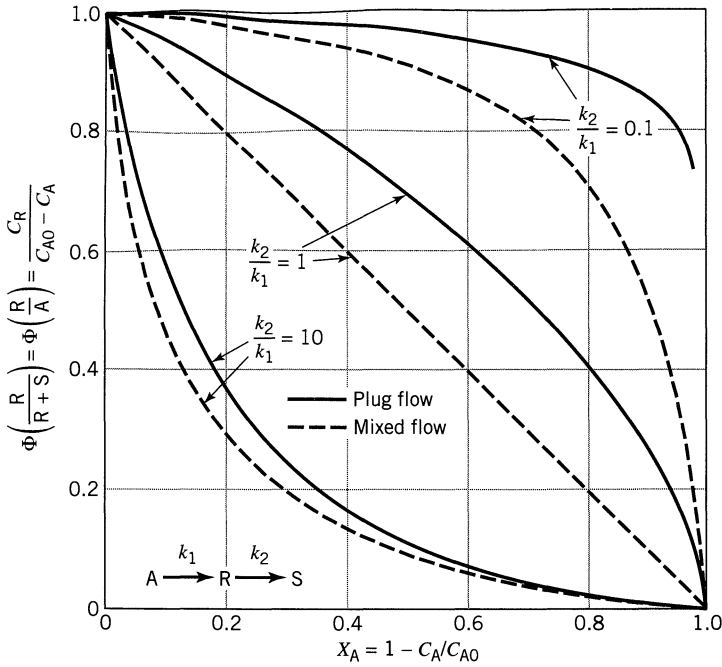
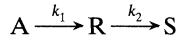
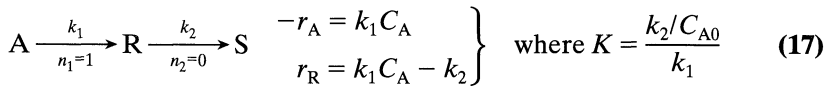


Figure 8.6 Comparison of the fractional yields of R in mixed flow and plug flow reactors for the unimolecular-type reactions



8.2 FIRST-ORDER FOLLOWED BY ZERO-ORDER REACTION

Let the reactions be



For batch or plug flow with $C_{R0} = C_{S0} = 0$ integration gives

$$\boxed{\frac{C_A}{C_{A0}} = e^{-k_1 t}} \quad (18)$$

and

$$\boxed{\frac{C_R}{C_{A0}} = 1 - e^{-k_1 t} - \frac{k_2}{C_{A0}} t} \quad (19)$$

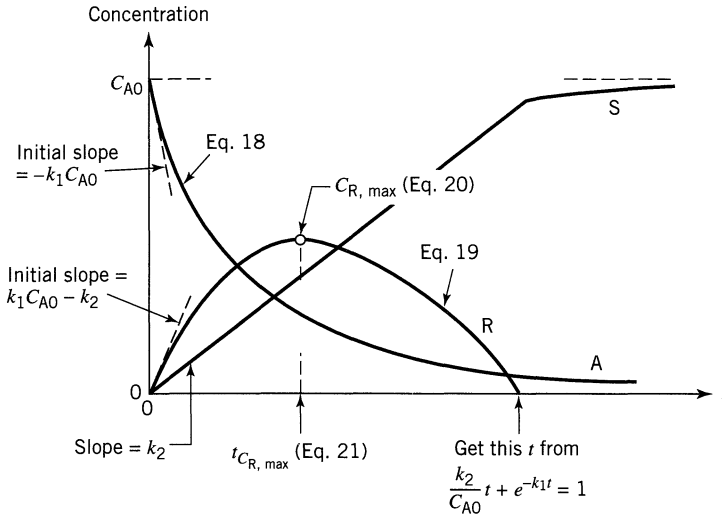


Figure 8.7 Product distribution for the reactions $A \xrightarrow{n=1} R \xrightarrow{n=0} S$

The maximum concentration of intermediate, $C_{R,max}$, and the time when this occurs is found to be

$$\boxed{\frac{C_{R,max}}{C_{A0}} = 1 - K(1 - \ln K)} \quad (20)$$

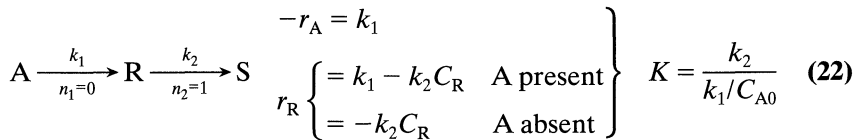
and

$$\boxed{t_{R,max} = \frac{1}{k_1} \ln \frac{1}{K}} \quad (21)$$

Graphically we show these findings in Fig. 8.7.

8.3 ZERO-ORDER FOLLOWED BY FIRST-ORDER REACTION

Let the reactions be



for batch or plug flow with $C_{R0} = C_{S0} = 0$ integration gives

$$\boxed{\frac{C_A}{C_{A0}} = 1 - \frac{k_1 t}{C_{A0}}} \quad (23)$$

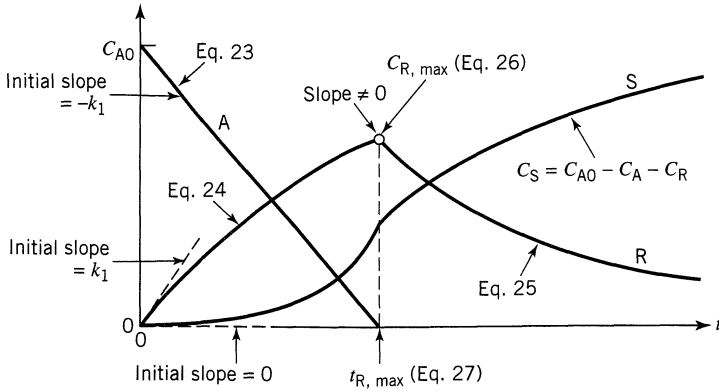


Figure 8.8 Product distribution for the reactions $A \xrightarrow{n=0} R \xrightarrow{n=1} S$

and

$$\frac{C_R}{C_{A0}} \begin{cases} = \frac{1}{K} (1 - e^{-k_2 t}) & t < \frac{C_{A0}}{k_1} \\ = \frac{1}{K} (e^{K - k_2 t} - e^{-k_2 t}) & t > \frac{C_{A0}}{k_1} \end{cases} \quad (24)$$

(25)

The maximum concentration of intermediate, $C_{R,\max}$, and the time when this occurs is found to be

$$\frac{C_{R,\max}}{C_{A0}} = \frac{1 - e^{-K}}{K} \quad (26)$$

and

$$t_{R,\max} = \frac{C_{A0}}{k_1} \quad (27)$$

Graphically we show these findings in Fig. 8.8.

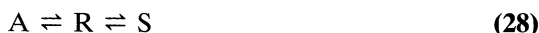
8.4 SUCCESSIVE IRREVERSIBLE REACTIONS OF DIFFERENT ORDERS

In principle, concentration-time curves can be constructed for successive reactions of different orders. For the plug flow or batch reactor and for the mixed reactor explicit solutions are difficult to obtain; thus, numerical methods provide the best tool for treating such reactions.

For these reactions the concentration-time curves are of little generality for they are dependent on the concentration of reactant in the feed. As with reactions in parallel, a rise in reactant concentration favors the higher-order reaction; a lower concentration favors the lower-order reaction. This causes a shift in $C_{R,\max}$, and this property can be used to improve the product distribution.

8.5 REVERSIBLE REACTIONS

Solution of the equations for successive reversible reactions is quite formidable even for the first-order case; thus, we illustrate only the general characteristics for a few typical cases. Consider the reversible first-order reactions



and



Figures 8.9 and 8.10 display the concentration time curves for the components in batch or plug flow for different values of the rate constants.

Figure 8.9 shows that the concentration of intermediate in reversible series reactions need not pass through a maximum, while Fig. 8.10 shows that a product may pass through a maximum concentration typical of an intermediate in the irreversible series reaction; however, the reactions may be of a different kind. A comparison of these figures shows that many of the curves are similar in shape, making it difficult to select a mechanism of reaction by experiment, especially if the kinetic data are somewhat scattered. Probably the best clue to distinguishing between parallel and series reactions is to examine initial rate data—data obtained for very small conversion of reactant. For series reactions the time-concentration curve for S has a zero initial slope, whereas for parallel reactions this is not so.

8.6 IRREVERSIBLE SERIES-PARALLEL REACTIONS

Multiple reactions that consist of steps in series and steps in parallel are called series-parallel reactions. From the point of view of proper contacting, these reactions are more interesting than the simpler types already considered because a larger choice of contacting is usually possible, leading to much wider differences in product distribution. Thus, design engineers are dealing with a more flexible system and this affords them the opportunity to display their talents in devising the best of the wide variety of possible contacting patterns. Let us develop our ideas with a reaction type that represents a broad class of industrially important reactions. We will then generalize our findings to other series-parallel reactions.

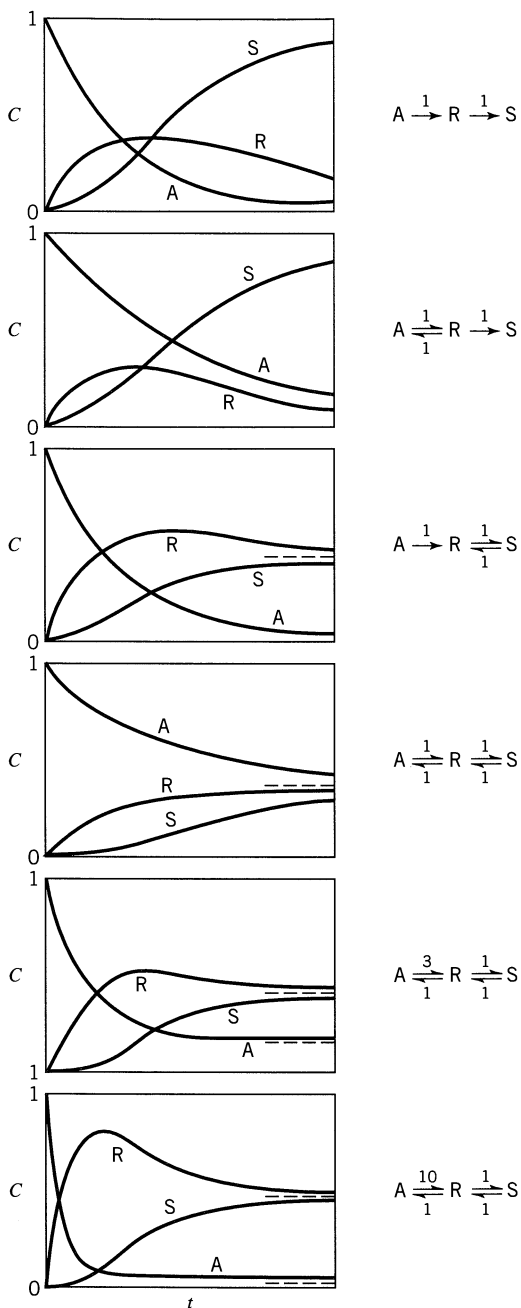
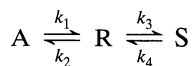


Figure 8.9 Concentration-time curves for the elementary reversible reactions



From Jungers et al. (1958), p. 207.

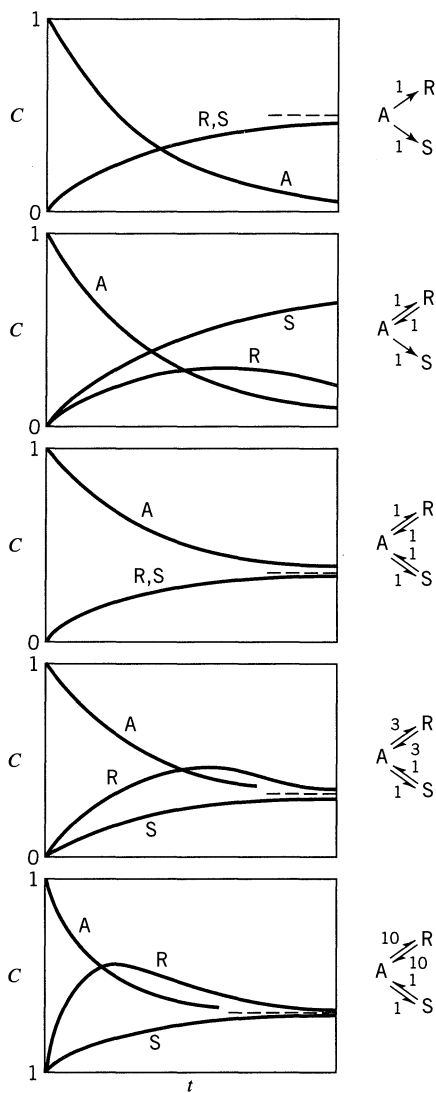
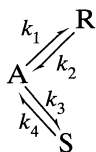


Figure 8.10 Concentration-time curves for the elementary reversible parallel reactions

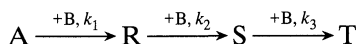


From Jungers et al. (1958), p. 207.

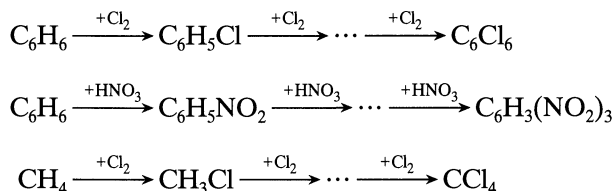
For the reaction set consider the successive attack of a compound by a reactive material. The general representation of these reactions is



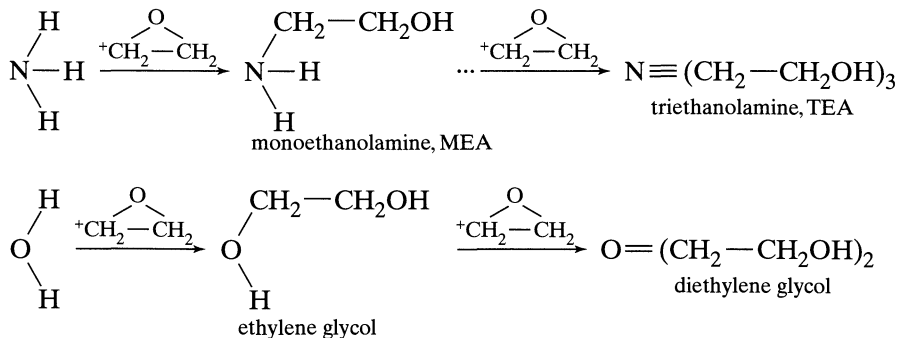
or



where A is the compound to be attacked, B is the reactive material, and R, S, T, etc., are the polysubstituted materials formed during reaction. Examples of such reactions may be found in the successive substitutive halogenation (or nitration) of hydrocarbons, say benzene or methane, to form monohalo, dihalo, trihalo, etc., derivatives as shown below:



Another important example is the addition of alkene oxides, say ethylene oxide, to compounds of the proton donor class such as amines, alcohols, water, and hydrazine to form monoalkoxy, dialkoxy, trialkoxy, etc., derivatives, some examples of which are shown below:



Such processes are frequently bimolecular, irreversible, hence second-order kinetically. When occurring in the liquid phase they are also essentially constant-density reactions.

Two-Step Irreversible Series-Parallel Reactions

We first consider the two-step reaction where the first substitution product is desired. Actually for an n -step reaction the third and succeeding reactions do not occur to any appreciable extent and may be ignored if the mole ratio of A to B is high (see qualitative treatment given next). The reaction set considered is thus



With the assumption that the reaction is irreversible, bimolecular, and of constant density, the rate expressions are given by

$$r_A = \frac{dC_A}{dt} = -k_1 C_A C_B \quad (32)$$

$$r_B = \frac{dC_B}{dt} = -k_1 C_A C_B - k_2 C_R C_B \quad (33)$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A C_B - k_2 C_R C_B \quad (34)$$

$$r_S = \frac{dC_S}{dt} = k_2 C_R C_B \quad (35)$$

Qualitative Discussion About Product Distribution. To get the “feel” for what takes place when A and B react according to Eq. 31, imagine that we have two beakers, one containing A and the other containing B. Should it make any difference in the product distribution how we mix A and B? To find out, consider the following ways of mixing the reactants: (a) add A slowly to B, (b) add B slowly to A, and finally (c) mix A and B together rapidly.

(a) Add A Slowly to B. For the first alternative pour A a little at a time into the beaker containing B, stirring thoroughly and making sure that all the A is used up and that the reaction stops before the next bit is added. With each addition a bit of R is produced in the beaker. But this R finds itself in an excess of B so it will react further to form S. The result is that at no time during the slow addition will A and R be present in any appreciable amount. The mixture becomes progressively richer in S and poorer in B. This continues until the beaker contains only S. Figure 8.11 shows this progressive change.

(b) Add B Slowly to A. Now pour B a little at a time into the beaker containing A, again stirring thoroughly. The first bit of B will be used up, reacting with A to form R. This R cannot react further for there is now no B present in the

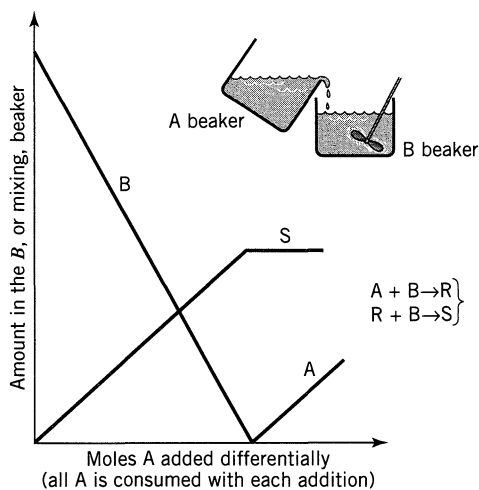
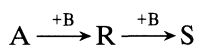


Figure 8.11 Distribution of materials in the B beaker for the method of mixing shown.

mixture. With the next addition of B, both A and R will compete with each other for the B added, and since A is in very large excess it will react with most of the B, producing even more R. This process will be repeated with progressive buildup of R and depletion of A until the concentration of R is high enough so that it can compete favorably with A for the B added. When this happens, the concentration of R reaches a maximum, then decreases. Finally, after addition of 2 moles of B for each mole of A, we end up with a solution containing only S. This progressive change is shown in Fig. 8.12.

(c) Mix A and B Rapidly. Now consider the third alternative where the contents of the two beakers are rapidly mixed together, the reaction being slow enough so that it does not proceed to any appreciable extent before the mixture becomes uniform. During the first few reaction increments R finds itself competing with a large excess of A for B and hence it is at a disadvantage. Carrying through this line of reasoning, we find the same type of distribution curve as for the mixture in which B is added slowly to A. This situation is shown in Fig. 8.12.

The product distribution of Figs. 8.11 and 8.12 are completely different. Thus, when A is kept uniform in composition as it reacts, as in Fig. 8.12, then R is formed. However, when fresh A is mixed with partly reacted mixture, as in Fig. 8.11, then no intermediate R forms. But this is precisely the behavior of reactions in series. Thus, as far as A, R, and S are concerned, we may view the reactions of Eq. 31 as



A second observation of Fig. 8.12 is that the concentration level of B, whether high or low, has no effect on the path of the reaction and on the distribution of

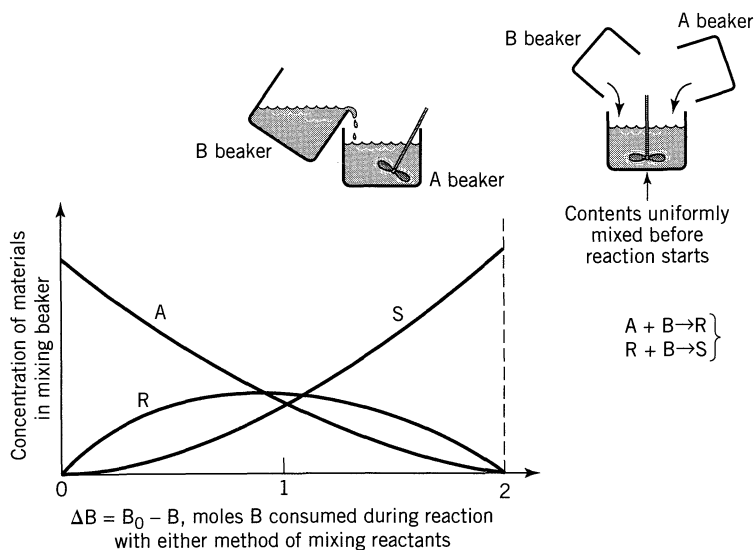
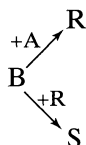


Figure 8.12 Distribution of materials in the mixing beaker for either of the methods of mixing shown.

products. But this is precisely the behavior of parallel reactions of the same order. So with respect to B, Eq. 31 can be looked at as



From this discussion we propose the general rule:

Irreversible series-parallel reactions can be analyzed in terms of their constituent series reactions and parallel reactions in that optimum contacting for favorable product distribution is the same as for the constituent reactions.

For the reactions of Eq. 31 where R is desired this rule shows that the best way of contacting A and B is to react A uniformly, while adding B in any convenient way.

This is a powerful generalization which, without needing specific values for the rate constants, can already show in many cases which are the favorable contacting patterns. It is essential, however, to have the proper representation of the stoichiometry and form of rate equation. Example 8.6 and many of the problems of Chapter 10 apply these generalizations.

Quantitative Treatment, Plug Flow or Batch Reactor. Here we quantitatively treat the reactions of Eq. 31 with the understanding that R, the intermediate, is the desired product, and that the reaction is slow enough so that we may ignore the problems of partial reaction during the mixing of reactants.

In general, taking the ratio of two rate equations eliminates the time variable and gives information on the product distribution. So dividing Eq. 34 by Eq. 32 we obtain the first-order linear differential equation

$$\frac{r_R}{r_A} = \frac{dC_R}{dC_A} = -1 + \frac{k_2 C_R}{k_1 C_A} \quad (36)$$

whose method of solution is shown in Chapter 3. With no R present in the feed the limits of integration are C_{A0} to C_A for A and $C_{R0} = 0$ for R, and the solution of this differential equation is

$$\boxed{\begin{aligned} \frac{C_R}{C_{A0}} &= \frac{1}{1 - k_2/k_1} \left[\left(\frac{C_A}{C_{A0}} \right)^{k_2/k_1} - \frac{C_A}{C_{A0}} \right], & \frac{k_2}{k_1} &\neq 1 \\ \frac{C_R}{C_{A0}} &= \frac{C_A}{C_{A0}} \ln \frac{C_{A0}}{C_A}, & \frac{k_2}{k_1} &= 1 \end{aligned}} \quad (37)$$

with maximum C_R at

$$\boxed{\begin{aligned} \frac{C_{R,\max}}{C_{A0}} &= \left(\frac{k_1}{k_2} \right)^{k_2/(k_2-k_1)}, & \frac{k_2}{k_1} &\neq 1 \\ \frac{C_{R,\max}}{C_{A0}} &= \frac{1}{e} = 0.368 & \frac{k_2}{k_1} &= 1 \end{aligned}} \quad (38)$$

This gives the relationship between C_R and C_A in a batch or in a plug flow reactor. To find the concentrations of the other components, simply make a material balance. An A balance gives

$$C_{A0} + C_{R0} + C_{S0} = C_A + C_R + C_S \quad (39)$$

or

$$\Delta C_A + \Delta C_R + \Delta C_S = 0$$

from which C_S can be found as a function of C_A and C_R . Finally, a balance about B gives

$$\Delta C_B + \Delta C_R + 2\Delta C_S = 0 \quad (40)$$

from which C_B can be found.

Quantitative Treatment, Mixed Flow. Writing the design equation for mixed flow in terms of A and R gives

$$\tau_m = \frac{C_{A0} - C_A}{-r_A} = \frac{-C_R}{-r_R}$$

or

$$\tau_m = \frac{C_{A0} - C_A}{k_1 C_A C_B} = \frac{-C_R}{k_2 C_R C_B - k_1 C_A C_B}$$

Rearranging, we obtain

$$\frac{-C_R}{C_{A0} - C_A} = -1 + \frac{k_2 C_R}{k_1 C_A}$$

which is the difference equation corresponding to the differential equation, Eq. 36. Writing C_R in terms of C_A then gives

$$\boxed{\begin{aligned} C_R &= \frac{C_A(C_{A0} - C_A)}{C_A + (k_2/k_1)(C_{A0} - C_A)} \\ \frac{C_{R,\max}}{C_{A0}} &= \frac{1}{[1 + (k_2/k_1)^{1/2}]^2} \end{aligned}} \quad (41)$$

with

Equations 39 and 40, material balances about A and B in plug flow, hold equally well for mixed flow and serve to complete the set of equations giving complete product distribution in this reactor.

Graphical Representation. Figures 8.13 and 8.14, time-independent plots, show the distribution of materials in plug and mixed flow and are prepared from Eqs. 37 to 41. As mentioned earlier, A, R, and S behave like the components in first-order reactions in series. Comparing Figs. 8.13 and 8.14 with Figs. 8.3*b* and 8.5*b*, we see that the distribution of these materials is the same in both cases, plug flow again giving a higher concentration of intermediate than mixed flow. The lines of slope 2 on these charts show the amount of B consumed to reach any particular point on the curve. It makes no difference whether B is added all at one time as in a batch reactor or a little at a time as in a semibatch reactor; in either case the same point on the chart will be reached when the same total amount of B is consumed.

These figures indicate that no matter what reactor system is selected, when the fractional conversion of A is low the fractional yield of R is high. Thus, if it is possible to separate R cheaply from a product stream, the optimum setup for producing R is to have small conversions per pass coupled with a separation of R and recycle of unused A. The actual mode of operation will, as usual, depend on the economics of the system under study.

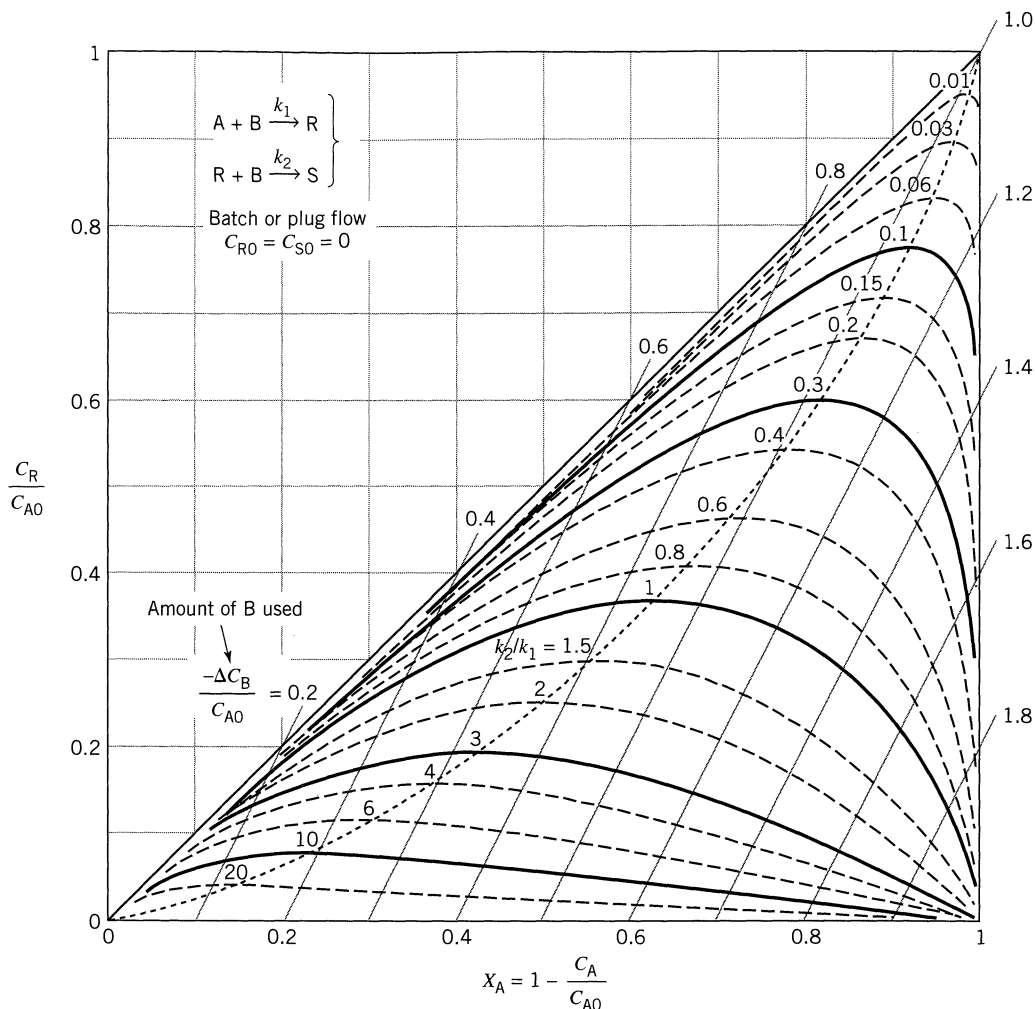
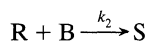
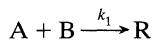


Figure 8.13 Distribution of materials in a batch or plug flow reactor for the elementary series-parallel reactions



Experimental Determination of the Kinetics of Reaction. The ratio k_2/k_1 may be found by analyzing the products of reaction from an experiment, and locating the corresponding point on the appropriate design chart. The simplest way to do this is to use different ratios of B to A in a batch reactor, allowing the reaction to go to completion each time. For each run a value of k_2/k_1 can be determined.

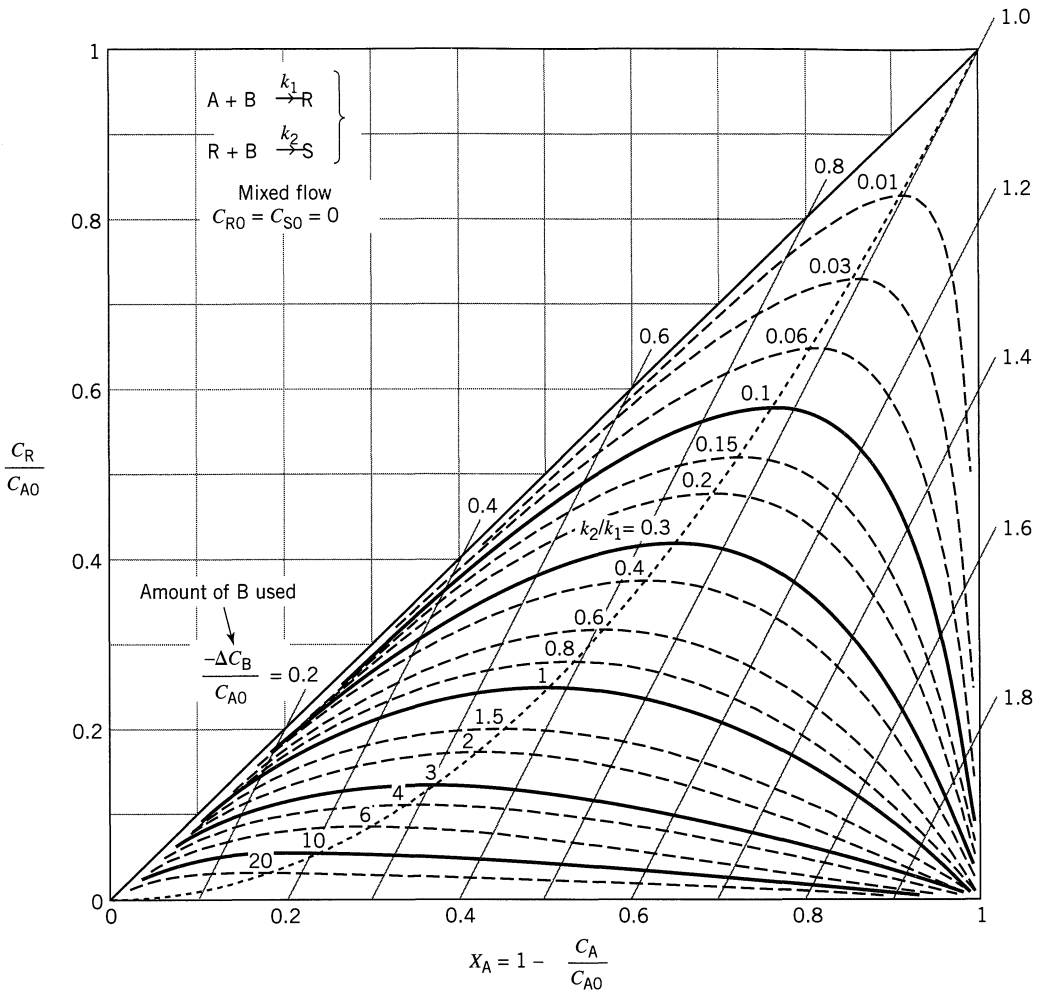
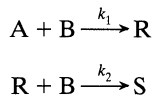


Figure 8.14 Distribution of materials in a mixed flow reactor for the elementary series-parallel reactions

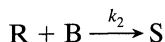
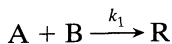


The best mole ratios to use are those where the lines of constant k_2/k_1 are furthest apart, or when $-(\Delta B/A_0) \approx 1.0$, or close to equimolar ratios.

With k_2/k_1 known, all that is needed is k_1 which must be found by kinetic experiments. The simplest procedure is to use a large excess of B in which case the disappearance of A follows first-order kinetics.

EXAMPLE 8.2 KINETICS OF SERIES-PARALLEL REACTION

From each of the following experiments, what can we say about the rate constants of the multiple reactions



- (a) Half a mole of B is poured bit by bit, with stirring, into a flask containing a mole of A. The reaction proceeds slowly, and when B is entirely consumed 0.67 mole of A remains unreacted.
- (b) One mole of A and 1.25 moles of B are rapidly mixed, and the reaction is slow enough so that it does not proceed to any appreciable extent before homogeneity in composition is achieved. On completion of the reaction, 0.5 mole of R is found to be present in the mixture.
- (c) One mole of A and 1.25 moles of B are rapidly brought together. The reaction is slow enough so that it does not proceed to any appreciable extent before homogeneity in A and B is achieved. At the time when 0.9 mole of B is consumed, 0.3 mole of S is present in the mixture.

SOLUTION

The sketches in Fig. E8.2 show how Fig. 8.13 is used to find the desired information. Thus we find:

(a) $\underline{k_2/k_1 = 4}$, (b) $\underline{k_2/k_1 = 0.4}$, (c) $\underline{k_2/k_1 = 1.45}$

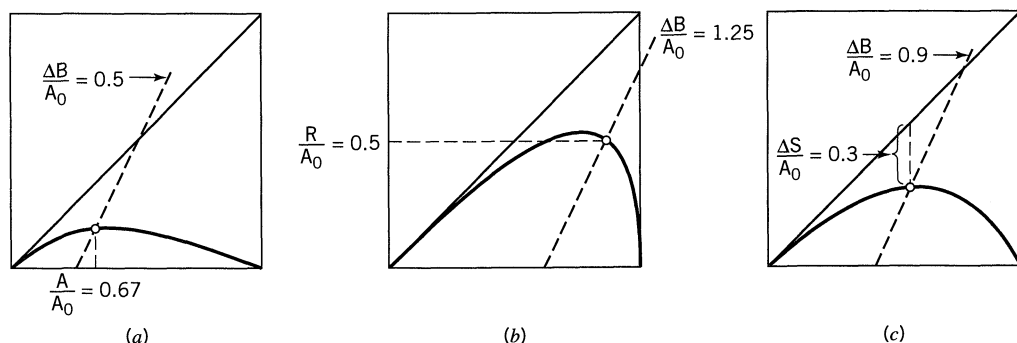


Figure E8.2

Extensions and Applications

Three or More Reactions. Analysis of three or more reactions can be made by procedures analogous to those presented. Of course, the mathematics becomes more involved; however, much of the extra labor can be avoided by selecting experimental conditions in which only two reactions need be considered at any time. Figure 8.15 shows product distribution curves for one such reaction set, the progressive chlorination of benzene.

Catipovic and Levenspiel (1979) have developed charts to represent the first three steps of an n -step reaction sequence. Beyond three steps, simple performance charts cannot be prepared.

Again, as with the two-reaction set, we find that a plug flow reactor yields a higher maximum concentration of any intermediate than does a mixed flow reactor.

Polymerization. The field of polymerization affords an opportunity for a fruitful application of these ideas. Often hundreds or even thousands of reactions in series occur in the formation of polymers, and the type of crosslinking and molecular weight distribution of these products are what gives these materials their particular physical properties of solubility, density, flexibility, etc.

Since the mode of mixing of monomers with their catalysts profoundly affects product distribution, great importance must be paid to this factor if the product is to have the desired physical and chemical properties. Denbigh (1947, 1951) considered some of the many aspects of this problem, and Fig. 8.16 shows for various kinetics how reactor type influences the molecular weight distribution of products.

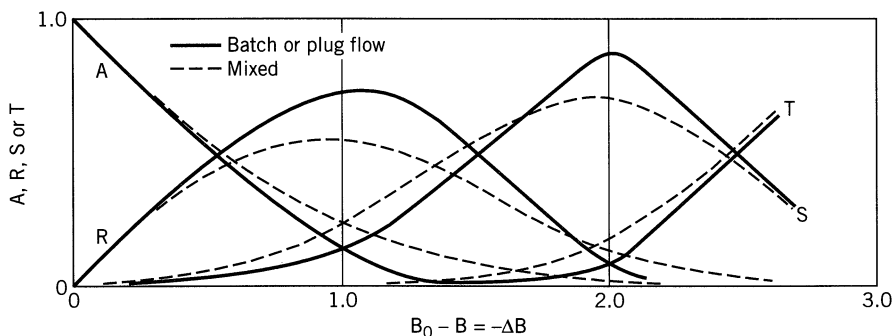
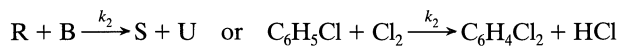


Figure 8.15 Product distribution in the progressive chlorination of benzene:



With $k_2/k_1 = 1/8$ and $k_3/k_1 = 1/240$; from R. B. MacMullin (1948).

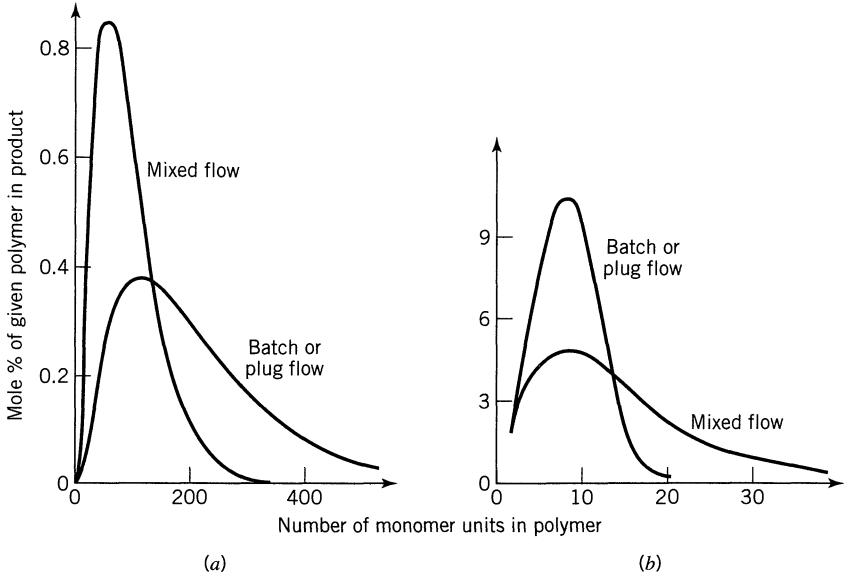
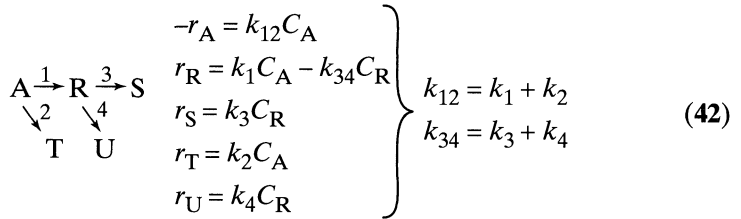


Figure 8.16 Type of flow and kinetics influence the molecular weight distribution of polymer: (a) duration of polymerization reaction (life of active polymer) is short compared to the reactor holding time; (b) duration of polymerization reaction is long compared to the reactor holding time, or where polymerization has no termination reaction. Adapted from Denbigh (1947).

8.7 THE DENBIGH REACTIONS AND THEIR SPECIAL CASES

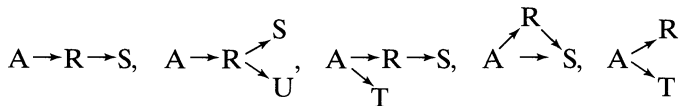
Denbigh (1958) was the first to treat the following rather general reaction scheme



with

$$C_{A0} + C_{R0} + C_{S0} + C_{T0} + C_{U0} = C_A + C_R + C_S + C_T + C_U \quad (43)$$

The performance equations for this reaction scheme reduce directly to all the special cases, for example



This scheme has wide application to a whole host of real reacting systems.

These rate equations are all of first order and so to develop the performance expressions does not involve complex mathematics, although it may be a tedious task. In our treatment we will not present the detailed calculation steps, but will just present the final results.

Batch or Plug Flow Reactors. Integration gives the performance equations for this system

$$\frac{C_A}{C_{A0}} = \exp(-k_{12}t) \quad (44)$$

$$\frac{C_R}{C_{A0}} = \frac{k_1}{k_{34} - k_{12}} [\exp(-k_{12}t) - \exp(-k_{34}t)] + \frac{C_{R0}}{C_{A0}} \exp(-k_{34}t) \quad (45)$$

$$\begin{aligned} \frac{C_S}{C_{A0}} = \frac{k_1 k_3}{k_{34} - k_{12}} \left[\frac{\exp(-k_{34}t)}{k_{34}} - \frac{\exp(-k_{12}t)}{k_{12}} \right] + \frac{k_1 k_3}{k_{12} k_{34}} \\ + \frac{C_{R0} k_3}{C_{A0} k_{34}} [1 - \exp(-k_{34}t)] + \frac{C_{S0}}{C_{A0}} \end{aligned} \quad (46)$$

$$\frac{C_T}{C_{A0}} = \frac{k_2}{k_{12}} [1 - \exp(-k_{12}t)] + \frac{C_{T0}}{C_{A0}} \quad (47)$$

$$\frac{C_U}{C_{A0}} \dots \text{same as } \frac{C_S}{C_{A0}} \text{ but with } k_3 \leftrightarrow k_4 \text{ and } C_{S0} \leftrightarrow C_{U0}$$

For the special case where $C_{R0} = C_{S0} = C_{T0} = C_{U0} = 0$ the above expressions simplify. We also can find $C_R = f(C_A)$, thus

$$\frac{C_R}{C_{A0}} = \frac{k_1}{k_{12} - k_{34}} \left[\left(\frac{C_A}{C_{A0}} \right)^{k_{34}/k_{12}} - \frac{C_A}{C_{A0}} \right] \quad (48)$$

and

$$\frac{C_{R,\max}}{C_{A0}} = \frac{k_1}{k_{12}} \left(\frac{k_{12}}{k_{34}} \right)^{k_{34}/(k_{34} - k_{12})} \quad (49)$$

at

$$t_{\max} = \frac{\ln(k_{34}/k_{12})}{k_{34} - k_{12}} \quad (50)$$

For $C_{R0} = C_{S0} = C_{T0} = C_{U0} = 0$ the behavior of the system is displayed as shown in Fig. 8.17. This figure also shows $C_{R,\max}$ and the time when this occurs in terms of the rate constants.

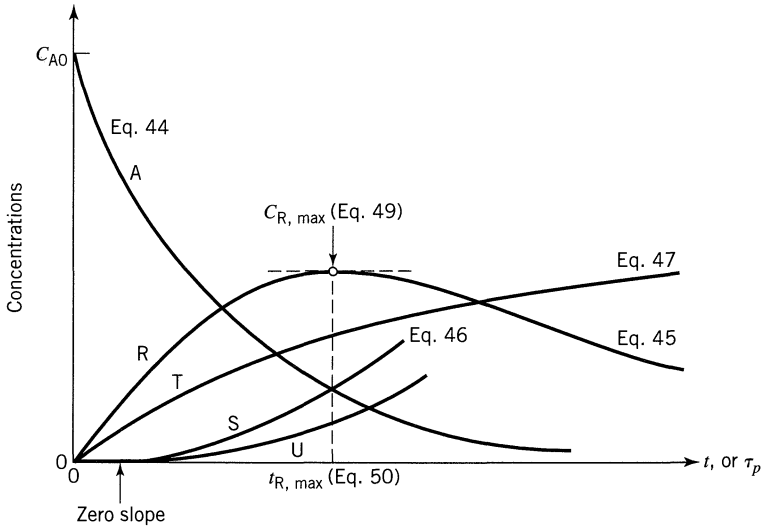


Figure 8.17 Progress of the Denbigh reaction scheme in a plug flow reactor for $C_{R0} = C_{S0} = C_{T0} = C_{U0} = 0$.

Mixed Flow Reactors. Using the mixed flow performance equation with these rates gives

$$\frac{C_A}{C_{A0}} = \frac{1}{(1 + k_{12}\tau_m)} \quad (51)$$

$$\frac{C_R}{C_{A0}} = \frac{k_1\tau_m}{(1 + k_{12}\tau_m)(1 + k_{34}\tau_m)} + \frac{C_{R0}}{C_{A0}} \frac{1}{(1 + k_{34}\tau_m)} \quad (52)$$

$$\frac{C_S}{C_{A0}} = \frac{k_1k_3\tau_m^2}{(1 + k_{12}\tau_m)(1 + k_{34}\tau_m)} + \frac{C_{R0}}{C_{A0}} \frac{k_3\tau_m}{(1 + k_{34}\tau_m)} + \frac{C_{S0}}{C_{A0}} \quad (53)$$

$$\frac{C_T}{C_{A0}} = \frac{k_2\tau_m}{(1 + k_{12}\tau_m)} + \frac{C_{T0}}{C_{A0}} \quad (54)$$

$$\frac{C_U}{C_{A0}} \dots \text{same as } \frac{C_S}{C_{A0}} \text{ but with } k_3 \leftrightarrow k_4 \text{ and } C_{S0} \leftrightarrow C_{U0} \quad (55)$$

At the optimum

$$\frac{C_{Rmax}}{C_{A0}} = \left(\frac{k_1}{k_{12}}\right) \cdot \frac{1}{[(k_{34}/k_{12})^{1/2} + 1]^2} \quad (56)$$

at

$$\tau_{m,Rmax} = \frac{1}{(k_{12}/k_{34})^{1/2}} \quad (57)$$

Graphically, for $C_{R0} = C_{S0} = C_{T0} = C_{U0} = 0$, Fig. 8.18 shows the behavior of this system.

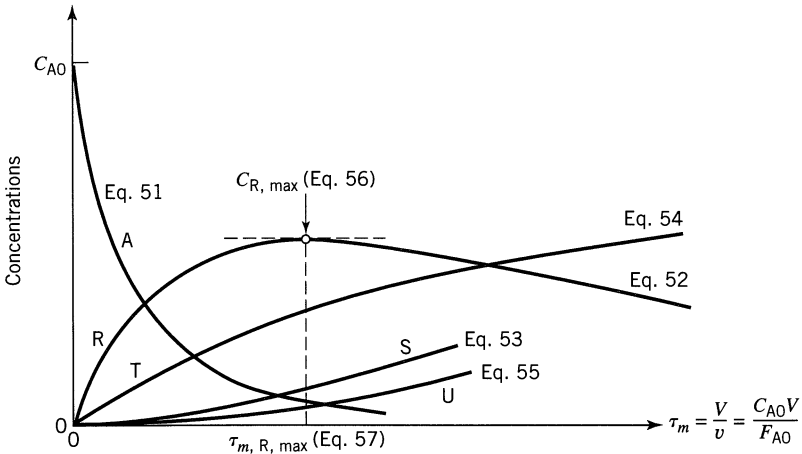
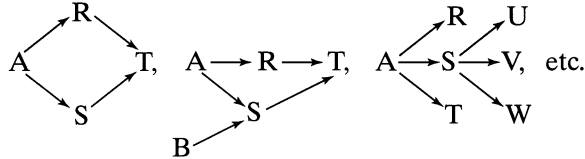


Figure 8.18 Progress of the Denbigh reaction scheme in a mixed flow reactor for $C_{R0} = C_{S0} = C_{T0} = C_{U0} = 0$.

Comments, Suggestions, and Extensions

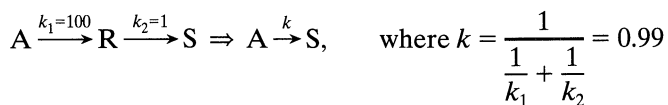
The equations of this chapter can be extended and applied directly to many other reaction schemes, for example



Some problems at the end of this chapter consider these extensions.

A careful examination of the shape of the C versus τ curves gives much useful information on the rate constants. Here are some clues:

- Look at the initial slope of the curves; measure the slopes. Are the initial slopes of produced materials zero or not?
- Measure the final concentration of all the reaction components.
- Find when an intermediate reaches its maximum concentration and measure this concentration.
- In searching for a model or mechanism for the reaction scheme make runs at different C_{A0} and different C_{B0}/C_{A0} .
- If possible, also make runs starting with intermediate. For example, for the reaction $A \rightarrow R \rightarrow S$ start with R alone and follow its disappearance.
- If the two steps of first-order reactions in series have very different values for their rate constants, we can approximate the overall behavior as follows:



- For schemes involving different reaction orders, for reversible reactions, and for a very-many-step scheme typical of polymerizations, analysis becomes complicated.
- The key to optimum design for multiple reactions is proper contacting and proper flow pattern of fluids within the reactor. These requirements are determined by the stoichiometry and observed kinetics. Usually qualitative reasoning alone can already determine the correct contacting scheme. This is discussed further in Chapter 10. However, to determine the actual equipment size requires quantitative considerations.

EXAMPLE 8.3 EVALUATE THE KINETICS FROM A BATCH EXPERIMENT

Japanese researchers very carefully followed the oxidation of sodium sulfide Na_2S (A) to sodium thiosulfate $\text{Na}_2\text{S}_2\text{O}_3$ (R) in a batch reactor. Intermediates were measured and the results found were sketched in Fig. E8.3.

- Think up a simple network of reactions, all of first-order, to represent this oxidation.
- Evaluate the rate constants of this network.

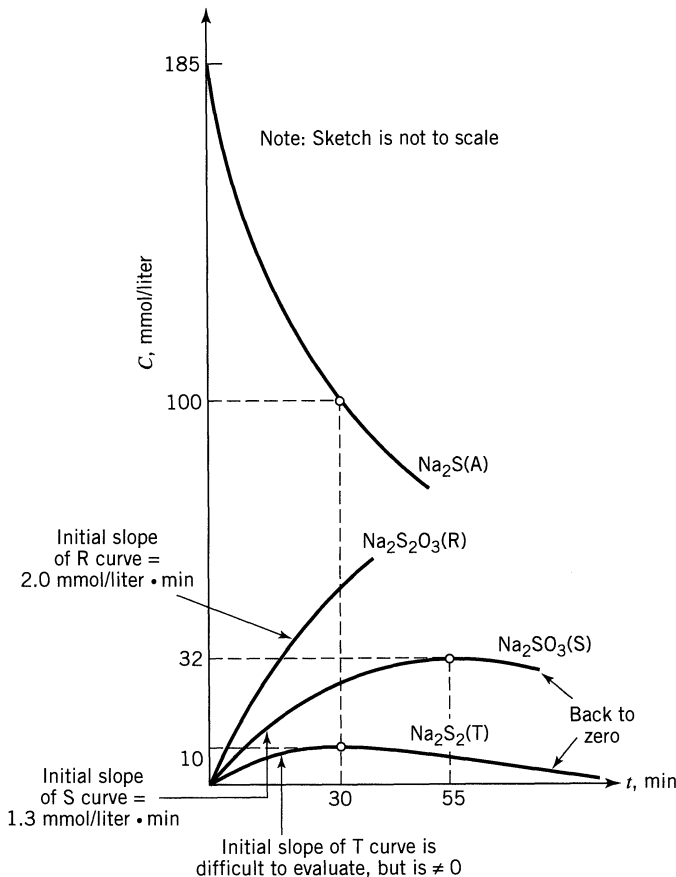
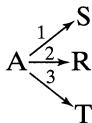


Figure E8.3

SOLUTION

This problem draws on a number of techniques.

(a) First, Look for Clues in the Graph. We first note that the initial slopes of the R, S, and T curves are all nonzero, suggesting that these compounds are formed directly from A, or



Next, since there is no S and T in the final product, our suggested reaction scheme is



(b) Evaluate the Rate Constants. Noting that A disappears by first-order kinetics, we have

$$\ln \frac{C_{A0}}{C_A} = \ln \frac{185}{100} = (k_1 + k_2 + k_3)t = k_{123}t = k_{123}(30)$$

from which

$$k_{123} = \underline{\underline{0.0205 \text{ min}^{-1}}}$$

From the initial rate for formation of R

$$\frac{dC_R}{dt} = k_2 C_{A0}$$

or

$$k_2 = \frac{dC_R/dt}{C_{A0}} = \frac{2.0}{185} = \underline{\underline{0.0108 \text{ min}^{-1}}}$$

Similarly for S

$$k_1 = \frac{dC_S/dt}{C_{A0}} = \frac{1.3}{185} = \underline{\underline{0.0070 \text{ min}^{-1}}}$$

So by difference

$$k_3 = k_{123} - k_1 - k_2 = 0.0205 - 0.0108 - 0.0070 = \underline{\underline{0.0027 \text{ min}^{-1}}}$$

Next, let us look at the maxima of the S and T curves. For S, by an extension of Eq. 49, we can write

$$\frac{C_{S\max}}{C_{A0}} = \frac{k_1}{k_{123}} \left(\frac{k_{123}}{k_4} \right)^{k_4/(k_4 - k_{123})}$$

or

$$\frac{32}{185} = \frac{0.0070}{0.0205} \left(\frac{0.0205}{k_4} \right)^{k_4/(k_4 - 0.0205)}$$

Solving for k_4 by trial and error gives

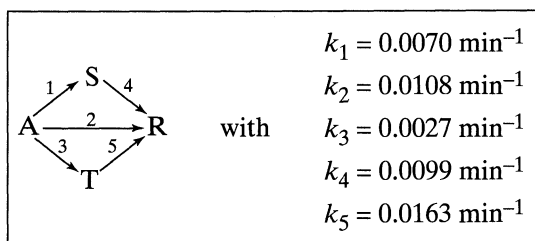
$$\underline{\underline{k_4 = 0.0099 \text{ min}^{-1}}}$$

Similarly for T

$$\frac{10}{185} = \frac{0.0027}{0.0205} \left(\frac{0.0205}{k_5} \right)^{k_5/(k_5 - 0.0205)}$$

$$\underline{\underline{k_5 = 0.0163 \text{ min}^{-1}}}$$

So we end up with the following kinetic scheme



(b)

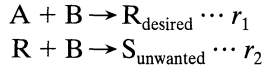
This problem was prepared by David L. Cates (1988).

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 Denbigh, K. G., *Trans. Faraday Soc.*, **43**, 648 (1947).
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PROBLEMS

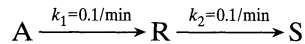
- 8.1. Starting with separate feeds of reactant A and B of given concentration (no dilution with inerts permitted), for the competitive-consecutive reactions with stoichiometry and rate as shown



sketch the best contacting patterns for both continuous and noncontinuous operations:

$$\begin{array}{ll} \text{(a)} & r_1 = k_1 C_A C_B^2 \\ & r_2 = k_2 C_R C_B \\ \text{(b)} & r_1 = k_1 C_A C_B \\ & r_2 = k_2 C_R C_B^2 \\ \text{(c)} & r_1 = k_1 C_A C_B \\ & r_2 = k_2 C_R^2 C_B \\ \text{(d)} & r_1 = k_1 C_A^2 C_B \\ & r_2 = k_2 C_R C_B \end{array}$$

- 8.2. Under appropriate conditions A decomposes as follows:



R is to be produced from 1000 liter/hr of feed in which $C_{A0} = 1$ mol/liter, $C_{R0} = C_{S0} = 0$.

- (a) What size of plug flow reactor will maximize the concentration of R, and what is that concentration in the effluent stream from this reactor?
 (b) What size of mixed flow reactor will maximize the concentration of R, and what is $C_{R,\text{max}}$ in the effluent stream from this reactor?

Pure A ($C_{A0} = 100$) is fed to a mixed flow reactor, R and S are formed, and the following outlet concentrations are recorded. Find a kinetic scheme to fit this data.

8.3. Run	C_A	C_R	C_S
1	75	15	10
2	25	45	30

8.4. Run	C_A	C_R	C_S
1	50	$33\frac{1}{3}$	$16\frac{2}{3}$
2	25	30	45

8.5. Run	C_A	C_R	C_S	t, min
1	50	40	10	5
2	20	40	40	20

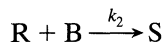
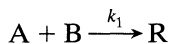
8.6. In grinding a continuous flow of pigments for paint, our company finds that too many too-small and too many too-large particles exit from our well-mixed grinder. A multistage grinder, approximating plug flow, could also have been used, but wasn't. Anyway, in either type of grinder the pigments are progressively ground into smaller and smaller particles.

At present, the exit stream from our well-mixed grinder contains 10% too-large ($d_p > 147 \mu\text{m}$); 32% just-right ($d_p = 38 - 147 \mu\text{m}$); and 58% too-small ($d_p < 38 \mu\text{m}$) particles.

- (a) Can you suggest a better grinding scheme for our present unit, and what would it give?
 (b) How about the multistage grinder? How would it do?

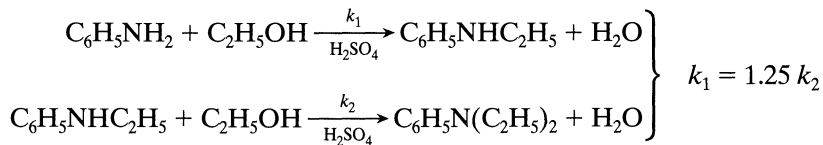
By "better" we mean giving more just right-sized pigment in the product stream. Also, separation and recycle of the size cuts is not practical.

8.7. Consider the following elementary reactions:



- (a) One mole A and 3 moles B are rapidly mixed together. The reaction is very slow, allowing analysis of compositions at various times. When 2.2 moles B remain unreacted, 0.2 mole S is present in the mixture. What should be the composition of the mixture (A, B, R, and S) when the amount of S present is 0.6 mole?
 (b) One mole A is added bit by bit with constant stirring to 1 mole B. Left overnight and then analyzed, 0.5 mole S is found. What can we say about k_2/k_1 ?
 (c) One mole A and 1 mole B are thrown together and mixed in a flask. The reaction is very rapid and goes to completion before any rate measurements can be made. On analysis of the products of reaction 0.25 mole S is found to be present. What can we say about k_2/k_1 ?

8.8. The liquid phase reaction of aniline with ethanol produces wanted monoethylaniline and unwanted diethylaniline



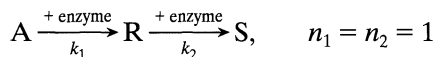
- (a) An equimolar feed is introduced into a batch reactor, and reaction is allowed to proceed to completion. Find the concentration of reactants and products at the end of the run.
 (b) Find the ratio of mono- to diethylaniline produced in a mixed flow

reactor for an alcohol-to-aniline feed ratio of 2 to 1 for 70% conversion of alcohol.

- (c) For an equimolar feed to a plug flow reactor, what will be the conversion of the two reactants when the concentration of monoethylaniline is at its highest?

- 8.9. Monoethylaniline can also be produced in the vapor phase in a fluidized bed using natural bauxite as the solid catalyst. The elementary reactions are shown in the previous problem. Using an equimolar feed of aniline and ethanol, the fluidized bed produces 3 parts monoethylaniline to 2 parts diethylaniline for a 40% conversion of aniline. Assuming mixed flow of gas in the fluidized bed, find k_2/k_1 and the concentration ratio of reactants and products at the exit of the reactor.

Under the action of mixed enzymes reactant A is converted to products as follows:



where the rate constants are dependent on the pH of the system.

- (a) What reactor set-up (plug flow, mixed flow, or staged mixed flow units) and what uniform pH level would you use?
- (b) If it were possible to change the pH level along the plug flow reactor, or from stage to stage in mixed flow units, in what direction would you change the pH level?
- 8.10. $k_1 = \text{pH}^2 - 8 \text{ pH} + 23$ with $2 < \text{pH} < 6$, and R the desired product
 $k_2 = \text{pH} + 1$
- 8.11. $k_1 = \text{pH} + 1$ with $2 < \text{pH} < 6$, and S the desired product
 $k_2 = \text{pH}^2 - 8 \text{ pH} + 23$

- 8.12. The progressive chlorination of *o*- and *p*-dichlorobenzene proceed with second-order rate, as shown in Fig. P8.12.

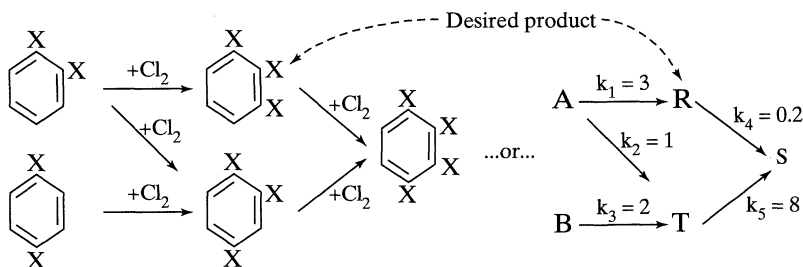


Figure P8.12

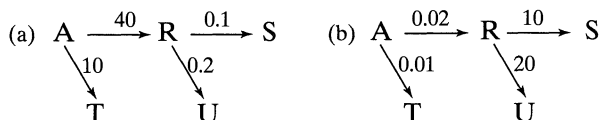
For a single-feed stream having $C_{A0} = 2$, $C_{B0} = 1$, and 1, 2, 3-trichlorobenzene as the desired product

(a) Tell which kind of flow reactor is best.

(b) In this reactor find $C_{R,max}$.

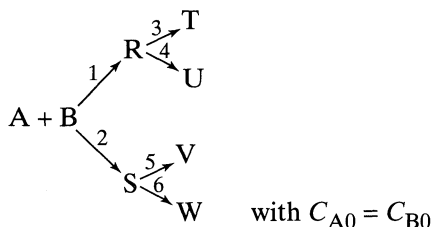
See T. E. Corrigan, *Chem. Eng.*, **201**, March 1956, for discussion of this process.

- 8.13.** Consider the following first order decompositions with rate constants as shown



If a colleague reports that $C_S = 0.2 C_{A0}$ in the exit stream of a plug flow reactor, what can you say about the concentration of the other reactor components, A, R, T, and U in the exit stream?

- 8.14.** Chemicals A and B are thrown into a vat and react away according to the following elementary reactions:



What can you say about these six rate constants if an analysis of the mixture shows that

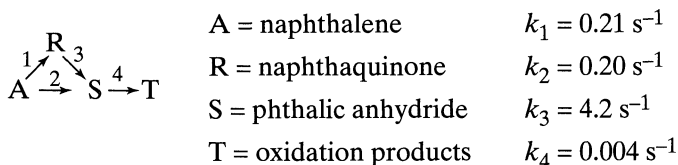
$$\begin{array}{ll} C_T = 5 \text{ mol/liter} & C_U = 1 \text{ mol/liter} \\ C_V = 9 \text{ mol/liter} & C_W = 3 \text{ mol/liter} \end{array}$$

at the time

(a) when reaction is incomplete?

(b) when reaction is complete?

- 8.15.** With a particular catalyst and at a given temperature, the oxidation of naphthalene to phthalic anhydride proceeds as follows:



What reactor type gives the maximum yield of phthalic anhydride? Roughly estimate this yield and the fractional conversion of naphthalene which will give this yield. Note the word “roughly”.

- 8.16.** Sandy’s Rock and Gravel Company wants to shift a mountain of gravel, estimated at about 20 000 tons, from one side of their yard to the other. For this they intend to use a power shovel to fill a hopper, which in turn feeds a belt conveyor. The latter then transports the gravel to the new location.

The shovel scoops up large amounts of gravel at first; however, as the gravel supply decreases, the handling capacity of the shovel also decreases because of the increased time required to move away from the hopper for a load and then return and dump. Roughly, then, we may estimate that the shovel’s gravel handling rate is proportional to the size of the pile still to be moved, its initial rate being 10 ton/min. The conveyor, on the other hand, transports the gravel at a uniform 5 ton/min. At first the shovel will work faster than the conveyor, then slower. Hence, the storage bin will first accumulate material, then empty.

- (a) What will be the largest amount of gravel in the bin?
- (b) When will this occur?
- (c) When will the rates of bin input and output be equal?
- (d) When will the bin become empty?

- 8.17.** A large fully automated municipal incinerator is being designed. A survey estimates the garbage load to be 1440 tons/day. This will be harvested by a fleet of compaction trucks which will disgorge their loads into an underground storage bin. A conveyor will then feed the garbage to the incinerator.

The proposed daily collection route is such that at the beginning of the working day (6 A.M. sharp!) relatively large quantities of garbage (average of 6 tons/min) are returned from nearby commercial areas. Subsequently, the supply will diminish as more remote suburban areas are serviced. It is assumed that the collection rate is proportional to the amount of garbage still to be collected, the initial rate being one truckload/min. The conveyor, on the other hand, will transport garbage at a uniform 1 ton/min to the incinerator. At the beginning of the working day, the trucks will work faster than the conveyor; later in the day, slower. Thus, each day the bin will accumulate material, then lose material.

To evaluate this operation, we need information. Please help us with this.

- (a) At what time of day will the trucks have collected 95% of the day’s garbage?
- (b) How much garbage would the storage bin be designed for?
- (c) At what time of day will the bin be fullest?
- (d) At what time of day will the bin be empty?

- 8.18.** Upper Slobbovians and Lower Slobbovians are always at it . . . , crushing skulls, slitting throats, and so on. . . . At any gathering the rate at which Upper Slobs are killed is directly proportional to the number of Lower

Slobs around, and vice versa. And at the end of any meeting of these friendly people, either Upper Slobs leave or Lower Slobs, but never both.

Last week ten Upper Slobs happened upon three Lower Slobs, and when it was over eight Upper Slobs lived to tell of their exciting victory.

- (a) From this encounter, how would you rate Upper and Lower Slobs as fighters? For example, would you say that they were equally good or that one Upper Slob is as good as 2.3 Lower Slobs, or what?
- (b) What would be the outcome of a friendly meeting of ten Upper Slobs with ten Lower Slobs?

- 8.19.** Chemical X, a powdered solid, is slowly and continuously fed for half an hour into a well-stirred vat of water. The solid quickly dissolves and hydrolyses to Y, which then slowly decomposes to Z as follows



The volume of liquid in the vat stays close to 3 m^3 throughout this operation, and if no reaction of Y to Z occurred, the concentration of Y in the vat would be 100 mol/m^3 at the end of the half-hour addition of X.

- (a) What is the maximum concentration of Y in the vat and at what time is this maximum reached?
- (b) What is the concentration of product Z in the vat after 1 hour?

Problem prepared by Bhaskar Chandan (1990).

- 8.20.** When oxygen is bubbled through a high-temperature batch of A-containing liquid material, A oxidizes slowly to give a slowly decomposing intermediate X and final product R. Here are the results of an experiment:

$t, \text{ min}$	$C_A, \text{ mol/m}^3$	$C_R, \text{ mol/m}^3$
0	100	0
0.1	95.8	1.4
2.5	35	26
5	12	41
7.5	4.0	52
10	1.5	60
20	negligible	80
∞	0	100

We have no way of analyzing for X; however, we are safe in assuming that at any time $C_A + C_R + C_X = C_{A0}$. What can we say about the mechanism and kinetics of this oxidation? Hint: plot the data and examine the plot.

- 8.21.** Chemical A reacts to form R ($k_1 = 6 \text{ hr}^{-1}$) and R reacts away to form S ($k_2 = 3 \text{ hr}^{-1}$). In addition R slowly decomposes to form T ($k_3 = 1 \text{ hr}^{-1}$). If a solution containing 1.0 mol/liter of A is introduced into a batch reactor, how long would it take to reach $C_{R,\text{max}}$, and what would be $C_{R,\text{max}}$?

Chapter 9

Temperature and Pressure Effects

In our search for favorable conditions for reaction we have considered how reactor type and size influence the extent of conversion and distribution of products. The reaction temperature and pressure also influence the progress of reactions, and it is the role of these variables that we now consider.

We follow a three-step procedure: First, we must find how equilibrium composition, rate of reaction, and product distribution are affected by changes in operating temperatures and pressures. This will allow us to determine the optimum temperature progression, and it is this that we strive to approximate with a real design. Second, chemical reactions are usually accompanied by heat effects, and we must know how these will change the temperature of the reacting mixture. With this information we are able to propose a number of favorable reactor and heat exchange systems—those which closely approach the optimum. Finally, economic considerations will select one of these favorable systems as the best.

So, with the emphasis on finding the optimum conditions and then seeing how best to approach them in actual design rather than determining what specific reactors will do, let us start with discussions of single reactions and follow this with the special considerations of multiple reactions.

9.1 SINGLE REACTIONS

With single reactions we are concerned with conversion level and reactor stability. Questions of product distribution do not occur.

Thermodynamics gives two important pieces of information, the first being the heat liberated or absorbed for a given extent of reaction, the second being the maximum possible conversion. Let us briefly summarize these findings. A justification of the expressions to follow can be found in any standard thermodynamics texts for chemical engineers.

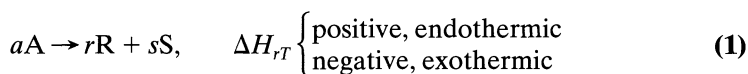
Heats of Reaction from Thermodynamics

The heat liberated or absorbed during reaction at temperature T_2 depends on the nature of the reacting system, the amount of material reacting, and the

temperature and pressure of the reacting system, and is calculated from the heat of reaction ΔH_r , for the reaction in question. When this is not known, it can in most cases be calculated from known and tabulated thermochemical data on heats of formation ΔH_f or heats of combustion ΔH_c of the reacting materials. These are tabulated at some standard temperature, T_1 , usually 25°C . As a brief reminder, consider the reaction



By convention we define the heat of reaction at temperature T as the heat transferred to the reacting system from the surroundings when a moles of A disappear to produce r moles of R and s moles of S with the system measured at the same temperature and pressure before and after the change. Thus



Heats of Reaction and Temperature. The first problem is to evaluate the heat of reaction at temperature T_2 knowing the heat of reaction at temperature T_1 . This is found by the law of conservation of energy as follows:

$$\left(\begin{array}{c} \text{heat absorbed} \\ \text{during reaction} \\ \text{at temperature} \\ T_2 \end{array} \right) = \left(\begin{array}{c} \text{heat added to} \\ \text{reactants to} \\ \text{change their} \\ \text{temperature} \\ \text{from } T_2 \text{ to } T_1 \end{array} \right) + \left(\begin{array}{c} \text{heat absorbed} \\ \text{during reaction} \\ \text{at temperature} \\ T_1 \end{array} \right) + \left(\begin{array}{c} \text{heat added to} \\ \text{products to} \\ \text{bring them} \\ \text{back to } T_2 \\ \text{from } T_1 \end{array} \right) \quad (2)$$

In terms of enthalpies of reactants and products this becomes

$$\Delta H_{r2} = -(H_2 - H_1)_{\text{reactants}} + \Delta H_{r1} + (H_2 - H_1)_{\text{products}} \quad (3)$$

where subscripts 1 and 2 refer to quantities measured at temperatures T_1 and T_2 , respectively. In terms of specific heats

$$\Delta H_{r2} = \Delta H_{r1} + \int_{T_1}^{T_2} \nabla C_p dT \quad (4)$$

where

$$\nabla C_p = rC_{pR} + sC_{pS} - aC_{pA} \quad (5)$$

When the molar specific heats are functions of temperatures as follows,

$$\begin{aligned} C_{pA} &= \alpha_A + \beta_A T + \gamma_A T^2 \\ C_{pR} &= \alpha_R + \beta_R T + \gamma_R T^2 \\ C_{pS} &= \alpha_S + \beta_S T + \gamma_S T^2 \end{aligned} \quad (6)$$

we obtain

$$\begin{aligned}\Delta H_{r2} &= \Delta H_{r1} + \int_{T_1}^{T_2} (\nabla\alpha + \nabla\beta T + \nabla\gamma T^2) dT \\ &= \Delta H_{r1} + \nabla\alpha(T_2 - T_1) + \frac{\nabla\beta}{2}(T_2^2 - T_1^2) + \frac{\nabla\gamma}{3}(T_2^3 - T_1^3)\end{aligned}\quad (7)$$

where

$$\begin{aligned}\nabla\alpha &= r\alpha_R + s\alpha_S - a\alpha_A \\ \nabla\beta &= r\beta_R + s\beta_S - a\beta_A \\ \nabla\gamma &= r\gamma_R + s\gamma_S - a\gamma_A\end{aligned}\quad (8)$$

Knowing the heat of reaction at any one temperature as well as the specific heats of reactants and products in the temperature range concerned allows us to calculate the heat of reaction at any other temperature. From this the heat effects of the reaction can be found.

EXAMPLE 9.1 ΔH_r AT VARIOUS TEMPERATURES

From the ΔH_c and ΔH_f tables, I've calculated that the standard heat of my gas-phase reaction at 25°C is as follows:



At 25°C the reaction is strongly exothermic. But this doesn't interest me because I plan to run the reaction at 1025°C. What is the ΔH_r at that temperature, and is the reaction still exothermic at that temperature?

Data. Between 25°C and 1025°C the average C_p values for the various reaction components are

$$\overline{C_{pA}} = 35 \text{ J/mol} \cdot \text{K} \quad \overline{C_{pB}} = 45 \text{ J/mol} \cdot \text{K} \quad \overline{C_{pR}} = 70 \text{ J/mol} \cdot \text{K}$$

SOLUTION

First, prepare a reaction map as shown in Fig. E9.1. Then an enthalpy balance for 1 mol A, 1 mol B, and 2 mol R gives

$$\begin{aligned}\Delta H_1 &= \Delta H_2 + \Delta H_3 + \Delta H_4 \\ &= (n\overline{C}_p \Delta T)_{\text{reactants}} + \Delta H_{r,25^\circ\text{C}} + (n\overline{C}_p \Delta T)_{\text{products}} \\ &= 1(35)(25 - 1025) + 1(45)(25 - 1025) + (-50\,000) + 2(70)(1025 - 25)\end{aligned}$$

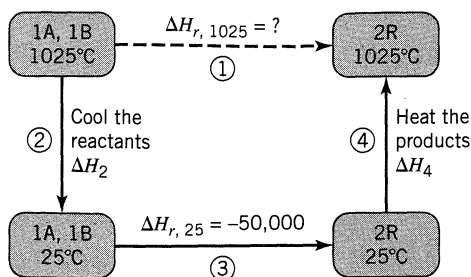


Figure E9.1

or

$$\Delta H_{r,1025^\circ\text{C}} = 10\,000\text{ J}$$

The reaction is $\left\{ \begin{array}{l} \underline{\underline{\text{exothermic at } 25^\circ\text{C}}} \\ \underline{\underline{\text{endothermic at } 1025^\circ\text{C}}} \end{array} \right.$

Equilibrium Constants from Thermodynamics

From the second law of thermodynamics equilibrium constants, hence equilibrium compositions of reacting systems, may be calculated. We must remember, however, that real systems do not necessarily achieve this conversion; therefore, the conversions calculated from thermodynamics are only suggested attainable values.

As a brief reminder, the standard free energy ΔG° for the reaction of Eq. 1 at temperature T is defined as

$$\Delta G^\circ = rG_{\text{R}}^\circ + sG_{\text{S}}^\circ - aG_{\text{A}}^\circ = -\mathbf{RT} \ln K = -\mathbf{RT} \ln \frac{\left(\frac{f}{f^\circ}\right)_{\text{R}}^r \left(\frac{f}{f^\circ}\right)_{\text{S}}^s}{\left(\frac{f}{f^\circ}\right)_{\text{A}}^a} \quad (9)$$

where f is the fugacity of the component at equilibrium conditions; f° is the fugacity of the component at the arbitrarily selected standard state at temperature T , the same one used in calculating ΔG° ; G° is the standard free energy of a reacting component, tabulated for many compounds; and K is the thermodynamic equilibrium constant for the reaction. Standard states at given temperature are commonly chosen as follows:

- Gases—pure component at one atmosphere, at which pressure ideal gas behavior is closely approximated
- Solid—pure solid component at unit pressure
- Liquid—pure liquid at its vapor pressure
- Solute in liquid—1 molar solution; or at such dilute concentrations that the activity is unity.

For convenience define

$$K_f = \frac{f_R^r f_S^s}{f_A^a}, \quad K_p = \frac{p_R^r p_S^s}{p_A^a}, \quad K_y = \frac{y_R^r y_S^s}{y_A^a}, \quad K_C = \frac{C_R^r C_S^s}{C_A^a} \quad (10)$$

and

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

Simplified forms of Eq. 9 can be obtained for various systems. For *gas reactions* standard states are usually chosen at a pressure of 1 atm. At this low pressure the deviation from ideality invariably is small; hence fugacity and pressure are identical and $f^\circ = p^\circ = 1$ atm. Thus

$$K = e^{-\Delta G^\circ/RT} = K_p \{p^\circ = 1 \text{ atm}\}^{-\Delta n} \quad (11)$$

The term in braces in this equation and in Eq. 13 is always unity but is retained to keep the equations dimensionally correct.

For any component i of an *ideal gas*

$$f_i = p_i = y_i \pi = C_i \mathbf{R}T \quad (12)$$

Hence

$$K_f = K_p$$

and

$$K = \frac{K_p}{\{p^\circ = 1 \text{ atm}\}^{\Delta n}} = \frac{K_y \pi^{\Delta n}}{\{p^\circ = 1 \text{ atm}\}^{\Delta n}} = \frac{K_c (\mathbf{R}T)^{\Delta n}}{\{p^\circ = 1 \text{ atm}\}^{\Delta n}} \quad (13)$$

For a *solid component* taking part in a reaction, fugacity variations with pressure are small and can usually be ignored. Hence

$$\left(\frac{f}{f^\circ}\right)_{\text{solid component}} = 1 \quad (14)$$

Equilibrium Conversion. The equilibrium composition, as governed by the equilibrium constant, changes with temperature, and from thermodynamics the rate of change is given by

$$\frac{d(\ln K)}{dT} = \frac{\Delta H_r}{\mathbf{R}T^2} \quad (15)$$

On integrating Eq. 15, we see how the equilibrium constant changes with temperature. When the heat of reaction ΔH_r can be considered to be constant in the temperature interval, integration yields

$$\boxed{\ln \frac{K_2}{K_1} = -\frac{\Delta H_r}{\mathbf{R}} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)} \quad (16)$$

When the variation of ΔH_r , must be accounted for in the integration we have

$$\ln \frac{K_2}{K_1} = \frac{1}{R} \int_{T_1}^{T_2} \frac{\Delta H_r}{T^2} dT \quad (17)$$

where ΔH_r is given by a special form of Eq. 4 in which subscript 0 refers to the base temperature

$$\Delta H_r = \Delta H_{r0} + \int_{T_0}^T \nabla C_p dT \quad (18)$$

Replacing Eq. 18 in Eq. 17 and integrating, while using the temperature dependency for C_p given by Eq. 8, gives

$$\begin{aligned} R \ln \frac{K_2}{K_1} = & \nabla \alpha \ln \frac{T_2}{T_1} + \frac{\nabla \beta}{2} (T_2 - T_1) + \frac{\nabla \gamma}{6} (T_2^2 - T_1^2) \\ & + (-\Delta H_{r0} + \nabla \alpha T_0 + \frac{\nabla \beta}{2} T_0^2 + \frac{\nabla \gamma}{3} T_0^3) \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \end{aligned} \quad (19)$$

These expressions allow us to find the variation of the equilibrium constant, hence, equilibrium conversion, with temperature.

The following conclusions may be drawn from thermodynamics. These are illustrated in part by Fig. 9.1.

1. The thermodynamic equilibrium constant is unaffected by the pressure of the system, by the presence or absence of inerts, or by the kinetics of the reaction, but is affected by the temperature of the system.
2. Though the thermodynamic equilibrium constant is unaffected by pressure or inerts, the equilibrium concentration of materials and equilibrium conversion of reactants can be influenced by these variables.

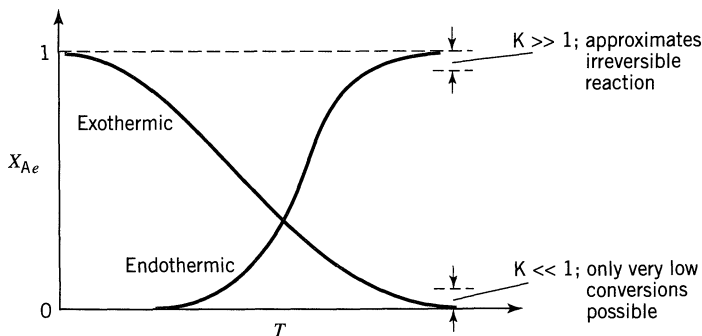
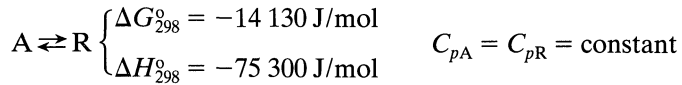


Figure 9.1 Effect of temperature on equilibrium conversion as predicted by thermodynamics (pressure fixed.)

3. $K \gg 1$ indicates that practically complete conversion may be possible and that the reaction can be considered to be irreversible. $K \ll 1$ indicates that reaction will not proceed to any appreciable extent.
4. For an increase in temperature, equilibrium conversion rises for endothermic reactions and drops for exothermic reactions.
5. For an increase in pressure in gas reactions, conversion rises when the number of moles decreases with reaction; conversion drops when the number of moles increases with reaction.
6. A decrease in inerts for all reactions acts in the way that an increase in pressure acts for gas reactions.

EXAMPLE 9.2**EQUILIBRIUM CONVERSION AT DIFFERENT TEMPERATURES**

- (a) Between 0°C and 100°C determine the equilibrium conversion for the elementary aqueous reaction



Present the results in the form of a plot of temperature versus conversion.

- (b) What restrictions should be placed on the reactor operating isothermally if we are to obtain a conversion of 75% or higher?

SOLUTION

- (a) With all specific heats alike, $\nabla C_p = 0$. Then from Eq. 4 the heat of reaction is independent of temperature and is given by

$$\Delta H_r = \Delta H_{r,298} = -75\,300 \text{ J/mol} \quad (\text{i})$$

From Eq. 9 the equilibrium constant at 25°C is given by

$$\begin{aligned} K_{298} &= \exp(-\Delta G_{298}^0 / \mathbf{RT}) \\ &= \exp\left(\frac{14\,130 \text{ J/mol}}{(8.314 \text{ J/mol} \cdot \text{K})(298\text{K})}\right) = 300 \end{aligned} \quad (\text{ii})$$

Since the heat of reaction does not change with temperature, the equilibrium constant K at any temperature T is now found from Eq. 16. Thus

$$\ln \frac{K}{K_{298}} = -\frac{\Delta H_r}{8.314} \left(\frac{1}{T} - \frac{1}{298} \right)$$

Rearranging gives

$$K = K_{298} \exp \left[\frac{-\Delta H_r}{\mathbf{R}} \left(\frac{1}{T} - \frac{1}{298} \right) \right]$$

Replacing K_{298} and ΔH_r from Eqs. (i) and (ii) gives on rearranging,

$$K = \exp \left[\frac{75\,300}{\mathbf{R}T} - 24.7 \right] \quad (\text{iii})$$

But at equilibrium

$$K = \frac{C_R}{C_A} = \frac{C_{A0} X_{Ae}}{C_{A0}(1 - X_{Ae})} = \frac{X_{Ae}}{1 - X_{Ae}}$$

or

$$X_{Ae} = \frac{K}{K + 1} \quad (\text{iv})$$

Putting T values into Eq. (iii), then K into Eq. (iv), as shown in Table E9.2 gives the changing equilibrium conversion as a function of temperature in the range of 0°C to 100°C . This result is displayed in Fig. E9.2.

(b) From the graph we see that the temperature must stay below 78°C if conversion of 75% or higher may be expected.

Table E9.2 Calculating $X_{Ae}(T)$ from Eqs. (iii) and (iv)

Selected Temperature		$K = \exp \left[\frac{75\,300}{\mathbf{R}T} - 24.7 \right]$ from Eq. (iii)	X_{Ae} from Eq. (iv)
$^\circ\text{C}$	K		
5	278	2700	0.999+
15	288	860	0.999
25	298	300	0.993
35	308	110	0.991
45	318	44.2	0.978
55	328	18.4	0.949
65	338	8.17	0.892
75	348	3.79	0.791
85	358	1.84	0.648
95	368	0.923	0.480

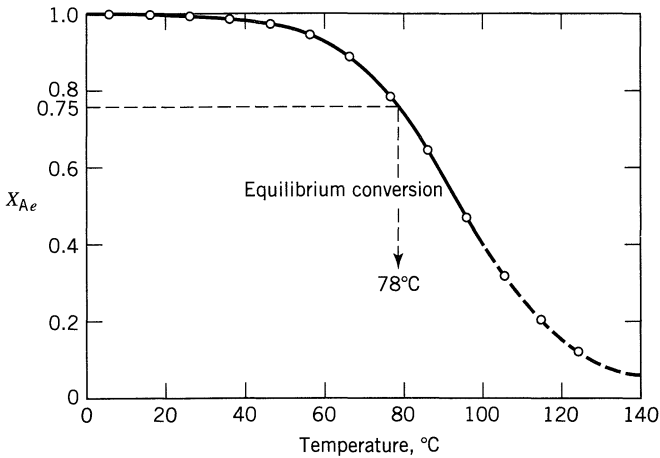


Figure E9.2

General Graphical Design Procedure

Temperature, composition, and reaction rate are uniquely related for any single homogeneous reaction, and this may be represented graphically in one of three ways, as shown in Fig. 9.2. The first of these, the composition-temperature plot, is the most convenient so we will use it throughout to represent data, to calculate reactor sizes, and to compare design alternatives.

For a given feed (fixed C_{A0} , C_{B0} , . . .) and using conversion of key component as a measure of the composition and extent of reaction, the X_A versus T plot has the general shape shown in Fig. 9.3. This plot can be prepared either from a thermodynamically consistent rate expression for the reaction (the rate must be zero at equilibrium) or by interpolating from a given set of kinetic data in conjunction with thermodynamic information on the equilibrium. Naturally, the reliability of all the calculations and predictions that follow are directly dependent on the accuracy of this chart. Hence, it is imperative to obtain good kinetic data to construct this chart.

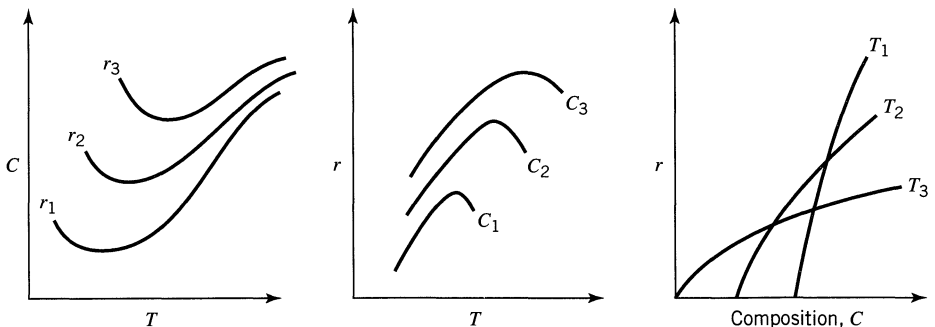


Figure 9.2 Different ways of representing the relationship of temperature, composition, and rate for a single homogeneous reaction.

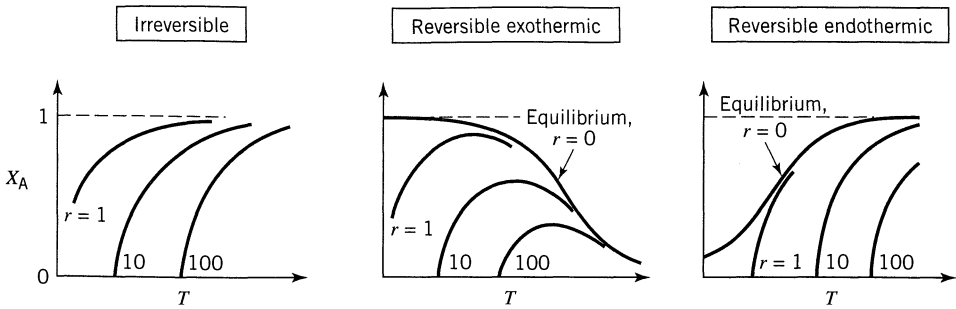


Figure 9.3 General shape of the temperature–conversion plot for different reaction types.

The size of reactor required for a given duty and for a given temperature progression is found as follows:

1. Draw the reaction path on the X_A versus T plot. This is the *operating line* for the operation.
2. Find the rates at various X_A along this path.

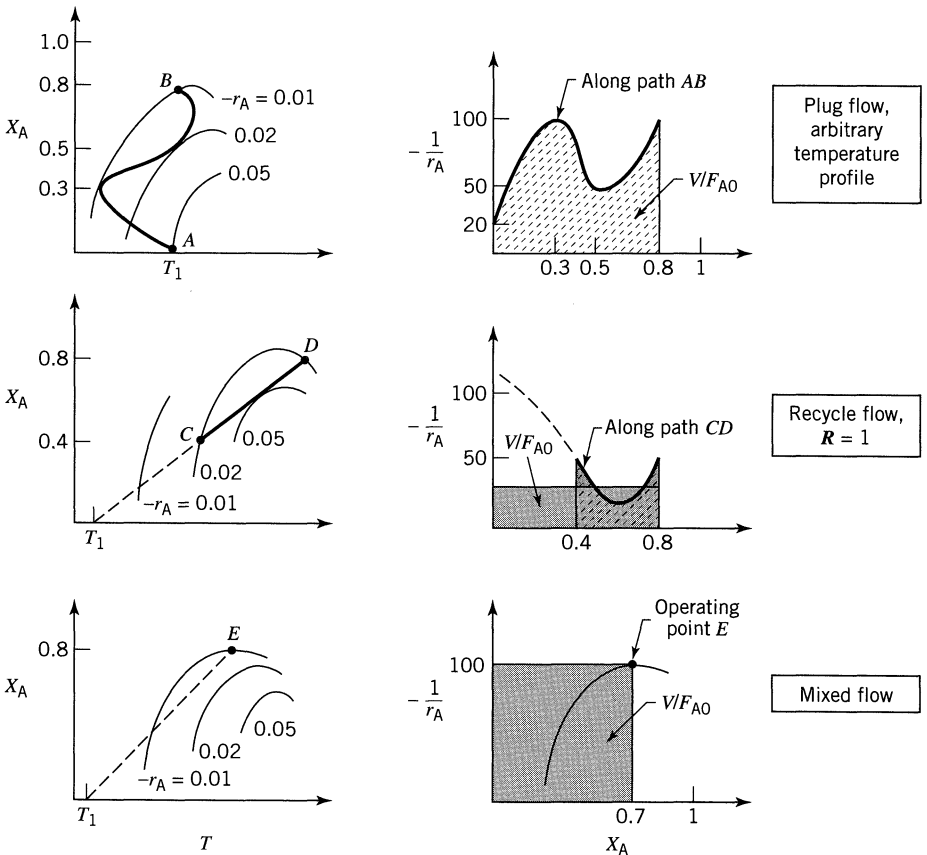


Figure 9.4 Finding the reactor size for different types of flow and for a feed temperature T_1 .

3. Plot the $1/(-r_A)$ versus X_A curve for this path.
4. Find the area under this curve. This gives V/F_{A0} .

For exothermic reactions we illustrate this procedure in Fig. 9.4 for three paths: path *AB* for plug flow with an arbitrary temperature profile, path *CD* for nonisothermal plug flow with 50% recycle, and point *E* for mixed flow. Note that for mixed flow the operating line reduces to a single point.

This procedure is quite general, applicable for any kinetics, any temperature progression, and any reactor type or any series of reactors. So, once the operating line is known, the reactor size can be found.

EXAMPLE 9.3 CONSTRUCTION OF THE RATE-CONVERSION-TEMPERATURE CHART FROM KINETIC DATA

With the system of Example 9.2 and starting with an R-free solution, kinetic experiments in a batch reactor give 58.1% conversion in 1 min at 65°C, 60% conversion in 10 min at 25°C. Assuming reversible first-order kinetics, find the rate expression for this reaction and prepare the conversion-temperature chart with reaction rate as parameter.

SOLUTION

Integrate the Performance Equation. For a reversible first-order reaction, the performance equation for a batch reactor is

$$t = C_{A0} \int \frac{dX_A}{-r_A} = C_{A0} \int \frac{dX_A}{k_1 C_A - k_2 C_R} = \frac{1}{k_1} \int_0^{X_A} \frac{dX_A}{1 - X_A/X_{Ae}}$$

According to Eq. 3.54 this integrates to give

$$\frac{k_1 t}{X_{Ae}} = -\ln \left(1 - \frac{X_A}{X_{Ae}} \right) \quad (\text{i})$$

Calculate the Forward Rate Constant. From the batch run at 65°C, noting from Example 9.2 that $X_{Ae} = 0.89$, we find with Eq. (i)

$$\frac{k_1 (1 \text{ min})}{0.89} = -\ln \left(1 - \frac{0.581}{0.89} \right)$$

or

$$k_{1,338} = 0.942 \text{ min}^{-1} \quad (\text{ii})$$

Similarly, for the batch run at 25°C we find

$$k_{1,298} = 0.0909 \text{ min}^{-1} \quad (\text{iii})$$

Assuming an Arrhenius temperature dependency, the ratio of forward rate constants at these two temperatures gives

$$\frac{k_{1,338}}{k_{1,298}} = \frac{0.942}{0.0909} = \frac{k_{10}e^{-E_1/R(338)}}{k_{10}e^{-E_1/R(298)}} \quad (\text{iv})$$

from which the activation energy of the forward reaction can be evaluated, giving

$$E_1 = 48\,900 \text{ J/mol}$$

Note that there are two activation energies for this reaction, one for the forward reaction, another for the reverse.

Now for the complete rate constant for the forward reaction. From either the numerator or the denominator of Eq. (iv) first evaluate k_{10} , then use it as shown below:

$$k_1 = 34 \times 10^6 \exp\left[\frac{-48\,900}{RT}\right] = \exp\left[17.34 - \frac{48\,900}{RT}\right]$$

Noting that $K = \frac{k_1}{k_2}$, thus $k_2 = \frac{k_1}{K}$, where K is given by Eq. (iii) of Example 9.2, we can find the value of k_2 .

Summary. For the reversible first-order reaction of Example 9.2 we have

$A \xrightleftharpoons[2]{1} R;$	$K = \frac{C_{Re}}{C_{Ae}}; \quad -r_A = r_R = k_1 C_A - k_2 C_R$
Equilibrium:	$K = \exp\left[\frac{75\,300}{RT} - 24.7\right]$
Rate constants:	$k_1 = \exp\left[17.34 - \frac{48\,900}{RT}\right], \quad \text{min}^{-1}$
	$k_2 = \exp\left[42.04 - \frac{124\,200}{RT}\right], \quad \text{min}^{-1}$

From these values the X_A versus T chart for any specific C_{A0} can be prepared and for this purpose the electronic computer is a great timesaver. Figure E9.3 is such a plot prepared for $C_{A0} = 1$ mol/liter and $C_{R0} = 0$.

Since we are dealing with first-order reactions this plot can be used for any C_{A0} value by properly relabeling the rate curves. Thus, for $C_{A0} = 10$ mol/liter simply multiply all the rate values on this graph by a factor of 10.

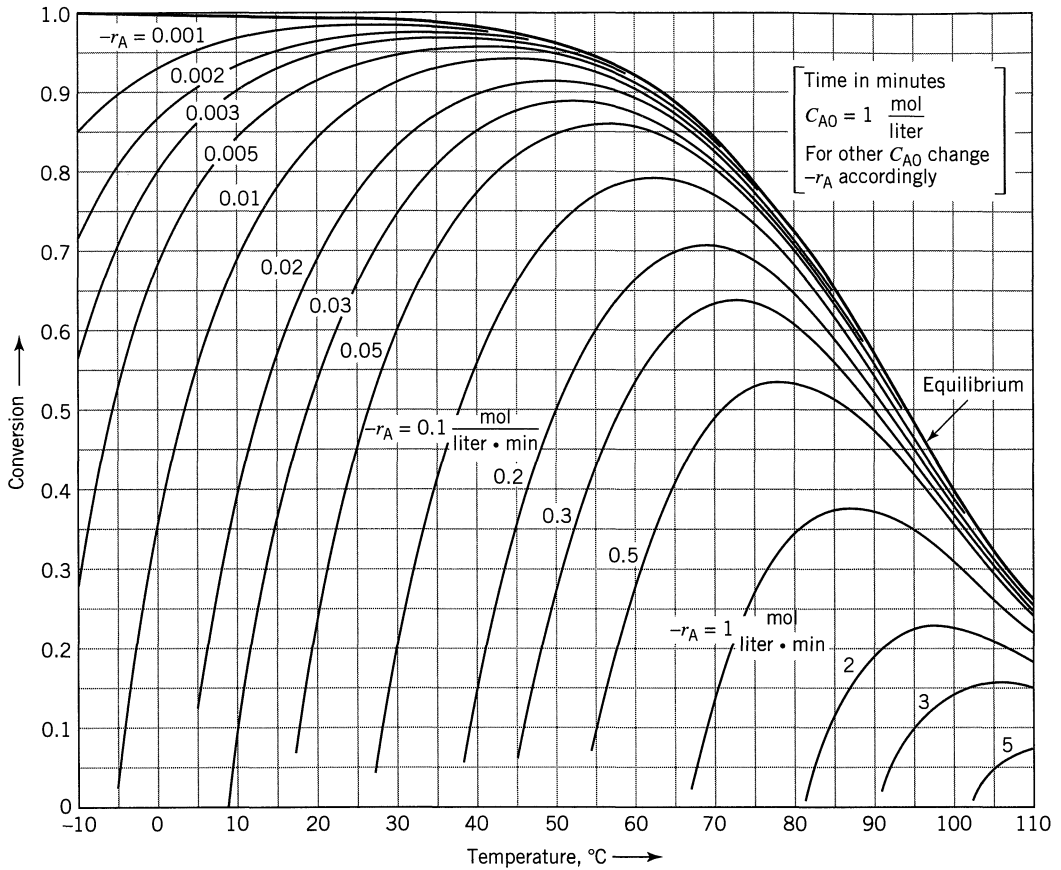


Figure E9.3

Optimum Temperature Progression

We define the optimum temperature progression to be that progression which minimizes V/F_{A0} for a given conversion of reactant. This optimum may be an isothermal or it may be a changing temperature: in time for a batch reactor, along the length of a plug flow reactor, or from stage to stage for a series of mixed flow reactors. It is important to know this progression because it is the ideal which we try to approach with a real system. It also allows us to estimate how far any real system departs from this ideal.

The optimum temperature progression in any type of reactor is as follows: At any composition, it will always be at the temperature where the rate is a maximum. The locus of maximum rates is found by examining the $r(T, C)$ curves of Fig. 9.4; Fig. 9.5 shows this progression.

For irreversible reactions, the rate always increases with temperature at any composition, so the highest rate occurs at the highest allowable temperature. This

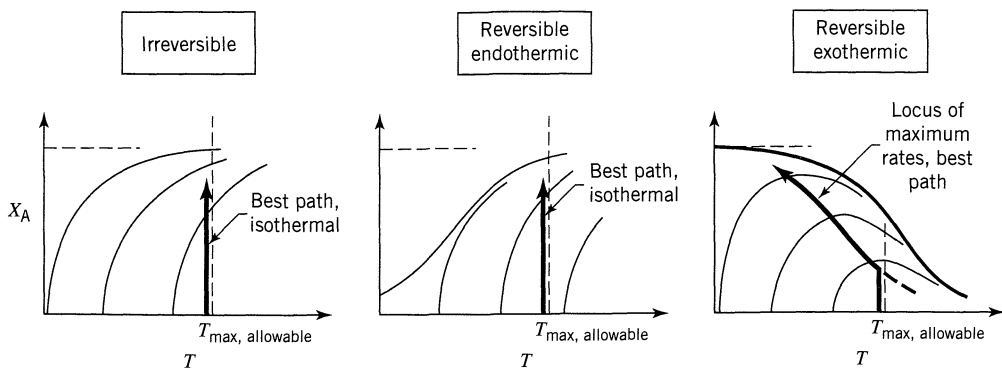


Figure 9.5 Operating lines for minimum reactor size.

temperature is set by the materials of construction or by the possible increasing importance of side reactions.

For endothermic reactions a rise in temperature increases both the equilibrium conversion and the rate of reaction. Thus, as with irreversible reactions, the highest allowable temperature should be used.

For exothermic reversible reactions the situation is different, for here two opposing factors are at work when the temperature is raised—the rate of forward reaction speeds up but the maximum attainable conversion decreases. Thus, in general, a reversible exothermic reaction starts at a high temperature which decreases as conversion rises. Figure 9.5 shows this progression, and its precise values are found by connecting the maxima of the different rate curves. We call this line the *locus of maximum rates*.

Heat Effects

When the heat absorbed or released by reaction can markedly change the temperature of the reacting fluid, this factor must be accounted for in design. Thus we need to use both the material and energy balance expressions, Eqs. 4.1 and 4.2, rather than the material balance alone, which was the starting point of all the analyses of isothermal operations of Chapters 5 through 8.

First of all, if the reaction is exothermic and if heat transfer is unable to remove all of the liberated heat, then the temperature of the reacting fluid will rise as conversion rises. By similar arguments, for endothermic reactions the fluid cools as conversion rises. Let us relate this temperature change with extent of conversion.

We start with adiabatic operations, later extending the treatment to account for heat interchange with the surroundings.

Adiabatic Operations

Consider either a mixed flow reactor, a plug flow reactor, or a section of plug flow reactor, in which the conversion is X_A , as shown in Fig. 9.6. In Chapters 5 and 6 one component, usually the limiting reactant, was selected as the basis for

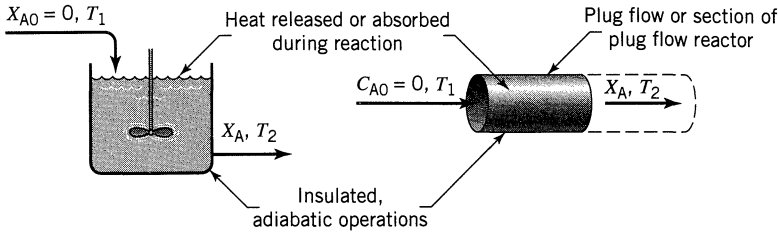


Figure 9.6 Adiabatic operations with large enough heat effect to cause a rise in temperature (exothermic) or drop in temperature (endothermic) in the reacting fluid.

all material balance calculations. The same procedure is used here, with limiting reactant A taken as the basis. Let

Subscripts 1, 2 refer to temperatures of entering and leaving streams.

C'_p, C''_p = Mean specific heat of unreacted feed stream and of *completely* converted product stream per mole of entering reactant A.

H', H'' = enthalpy of unreacted feed stream and of *completely* converted product stream per mole of entering reactant A.

ΔH_{ri} = heat of reaction per mole of entering reacting A, and at temperature T_i .

With T_1 as the reference temperature on which enthalpies and heats of reaction are based we have

Enthalpy of entering feed:

$$H'_1 = C'_p (T_1 - T_1) = 0 \text{ J/mol A}$$

Enthalpy of leaving stream:

$$H''_2 X_A + H'_2 (1 - X_A) = C''_p (T_2 - T_1) X_A + C'_p (T_2 - T_1) (1 - X_A) \text{ J/mol A}$$

Energy absorbed by reaction:

$$\Delta H_{r1} X_A \text{ J/mol A}$$

Replacing these quantities in the energy balance,

$$\text{input} = \text{output} + \text{accumulation} + \text{disappearance by reaction} \quad (4.2)$$

we obtain at steady state

$$0 = [C''_p (T_2 - T_1) X_A + C'_p (T_2 - T_1) (1 - X_A)] + \Delta H_{r1} X_A \quad (20)$$

By rearranging,

$$X_A = \frac{C_p'(T_2 - T_1)}{-\Delta H_{r1} - (C_p'' - C_p')(T_2 - T_1)} = \frac{C_p'\Delta T}{-\Delta H_{r1} - (C_p'' - C_p')\Delta T} \quad (21)$$

or, with Eq. 18

$$X_A = \frac{C_p'\Delta T}{-\Delta H_{r2}} = \left(\frac{\text{heat needed to raise feed stream to } T_2}{\text{heat released by reaction at } T_2} \right) \quad (22)$$

which for complete conversion becomes

$$-\Delta H_{r2} = C_p'\Delta T, \quad \text{for } X_A = 1 \quad (23)$$

The latter form of the equation simply states that the heat released by reaction just balances the heat necessary to raise the reactants from T_1 to T_2 .

The relation between temperature and conversion, as given by the energy balances of Eq. 21 or 22, is shown in Fig. 9.7. The resulting lines are straight for all practical purposes since the variation of the denominator term of these equa-

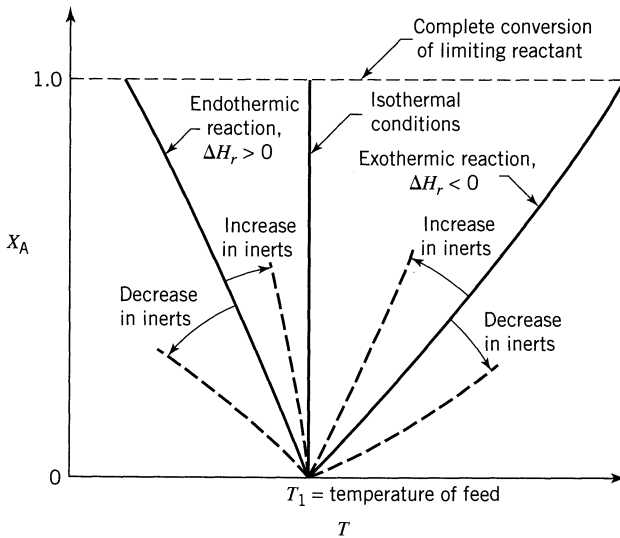


Figure 9.7 Graphical representation of energy balance equation for adiabatic operation. These are adiabatic operating lines.

tions is relatively small. When $C_p'' - C_p' = 0$, the heat of reaction is independent of temperature and Eqs. 21 and 22 reduce to

$$X_A = \frac{C_p \Delta T}{-\Delta H_r} \quad (24)$$

which are straight lines in Fig. 9.7.

This figure illustrates the shape of the energy balance curve for both endothermic and exothermic reactions for both mixed flow and plug flow reactors. This representation shows that whatever is the conversion at any point in the reactor, the temperature is at its corresponding value on the curve. For plug flow the fluid in the reactor moves progressively along the curve, for mixed flow the fluid immediately jumps to its final value on the curve. These are the *adiabatic operating lines* for the reactor. With increased inerts C_p rises, and these curves become more closely vertical. A vertical line indicates that temperature is unchanged as reaction proceeds. This then is the special case of isothermal reactions treated in Chapters 5 through 7.

The *size of reactor* needed for a given duty is found as follows. For plug flow tabulate the rate for various X_A along this adiabatic operating line, prepare the $1/(-r_A)$ versus X_A plot and integrate. For mixed flow simply use the rate at the conditions within the reactor. Figure 9.8 illustrates this procedure.

The *best adiabatic operations* of a single plug flow reactor are found by shifting the operating line (changing the inlet temperature) to where the rates have the highest mean value. For endothermic operations this means starting at the highest allowable temperature. For exothermic reactions this means straddling the locus of maximum rates as shown in Fig. 9.9. A few trials will locate the best inlet temperature, that which minimizes V/F_{A0} . For mixed flow the reactor should operate on the locus of maximum rates, again shown in Fig. 9.9.

The *best reactor type*, that which minimizes V/F_{A0} , is found directly from this X_A versus T graph. If the rate progressively decreases with conversion, then use plug flow. This is the case for endothermic reactions (Fig. 9.8a) and close to isothermal exothermic reactions. For exothermic reactions that have a large temperature rise during reaction, the rate rises from a very low value to a maximum at some intermediate X_A , then falls. This behavior is characteristic of autocatalytic reactions, thus recycle operations are best. Figure 9.10 illustrates two situations, one where plug flow is best, the other where large recycle or mixed flow is best. The slope of the operating line, $C_p/-\Delta H_r$, will determine which case one has at hand. Thus

1. for small $C_p/-\Delta H_r$ (pure gaseous reactants) mixed flow is best.
2. for large $C_p/-\Delta H_r$ (gas with much inerts, or liquid systems) plug flow is best.

Nonadiabatic Operations

For the adiabatic operating line of Fig. 9.7 to more closely approach the ideals of Fig. 9.5, we may want deliberately to introduce or remove heat from the reactor. In addition, there are heat losses to the surroundings to account for.

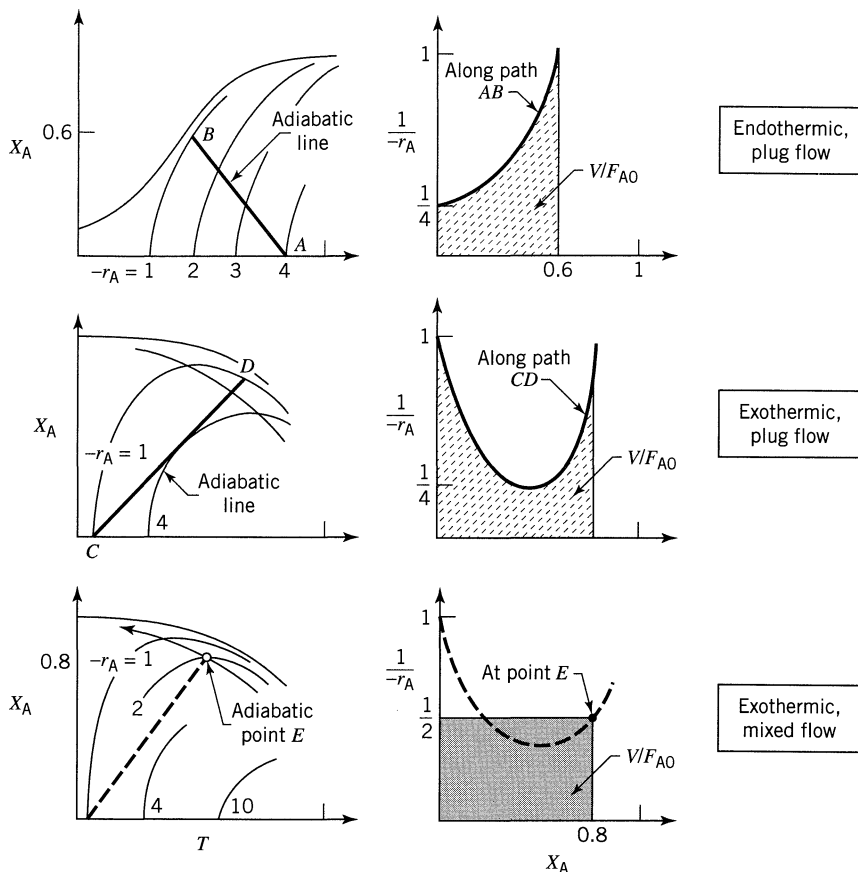


Figure 9.8 Finding reactor size for adiabatic operations of plug flow and mixed flow reactors.

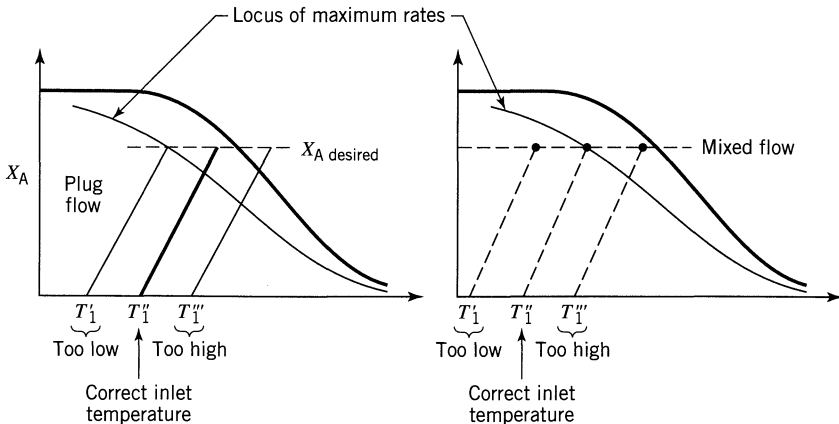


Figure 9.9 Best location for the adiabatic operating line. For plug flow, a trial and error search is needed to find this line; for mixed flow, no search is needed.

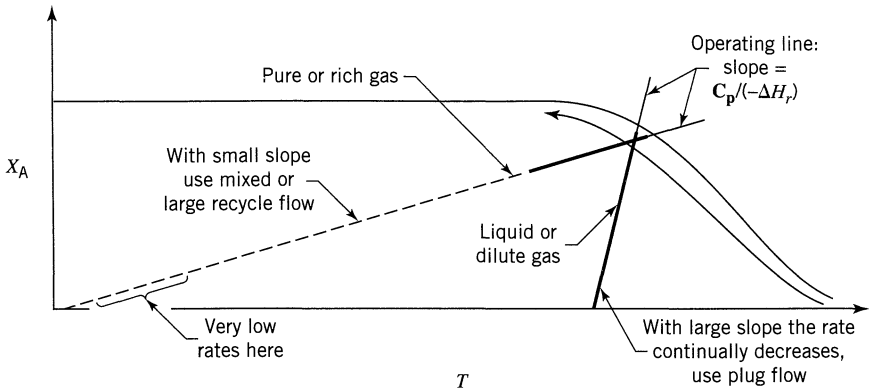


Figure 9.10 For exothermic reactions mixed flow is best where the temperature rise is large; plug flow is best for close to isothermal systems.

Let us see how these forms of heat interchange modify the shape of the adiabatic operating line.

Let Q be the total heat *added* to a reactor *per mole* of entering reactant A, and let this heat also include the losses to the surroundings. Then Eq. 20, the energy balance about the system, is modified to

$$Q = C_p''(T_2 - T_1)X_A + C_p'(T_2 - T_1)(1 - X_A) + \Delta H_{r1}X_A$$

which on rearrangement and with Eq. 18 gives

$$X_A = \frac{C_p'\Delta T - Q}{-\Delta H_{r2}} = \left(\frac{\text{net heat still needed after heat transfer to raise feed to } T_2}{\text{heat released by reaction at } T_2} \right) \quad (25)$$

and for $C_p'' = C_p'$, which often is a reasonable approximation

$$X_A = \frac{C_p\Delta T - Q}{-\Delta H_r} \quad (26)$$

With heat input proportional to $\Delta T = T_2 - T_1$ the energy balance line rotates about T_1 . This change is shown in Fig. 9.11. Other modes of heat addition or removal yield corresponding shifts in the energy balance line.

Using this modified operating line, the procedure for finding the reactor size and optimum operations follows directly from the discussion on adiabatic operations.

Comments and Extensions

Adiabatic operations of an exothermic reaction give a rising temperature with conversion. However, the desired progression is one of falling temperature. Thus,

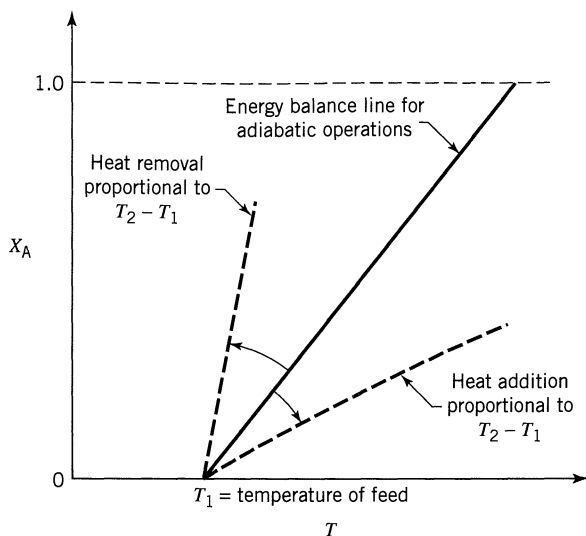


Figure 9.11 Sketch of the energy balance equation showing the shift in adiabatic line caused by heat exchange with surroundings.

very drastic heat removal may be needed to make the operating line approach the ideal, and many schemes may be proposed to do this. As an example, we may have heat exchange with the incoming fluid (see Fig. 9.12*a*), a case treated by van Heerden (1953, 1958). Another alternative is to have multistage operations with interstage cooling between adiabatic sections (see Fig. 9.12*b*). In general multistaging is used when it is impractical to effect the necessary heat exchange within the reactor itself. This is usually the case with gas-phase reactions with their relatively poor heat transfer characteristics. For endothermic reactions, multistaging with reheat between stages is commonly used to keep the temperature from dropping too low (see Fig. 9.12*c*).

Since the main use of these and many other forms of multistage operations is with solid catalyzed gas-phase reactions we discuss these operations in Chapter 19. Design for homogeneous reactions parallels that for catalytic reactions, so the reader is referred to Chapter 19 for the development.

Exothermic Reactions in Mixed Flow Reactors—A Special Problem

For exothermic reactions in mixed flow (or close to mixed flow) an interesting situation may develop in that more than one reactor composition may satisfy the governing material and energy balance equations. This means that we may not know which conversion level to expect. van Heerden (1953, 1958) was the first to treat this problem. Let us examine it.

First, consider reactant fluid fed at a given rate (fixed τ or V/F_{A0}) to a mixed flow reactor. At each reactor temperature there will be some particular conversion which satisfies the material balance equation, Eq. 5.11. At low temperature the rate is low so this conversion is low. At higher temperature the conversion

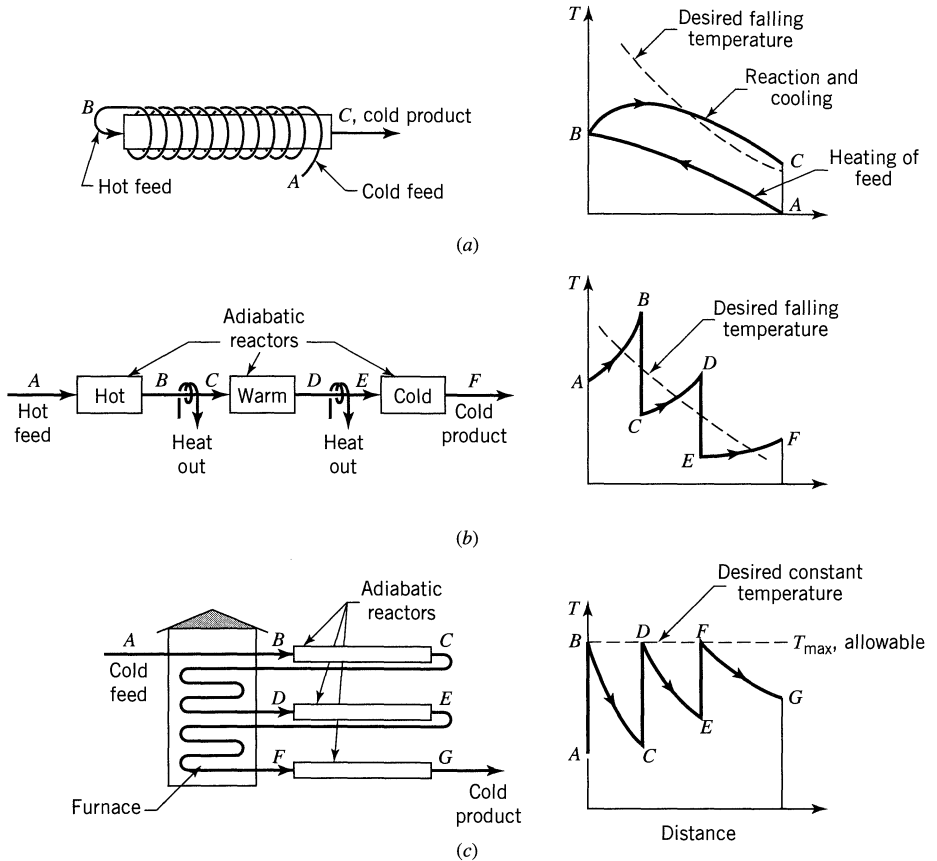


Figure 9.12 Ways of approaching the ideal temperature profile with heat exchange: (a) and (b) exothermic reaction; (c) endothermic reaction.

risers and approaches the equilibrium. At a still higher temperature we enter the region of falling equilibrium so the conversion for given τ will likewise fall. Figure 9.13 illustrates this behavior for different τ values. Note that these lines do not represent an operating line or a reaction path. Actually any point on these curves represents a particular solution of the material balance equations; thus, it represents an operating point for the mixed flow reactor.

Now, for a given feed temperature T_1 the intersection of the energy balance line with the S-shaped material balance line for the operating τ gives the conditions within the reactor. Here three cases may be distinguished. These are shown in Fig. 9.14 for *irreversible reactions*.

First, the energy balance line T_1A represents the situation where insufficient heat is liberated by reaction to raise the temperature to a high enough level for the reaction to be self-sustaining. Hence, conversion is negligible. At the other extreme, if we have more than enough heat liberated, the fluid will be hot and conversion essentially complete. This is shown as line T_1B . Finally, line T_1C indicates an intermediate situation which has three solutions to the material and

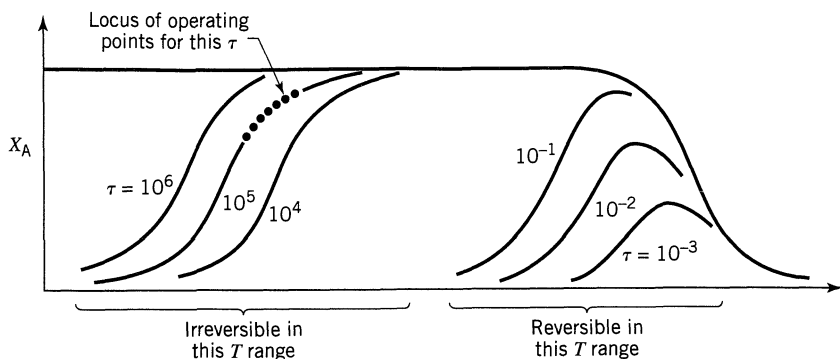


Figure 9.13 Conversion in a mixed flow reactor as a function of T and τ , from the material balance equation, Eq. 5.11.

energy balance equations, points M' , M'' , and M''' . However, point M'' is an unstable state because with a small rise in temperature the heat produced (with the rapidly rising material balance curve) is greater than the heat consumed by the reacting mixture (energy balance curve). The excess heat produced will make the temperature rise until M''' is reached. By similar reasoning, if the temperature drops slightly below M'' it will continue to drop until M' is reached. Thus, we look upon M'' as the ignition point. If the mixture can be raised above this temperature, then the reaction will be self-sustaining.

For *reversible exothermic reactions* the same three cases occur, as shown in Fig. 9.15. However, it can be seen that here there is an optimum operating temperature for the given τ value where conversion is maximized. Above or below this temperature the conversion drops; thus, proper control of heat removal is essential.

The type of behavior described here occurs in systems where the slope of the energy balance line, $C_p/-\Delta H_r$, is small; thus, large liberation of heat and pure reactants which leads to far from isothermal operations. van Heerden (1953, 1958) discusses and gives examples of this type of reacting system. In addition, though it is a much more complex situation, a gas flame illustrates well the

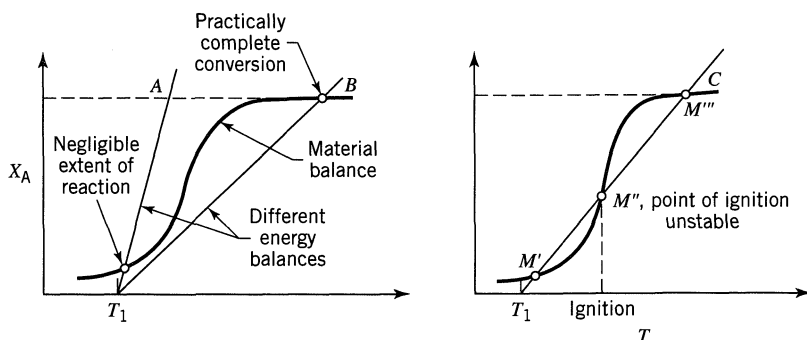


Figure 9.14 Three types of solutions to the energy and material balances for exothermic irreversible reactions.

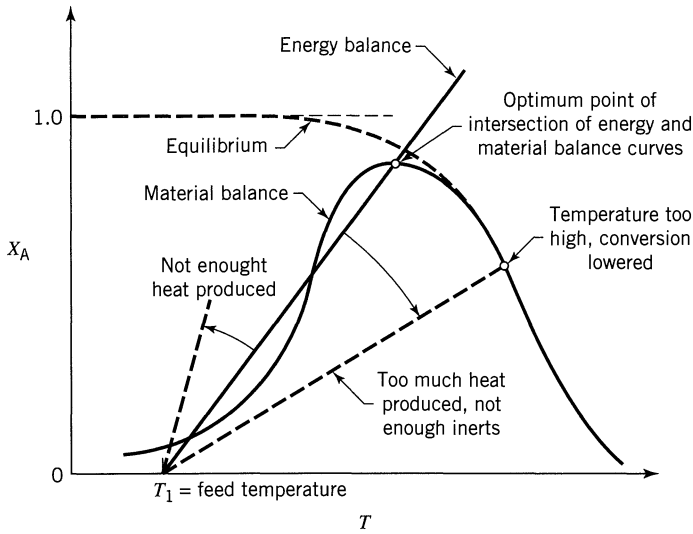


Figure 9.15 Solution of energy and material balances for reversible exothermic reaction.

multiple solutions discussed here: the unreacted state, the reacted state, and the ignition point.

Reactor dynamics, stability, and start-up procedures are particularly important for auto-induced reactions such as these. For example, a small change in feed rate (τ value), feed composition or temperature, or heat transfer rate may cause the reactor output to jump from one operating point to the other.

EXAMPLE 9.4 PERFORMANCE FOR THE OPTIMAL TEMPERATURE PROGRESSION

Using the optimal temperature progression in a plug flow reactor for the reaction of Examples 9.2 and 9.3,

- calculate the space time and volume needed for 80% conversion of a feed of $F_{A0} = 1000$ mol/min where $C_{A0} = 4$ mol/liter.
- plot the temperature and conversion profile along the length of the reactor.

Let the maximum allowable operating temperature be 95°C .

Note that Fig. E9.3 was prepared for $C_{A0} = 1$ mol/liter, not 4 mol/liter.

SOLUTION

(a) Minimum Space-Time. On the conversion-temperature graph (Fig. E9.3) draw the locus of maximum rates. Then, remembering the temperature restriction, draw the optimum path for this system (line *ABCDE* in Fig E9.4a) and

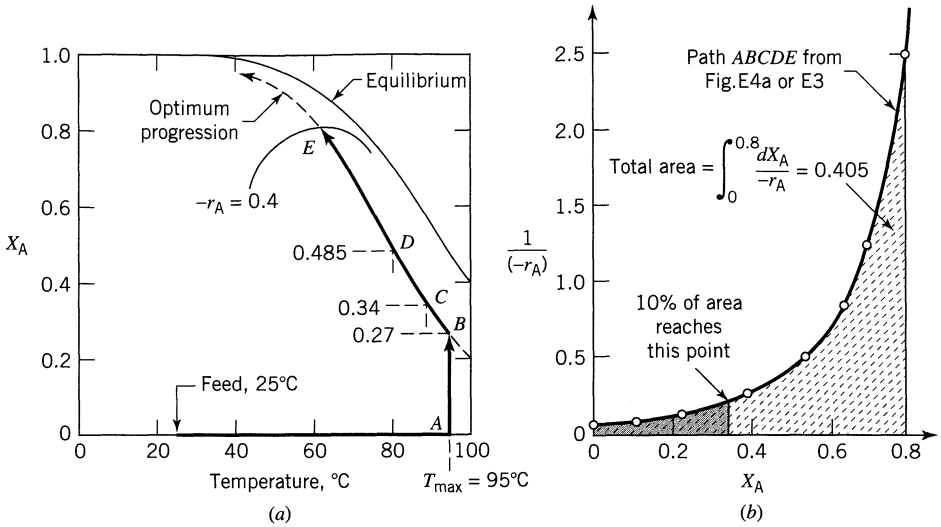


Figure E9.4a

Figure E9.4b

integrate graphically along this path to obtain

$$\frac{\tau}{C_{A0}} = \frac{V}{F_{A0}} = \int_0^{0.8} \frac{dX_A}{(-r_A)_{\text{optimum path ABCDE}}} = \left(\text{shaded area} \right) \text{ of Fig. E9.4b} = 0.405 \text{ liter/mol} \cdot \text{min}$$

Therefore

$$\underline{\underline{\tau}} = C_{A0} (\text{area}) = (4 \text{ mol/liter}) (0.405 \text{ liter} \cdot \text{min/mol}) = \underline{\underline{1.62 \text{ min}}}$$

and

$$\underline{\underline{V}} = F_{A0} (\text{area}) = (1000 \text{ mol/min}) (0.405 \text{ liter} \cdot \text{min/mol}) = \underline{\underline{405 \text{ liters}}}$$

(b) T and X_A Profiles Through the Reactor. Let us take 10% increments through the reactor by taking 10% increments in area under the curve of Fig. E9.4b. This procedure gives $X_A = 0.34$ at the 10% point, $X_A = 0.485$ at the 20% point, etc. The corresponding temperatures are then 362 K at $X_A = 0.34$ (point C), 354 K at $X_A = 0.485$ (point D), etc.

In addition we note that the temperature starts at 95°C, and at $X_A = 0.27$ (point B) it drops. Measuring areas in Fig. E9.4b we see that this happens after the fluid has passed 7% of the distance through the reactor.

In this manner the temperature and conversion profiles are found. The result is shown in Fig. E9.4c.

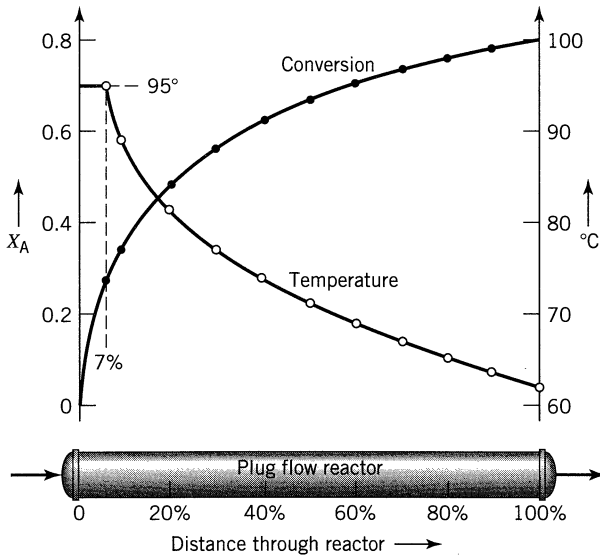


Figure E9.4c

EXAMPLE 9.5 OPTIMUM MIXED FLOW REACTOR PERFORMANCE

A concentrated aqueous A-solution of the previous examples ($C_{A0} = 4$ mol/liter, $F_{A0} = 1000$ mol/min) is to be 80% converted in a mixed flow reactor.

- What size of reactor is needed?
- What is the heat duty if feed enters at 25°C and product is to be withdrawn at this temperature?

Note that

$$C_{pA} = \frac{1000 \text{ cal}}{\text{kg} \cdot \text{K}} \cdot \frac{1 \text{ kg}}{1 \text{ liter}} \cdot \frac{1 \text{ liter}}{4 \text{ mol A}} = 250 \frac{\text{cal}}{\text{mol A} \cdot \text{K}}$$

SOLUTION

(a) Reactor Volume. For $C_{A0} = 4$ mol/liter we may use the X_A versus T chart of Fig. E9.3 as long as we multiply all rate values on this chart by 4.

Following Fig. 9.9 the mixed flow operating point should be located where the locus of optima intersects the 80% conversion line (point C on Fig. E9.5a). Here the reaction rate has the value

$$-r_A = 0.4 \text{ mol A converted/min} \cdot \text{liter}$$

From the performance equation for mixed flow reactors, Eq. 5.11, the volume required is given by

$$V = \frac{F_{A0} X_A}{(-r_A)} = \frac{(1000 \text{ mol/min})(0.80)}{0.4 \text{ mol/min} \cdot \text{liter}} = \underline{\underline{2000 \text{ liters}}}$$

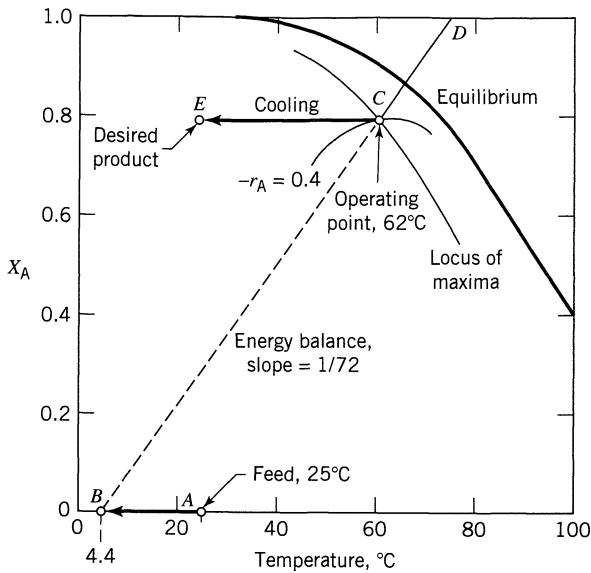


Figure E9.5a

(b) Heat Duty. Of course we can use joules in our calculations; however, since we are dealing with aqueous solutions it is simpler to use calories. Let us use calories. Then the slope of the energy balance line is

$$\text{slope} = \frac{C_p}{-\Delta H_r} = \frac{(250 \text{ cal/mol A} \cdot \text{K})}{18\,000 \text{ cal/mol A}} = \frac{1}{72} \text{ K}^{-1}$$

Drawing this line through point *C* (line *BCD*) we see that the feed must be cooled 20° (from point *A* to point *B*) before it enters and reacts adiabatically. Also, the product must be cooled 37°C (from point *C* to point *E*). Thus the heat duty is

$$\begin{aligned} \text{Precooler: } Q_{AB} &= (250 \text{ cal/mol A} \cdot \text{K})(20 \text{ K}) = 5000 \text{ cal/mol A fed} \\ &= (5000 \text{ cal/mol A})(1000 \text{ mol A/min}) = 5000\,000 \text{ cal/min} \\ &= \underline{\underline{348.7 \text{ kW}}} \end{aligned}$$

$$\begin{aligned} \text{Postcooler: } Q_{CE} &= (250)(37) = 9250 \text{ cal/mol A fed} \\ &= (9250)(1000) = 9250\,000 \text{ cal/min} \\ &= \underline{\underline{645.0 \text{ kW}}} \end{aligned}$$

Figure E9.5b shows two reasonable arrangements for the coolers.

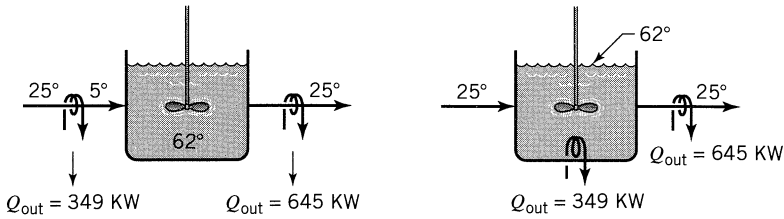


Figure E9.5b

EXAMPLE 9.6 ADIABATIC PLUG FLOW REACTOR PERFORMANCE

Find the size of adiabatic plug flow reactor to react the feed of Example 9.5 ($F_{A0} = 1000$ mol/min and $C_{A0} = 4$ mol/liter) to 80% conversion.

SOLUTION

Following the procedure of Fig. 9.9 draw trial operating lines (see Fig. E9.6a) with a slope of $\frac{1}{72}$ (from Example 9.5), and for each evaluate the integral

$$\int_0^{0.8} \frac{dX_A}{-r_A}$$

to find which is smallest. Figures E9.6a and b show this procedure for lines AB and CD. Line CD has the smaller area, is in fact closer to the minimum, and is

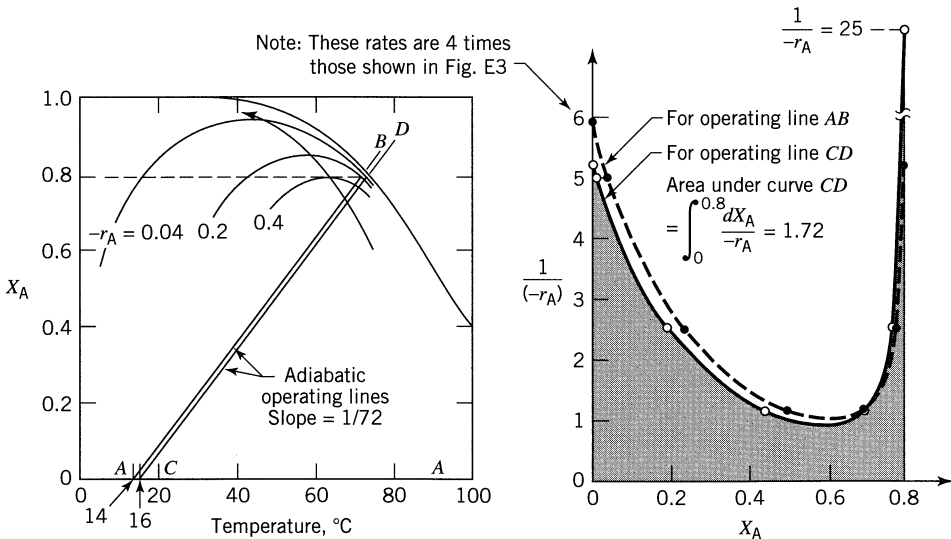


Figure E9.6

therefore the desired adiabatic operating line. So

$$\begin{aligned} \underline{V} &= F_{A0} \int_0^{0.8} \frac{dX_A}{-r_A} = F_{A0} (\text{area under curve } CD) \\ &= (1000 \text{ mol/min})(1.72 \text{ liter} \cdot \text{min/mol}) \\ &= \underline{\underline{1720 \text{ liters}}} \end{aligned}$$

This volume is somewhat smaller than the volume of mixed flow reactor (from Example 9.5) but it is still four times as large as the minimum possible (405 liters, from Example 9.4).

Regarding temperatures: Figure E6a shows that the feed must first be cooled to 16.0°C, it then passes through the adiabatic reactor and leaves at 73.6°C and 80% conversion.

EXAMPLE 9.7 ADIABATIC PLUG FLOW REACTOR WITH RECYCLE

Repeat Example 9.6 but now allow recycle to product stream.

SOLUTION

For operating line CD of Example 9.6 we find an optimum recycle area, shown in Fig. E9.7 as rectangle $EFGH$.

$$\text{Area} = (0.8 - 0)(1.5 \text{ liter} \cdot \text{min/mol}) = 1.2 \text{ liter} \cdot \text{min/mol}$$

$$\underline{V} = F_{A0} (\text{area}) = (1000 \text{ mol/min})(1.2 \text{ liter/mol} \cdot \text{min}) = \underline{\underline{1200 \text{ liter}}}$$

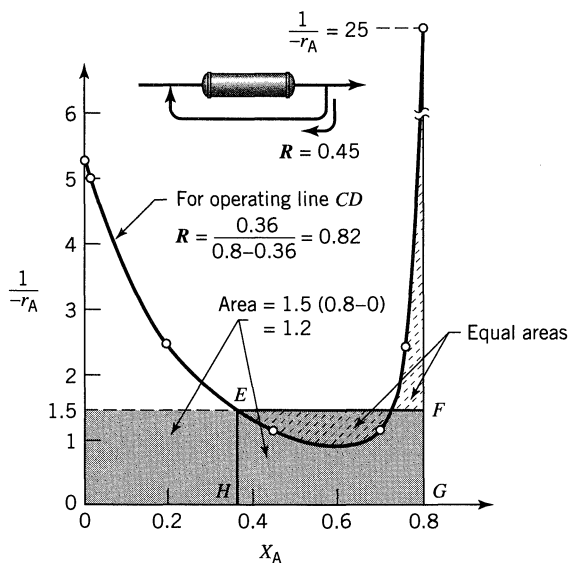


Figure E9.7

To summarize the results of these four examples, all of which are performing the same duty with the same feed

for the plug flow with optimal T progression	$V = 405$ liter (Example 4)
for the mixed flow reactor	$V = 2000$ liter (Example 5)
for the adiabatic plug flow reactor	$V = 1720$ liter (Example 6)
for the adiabatic recycle reactor	$V = 1200$ liter (Example 7)

9.2 MULTIPLE REACTIONS

As pointed out in the introduction to Chapter 7, in multiple reactions both reactor size and product distribution are influenced by the processing conditions. Since the problems of reactor size are no different in principle than those for single reactions and are usually less important than the problems connected with obtaining the desired product material, let us concentrate on the latter problem. Thus, we examine how to manipulate the temperature so as to obtain, first, a desirable product distribution, and second, the maximum production of desired product in a reactor with given space-time.

In our development we ignore the effect of concentration level by assuming that the competing reactions are all of the same order. This effect is studied in Chapter 7.

Product Distribution and Temperature

If two competing steps in multiple reactions have rate constants k_1 and k_2 , then the relative rates of these steps are given by

$$\frac{k_1}{k_2} = \frac{k_{10}e^{-E_1/RT}}{k_{20}e^{-E_2/RT}} = \frac{k_{10}}{k_{20}} e^{(E_2 - E_1)/RT} \propto e^{(E_2 - E_1)/RT} \quad (27)$$

This ratio changes with temperature depending on whether E_1 is greater or smaller than E_2 , so

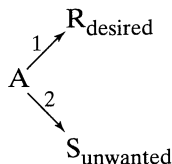
$$\text{when } T \text{ rises } \begin{cases} k_1/k_2 \text{ increases if } E_1 > E_2 \\ k_1/k_2 \text{ decreases if } E_1 < E_2 \end{cases}$$

Thus the reaction with larger activation energy is the more temperature-sensitive of the two reactions. This finding leads to the following general rule on the influence of temperature on the relative rates of competing reactions:

A high temperature favors the reaction of higher activation energy, a low temperature favors the reaction of lower activation energy.

Let us apply this rule to find the proper temperature of operations for various types of multiple reactions.

For *parallel reactions*



Step 1 is to be promoted, step 2 depressed, so k_1/k_2 is to be made as large as possible. Thus, from the above rule

$$\left. \begin{array}{l} \text{if } E_1 > E_2 \text{ use high } T \\ \text{if } E_1 < E_2 \text{ use low } T \end{array} \right\} \quad (28)$$

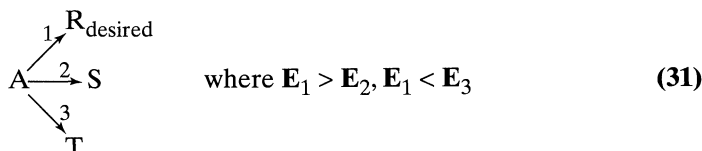
For *reactions in series*



the production of R is favored if k_1/k_2 is increased. Thus

$$\left. \begin{array}{l} \text{if } E_1 > E_2 \text{ use high } T \\ \text{if } E_1 < E_2 \text{ use low } T \end{array} \right\} \quad (30)$$

For the general series-parallel reaction we introduce two additional considerations. First of all for *parallel steps* if one requirement is for a high temperature and another is for a low temperature, then a particular intermediate temperature is best in that it gives the most favorable product distribution. As an example, consider the reactions



Now, $E_1 > E_2$ requires a high T , $E_1 < E_3$ requires a low T , and it can be shown that the most favorable product distribution is obtained when the temperature satisfies the following condition

$$\frac{1}{T_{\text{opt}}} = \frac{\text{R}}{E_3 - E_2} \ln \left[\frac{E_3 - E_1 k_{30}}{E_1 - E_2 k_{20}} \right] \quad (32)$$

Second, for *steps in series* if an early step needs a high temperature and a later step needs a low temperature, then a falling progression of temperatures should be used. Analogous arguments hold for other progressions.

The problems at the end of this chapter verify some of the qualitative findings on T_{opt} and also show some possible extension.

Comments

This discussion of multiple reactions shows that the relative size of the activation energies will tell which temperature level or progression is favored, just as Chapter 7 showed what concentration level or progression and what state of mixing is best. Although the general pattern of low, high, falling, or rising temperature can usually be determined without much difficulty, calculation of the optimum is not easy.

In experimentation we usually meet with the inverse of the situation outlined here in that we observe product distributions from experiment, and from this we wish to find the stoichiometry, kinetics, and the most favorable operating conditions. The generalizations of this chapter should be helpful in this inductive search.

Finally, when the reactions are of different order and of different activation energies, we must combine the methods of Chapters. 7, 8, and 9. Jackson et al. (1971) treat a particular system of this type and find that the optimum policy requires adjusting only one of the two factors, temperature or concentration, while keeping the other at its extreme. Which factor to adjust depends on whether the change in product distribution is more temperature dependent or concentration dependent. It would be interesting to know whether this finding represents a general conclusion.

REFERENCES

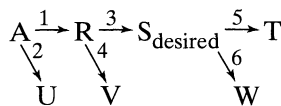
- Jackson, R., Obando, R., and Senior, M. G., *Chem. Eng. Sci.*, **26**, 853 (1971).
van Heerden, C., *Ind. Eng. Chem.*, **45**, 1242 (1953).
van Heerden, C., *Chem. Eng. Sci.*, **8**, 133 (1958).

PROBLEMS

Examples 9.4 through 9.7 illustrate the approach to problems dealing with nonisothermal reactors. Chapter 19 extends this approach to multistage operations of solid catalyzed reactions.

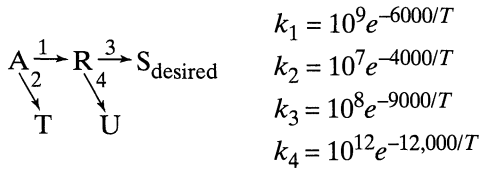
To reinforce these concepts, Problems 9.1 through 9.9 ask the reader to redo these examples with one or more changes. In many of these problems there is no need to redo the whole problem, just indicate where changes are needed in text and graphs.

- 9.1. For the reaction system of Example 9.4
- find τ needed for 60% conversion of reactant using the optimal temperature progression in the plug flow reactor.
 - also find the exit temperature of fluid from the reactor.
- Use whatever information you need from Example 9.4.
- 9.2. For the mixed flow reactor system of Example 9.5, we wish to get 70% conversion in the smallest size of reactor. Sketch your recommended system and on it indicate the temperature of the flowing stream entering and leaving the reactor as well as τ , the space time needed.
- 9.3. For the optimum temperature progression in a plug flow reactor in Example 9.4 ($C_{A0} = 4$ mol/liter, $F_{A0} = 1000$ mol A/min, $X_A = 0.8$, $T_{\min} = 5^\circ\text{C}$, $T_{\max} = 95^\circ\text{C}$) and feed and product both at 25°C , how much heating and cooling would be needed
- for the feed stream?
 - in the reactor itself?
 - for the stream leaving the reactor?
- 9.4. We plan to run the reaction of Example 9.4 ($C_{A0} = 4$ mol/liter, $F_{A0} = 1000$ mol/min) in a plug flow reactor kept at 40°C throughout to 90% conversion. Find the volume of reactor needed.
- 9.5. Redo Example 9.4
- 9.6. Redo Example 9.5
- 9.7. Redo Example 9.6
- 9.8. Redo Example 9.7
- where $C_{A0} = 4$ mol/liter is replaced by $C_{A0} = 1$ mol/liter, and
 where F_{A0} remains unchanged at 1000 mol A/min.
- 9.9. We wish to run the reaction of Example 9.4 in a mixed flow reactor to 95% conversion for a feed concentration $C_{A0} = 10$ mol/liter and feed rate of $v = 100$ liter/min. What size of reactor would we need?
- 9.10. Qualitatively find the optimum temperature progression to maximize C_S for the reaction scheme



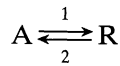
Data: $E_1 = 10$, $E_2 = 25$, $E_3 = 15$, $E_4 = 10$, $E_5 = 20$, $E_6 = 25$

9.11. The first-order reactions



are to be run in two mixed flow reactors in series anywhere between 10 and 90°C. If the reactors may be kept at different temperatures, what should these temperatures be for maximum fractional yield of S? Find this fractional yield.

9.12. The reversible first-order gas reaction



is to be carried out in a mixed flow reactor. For operations at 300 K the volume of reactor required is 100 liters for 60% conversion of A. What should be the volume of the reactor for the same feed rate and conversion but with operations at 400 K?

Data: $k_1 = 10^3 \exp[-2416/T]$

$$\Delta C_p = C_{pR} - C_{pA} = 0$$

$$\Delta H_r = -8000 \text{ cal/mol at } 300 \text{ K}$$

$$K = 10 \text{ at } 300 \text{ K}$$

Feed consists of pure A

Total pressure stays constant

Chapter 10

Choosing the Right Kind of Reactor

So far we have concentrated on homogeneous reactions in ideal reactors. The reason is two-fold; because this is the simplest of systems to analyze and is the easiest to understand and master; also because the rules for good reactor behavior for homogeneous systems can often be applied directly to heterogeneous systems.

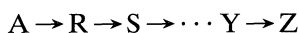
The important lessons learned in the first nine chapters of this book should guide us right away, or with a very minimum of calculations, to the optimum reactor system. Previously we have come up with six general rules. Let us present them and then practice using them.

Rule 1. For Single Reactions

To minimize the reactor volume, keep the concentration as high as possible for a reactant whose order is $n > 0$. For components where $n < 0$ keep the concentration low.

Rule 2. For Reactions in Series

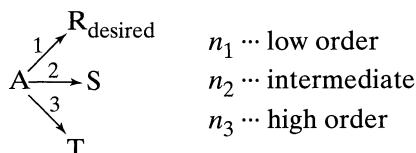
Consider reactions in series, as shown:



To maximize any intermediate, do not mix fluids that have different concentrations of the active ingredients—reactant or intermediates. See Fig. 10.1.

Rule 3. For Parallel Reactions

Consider the parallel reactions with reaction orders n_i



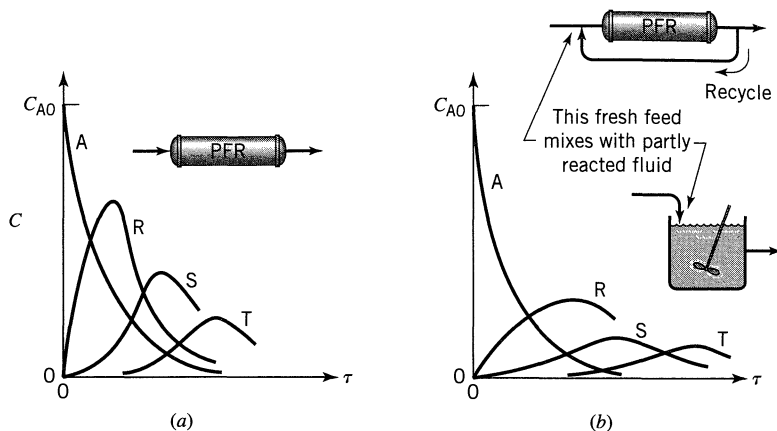


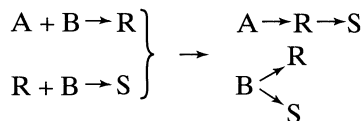
Figure 10.1 (a) Plug flow (no intermixing) gives the most of all the intermediates. (b) Intermixing depresses the formation of all intermediates.

To get the best product distribution,

- low C_A favors the reaction of lowest order
- high C_A favors the reaction of highest order
- If the desired reaction is of intermediate order then some intermediate C_A will give the best product distribution.
- For reactions all of the same order the product distribution is not affected by the concentration level.

Rule 4. Complex Reactions

These networks can be analyzed by breaking them down into their simple series and simple parallel components. For example, for the following elementary reactions, where R is the desired product, the breakdown is as follows:



This breakdown means that A and R should be in plug flow, without any recycle, while B can be introduced as you wish, at any concentration level, since it will not affect the product distribution.

Rule 5. Continuous versus Noncontinuous Operations

Any product distribution that can be obtained in continuous steady-state flow operations can be gotten in a non-flow operation and vice versa. Figure 10.2 illustrates this.

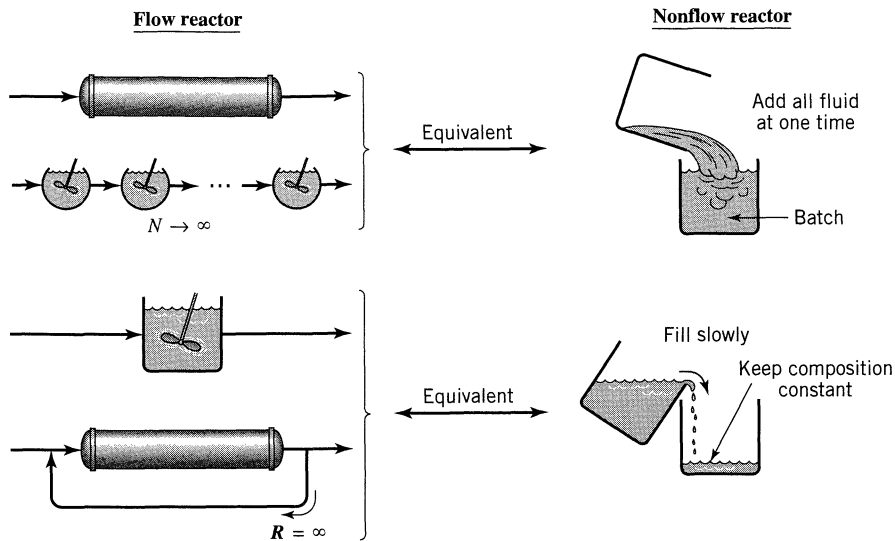
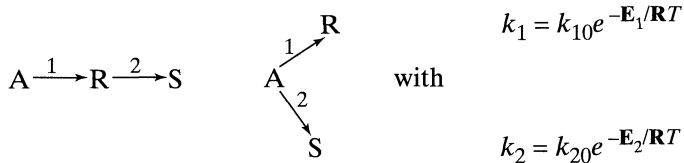


Figure 10.2 Correspondence between the residence time distribution of steady flow and either non-flow, batch or semibatch systems.

Rule 6. Effect of Temperature on Product Distribution

Given



a high temperature favors the reaction with larger E , while a low temperature favors the reaction with smaller E .

Let us now see how these six rules can be used to guide us to the optimum.

Optimum Operation of Reactors

In reactor operations the word “optimum” can have different meanings. Let us look at two definitions which are particularly useful.

Feed a stream containing reactant A to a reactor and let R, S, T, ... be formed, with R being the desired product. Then by optimum

1. we could mean maximizing the overall fractional yield of R, or

$$\Phi\left(\frac{R}{A}\right) = \left(\frac{\text{moles R formed}}{\text{moles of A consumed}} \right)_{\max} \quad (1)$$

2. we could mean running the reactor system so that the production of R is maximized, or

$$(\text{Prod R})_{\max} = \left(\frac{\text{moles of R formed}}{\text{moles of A fed to the system}} \right)_{\max} \quad (2)$$

For reactions in series we calculate the maximum production rate of R directly, as shown in Chapter 8. However, for reactions in parallel we find it useful to first evaluate the instantaneous fractional yield of R, or

$$\varphi\left(\frac{\text{R}}{\text{A}}\right) = \left(\frac{\text{moles R formed}}{\text{moles A consumed}} \right) \quad (3)$$

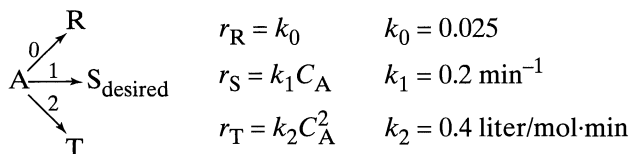
and then proceed to find the optimum. This procedure is shown in Chapter 7.

If unused reactant can be separated from the exit stream, reconcentrated to feed conditions and then recycled, then

$$(\text{Prod R})_{\max} = \Phi(\text{R/A})_{\text{opt}} \quad (4)$$

EXAMPLE 10.1 THE TRAMBOUZE REACTIONS (1958).

The elementary reactions



are to be run in four equal-size MFR's (mixed flow reactors), connected any way you wish. The feed is $C_{\text{A}0} = 1$, the feed flow rate is $v = 100$ liters/min.

The best scheme that the computer could come up with to maximize the fractional yield of S, or $\Phi(\text{S/A})$ [see problem 5, *Chem. Eng. Sci.*, **45**, 595–614 (1990)], is shown in Fig. E10.1a.

- (a) How would you arrange a four-MFR system?
 (b) With your best system what should be the volume of your four reactors?

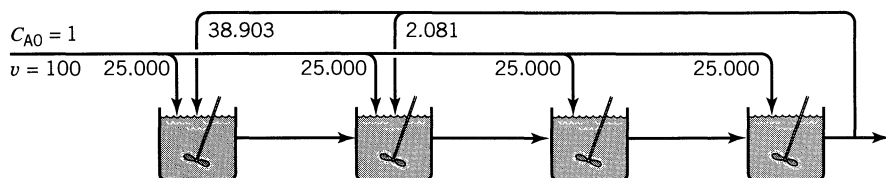


Figure E10.1a

SOLUTION

- (a) First of all, the computer solution looks somewhat complicated from the engineering point of view. But never mind, let us proceed with our calculations. The instantaneous fractional yield, $\varphi(S/A)$, is

$$\varphi(S/A) = \frac{k_1 C_A}{k_0 + k_1 C_A + k_2 C_A^2} = \frac{0.2 C_A}{0.025 + 0.2 C_A + 0.4 C_A^2} \quad (i)$$

To maximize $\varphi(S/A)$ put

$$\frac{d\varphi}{dC_A} = 0 = \frac{0.2(0.025 + 0.2 C_A + 0.4 C_A^2) - 0.2 C_A (0.2 + 0.8 C_A)}{(- -)^2}$$

Solving gives

$$\underline{\underline{C_{A\text{opt}} = 0.25}}$$

So from Eq. (i), at $C_{A\text{opt}}$,

$$\underline{\underline{C_{S\text{opt}} = \Phi(S/A)(C_{A0} - C_{A\text{opt}}) = 0.5(1 - 0.25) = 0.375}}$$

Thus the best way of running these four reactors is to keep the conditions at the optimum in all four units. One such design is shown in Fig. E10.1b. Problem P20 shows another design, and so does Fig. E10.1a.

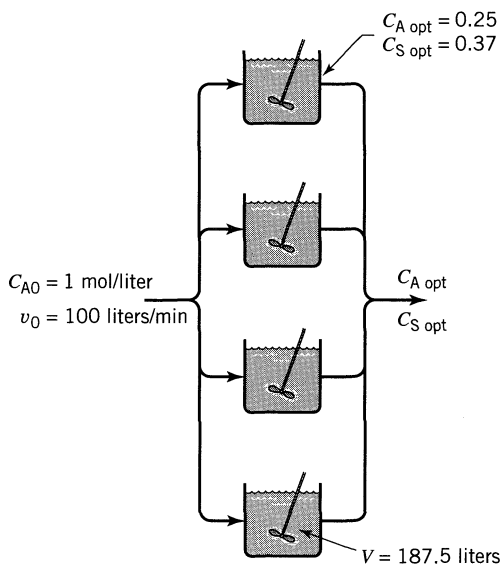


Figure E10.1b

(b) The volume per MFR comes from the performance equation

$$\tau = \frac{V}{v} = \frac{C_{A0} - C_A}{-r_A}$$

or

$$V = \frac{v(C_{A0} - C_A)}{-r_A} = \frac{(100/4)(1.00 - 0.25)}{0.025 + 0.2(0.25) + 0.4(0.25)^2}$$

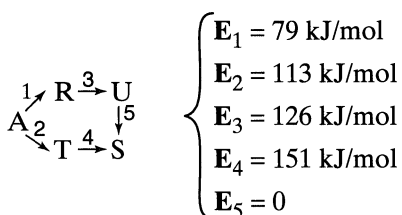
$$= 187.5 \text{ liters}$$

Therefore, for the four reactor system

$$\underline{V_{\text{total}}} = 187.5 \times 4 = \underline{\underline{750 \text{ liters}}}$$

EXAMPLE 10.2 TEMPERATURE PROGRESSION FOR MULTIPLE REACTIONS

Consider the following scheme of elementary reactions:



What temperature progression would you recommend if the desired product is:

(a) R, (b) S, (c) T, (d) U

and if reactor size is not important?

This industrially important reaction scheme is reported by Binns et al. (1969) and is used by Husain and Gangiah (1976, p. 245). In this problem we interchanged two of the reported E values to make the problem more interesting.

SOLUTION

(a) **Intermediate R is Desired.** We want step 1 fast compared to step 2, and we want step 1 fast compared to step 3.

Since $E_1 < E_2$ and $E_1 < E_3$ use a low temperature and plug flow.

(b) **Final Product S is Desired.** Here speed is all that matters.

So use a high temperature and plug flow.

(c) **Intermediate T is Desired.** We want step 2 fast compared to step 1, and we want step 2 fast compared to step 4.

Since $E_2 > E_1$ and $E_2 < E_4$ use a falling temperature and plug flow

(d) **Intermediate U is Desired.** We want step 1 fast compared to step 2, and step 3 fast compared to step 5.

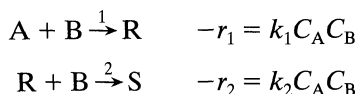
Since $E_1 < E_2$ and $E_3 > E_5$ use a rising temperature and plug flow

REFERENCES

- Binns, D.T., Kantyka, T.A., and Welland, R.C., *Trans. I. Chem. E.*, **47**, T53 (1969).
 Husain, A., and Gangiah, K., *Optimization Techniques for Chemical Engineers*, Macmillan of India, Delhi (1976).
 Trambouze, P.J., and Piret, E.L., *AIChE J.*, **5**, 384 (1959).
 van der Vusse, J.G., *Chem. Eng. Sci.*, **19**, 994 (1964).

PROBLEMS

10.1. Given the two reactions



where R is the desired product and is to be maximized. Rate the four schemes shown in Fig. P10.1—either “good” or “not so good.” Please, no complicated calculations, just reason it out.

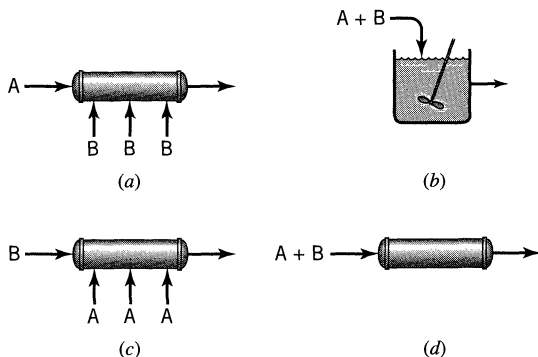


Figure P10.1

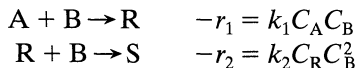
10.2. Repeat Problem 1 with just one change

$$-r_2 = k_2 C_R C_B^2$$

10.3. Repeat Problem 1 with just one change

$$-r_2 = k_1 C_R^2 C_B$$

10.4. For the reactions



where R is the desired product, which of the following ways of running a batch reactor is favorable, which is not? See Fig. P10.4.

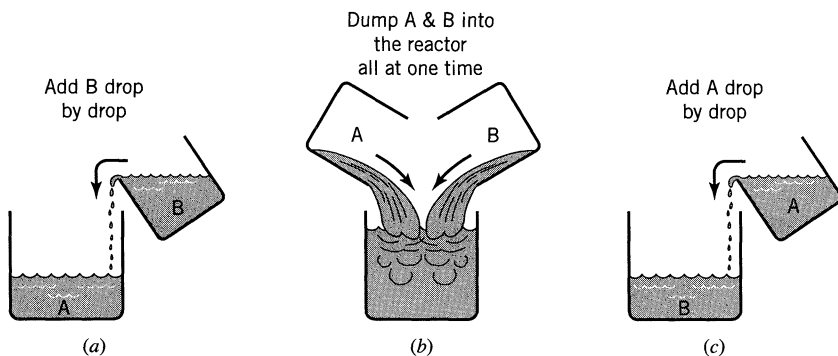


Figure P10.4

10.5. *The Oxidation of Xylene.* The violent oxidation of xylene simply produces CO_2 and H_2O ; however, when oxidation is gentle and carefully controlled, it can also produce useful quantities of valuable phthalic anhydride as shown in Fig. P10.5. Also, because of the danger of explosion, the fraction

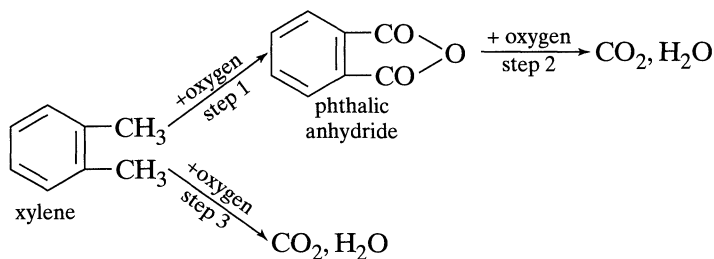
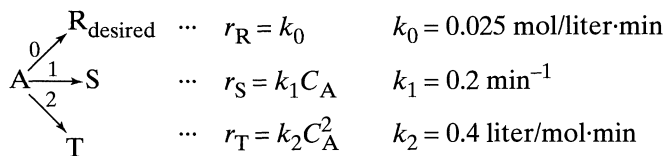


Figure P10.5

of xylene in the reacting mixture must be kept below 1%. Naturally, the problem in this process is to obtain a favorable product distribution.

- In a plug flow reactor what values of the three activation energies would require that we operate at the maximum allowable temperature?
- Under what circumstances should the plug flow reactor have a falling temperature progression?

10.6. The Tramouze Reactions—Reactions in parallel. Given the set of elementary reactions with a feed of $C_{A0} = 1$ mol/liter and $v = 100$ liters/min we wish to maximize the fractional yield, not the production of S, in a reactor arrangement of your choice.



The computer, going through a multidimensional search [see problem 3, *Chem. Eng. Sci.*, **45**, 595–614 (1990)] came up with the arrangement of Fig. P10.6, which the authors claim is a LOCAL optimum, or a STATIONARY POINT. We are not interested in LOCAL optima, if such things exist. We are interested in finding the GLOBAL optimum. So with this in mind,

- do you judge that the arrangement of Fig. P10.6 is the best set up?
- if not, suggest a better scheme. Sketch your scheme and calculate the volume of the reactors you plan to use.

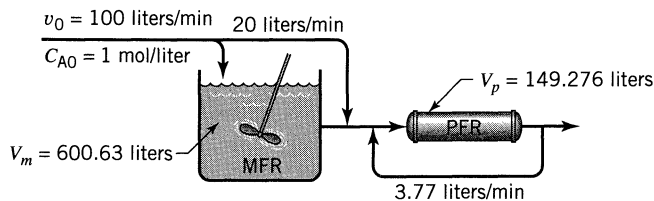
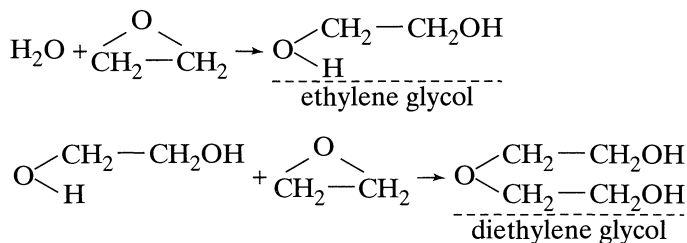


Figure P10.6

10.7. For the set of elementary reactions of Problem 10.6, with a feed of $C_{A0} = 1$ mol/liter and $v = 100$ liters/min we now wish to maximize the production rate of intermediate S (not the fractional yield) in a reactor arrangement of your choice. Sketch your chosen reactor scheme and determine $C_{S,\max}$ obtainable.

10.8. Automobile Antifreeze. Ethylene glycol and diethylene glycol are used as automobile antifreeze, and are produced by the reactions of ethylene oxide with water, as follows:



A mole of either glycol in water is as effective as the other in reducing the freezing point of water; however, on a molar basis the diethylene glycol is twice as expensive as the ethylene glycol. So we want to maximize ethylene glycol, and minimize the diethylene glycol in the mixture.

One of the country's largest suppliers produced millions of kilograms of antifreeze annually in reactors shown in Fig. P10.8a. One of the company's engineers suggested that they replace their reactors with one of the type shown in Fig. P10.8b. What do you think of this suggestion?

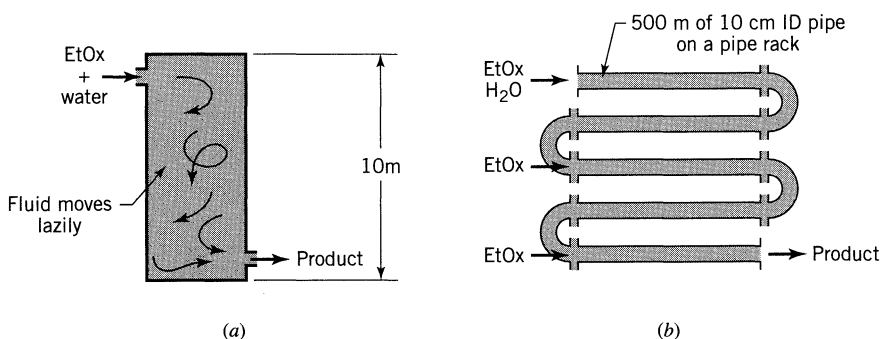
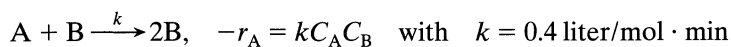


Figure P10.8a & P10.8b

10.9. The Homogeneous Catalytic Reaction. Consider the elementary reaction



For the following feed and reactor space time

Flow rate	$v = 100 \text{ liters/min}$
Feed composition	$\begin{cases} C_{\text{A}0} = 0.45 \text{ mol/liter} \\ C_{\text{B}0} = 0.55 \text{ mol/liter} \end{cases}$
Space time	$\tau = 1 \text{ min}$

we want to maximize the concentration of B in the product stream. Our clever computer [see problem 8, *Chem. Eng. Sci.*, **45**, 595–614 (1990)] gives the design of Fig. P10.9 as its best try.

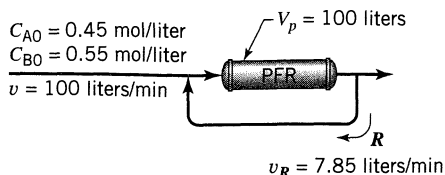


Figure P10.9

Do you think that this is the best way to run this reaction? If not, suggest a better scheme. Do not bother to calculate reactor size, recycle rate, etc. Just indicate a better scheme.

- 10.10. To Color Cola Drinks.** When viscous corn syrup is heated it caramelizes (turns a deep dark brown). However, if it is heated a bit too long it transforms into carbon

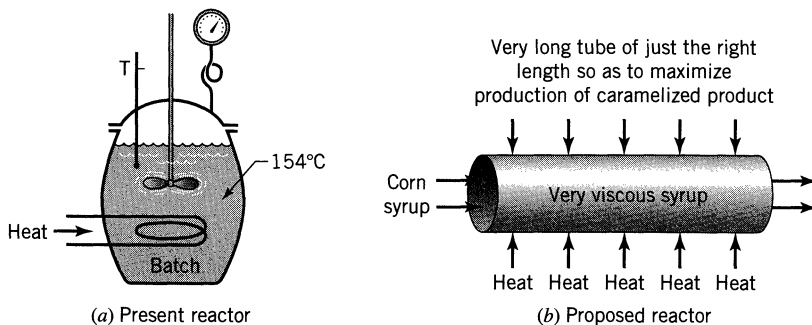
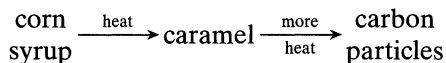


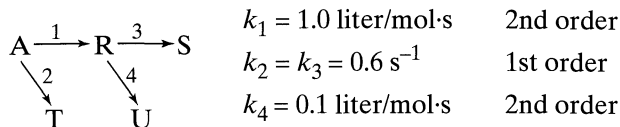
Figure P10.10 (a) Present reactor; (b) Proposed design.

The caramelized liquid is sent by railroad tank cars to the cola syrup formulators, who then test the solution for quality. If it is too light in color—penalty; if it has too many carbon particles per unit volume, then the whole tank car is rejected. There is thus a delicate balance between underreacting and overreacting.

At present a batch of corn syrup is heated at 154°C in a vat for a precise time. Then it is rapidly discharged and cooled, the vat is thoroughly cleaned (very labor intensive), and then is recharged.

The company wants to reduce costs and replace this costly labor intensive batch operation with a continuous flow system. Of course it will be a tubular reactor (rule 2). What do you think of their idea? Comment please, as you sit and sip your Coke or Pepsi.

10.11. The Denbigh Reactions. We intend to run the reactions below:



in a flow system under the following conditions

$$\begin{array}{ll}
 \text{Feed flow rate} & v = 100 \text{ liters/s} \\
 \text{Feed composition} & \begin{cases} C_{A0} = 6 \text{ mol/liter} \\ C_{R0} = 0.6 \text{ mol/liter} \end{cases}
 \end{array}$$

We want to maximize the concentration ratio of C_R/C_T in the product stream.

As reported [see problem 7, *Chem. Eng. Sci.*, **45**, 595–614 (1990)], the attack on this problem used 2077 continuous variables, 204 integer variables, 2108 constraints, and gave as an optimal solution the design shown in Fig. P10.11.

- Do you think you could do better? If so, what reactor design would you suggest we use, and what C_R/C_T would you expect to obtain?
- If you wished to minimize the ratio of C_R/C_T , how would you go about it?

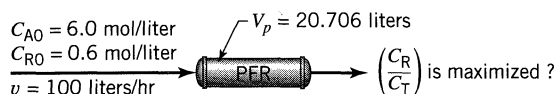
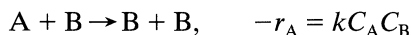


Figure P10.11

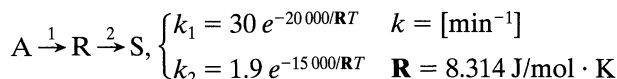
10.12. For the homogeneous catalytic reaction



and with a feed of $C_{A0} = 90 \text{ mol/m}^3$, $C_{B0} = 10 \text{ mol/m}^3$ we want about 44% conversion of reactant A. What flow reactor or combination of flow reactors is best in that it gives the smallest total volume of reactors needed? There is no need to try to calculate the size of reactors needed; just determine the type of reactor system that is best and the type of flow that should be used.

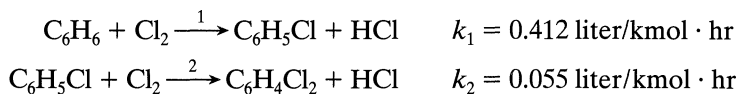
10.13. Repeat Problem 12 with just one change. We need 90% conversion of reactant A.

- 10.14.** Repeat Problem 12 with just one change. We only want about 20% conversion of reactant A.
- 10.15.** We want to produce R from A in a batch reactor with a run time no greater than 2 hours and at a temperature somewhere between 5 and 90°C. The kinetics of this liquid first-order reaction system is as follows:



Determine the optimum temperature (to give $C_{R_{\max}}$) and run time to use, and the corresponding conversion of A to R.

- 10.16. Reactor-Separator-Recycle System—Benzene Chlorination.** Here the elementary reactions are



The desired product is monochlorobenzene. Also assume that any unreacted benzene in the product stream can be cleanly separated and reused as desired.

With the requirement that we only use PFRs, a minimum of three, in any arrangement, plus separator and recycle of unused reactant, the best of which was determined by the computer [see case 3, *Chem. Eng. Sci.*, **46**, 1361–1383 (1991)] is shown in Fig. P10.16.

Can you do better? There is no need to calculate volumes and flow rates. Just come up with an improved scheme.

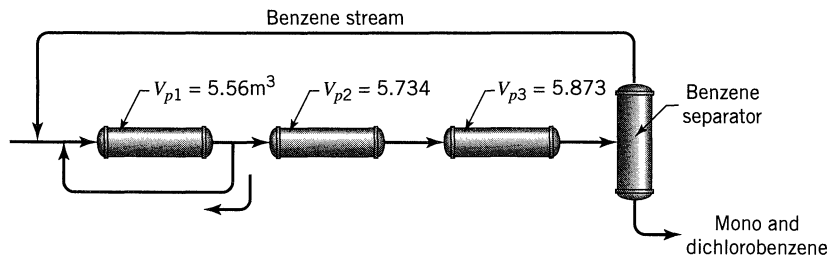
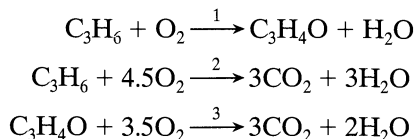


Figure P10.16

- 10.17. Acrolein Production.** Adams et al. [*J. Catalysis*, **3**, 379 (1964)] studied the catalytic oxidation of propylene on bismuth molybdate catalyst to form acrolein. With a feed of propylene and oxygen and reaction at 460°C, the following three reactions occur.

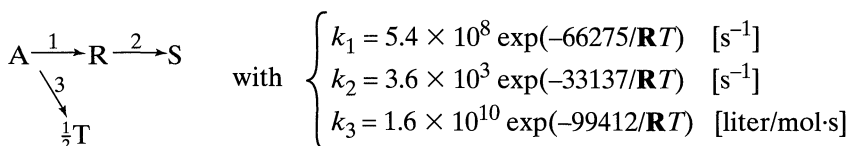


The reactions are all of first order in olefin and independent of oxygen and of reaction products, and with reaction rate ratios

$$\frac{k_2}{k_1} = 0.1, \quad \frac{k_3}{k_1} = 0.25$$

If no cooling is needed to keep the reaction close to 460°C and if no separation and recycle of unused C_3H_6 is allowed, what kind of contactor would you suggest be used and what should be the maximum expected production rate of acrolein from this reactor?

10.18. Nonisothermal van der Vusse Reactions (1964). Consider the following reactions:



where the Arrhenius activation energy is given in units of J/mol, C_R is to be maximized and $C_{A0} = 1$ mol/liter.

Insisting on using three MFR's with τ_i between 0.1 and 20 s [see example 2, *AIChE J*, **40**, 849 (1994)], with possible intercooling and a temperature range between 360 K and 396 K, the best scheme calculated by the computer is shown in Fig. P10.18.

- (a) Do you like this design? If not, what do you suggest we do with this three-reactor system? Please retain the three MFR's.
- (b) What C_R/C_{A0} could be obtained and what τ should be used with the best reactor scheme (plug, mixed, or combined) and with ideal heat transfer?

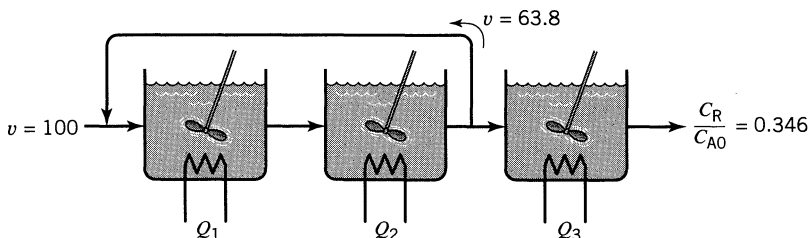
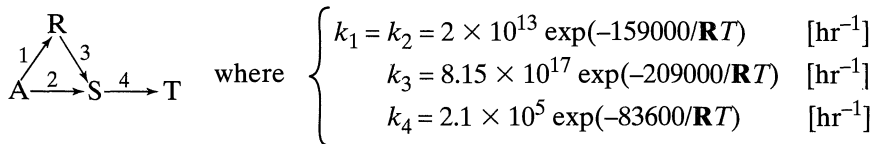


Figure P10.18

10.19. Phthalic Anhydride from Naphthalene. The accepted mechanism for the highly exothermic solid catalyzed oxidation of naphthalene to produce phthalic anhydride is



and where

A = naphthalene (reactant)
 R = naphthaquinone (postulated intermediate)
 S = phthalic anhydride (desired product)
 T = CO₂ + H₂O (waste products)

and the Arrhenius activation energy is given in units of J/mol. This reaction is to be run somewhere between 900 K and 1200 K.

A local optimum reactor setup discovered by the computer [see example 1, *Chem. Eng. Sci.*, **49**, 1037–1051 (1994)] is shown in Fig. P10.19.

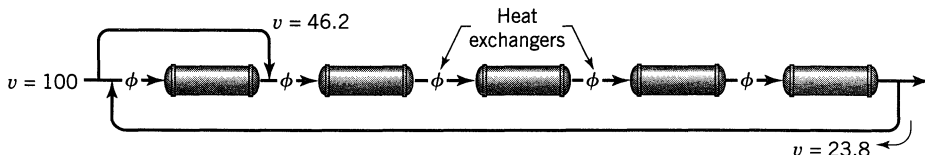


Figure P10.19

- (a) Do you like this design? Could you do better? If so, how?
 (b) If you could keep the whole of your reactors at whatever temperature and τ value desired, and if recycle is allowed, how much phthalic anhydride could be produced per mole of naphthalene reacted?

Suggestion: Why not determine the values of k_1 , k_2 , k_3 , and k_4 for both extremes of temperature, look at the values, and then proceed with the solution?

10.20. Professor Turton dislikes using reactors in parallel, and he cringed when he saw my recommended “best” design for Example 10.1. He much prefers using reactors in series, and so for that example he suggests using the design of Figure E10.1a, *but without any recycle* of fluid.

Determine the fractional yield of S, Φ (S/A), obtainable with Turton’s design, and see if it matches that found in Example 10.1.

Part II

Flow Pattern, Contacting, and Non-Ideal Flow

- Chapter 11** Basics of Non-Ideal Flow /257
- Chapter 12** Compartment Models /283
- Chapter 13** The Dispersion Model /293
- Chapter 14** The Tanks-in-Series Model /321
- Chapter 15** The Convection Model for Laminar Flow /339
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Chapter 11

Basics of Non-Ideal Flow

So far we have treated two flow patterns, plug flow and mixed flow. These can give very different behavior (size of reactor, distribution of products). We like these flow patterns and in most cases we try to design equipment to approach one or the other because

- one or the other often is optimum no matter what we are designing for.
- these two patterns are simple to treat.

But real equipment always deviates from these ideals. How to account for this? That is what this and the following chapters are about.

Overall three somewhat interrelated factors make up the contacting or flow pattern:

1. the **RTD** or residence time distribution of material which is flowing through the vessel
2. the **state of aggregation** of the flowing material, its tendency to clump and for a group of molecules to move about together
3. the **earliness and lateness of mixing** of material in the vessel.

Let us discuss these three factors in a qualitative way at first. Then, this and the next few chapters treat these factors and show how they affect reactor behavior.

The Residence Time Distribution, RTD

Deviation from the two ideal flow patterns can be caused by channeling of fluid, by recycling of fluid, or by creation of stagnant regions in the vessel. Figure 11.1 shows this behavior. In all types of process equipment, such as heat exchangers, packed columns, and reactors, this type of flow should be avoided since it always lowers the performance of the unit.

If we know precisely what is happening within the vessel, thus if we have a complete velocity distribution map for the fluid in the vessel, then we should, in principle, be able to predict the behavior of a vessel as a reactor. Unfortunately, this approach is impractical, even in today's computer age.

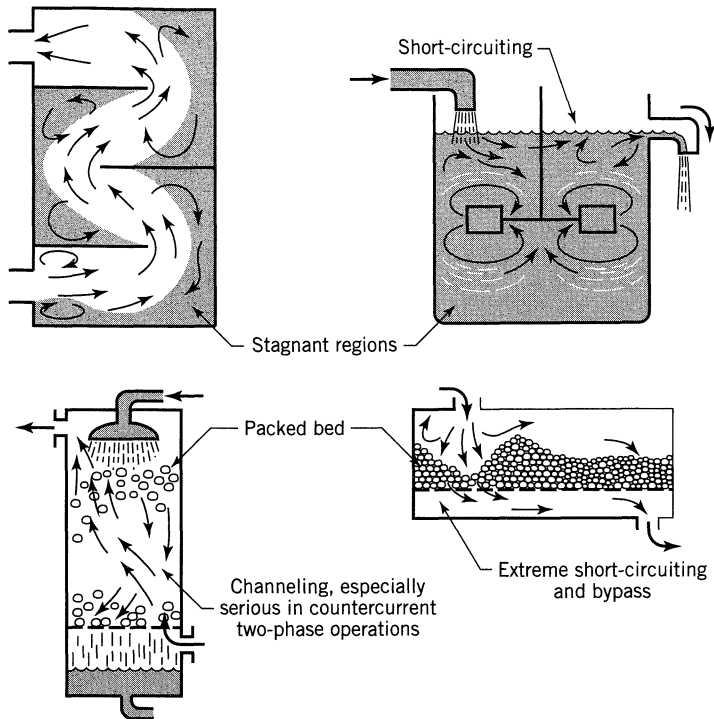


Figure 11.1 Nonideal flow patterns which may exist in process equipment.

Setting aside this goal of complete knowledge about the flow, let us be less ambitious and see what it is that we actually need to know. In many cases we really do not need to know very much, simply how long the individual molecules stay in the vessel, or more precisely, the distribution of residence times of the flowing fluid. This information can be determined easily and directly by a widely used method of inquiry, the stimulus-response experiment.

This chapter deals in large part with the residence time distribution (or RTD) approach to nonideal flow. We show when it may legitimately be used, how to use it, and when it is not applicable what alternatives to turn to.

In developing the “language” for this treatment of nonideal flow (see Danckwerts, 1953), we will only consider the steady-state flow, without reaction and without density change, of a single fluid through a vessel.

State of Aggregation of the Flowing Stream

Flowing material is in some particular state of aggregation, depending on its nature. In the extremes these states can be called *microfluids* and *macrofluids*, as sketched in Fig. 11.2.

Single-Phase Systems. These lie somewhere between the extremes of macro- and microfluids.

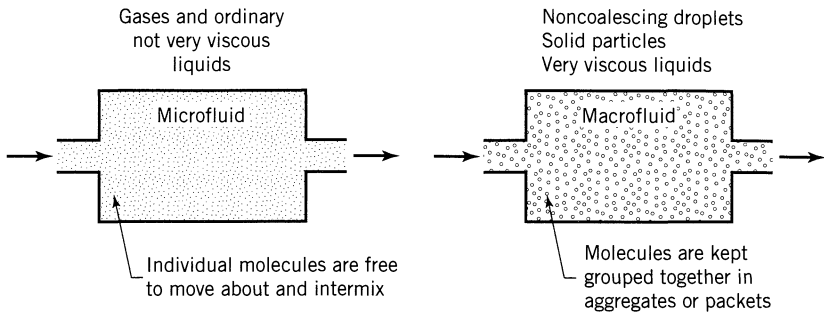


Figure 11.2 Two extremes of aggregation of fluid.

Two-Phase Systems. A stream of solids always behaves as a macrofluid, but for gas reacting with liquid, either phase can be a macro- or microfluid depending on the contacting scheme being used. The sketches of Fig. 11.3 show completely opposite behavior. We treat these two phase reactors in later chapters.

Earliness of Mixing

The fluid elements of a single flowing stream can mix with each other either early or late in their flow through the vessel. For example, see Fig. 11.4.

Usually this factor has little effect on overall behavior for a single flowing fluid. However, for a system with two entering reactant streams it can be very important. For example, see Fig. 11.5.

Role of RTD, State of Aggregation, and Earliness of Mixing in Determining Reactor Behavior

In some situations one of these three factors can be ignored; in others it can become crucial. Often, much depends on the time for reaction, \bar{t}_{rx} , the time for

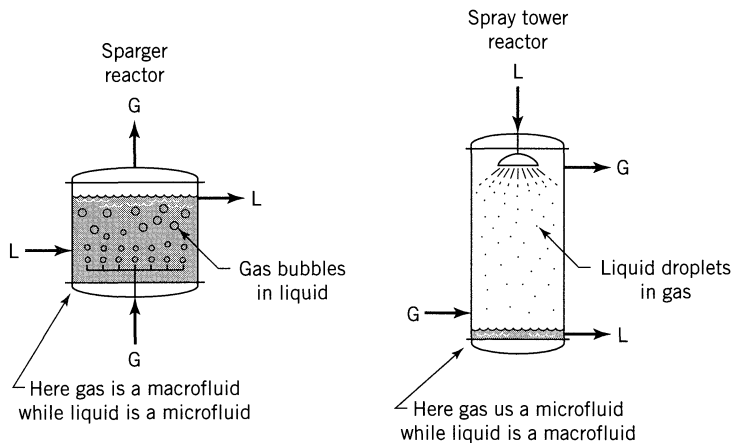


Figure 11.3 Examples of macro- and microfluid behavior.

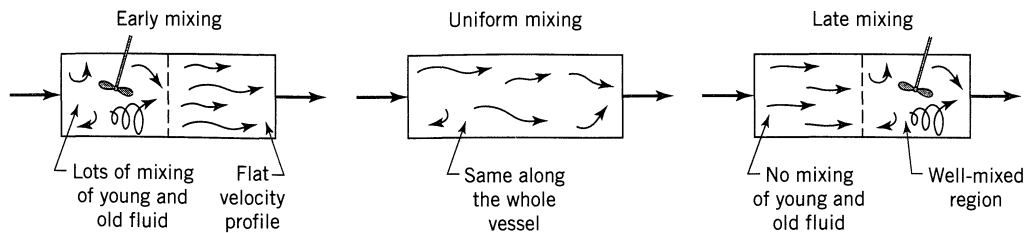


Figure 11.4 Examples of early and of late mixing of fluid.

mixing \bar{t}_{mix} , and the time for stay in the vessel \bar{t}_{stay} . In many cases \bar{t}_{stay} has a meaning somewhat like \bar{t}_{mix} but somewhat broader.

11.1 E, THE AGE DISTRIBUTION OF FLUID, THE RTD

It is evident that elements of fluid taking different routes through the reactor may take different lengths of time to pass through the vessel. The distribution of these times for the stream of fluid leaving the vessel is called the exit age distribution E , or the residence time distribution RTD of fluid. E has the units of time^{-1} .

We find it convenient to represent the RTD in such a way that the area under the curve is unity, or

$$\int_0^{\infty} E dt = 1 \quad [-]$$

This procedure is called normalizing the distribution, and Fig. 11.6 shows this.

We should note one restriction on the E curve—that the fluid only enters and only leaves the vessel one time. This means that there should be no flow or diffusion or upflow eddies at the entrance or at the vessel exit. We call this the *closed* vessel boundary condition. Where elements of fluid can cross the vessel boundary more than one time we call this the *open* vessel boundary condition.

With this representation the fraction of exit stream of age* between t and $t + dt$ is

$$E dt \quad [-]$$

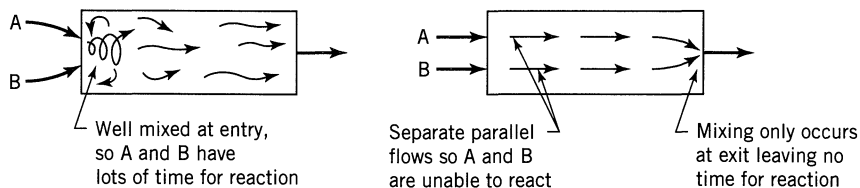


Figure 11.5 Early or late mixing affects reactor behavior.

* The term “age” for an element of the exit stream refers to the time spent by that element in the vessel.

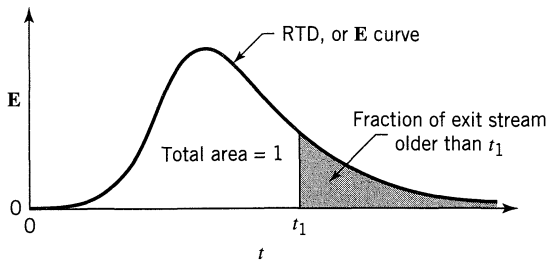


Figure 11.6 The exit age distribution curve E for fluid flowing through a vessel; also called the residence time distribution, or RTD.

the fraction younger than age t_1 is

$$\int_0^{t_1} E dt \quad [-] \quad (1)$$

whereas the fraction of material older than t_1 , shown as the shaded area in Fig. 11.6, is

$$\int_{t_1}^{\infty} E dt = 1 - \int_0^{t_1} E dt \quad [-] \quad (2)$$

The E curve is the distribution needed to account for nonideal flow.

Experimental Methods (Nonchemical) for Finding E

The simplest and most direct way of finding the E curve uses a physical or nonreactive tracer. For special purposes, however, we may want to use a reactive tracer. This chapter deals in detail with the nonreactive tracer, and for this all sorts of experiments can be used. Figure 11.7 shows some of these. Because the pulse and the step experiments are easier to interpret, the periodic and random harder, here we only consider the pulse and the step experiment.

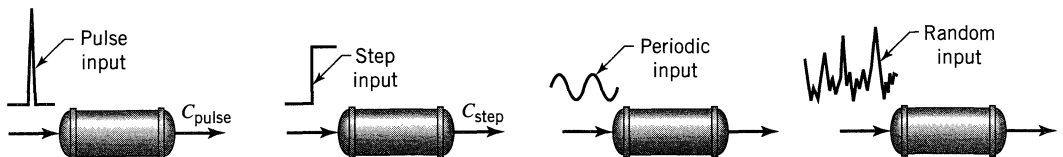


Figure 11.7 Various ways of studying the flow pattern in vessels.

We next discuss these two experimental methods for finding the **E** curve. We then show how to find reactor behavior knowing the **E** curve for the reactor.

The Pulse Experiment

Let us find the **E** curve for a vessel of volume $V \text{ m}^3$ through which flows $v \text{ m}^3/\text{s}$ of fluid. For this instantaneously introduce M units of tracer (kg or moles) into the fluid entering the vessel, and record the concentration-time of tracer leaving the vessel. This is the C_{pulse} curve. From the material balance for the vessel we find

$$\left(\begin{array}{l} \text{Area under the} \\ C_{\text{pulse}} \text{ curve} \end{array} \right): \quad A = \int_0^\infty C \, dt \cong \sum_i C_i \Delta t_i = \frac{M}{v} \quad \left[\frac{\text{kg} \cdot \text{s}}{\text{m}^3} \right] \quad (3)$$

$$\left(\begin{array}{l} \text{Mean of the} \\ C_{\text{pulse}} \text{ curve} \end{array} \right): \quad \bar{t} = \frac{\int_0^\infty tC \, dt}{\int_0^\infty C \, dt} \cong \frac{\sum_i t_i C_i \Delta t_i}{\sum_i C_i \Delta t_i} = \frac{V}{v} \quad [\text{s}] \quad (4)$$

All this is shown in Fig. 11.8.

To find the **E** curve from the C_{pulse} curve simply change the concentration scale such that the area under the curve is unity. Thus, simply divide the concentration readings by M/v , as shown in Fig. 11.9.

$$E = \frac{C_{\text{pulse}}}{M/v} \quad (5a)$$

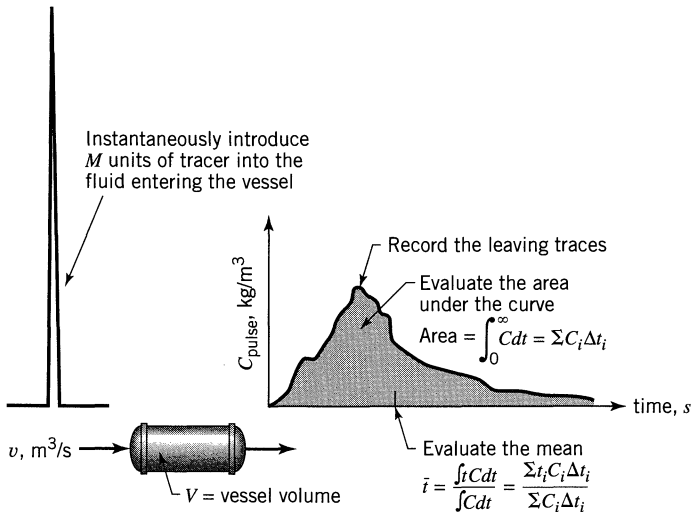


Figure 11.8 The useful information obtainable from the pulse trace experiment.

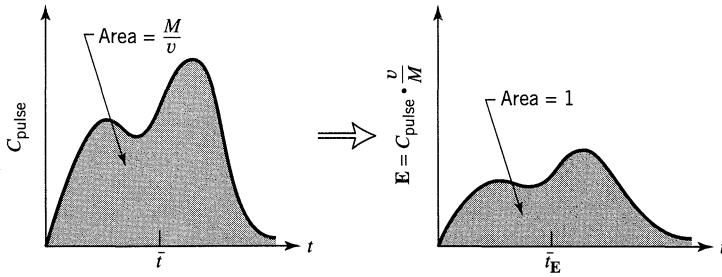


Figure 11.9 Transforming an experimental C_{pulse} curve into an \mathbf{E} curve.

We have another RTD function \mathbf{E}_θ . Here time is measured in terms of mean residence time $\theta = t/\bar{t}$. Thus

$$\mathbf{E}_\theta = \bar{t}\mathbf{E} = \frac{V}{v} \cdot \frac{C_{\text{pulse}}}{M/v} = \frac{V}{M} C_{\text{pulse}} \quad (5b)$$

\mathbf{E}_θ is a useful measure when dealing with flow models which come up in Chapters 13, 14, and 15. Figure 11.10 shows how to transform \mathbf{E} into \mathbf{E}_θ .

One final reminder, the relationship between C_{pulse} and the \mathbf{E} curves only holds exactly for vessels with *closed* boundary conditions.

The Step Experiment

Consider $v \text{ m}^3/\text{s}$ of fluid flowing through a vessel of volume V . Now at time $t = 0$ switch from ordinary fluid to fluid with tracer of concentration $C_{\text{max}} = \left[\frac{\text{kg or mol}}{\text{m}^3} \right]$, and measure the outlet tracer concentration C_{step} versus t , as shown in Fig. 11.11.

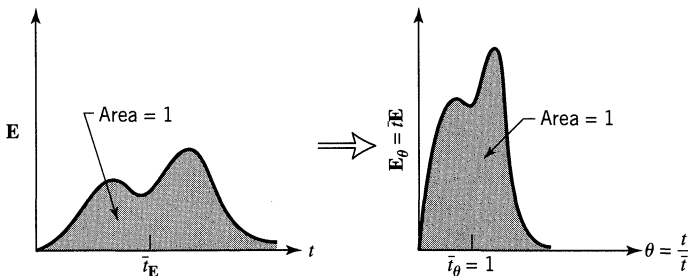


Figure 11.10 Transforming an \mathbf{E} curve into an \mathbf{E}_θ curve.

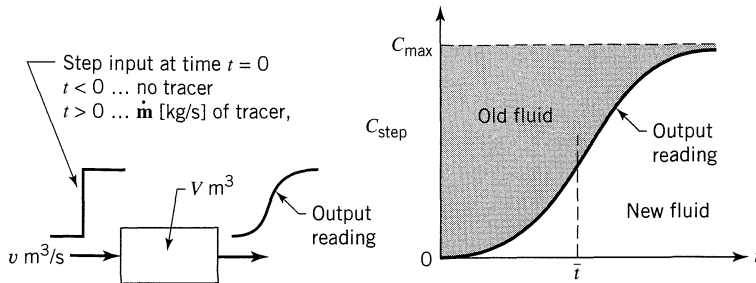


Figure 11.11 Information obtainable from a step tracer experiment.

A material balance relates the different measured quantities of the output curve of a step input

$$C_{\max} = \frac{\dot{m}}{v} \left[\frac{\text{kg} \cdot \text{s}}{\text{m}^3} \right]$$

and

$$\left(\begin{array}{l} \text{shaded area} \\ \text{of Fig. 11.11} \end{array} \right) = C_{\max} \bar{t} = \frac{\dot{m}V}{v^2} \left[\frac{\text{kg} \cdot \text{s}^2}{\text{m}^3} \right] \quad (6)$$

$$\bar{t} = \frac{\int_0^{C_{\max}} t dC_{\text{step}}}{\int_0^{C_{\max}} dC_{\text{step}}} = \frac{1}{C_{\max}} \int_0^{C_{\max}} t dC_{\text{step}}$$

where \dot{m} [kg/s] is the flow rate of tracer in the entering fluid.

The dimensionless form of the C_{step} curve is called the **F** curve. It is found by having the tracer concentration rise from zero to unity, as shown in Fig. 11.12.

Relationship between the F and E Curves

To relate **E** with **F** imagine a steady flow of white fluid. Then at time $t = 0$ switch to red and record the rising concentration of red fluid in the exit stream, the **F**

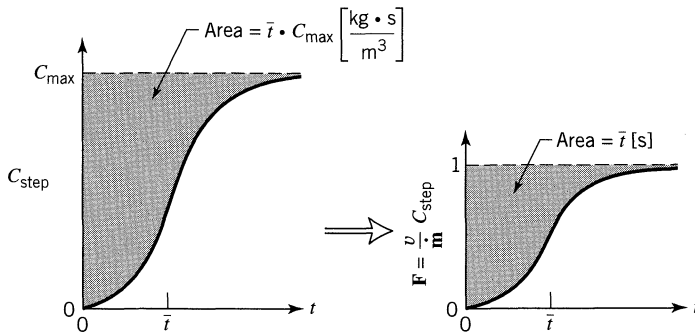


Figure 11.12 Transforming an experimental C_{step} curve to an **F** curve.

curve. At any time $t > 0$ red fluid and only red fluid in the exit stream is younger than age t . Thus we have

$$\left(\begin{array}{c} \text{fraction of red fluid} \\ \text{in the exit stream} \end{array} \right) = \left(\begin{array}{c} \text{fraction of exit stream} \\ \text{younger than age } t \end{array} \right)$$

But the first term is simply the \mathbf{F} value, while the second is given by Eq. 1. So we have, at time t ,

$$\mathbf{F} = \int_0^t \mathbf{E} dt \quad (7)$$

and on differentiating

$$\frac{d\mathbf{F}}{dt} = \mathbf{E} \quad (8)$$

In graphical form this relationship is shown in Fig. 11.13.

These relationships show how stimulus-response experiments, using either step or pulse inputs can conveniently give the RTD and mean flow rate of fluid in the vessel. We should remember that these relationships only hold for closed vessels. When this boundary condition is not met, then the C_{pulse} and \mathbf{E} curves differ. The C_{pulse} curves of the convection model (see Chap. 15) clearly show this.

Figure 11.14 shows the shapes of these curves for various types of flow.

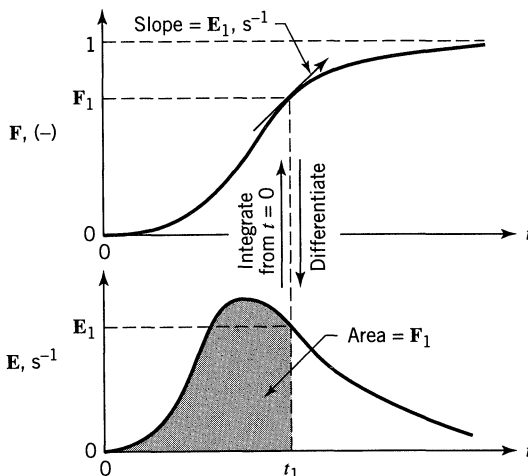


Figure 11.13 Relationship between the \mathbf{E} and \mathbf{F} curves.

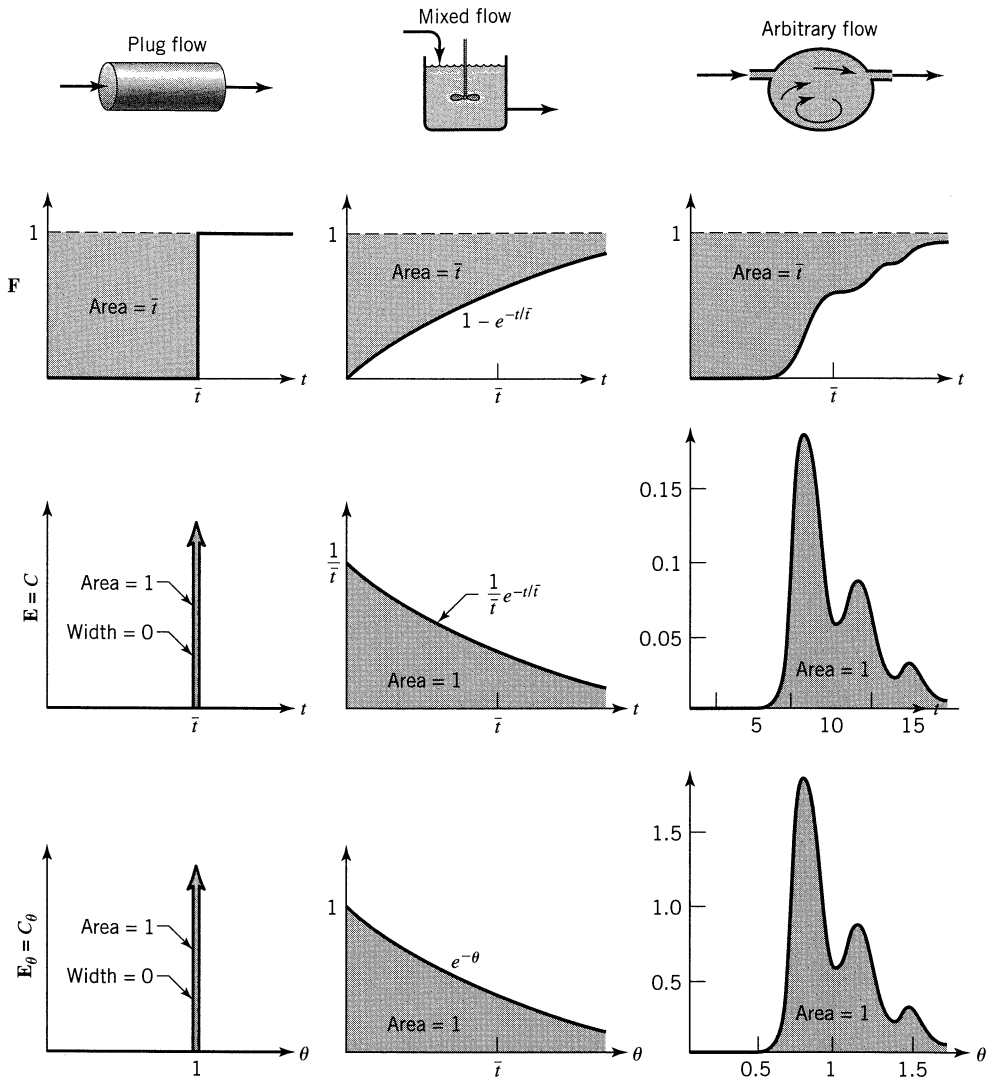


Figure 11.14 Properties of the E and F curves for various flows. Curves are drawn in terms of ordinary and dimensionless time units. Relationship between curves is given by Eqs. 7 and 8.

At any time these curves are related as follows:

$$\begin{aligned}
 \mathbf{E} &= \frac{v}{\dot{m}} \cdot C_{\text{pulse}}, & \mathbf{F} &= \frac{v}{\dot{m}} \cdot C_{\text{step}}, & \mathbf{E} &= \frac{d\mathbf{F}}{dt}, \\
 \bar{t} &= \frac{V}{v}, & \theta &= \frac{t}{\bar{t}}, & \bar{\theta}_E &= 1, & \mathbf{E}_\theta &= \bar{t}\mathbf{E} \\
 \theta, \mathbf{E}_\theta, \mathbf{F} \dots & \text{all dimensionless, } & \mathbf{E} &= [\text{time}^{-1}]
 \end{aligned}$$

(9)

EXAMPLE 11.1 FINDING THE RTD BY EXPERIMENT

The concentration readings in Table E11.1 represent a continuous response to a pulse input into a closed vessel which is to be used as a chemical reactor. Calculate the mean residence time of fluid in the vessel t , and tabulate and plot the exit age distribution E .

Table E11.1

Time t , min	Tracer Output Concentration, C_{pulse} gm/liter fluid
0	0
5	3
10	5
15	5
20	4
25	2
30	1
35	0

SOLUTION

The mean residence time, from Eq. 4, is

$$\bar{t} = \frac{\sum t_i C_i \Delta t_i}{\sum C_i \Delta t_i} \frac{\Delta t = \text{constant}}{\sum C_i} = \frac{5 \times 3 + 10 \times 5 + 15 \times 5 + 20 \times 4 + 25 \times 2 + 30 \times 1}{3 + 5 + 5 + 4 + 2 + 1} = 15 \text{ min}$$

The area under the concentration-time curve,

$$\text{Area} = \sum C \Delta t = (3 + 5 + 5 + 4 + 2 + 1)5 = 100 \text{ gm} \cdot \text{min/liter}$$

gives the total amount of tracer introduced. To find E , the area under this curve must be unity; hence, the concentration readings must each be divided by the total area, giving

$$E = \frac{C}{\text{area}}$$

Thus we have

$E = \frac{C}{\text{area}}, \text{min}^{-1}$	t, min	0	5	10	15	20	25	30
		0	0.03	0.05	0.05	0.04	0.02	0.01

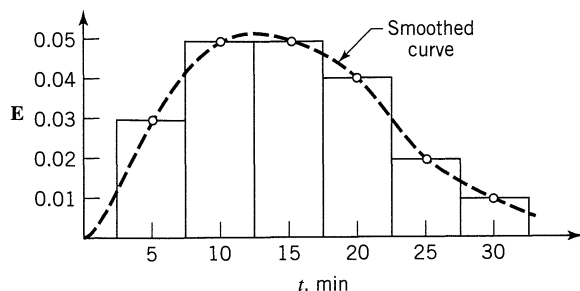


Figure E11.1

Figure E11.1 is a plot of this distribution.

EXAMPLE 11.2 FINDING THE E CURVE FOR LIQUID FLOWING THROUGH A VESSEL

A large tank (860 liters) is used as a gas-liquid contactor. Gas bubbles up through the vessel and out the top, liquid flows in at one part and out the other at 5 liters/s. To get an idea of the flow pattern of liquid in this tank a pulse of tracer ($M = 150$ gm) is injected at the liquid inlet and measured at the outlet, as shown in Fig. E11.2a.

- Is this a properly done experiment?
- If so, find the liquid fraction in the vessel.
- Determine the E curve for the liquid.
- Qualitatively what do you think is happening in the vessel?

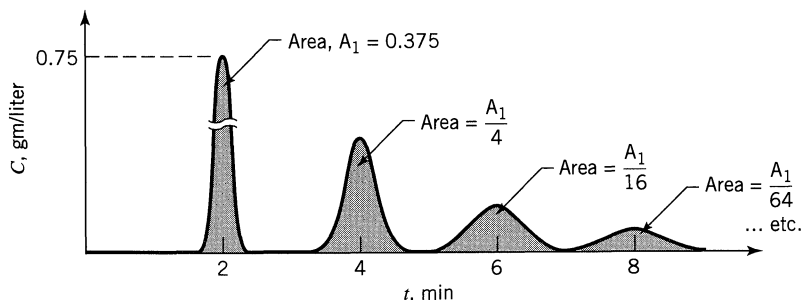


Figure E11.2a

SOLUTION

- Check the material balance against the tracer curve. From the material balance, Eq. 3, we should have

$$\text{Area} = \frac{M}{v} = \frac{150 \text{ gm}}{5 \text{ liters/s}} = 30 \frac{\text{gm} \cdot \text{s}}{\text{liter}} = 0.5 \frac{\text{gm} \cdot \text{min}}{\text{liter}}$$

From the tracer curve

$$\text{Area} = A_1 \left(1 + \frac{1}{4} + \frac{1}{16} + \dots \right) = 0.375 \left(\frac{4}{3} \right) = 0.5 \frac{\text{gm} \cdot \text{min}}{\text{liter}}$$

These values agree. The results are consistent. (a)

(b) For the liquid, Eq. 4 gives

$$\bar{t}_l = \frac{\int tC dt}{\int C dt} = \frac{1}{0.5} \left[2A_1 + 4 \times \frac{A_1}{4} + 6 \times \frac{A_1}{16} + 8 \times \frac{A_1}{64} + \dots \right] = 2.67 \text{ min}$$

Thus the liquid volume in the vessel is

$$V_l = \bar{t}_l v_l = 2.67(5 \times 60) = 800 \text{ liters}$$

and the volume fraction of phases is

$$\left. \begin{array}{l} \text{Fraction of liquid} = \frac{800}{860} = 93\% \\ \text{Fraction of gas} = 7\% \end{array} \right\} \text{(b)}$$

(c) Finally, from Eq. 5 we find the **E** curve, or

$$\mathbf{E} = \frac{C_{\text{pulse}}}{M/v} = \frac{0.75}{0.5} C = 1.5 C$$

Thus the **E** curve for the liquid is as shown in Fig. E11.2b. (c)

(d) The vessel has a strong recirculation of liquid, probably induced by the rising bubbles. (d)

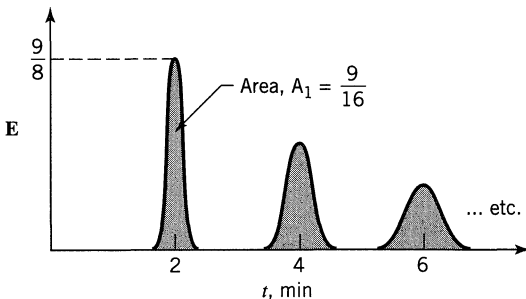


Figure E11.2b

The Convolution Integral

Suppose we introduce into a vessel a one-shot tracer signal C_{in} versus t as shown in Fig. 11.15. In passing through the vessel the signal will be modified to give an output signal C_{out} versus t . Since the flow with its particular RTD is responsible for this modification let us relate C_{in} , \mathbf{E} , and C_{out} .

Focus attention on tracer leaving at time about t . This is shown as the narrow rectangle B in Fig. 11.15. We may then write

$$\left(\begin{array}{l} \text{tracer leaving} \\ \text{in rectangle } B \end{array} \right) = \left(\begin{array}{l} \text{all the tracer entering } t' \text{ seconds earlier than } t, \\ \text{and staying for time } t' \text{ in the vessel} \end{array} \right)$$

We show the tracer which enters t' seconds earlier than t as the narrow rectangle A . In terms of this rectangle the above equation may be written

$$\left(\begin{array}{l} \text{tracer leaving} \\ \text{in rectangle } B \end{array} \right) = \sum_{\substack{\text{all rectangles} \\ A \text{ which enter} \\ \text{earlier than} \\ \text{time } t}} \left(\begin{array}{l} \text{tracer in} \\ \text{rectangle} \\ A \end{array} \right) \left(\begin{array}{l} \text{fraction of tracer in } A \\ \text{which stays for about} \\ t' \text{ seconds in the vessel} \end{array} \right)$$

In symbols and taking limits (shrinking the rectangles) we obtain the desired relationship, which is called the convolution integral

$$C_{out}(t) = \int_0^t C_{in}(t-t')\mathbf{E}(t')dt' \tag{10a}$$

In what can be shown to be equivalent form we also have

$$C_{out}(t) = \int_0^t C_{in}(t')\mathbf{E}(t-t')dt' \tag{10b}$$

We say that C_{out} is the *convolution* of \mathbf{E} with C_{in} and we write concisely

$$C_{out} = \mathbf{E} * C_{in} \quad \text{or} \quad C_{out} = C_{in} * \mathbf{E} \tag{10c}$$

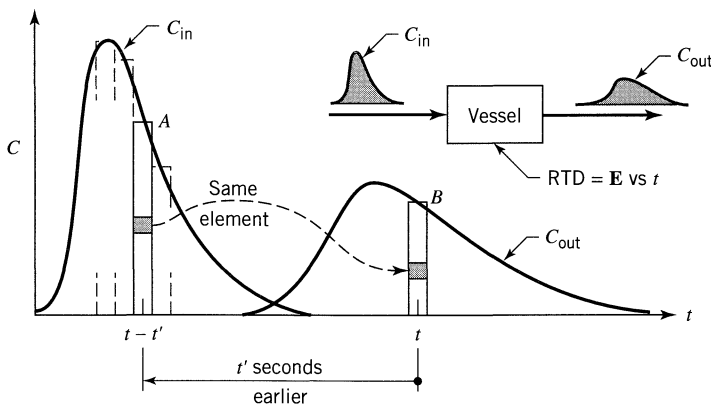


Figure 11.15 Sketch showing derivation of the convolution integral.

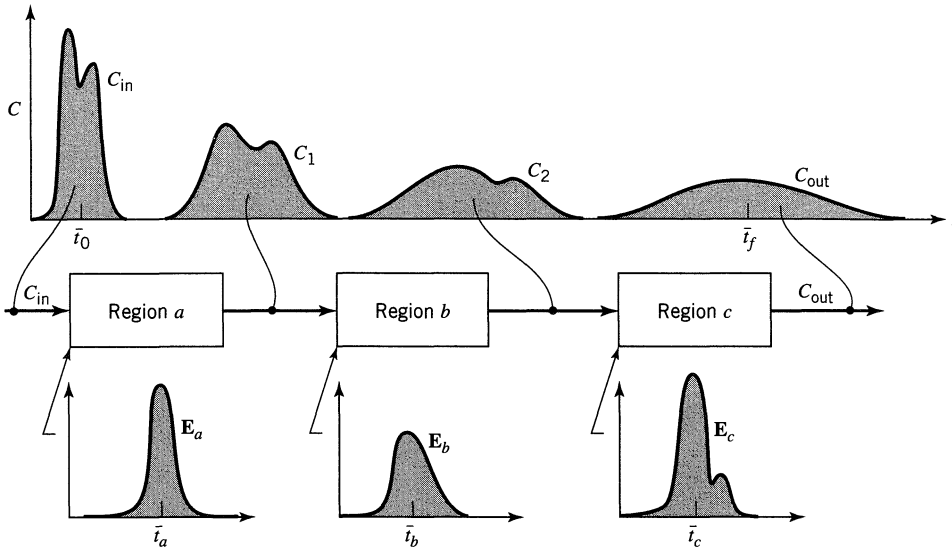


Figure 11.16 Modification of an input tracer signal C_{in} on passing through three successive regions.

Application of These Tools. To illustrate the uses of these mathematical tools consider three independent* flow units a , b , and c , which are closed and connected in series (see Fig. 11.16).

Problem 1. If the input signal C_{in} is measured and the exit age distribution functions E_a , E_b , and E_c are known, then C_1 is the convolution of E_a with C_{in} and so on, thus

$$C_1 = C_{in} * E_a, \quad C_2 = C_1 * E_b, \quad C_{out} = C_2 * E_c$$

and on combining

$$C_{out} = C_{in} * E_a * E_b * E_c \quad (11)$$

Thus we can determine the output from a multiregion flow unit.

Problem 2. If we measure C_{in} and C_{out} and know E_a and E_c we can then extract the unknown E_b . This type of problem is of particular importance in experimentation where the entrance region and collection region for tracer are both large compared with the experimental section.

It is a straightforward matter to convolute; however, to *deconvolute*, to find one of the distribution functions under the integral, is difficult. Thus Problem 2 is harder to treat than Problem 1 and requires using a computer.

* By independence we mean that the fluid loses its memory as it passes from vessel to vessel. Thus, a faster-moving fluid element in one vessel does not remember this fact in the next vessel and doesn't preferentially flow faster (or slower) there. Laminar flow often does not satisfy this requirement of independence; however, complete (or lateral) mixing of fluid between units satisfies this condition.

In some cases, however, we can in essence deconvolute. This special situation is considered at the end of Chapter 14 and is illustrated with an example there.

Example 11.3 illustrates convolution; Example 14.4 illustrates deconvolution.

EXAMPLE 11.3 CONVOLUTION

Let us illustrate the use of the convolution equation, Eq. 10, with a very simple example in which we want to find C_{out} given C_{in} and the **E** curve for the vessel, as shown in Fig. E11.3a.

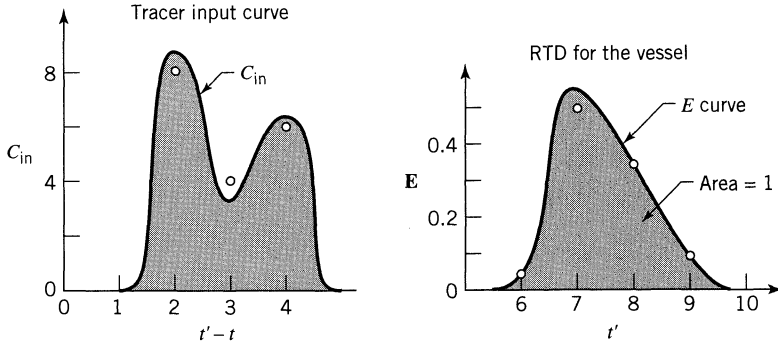


Figure E11.3a

SOLUTION

First of all, take 1 min time slices. The given data are then

$t' - t$	C_{in}	t'	E
0	0	5	0
1	0	6	0.05
2	8	7	0.50
3	4	8	0.35
4	6	9	0.10
5	0	10	0

Note: The area under the **E** curve is unity.

Now the first bit of tracer leaves at 8 min, the last bit at 13 min. Thus, applying the convolution integral, in discrete form, we have

t	C_{out}	
7	0	= 0
8	8×0.05	= 0.4
9	$8 \times 0.5 + 4 \times 0.05$	= 4.2
10	$8 \times 0.35 + 4 \times 0.5 + 6 \times 0.05$	= 5.1
11	$8 \times 0.10 + 4 \times 0.35 + 6 \times 0.5$	= 5.2
12	$4 \times 0.10 + 6 \times 0.35$	= 2.5
13	6×0.10	= 0.6
14		= 0

The C_{in} , E , and C_{out} curves, in discrete and in continuous form, are shown in Fig. E11.3b. Note that the area under the C_{out} curve equals the area under the C_{in} curve.

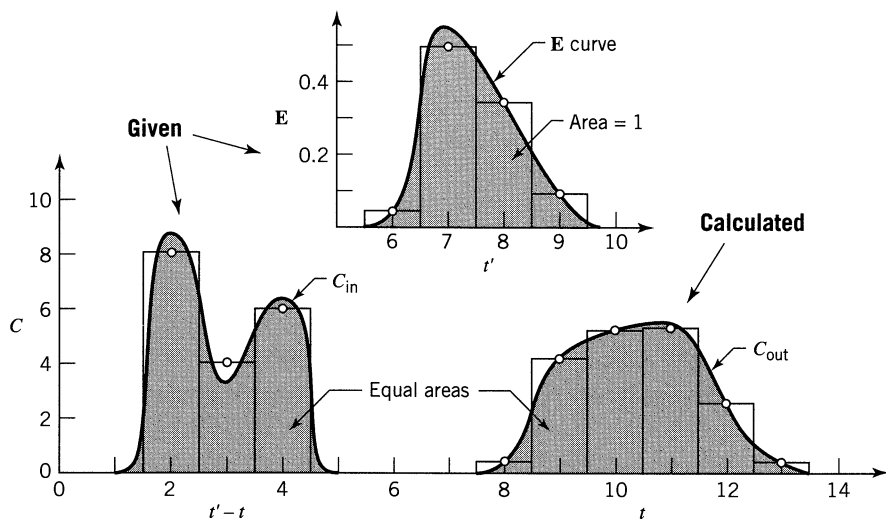


Figure E11.3b

11.2 CONVERSION IN NON-IDEAL FLOW REACTORS

To evaluate reactor behavior in general we have to know four factors:

1. the kinetics of the reaction
2. the RTD of fluid in the reactor
3. the earliness or lateness of fluid mixing in the reactor
4. whether the fluid is a micro or macro fluid

For *microfluids* in plug or mixed flow we have developed the equations in the earlier chapters. For intermediate flow we will develop appropriate models in Chapters 12, 13, and 14.

To consider the *early and late mixing of a microfluid*, consider the two flow patterns shown in Fig. 11.17 for a reactor processing a second-order reaction. In (a) the reactant starts at high concentration and reacts away rapidly because $n > 1$. In (b) the fluid drops immediately to a low concentration. Since the rate of reaction drops more rapidly than does the concentration you will end up with a lower conversion. Thus, for microfluids

Late mixing favors reactions where $n > 1$

Early mixing favors reactions where $n < 1$

(12)

For *macrofluids*, imagine little clumps of fluid staying for different lengths of time in the reactor (given by the E function). Each clump reacts away as a little

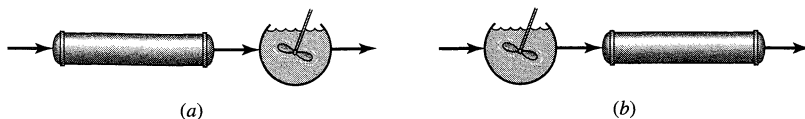


Figure 11.17 This shows the latest and the earliest mixing we can have for a given RTD.

batch reactor, thus fluid elements will have different compositions. So the mean composition in the exit stream will have to account for these two factors, the kinetics and the RTD. In words, then

$$\left(\begin{array}{c} \text{mean concentration} \\ \text{of reactant} \\ \text{in exit stream} \end{array} \right) = \sum_{\text{all elements of exit stream}} \left(\begin{array}{c} \text{concentration of} \\ \text{reactant remaining} \\ \text{in an element of} \\ \text{age between } t \\ \text{and } t + dt \end{array} \right) \left(\begin{array}{c} \text{fraction of exit} \\ \text{stream which is} \\ \text{of age between } t \\ \text{and } t + dt \end{array} \right)$$

In symbols this becomes

$$\left(\frac{\bar{C}_A}{C_{A0}} \right)_{\text{at exit}} = \int_0^{\infty} \left(\frac{C_A}{C_{A0}} \right)_{\text{for an element or little batch of fluid of age } t} \cdot \mathbf{E} dt$$

or in terms of conversions

$$\bar{X}_A = \int_0^{\infty} (X_A)_{\text{element}} \cdot \mathbf{E} dt \quad (13)$$

or in a form suitable for numerical integration

$$\frac{\bar{C}_A}{C_{A0}} = \sum_{\text{all age intervals}} \left(\frac{C_A}{C_{A0}} \right)_{\text{element}} \cdot \mathbf{E} \Delta t$$

From Chapter 3 on batch reactors we have

- for first-order reactions $\left(\frac{C_A}{C_{A0}} \right)_{\text{element}} = e^{-kt} \quad (14)$

- for second-order reactions $\left(\frac{C_A}{C_{A0}} \right)_{\text{element}} = \frac{1}{1 + kC_{A0}t} \quad (15)$

- for an n th-order reaction $\left(\frac{C_A}{C_{A0}} \right)_{\text{element}} = [1 + (n-1)C_{A0}^{n-1}kt]^{1/1-n} \quad (16)$

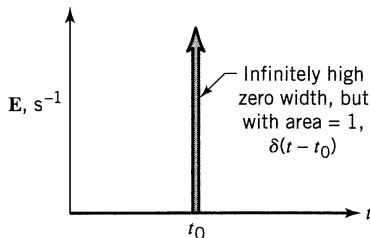


Figure 11.18 The E function for plug flow.

These are terms to be introduced into the performance equation, Eq. 13. Also, further on in this chapter we will show that for first-order reactions, the macrofluid equation is identical to the batch or to the microfluid equation.

We continue this discussion in Chapter 16.

The Dirac Delta Function, $\delta(t - t_0)$. One E curve which may puzzle us is the one which represents plug flow. We call this the Dirac δ function, and in symbols we show it as

$$\delta(t - t_0) \quad (17)$$

which says that the pulse occurs at $t = t_0$, as seen in Fig. 11.18.

The two properties of this function which we need to know are

$$\text{Area under the curve: } \int_0^{\infty} \delta(t - t_0) dt = 1 \quad (18)$$

$$\text{Any integration with a } \delta \text{ function: } \int_0^{\infty} \delta(t - t_0) f(t) dt = f(t_0) \quad (19)$$

Once we understand what this means we will see that it is easier to integrate with a δ function than with any other. For example,

$$\int_0^{\infty} \delta(t - 5) t^6 dt = 5^6 \quad (\text{just replace } t_0 \text{ by } 5)$$

$$\int_0^3 \delta(t - 5) t^6 dt = 0$$

EXAMPLE 11.4 CONVERSION IN REACTORS HAVING NON-IDEAL FLOW

The vessel of Example 11.1 is to be used as a reactor for a liquid decomposing with rate

$$-r_A = kC_A, \quad k = 0.307 \text{ min}^{-1}$$

Find the fraction of reactant unconverted in the real reactor and compare this with the fraction unconverted in a plug flow reactor of the same size.

SOLUTION

For the *plug flow reactor* with negligible density change we have

$$\tau = C_{A0} \int_0^{X_A} \frac{dX_A}{-r_A} = -\frac{1}{k} \int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \frac{1}{k} \ln \frac{C_{A0}}{C_A}$$

and with τ from Example 11.1

$$\frac{C_A}{C_{A0}} = e^{-k\tau} = e^{-(0.307)(15)} = e^{-4.6} = \underline{\underline{0.01}}$$

Thus the fraction of reactant unconverted in a plug flow reactor equals 1.0%.

For the *real reactor* the fraction unconverted, given by Eq. 13 for macrofluids, is found in Table E11.4. Hence the fraction of reactant unconverted in the real reactor

$$\frac{C_A}{C_{A0}} = \underline{\underline{0.047}}$$

Table E11.4

t	\mathbf{E}	kt	e^{-kt}	$e^{-kt}\mathbf{E} \Delta t$
5	0.03	1.53	0.2154	(0.2154)(0.03)(5) = 0.0323
10	0.05	3.07	0.0464	0.0116
15	0.05	4.60	0.0100	0.0025
20	0.04	6.14	0.0021	0.0004
25	0.02	7.68	0.0005	0.0001
30	0.01	9.21	0.0001	0
<div style="display: flex; align-items: center; justify-content: center;"> } given </div>				$\frac{C_A}{C_{A0}} = \sum e^{-kt}\mathbf{E} \Delta t = \underline{\underline{0.0469}}$

From the table we see that the unconverted material comes mostly from the early portion of the \mathbf{E} curve. This suggests that channeling and short-circuiting can seriously hinder attempts to achieve high conversion in reactors.

Note that since this is a first-order reaction we can treat it as a microfluid, or a macrofluid, whatever we wish. In this problem we solved the plug flow case as a microfluid, and we solved the nonideal case as a macrofluid.

EXAMPLE 11.5 REACTION OF A MACROFLUID

Dispersed noncoalescing droplets ($C_{A0} = 2$ mol/liter) react ($A \rightarrow R$, $-r_A = kC_A^2$, $k = 0.5$ liter/mol·min) as they pass through a contactor. Find the average concentration of A remaining in the droplets leaving the contactor if their RTD is given by the curve in Fig. E11.5.

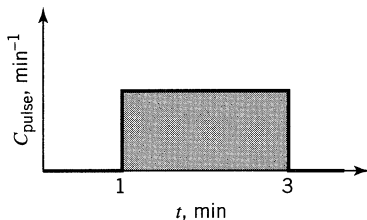


Figure E11.5

SOLUTION

Equation 13 is the pertinent performance equation. Evaluate terms in this expression. For

$$-r_A = kC_A^2, \quad k = 0.5 \text{ liter/mol} \cdot \text{min}$$

The batch equation from Chapter 3 is

$$\frac{C_A}{C_{A0}} = \frac{1}{1 + kC_{A0}t} = \frac{1}{1 + 0.5(2)t} = \frac{1}{1 + t}$$

With $E = 0.5$ for $1 < t < 3$, Eq. 13 becomes

$$\frac{\bar{C}_A}{C_{A0}} = \int_0^{\infty} \left(\frac{C_A}{C_{A0}} \right)_{\text{batch}} E dt = \int_1^3 \frac{1}{1 + t} \cdot (0.5) dt = 0.5 \ln 2 = 0.347$$

So

$$\bar{X}_A = 1 - 0.347 = 0.653, \quad \text{or} \quad \underline{\underline{65\%}}$$

REFERENCE

Danckwerts, P. V., *Chem. Eng. Sci.*, **2**, 1 (1953).

PROBLEMS

- 11.1. A pulse input to a vessel gives the results shown in Fig. P11.1.
 (a) Check the material balance with the tracer curve to see whether the results are consistent.
 (b) If the result is consistent, determine \bar{t} , V and sketch the E curve.

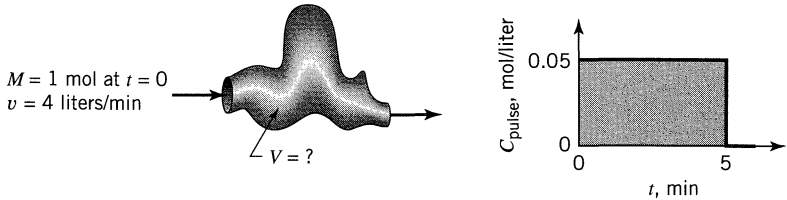


Figure P11.1

- 11.2. Repeat Problem P11.1 with one change: The tracer curve is now as shown in Fig. P11.2.

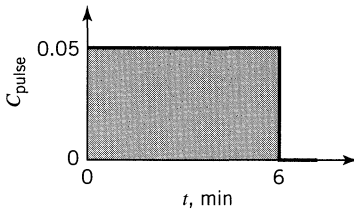


Figure P11.2

- 11.3. A pulse input to a vessel gives the results shown in Fig. P11.3.
 (a) Are the results consistent? (Check the material balance with the experimental tracer curve.)
 (b) If the results are consistent, determine the amount of tracer introduced M , and the E curve.

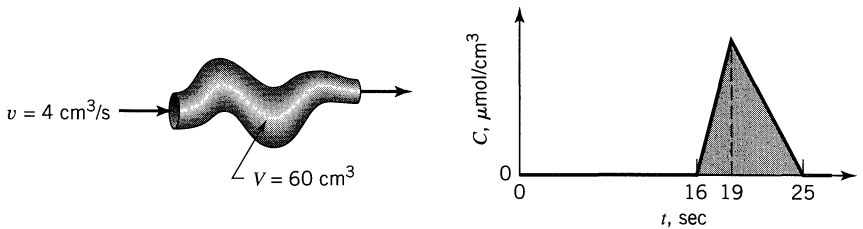


Figure P11.3

- 11.4. A step experiment is made on a reactor. The results are shown in Fig. P11.4.
 (a) Is the material balance consistent with the tracer curve?
 (b) If so, determine the vessel volume V , \bar{t} , the F curve, and the E curve.

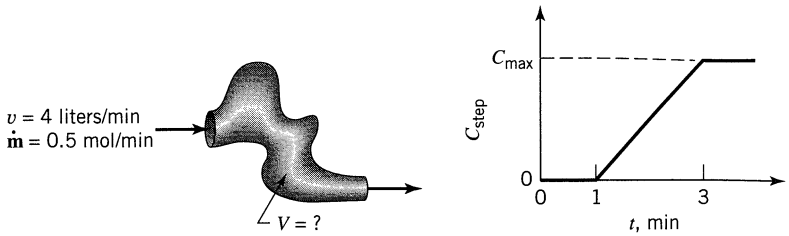


Figure P11.4

- 11.5. A batch of radioactive material is dumped into the Columbia River at Hanford, Washington. At Bonneville Dam, about 400 km downstream the flowing waters ($6000 \text{ m}^3/\text{s}$) are monitored for a particular radioisotope ($t_{1/2} > 10 \text{ yr}$) and the data of Fig. P11.5 are obtained.
- How many units of this tracer were introduced into the river?
 - What is the volume of Columbia River waters between Bonneville Dam and the point of introduction of tracer?

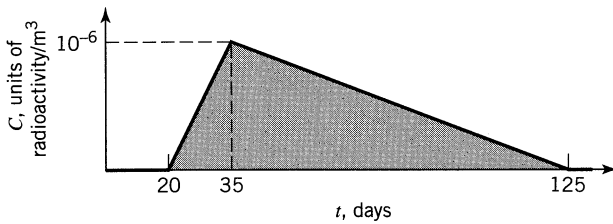


Figure P11.5

- 11.6. A pipeline (10 cm I.D., 19.1 m long) simultaneously transports gas and liquid from here to there. The volumetric flow rate of gas and liquid are $60\,000 \text{ cm}^3/\text{s}$ and $300 \text{ cm}^3/\text{s}$, respectively. Pulse tracer tests on the fluids flowing through the pipe give results as shown in Fig. P11.6. What fraction of the pipe is occupied by gas and what fraction by liquid?

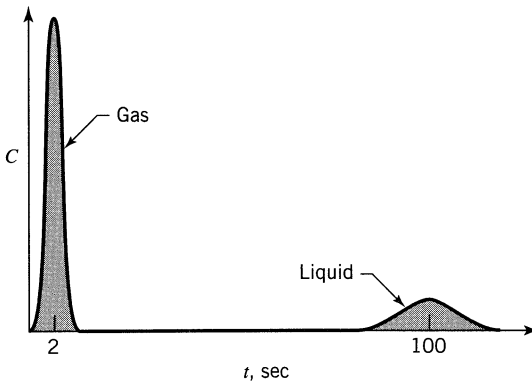
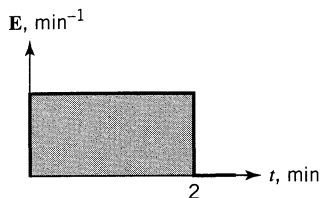


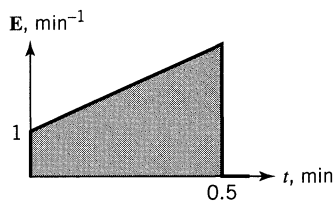
Figure P11.6

A liquid macrofluid reacts according to $A \rightarrow R$ as it flows through a vessel. Find the conversion of A for the flow patterns of Figs. P11.7 to P11.11 and kinetics as shown.

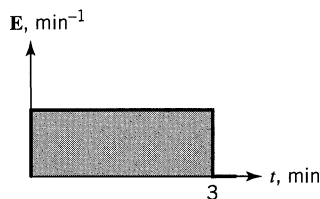
11.7. $C_{A0} = 1 \text{ mol/liter}$
 $-r_A = kC_A^{0.5}$
 $k = 2 \text{ mol}^{0.5}/\text{liter}^{0.5} \cdot \text{min}$



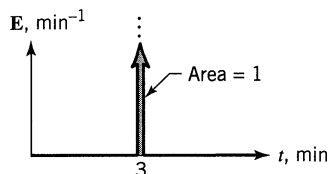
11.8. $C_{A0} = 2 \text{ mol/liter}$
 $-r_A = kC_A^2$
 $k = 2 \text{ liter/mol} \cdot \text{min}$



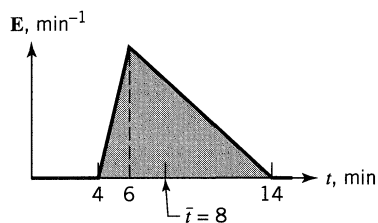
11.9. $C_{A0} = 6 \text{ mol/liter}$
 $-r_A = k$
 $k = 3 \text{ mol/liter} \cdot \text{min}$



11.10. $C_{A0} = 4 \text{ mol/liter}$
 $-r_A = k$
 $k = 1 \text{ mol/liter} \cdot \text{min}$

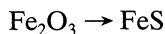


11.11. $C_{A0} = 0.1 \text{ mol/liter}$
 $-r_A = k$
 $k = 0.03 \text{ mol/liter} \cdot \text{min}$



Figures P11.7, P11.8, P11.9, P11.10, P11.11

11.12–11.14. Hydrogen sulfide is removed from coal gas by contact with a moving bed of iron oxide particles which convert to the sulfide as follows:



In our reactor the fraction of oxide converted in any particle is determined by its residence time t and the time needed for complete conversion of

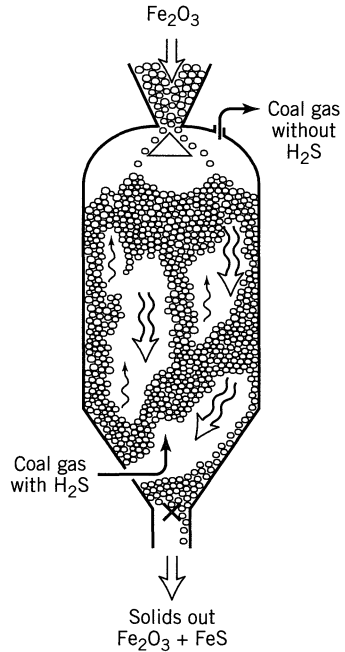
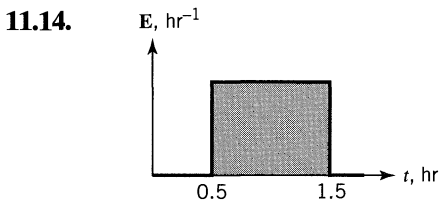
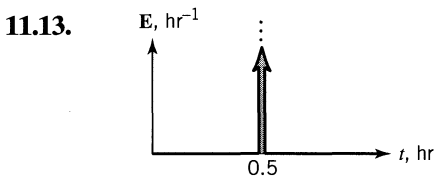
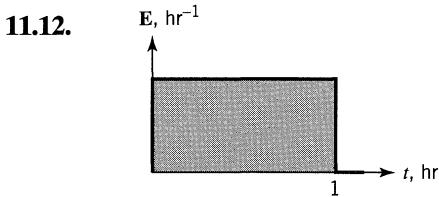
the particle τ , and this is given by

$$1 - X = \left(1 - \frac{t}{\tau}\right)^3 \quad \text{when } t < 1 \text{ hr, and with } \tau = 1 \text{ hr}$$

and

$$X = 1 \quad \text{when } t \geq 1 \text{ hr}$$

Find the conversion of iron oxide to sulfide if the RTD of solids in the contactor is approximated by the curve of Fig. P11.12, P11.13, or P11.14.



Figures P11.12, P11.13, P11.14

11.15. Cold solids flow continuously into a fluidized bed where they disperse rapidly enough so that they can be taken as well mixed. They then heat up, they devolatilize slowly, and they leave. Devolatilization releases gaseous A which then decomposes by first-order kinetics as it passes through the bed. When the gas leaves the bed decomposition of gaseous A stops. From the following information determine the fraction of gaseous A which has decomposed.

Data: Since this is a large-particle fluidized bed containing cloudless bubbles, assume plug flow of gas through the unit. Also assume that the volume of gases released by the solids is small compared to the volume of carrier gas passing through the bed.

Mean residence time in the bed:

$$\bar{t}_s = 15 \text{ min}, \bar{t}_g = 2 \text{ s for carrier gas}$$

For the reaction: $\text{A} \rightarrow \text{products}$, $-r_A = kC_A$, $k = 1 \text{ s}^{-1}$

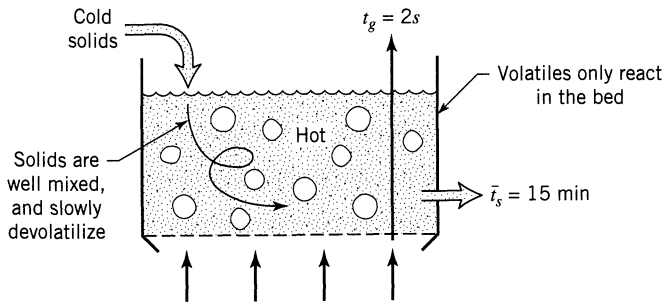
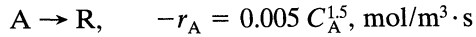


Figure P11.15

11.16. Reactant A ($C_{A0} = 64 \text{ mol/m}^3$) flows through a plug flow reactor ($\tau = 50 \text{ s}$), and reacts away as follows:



Determine the conversion of A if the stream is:

- (a) a microfluid,
- (b) a macrofluid.

Chapter 12

Compartment Models

Flow models can be of different levels of sophistication and the compartment models of this chapter are the next stage beyond the very simplest, those that assume the extremes of plug flow and mixed flow. In the compartment models we consider the vessel and the flow through it as follows:

$$\text{Total volume } \cdot \cdot \cdot \left\{ \begin{array}{l} V_p \text{—plug flow region} \\ V_m \text{—mixed flow region} \\ V_d \text{—dead or stagnant region within the vessel} \end{array} \right\} V_a \text{—active volume}$$

V

$$\text{Total throughflow } \cdot \cdot \cdot \left\{ \begin{array}{l} v_a \text{—active flow, that through the plug and mixed flow regions} \\ v_b \text{—bypass flow} \\ v_r \text{—recycle flow} \end{array} \right.$$

v

By comparing the **E** curve for the real vessel with the theoretical curves for various combinations of compartments and throughflow, we can find which model best fits the real vessel. Of course, the fit will not be perfect; however, models of this kind are often a reasonable approximation to the real vessel.

Figure 12.1, on the next few pages, shows what the **E** curves look like for various combinations of the above elements—certainly not all combinations.

Hints, Suggestions, and Possible Applications

- (a) If we know M (kilograms of tracer introduced in the pulse) we can make a material balance check. Remember that $M = v$ (area of curve). However, if we only measure the output C on an arbitrary scale, we cannot find M or make this material balance check.

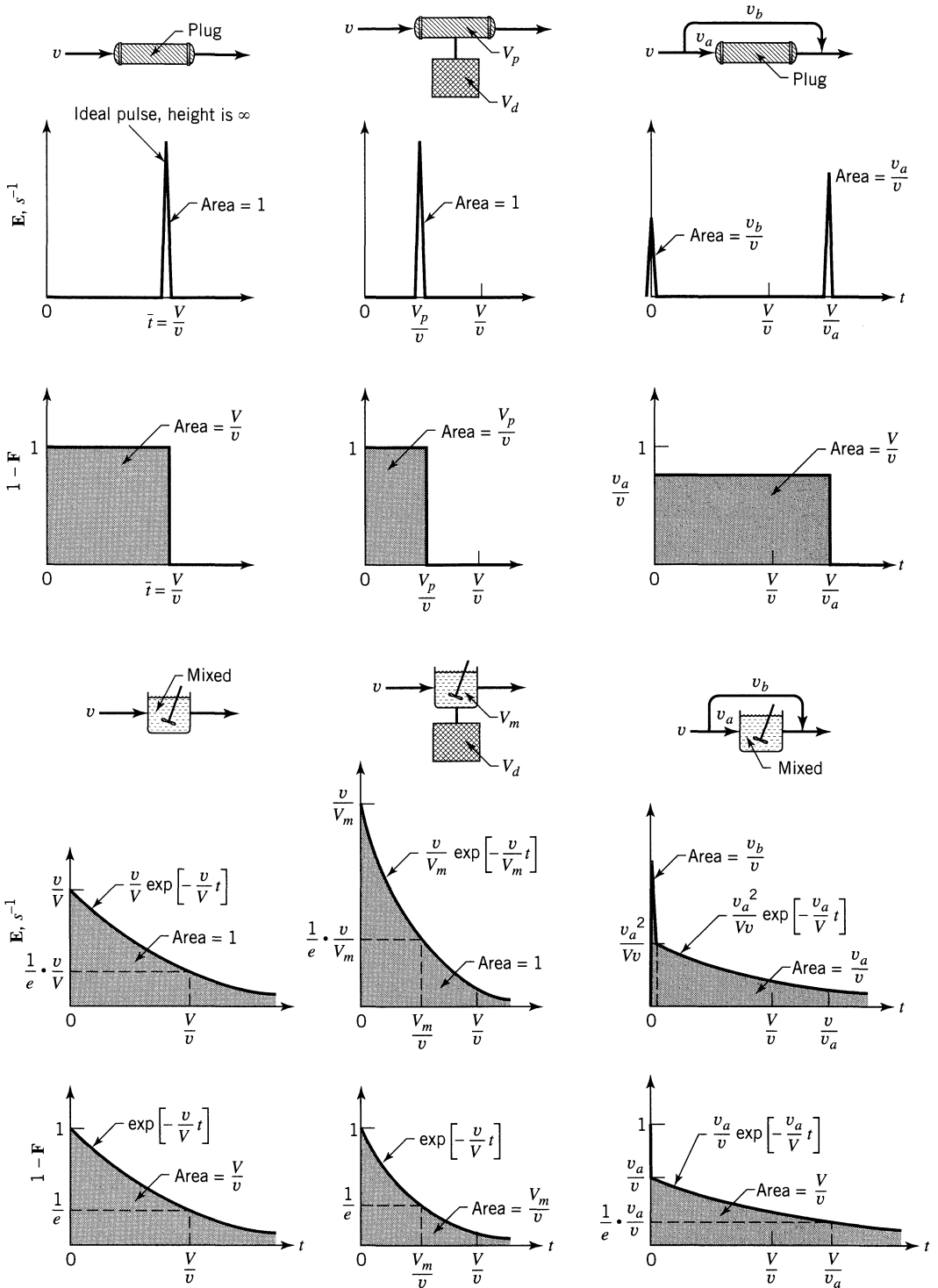


Figure 12.1 Various compartment flow models.

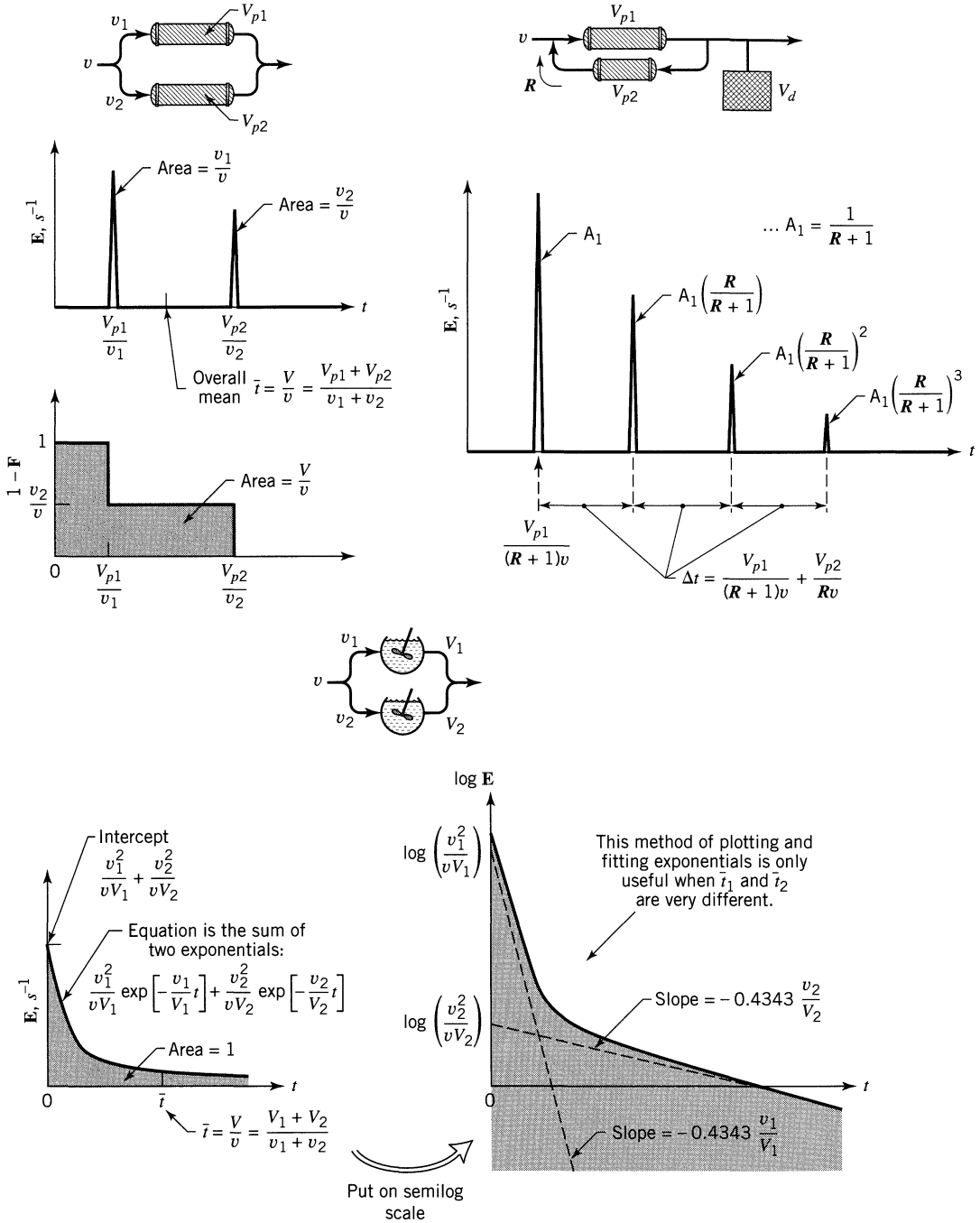


Figure 12.1 (Continued)

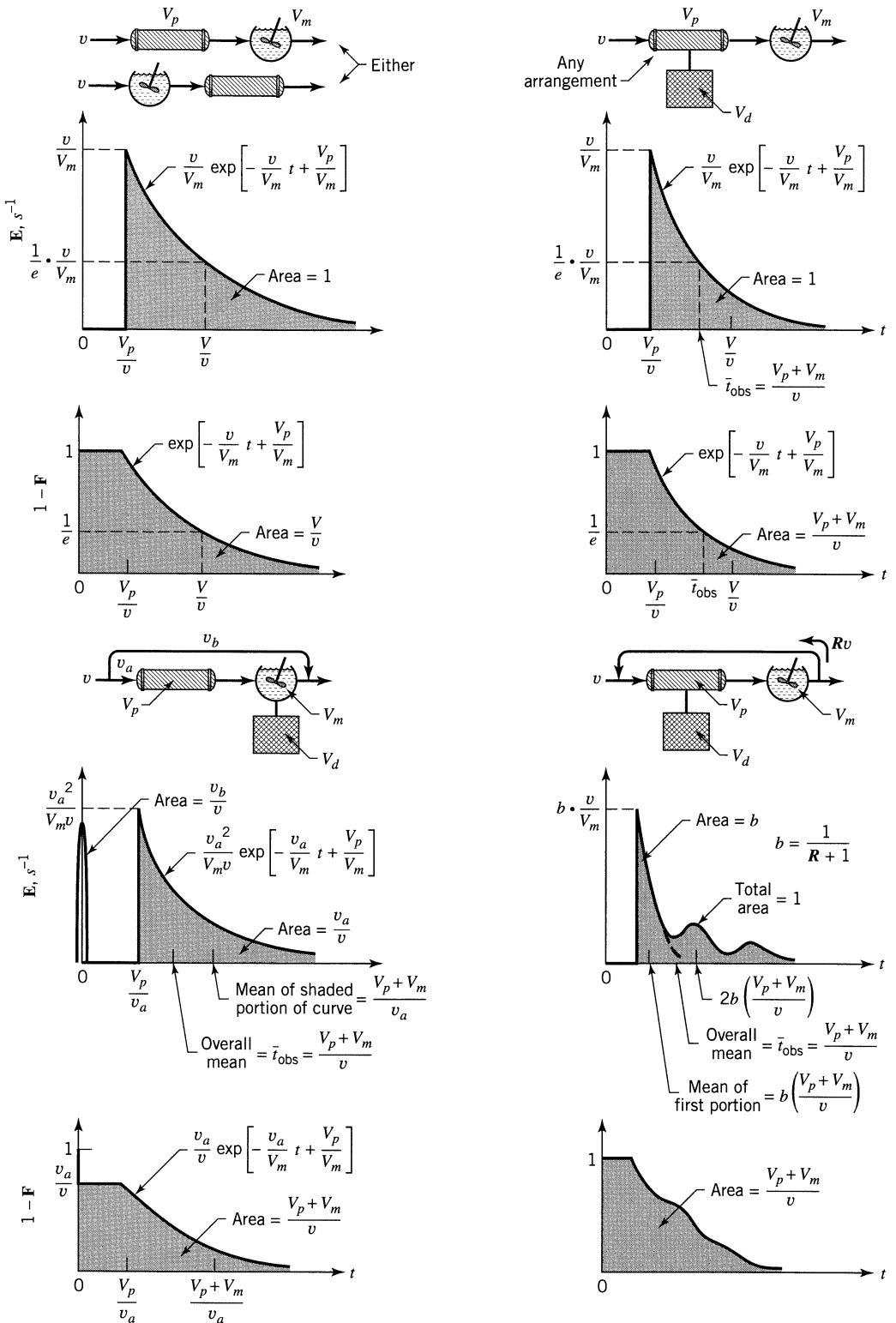


Figure 12.1 (Continued)

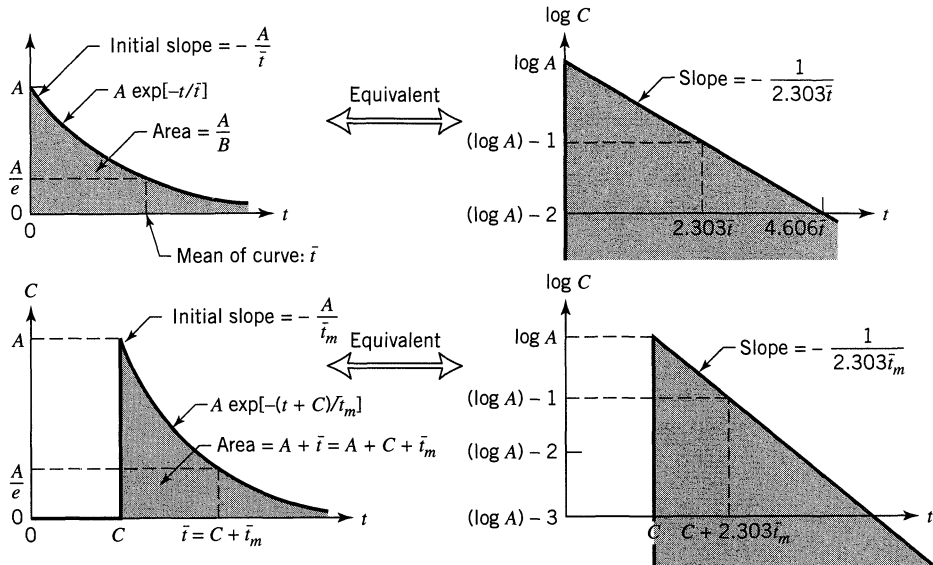


Figure 12.2 Properties of exponential decay tracer curves.

- (b) We must know both V and v if we want to properly evaluate all the elements of a model, including dead spaces. If we only measure \bar{t}_{obs} , we cannot find the size of these stagnant regions and must ignore them in our model building. Thus

$$\begin{array}{l}
 \text{If the real vessel} \\
 \text{has dead spaces:} \\
 \\
 \text{If the real vessel} \\
 \text{has no dead spaces:}
 \end{array}
 \quad
 \begin{array}{l}
 \bar{t}_{\text{obs}} < \bar{t} \\
 \\
 \bar{t}_{\text{obs}} = \bar{t}
 \end{array}
 \quad
 \cdots \text{ where }
 \begin{cases}
 \bar{t} = \frac{V}{v} \\
 \bar{t}_{\text{obs}} = \frac{V_{\text{active}}}{v}
 \end{cases}$$

- (c) The semilog plot is a convenient tool for evaluating the flow parameters of a mixed flow compartment. Just draw the tracer response curve on this plot, find the slope and intercept and this gives the quantities A , B , and C , as shown in Fig. 12.2.

Diagnosing Reactor Ills

These combined models are useful for diagnostic purposes, to pinpoint faulty flow and suggest causes. For example, if you expect plug flow and you know $\bar{t} = V/v$, Fig. 12.3 shows what you could find.

If you expect mixed flow, Fig. 12.4 shows what you may find.

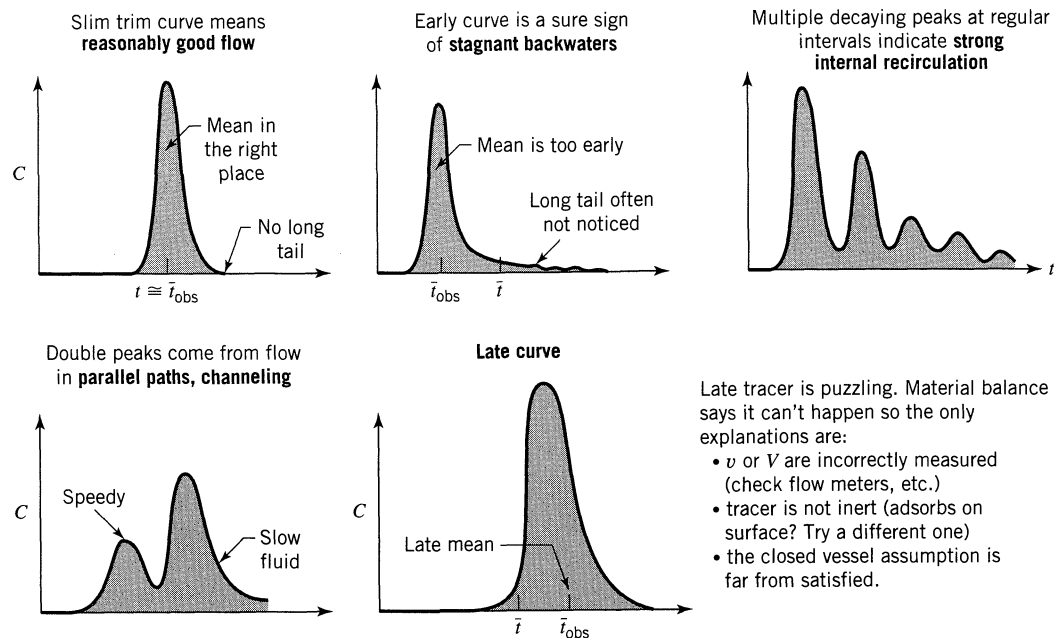


Figure 12.3 Misbehaving plug flow reactors.

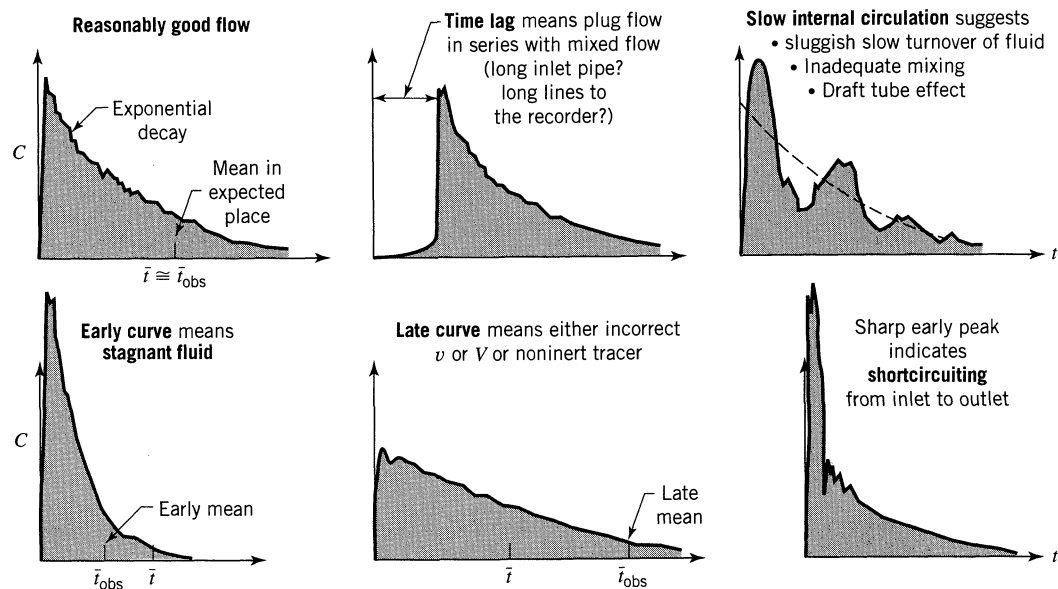


Figure 12.4 Misbehaving mixed flow reactors.

EXAMPLE 12.1 BEHAVIOR OF A G/L CONTACTOR

From the measured pulse tracer response curves (see figure), find the fraction of gas, of flowing liquid, and of stagnant liquid in the gas-liquid contactor shown in Fig. E12.1.

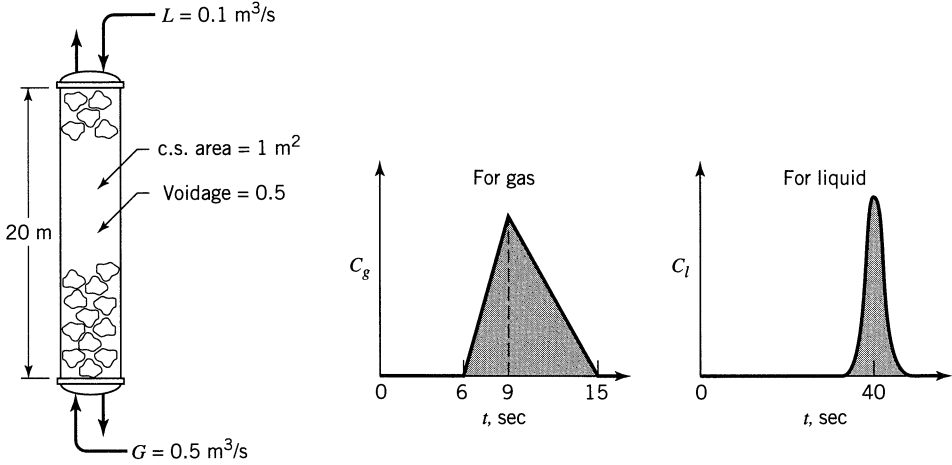


Figure E12.1

SOLUTION

To find V_g , V_l , and V_{stag} , first calculate \bar{t}_g and \bar{t}_l from the tracer curves. Thus from Fig. E12.1

$$\bar{t}_g = \frac{\sum tC}{\sum C} = \frac{8(9-6)(h/2) + 11(15-9)(h/2)}{(15-6)(h/2)} = 10 \text{ s}$$

and

$$\bar{t}_l = 40 \text{ s.}$$

Therefore

$$V_g = \bar{t}_g v_g = (10)(0.5) = 5 \text{ m}^3$$

$$V_l = \bar{t}_l v_l = 40(0.1) = 4 \text{ m}^3$$

In terms of void volume

$$\left. \begin{array}{l} \% G = 50\% \\ \% L = 40\% \\ \% \text{ stagnant} = 10\% \end{array} \right\} \leftarrow$$

EXAMPLE 12.2 CURING A MISBEHAVING REACTOR

At present our 6-m³ tank reactor gives 75% conversion for the first order reaction $A \rightarrow R$. However, since the reactor is stirred with an underpowered paddle turbine, we suspect incomplete mixing and poor flow patterns in the vessel. A pulse tracer shows that this is so and gives the flow model sketched in Fig. E12.2. What conversion can we expect if we replace the stirrer with one powerful enough to ensure mixed flow?

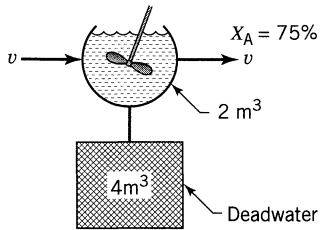


Figure E12.2

SOLUTION

Let subscript 1 represent today's reactor and subscript 2 represent the cured reactor. At present, from Chapter 5 for the MFR, we have

$$k\tau = \frac{C_{A0} - C_A}{C_A} = \frac{C_{A0}}{C_A} - 1 = \frac{1}{0.25} - 1 = 3$$

$$\text{But } k\tau_2 = 3 \quad k\tau_1 = 3 \times 3 = 9$$

Therefore

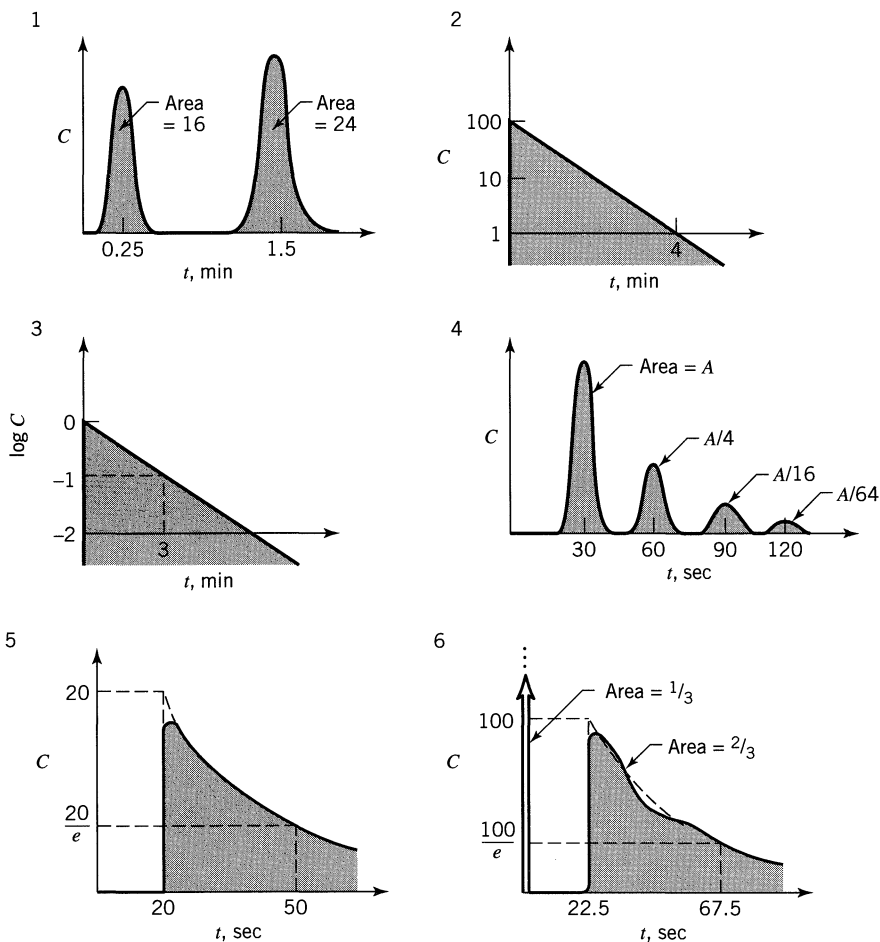
$$\frac{C_{A2}}{C_{A0}} = \frac{1}{k\tau_2 + 1} = \frac{1}{9 + 1} = 0.1$$

or

$$\underline{\underline{X_{A2} = 90\%}}$$

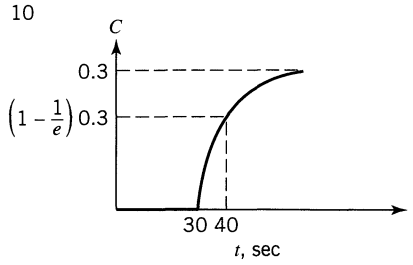
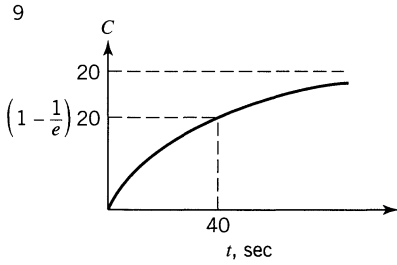
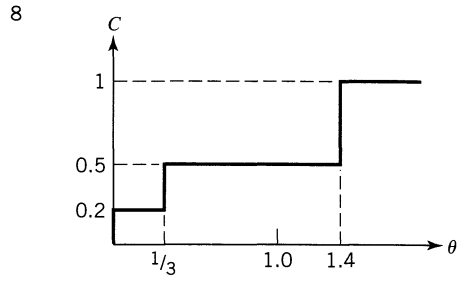
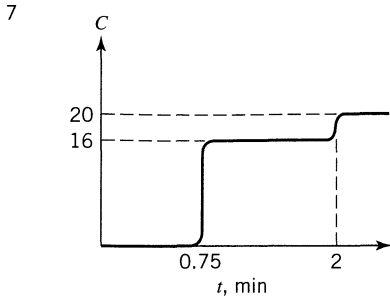
PROBLEMS

12.1. to 12.6. A pulse of concentrated NaCl solution is introduced as tracer into the fluid entering a vessel ($V = 1 \text{ m}^3, v = 1 \text{ m}^3/\text{min}$) and the concentration of tracer is measured in the fluid leaving the vessel. Develop a flow model to represent the vessel from the tracer output data sketched in Figs. P12.1 to P12.6.



Figures P12.1 through P12.6

12.7. to 12.10. A step input tracer test (switching from tap water to salt water, measuring the conductivity of fluid leaving the vessel) is used to explore the flow pattern of fluid through the vessel ($V = 1 \text{ m}^3, v = 1 \text{ m}^3/\text{min}$). Devise a flow model to represent the vessel from the data of Figs. P12.7 to P12.10.



Figures P12.7 through P12.10

12.11. The second order aqueous reaction $A + B \rightarrow R + S$ is run in a large tank reactor ($V = 6 \text{ m}^3$) and for an equimolar feed stream ($C_{A0} = C_{B0}$) conversion of reactants is 60%. Unfortunately, agitation in our reactor is rather inadequate and tracer tests of the flow within the reactor give the flow model sketched in Fig. P12.11. What size of mixed flow reactor will equal the performance of our present unit?

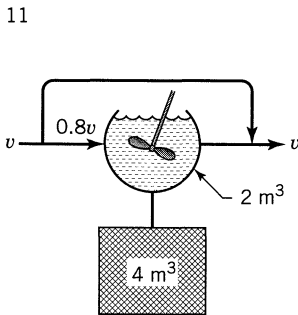


Figure P12.11

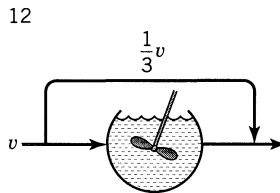


Figure P12.12

12.12. Repeat Example 12.2 with one change: The model for the present flow is as shown in Fig. P12.12.

Chapter 13

The Dispersion Model

Choice of Models

Models are useful for representing flow in real vessels, for scale up, and for diagnosing poor flow. We have different kinds of models depending on whether flow is close to plug, mixed, or somewhere in between.

Chapters 13 and 14 deal primarily with small deviations from plug flow. There are two models for this: the **dispersion model** and the **tanks-in-series** model. Use the one that is comfortable for you. They are roughly equivalent. These models apply to turbulent flow in pipes, laminar flow in very long tubes, flow in packed beds, shaft kilns, long channels, screw conveyers, etc.

For laminar flow in short tubes or laminar flow of viscous materials these models may not apply, and it may be that the parabolic velocity profile is the main cause of deviation from plug flow. We treat this situation, called the **pure convection model**, in Chapter 15.

If you are unsure which model to use go to the chart at the beginning of Chapter 15. It will tell you which model should be used to represent your setup.

13.1 AXIAL DISPERSION

Suppose an ideal pulse of tracer is introduced into the fluid entering a vessel. The pulse spreads as it passes through the vessel, and to characterize the spreading according to this model (see Fig. 13.1), we assume a diffusion-like process superimposed on plug flow. We call this **dispersion** or longitudinal dispersion to distinguish it from molecular diffusion. The dispersion coefficient **D** (m^2/s) represents this spreading process. Thus

- large **D** means rapid spreading of the tracer curve
- small **D** means slow spreading
- **D** = 0 means no spreading, hence plug flow

Also

$\left(\frac{\mathbf{D}}{uL}\right)$ is the dimensionless group characterizing the spread in the whole vessel.

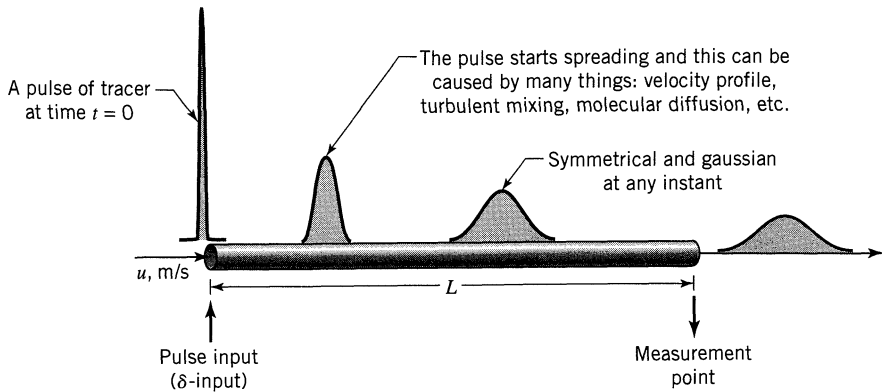


Figure 13.1 The spreading of tracer according to the dispersion model.

We evaluate \mathbf{D} or \mathbf{D}/uL by recording the shape of the tracer curve as it passes the exit of the vessel. In particular, we measure

\bar{t} = mean time of passage, or when the curve passes by the exit

σ^2 = variance, or a measure of the spread of the curve

These measures, \bar{t} and σ^2 , are directly linked by theory to \mathbf{D} and \mathbf{D}/uL . The mean, for continuous or discrete data, is defined as

$$\bar{t} = \frac{\int_0^{\infty} t C dt}{\int_0^{\infty} C dt} = \frac{\sum t_i C_i \Delta t_i}{\sum C_i \Delta t_i} \quad (1)$$

The variance is defined as

$$\sigma^2 = \frac{\int_0^{\infty} (t - \bar{t})^2 C dt}{\int_0^{\infty} C dt} = \frac{\int_0^{\infty} t^2 C dt}{\int_0^{\infty} C dt} - \bar{t}^2 \quad (2)$$

or in discrete form

$$\sigma^2 \cong \frac{\sum (t_i - \bar{t})^2 C_i \Delta t_i}{\sum C_i \Delta t_i} = \frac{\sum t_i^2 C_i \Delta t_i}{\sum C_i \Delta t_i} - \bar{t}^2 \quad (3)$$

The variance represents the square of the spread of the distribution as it passes the vessel exit and has units of (time)². It is particularly useful for matching experimental curves to one of a family of theoretical curves. Figure 13.2 illustrates these terms.

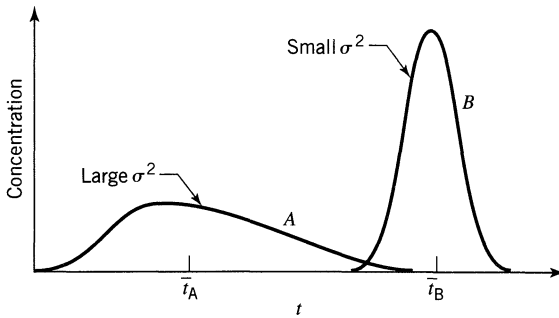


Figure 13.2

Consider plug flow of a fluid, on top of which is superimposed some degree of backmixing, the magnitude of which is independent of position within the vessel. This condition implies that there exist no stagnant pockets and no gross bypassing or short-circuiting of fluid in the vessel. This is called the dispersed plug flow model, or simply the **dispersion model**. Figure 13.3 shows the conditions visualized. Note that with varying intensities of turbulence or intermixing the predictions of this model should range from plug flow at one extreme to mixed flow at the other. As a result the reactor volume for this model will lie between those calculated for plug and mixed flow.

Since the mixing process involves a shuffling or redistribution of material either by slippage or eddies, and since this is repeated many, many times during the flow of fluid through the vessel we can consider these disturbances to be statistical in nature, somewhat as in molecular diffusion. For molecular diffusion in the x -direction the governing differential equation is given by Fick's law:

$$\frac{\partial C}{\partial t} = \mathcal{D} \frac{\partial^2 C}{\partial x^2} \quad (4)$$

where \mathcal{D} , the coefficient of molecular diffusion, is a parameter which uniquely characterizes the process. In an analogous manner we may consider all the contributions to intermixing of fluid flowing in the x -direction to be described

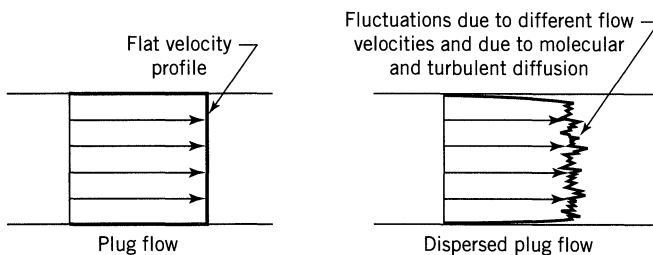


Figure 13.3 Representation of the dispersion (dispersed plug flow) model.

by a similar form of expression, or

$$\frac{\partial C}{\partial t} = \mathbf{D} \frac{\partial^2 C}{\partial x^2} \quad (5)$$

where the parameter \mathbf{D} , which we call the *longitudinal* or *axial dispersion coefficient*, uniquely characterizes the degree of backmixing during flow. We use the terms *longitudinal* and *axial* because we wish to distinguish mixing in the direction of flow from mixing in the lateral or radial direction, which is not our primary concern. These two quantities may be quite different in magnitude. For example, in streamline flow of fluids through pipes, axial mixing is mainly due to fluid velocity gradients, whereas radial mixing is due to molecular diffusion alone.

In dimensionless form where $z = (ut + x)/L$ and $\theta = t/\bar{t} = tu/L$, the basic differential equation representing this dispersion model becomes

$$\frac{\partial C}{\partial \theta} = \left(\frac{\mathbf{D}}{uL} \right) \frac{\partial^2 C}{\partial z^2} - \frac{\partial C}{\partial z} \quad (6)$$

where the dimensionless group $\left(\frac{\mathbf{D}}{uL} \right)$, called the vessel dispersion number, is the parameter that measures the extent of axial dispersion. Thus

$$\begin{aligned} \frac{\mathbf{D}}{uL} \rightarrow 0 & \quad \text{negligible dispersion, hence plug flow} \\ \frac{\mathbf{D}}{uL} \rightarrow \infty & \quad \text{large dispersion, hence mixed flow} \end{aligned}$$

This model usually represents quite satisfactorily flow that deviates not too greatly from plug flow, thus real packed beds and tubes (long ones if flow is streamline).

Fitting the Dispersion Model for Small Extents of Dispersion, $\mathbf{D}/uL < 0.01$

If we impose an idealized pulse onto the flowing fluid then dispersion modifies this pulse as shown in Fig. 13.1. For small extents of dispersion (if \mathbf{D}/uL is small) the spreading tracer curve does not significantly change in shape as it passes the measuring point (during the time it is being measured). Under these conditions the solution to Eq. 6 is not difficult and gives the symmetrical curve of Eq. 7 shown in Figs. 13.1 and 13.4.

$$C = \frac{1}{2\sqrt{\pi(\mathbf{D}/uL)}} \exp \left[-\frac{(1-\theta)^2}{4(\mathbf{D}/uL)} \right] \quad (7)$$

This represents a family of gaussian curves, also called error or Normal curves.

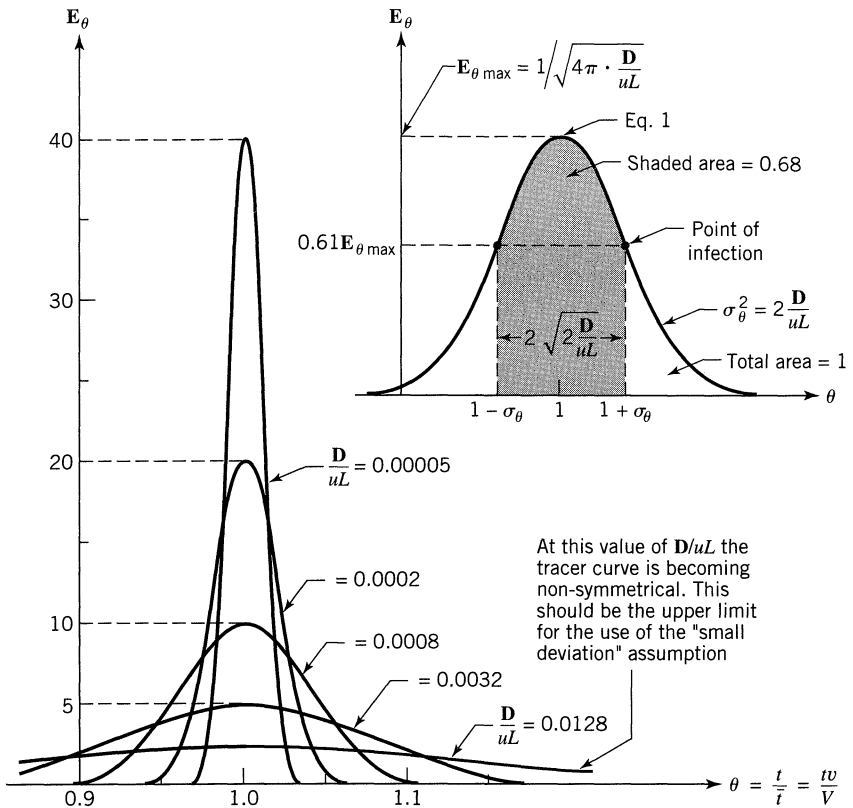


Figure 13.4 Relationship between D/uL and the dimensionless E_θ curve for small extents of dispersion, Eq. 7.

The equations representing this family are

$$\begin{aligned}
 E_\theta &= \bar{t} \cdot E = \frac{1}{\sqrt{4\pi(D/uL)}} \exp \left[-\frac{(1-\theta)^2}{4(D/uL)} \right] \\
 E &= \sqrt{\frac{u^3}{4\pi DL}} \exp \left[-\frac{(L-ut)^2}{4DLu} \right] \\
 \bar{t}_E &= \frac{V}{v} = \frac{L}{u} \quad \text{or} \quad \bar{\theta}_E = 1 \quad \text{mean of } E \text{ curve} \\
 \sigma_\theta^2 &= \frac{\sigma_t^2}{\bar{t}^2} = 2 \left(\frac{D}{uL} \right) \quad \text{or} \quad \sigma^2 = 2 \left(\frac{DL}{u^3} \right)
 \end{aligned} \tag{8}$$

Note that D/uL is the one parameter of this curve. Figure 13.4 shows a number of ways to evaluate this parameter from an experimental curve: by calculating its variance, by measuring its maximum height or its width at the point of inflection, or by finding that width which includes 68% of the area.

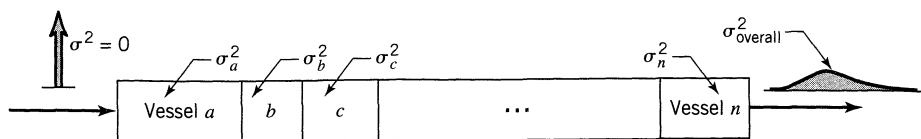


Figure 13.5 Illustration of additivity of means and of variances of the \mathbf{E} curves of vessels a, b, \dots, n .

Also note how the tracer spreads as it moves down the vessel. From the variance expression of Eq. 8 we find that

$$\sigma^2 \propto L \quad \text{or} \quad \left(\frac{\text{width of tracer}}{\text{curve}} \right)^2 \propto L$$

Fortunately, for small extents of dispersion numerous simplifications and approximations in the analysis of tracer curves are possible. First, the shape of the tracer curve is insensitive to the boundary condition imposed on the vessel, whether closed or open (see above Eq. 11.1). So for both closed and open vessels $C_{\text{pulse}} = \mathbf{E}$ and $C_{\text{step}} = \mathbf{F}$.

For a series of vessels the \bar{t} and σ^2 of the individual vessels are additive, thus, referring to Fig. 13.5 we have

$$\bar{t}_{\text{overall}} = \bar{t}_a + \bar{t}_b + \dots = \frac{V_a}{v} + \frac{V_b}{v} + \dots = \left(\frac{L}{u} \right)_a + \left(\frac{L}{u} \right)_b + \dots \quad (9)$$

and

$$\sigma_{\text{overall}}^2 = \sigma_a^2 + \sigma_b^2 + \dots = 2 \left(\frac{DL}{u^3} \right)_a + 2 \left(\frac{DL}{u^3} \right)_b + \dots \quad (10)$$

The additivity of times is expected, but the additivity of variance is not generally expected. This is a useful property since it allows us to subtract for the distortion of the measured curve caused by input lines, long measuring leads, etc.

This additivity property of variances also allows us to treat any one-shot tracer input, no matter what its shape, and to extract from it the variance of the \mathbf{E} curve of the vessel. So, on referring to Fig. 13.6, if we write for a one-shot input

$$\Delta\sigma^2 = \sigma_{\text{out}}^2 - \sigma_{\text{in}}^2 \quad (11)$$

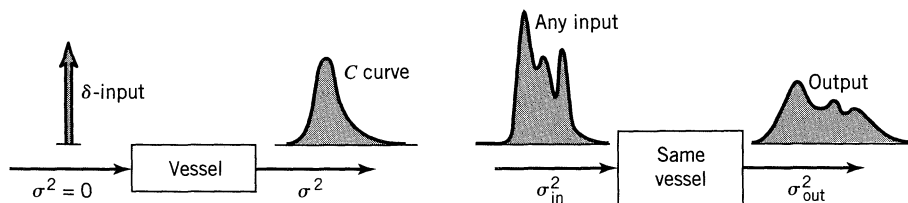


Figure 13.6 Increase in variance is the same in both cases, or $\sigma^2 = \sigma_{\text{out}}^2 - \sigma_{\text{in}}^2 = \Delta\sigma^2$.

Aris (1959) has shown, for small extents of dispersion, that

$$\frac{\sigma_{\text{out}}^2 - \sigma_{\text{in}}^2}{(\bar{t}_{\text{out}} - \bar{t}_{\text{in}})^2} = \frac{\Delta\sigma^2}{(\Delta\bar{t})^2} = \Delta\sigma_{\theta}^2 = 2\left(\frac{\mathbf{D}}{uL}\right) \quad (12)$$

Thus no matter what the shape of the input curve, the \mathbf{D}/uL value for the vessel can be found.

The goodness of fit for this simple treatment can only be evaluated by comparison with the more exact but much more complex solutions. From such a comparison we find that the maximum error in estimate of \mathbf{D}/uL is given by

$$\text{error} < 5\% \text{ when } \frac{\mathbf{D}}{uL} < 0.01$$

Large Deviation from Plug Flow, $\frac{\mathbf{D}}{uL} > 0.01$

Here the pulse response is broad and it passes the measurement point slowly enough that it changes shape—it spreads—as it is being measured. This gives a nonsymmetrical \mathbf{E} curve.

An additional complication enters the picture for large \mathbf{D}/uL : What happens right at the entrance and exit of the vessel strongly affects the shape of the tracer curve as well as the relationship between the parameters of the curve and \mathbf{D}/uL .

Let us consider two types of boundary conditions: either the flow is undisturbed as it passes the entrance and exit boundaries (we call this the open b.c.), or you have plug flow outside the vessel up to the boundaries (we call this the closed b.c.). This leads to four combinations of boundary conditions, closed-closed, open-open, and mixed. Figure 13.7 illustrates the closed and open extremes, whose RTD curves are designated as \mathbf{E}_{cc} and \mathbf{E}_{oo} .

Now only one boundary condition gives a tracer curve which is identical to the \mathbf{E} function and which fits all the mathematics of Chapter 11, and that is the closed vessel. For all other boundary conditions you do not get a proper RTD.

In all cases you can evaluate \mathbf{D}/uL from the parameters of the tracer curves; however, each curve has its own mathematics. Let us look at the tracer curves for closed and for the open boundary conditions.

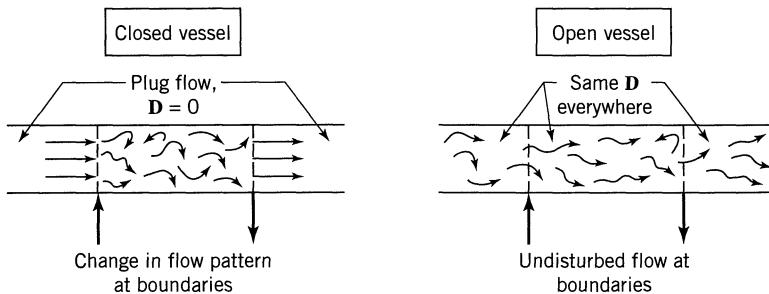


Figure 13.7 Various boundary conditions used with the dispersion model.

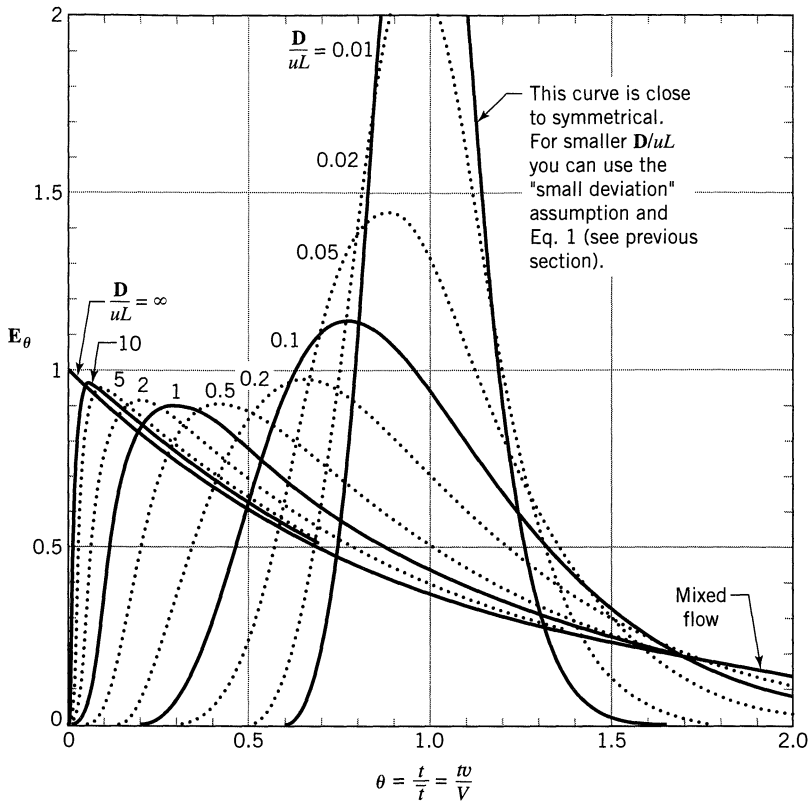


Figure 13.8 Tracer response curves for closed vessels and large deviations from plug flow.

Closed Vessel. Here an analytic expression for the **E** curve is not available. However, we can construct the curve by numerical methods, see Fig. 13.8, or evaluate its mean and variance exactly, as was first done by van der Laan (1958). Thus

$$\begin{aligned}
 \bar{t}_E = \bar{t} = \frac{V}{v} \quad \dots \text{ or } \dots \quad \bar{\theta}_E = \frac{\bar{t}_E}{\bar{t}} = \frac{\bar{t}_E v}{V} = 1 \\
 \sigma_\theta^2 = \frac{\sigma_t^2}{\bar{t}^2} = 2\left(\frac{D}{uL}\right) - 2\left(\frac{D}{uL}\right)^2 [1 - e^{-uL/D}]
 \end{aligned}
 \tag{13}$$

Open Vessel. This represents a convenient and commonly used experimental device, a section of long pipe (see Fig. 13.9). It also happens to be the only physical situation (besides small D/uL) where the analytical expression for the **E** curve is not too complex. The results are given by the response curves shown

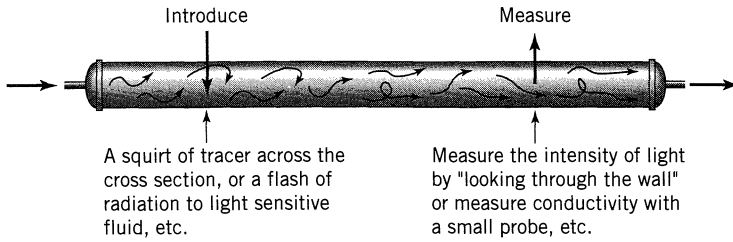


Figure 13.9 The open-open vessel boundary condition.

in Fig. 13.10, and by the following equations, first derived by Levenspiel and Smith (1957).

$$E_{\theta,oo} = \frac{1}{\sqrt{4\pi(D/uL)}} \exp\left[-\frac{(1-\theta)^2}{4\theta(D/uL)}\right] \quad (14)$$

$$E_{t,oo} = \frac{u}{\sqrt{4\pi Dt}} \exp\left[-\frac{(L-ut)^2}{4Dt}\right]$$

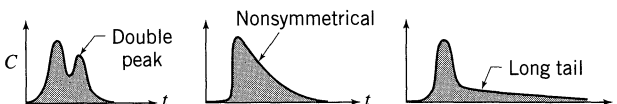
$$\bar{\theta}_{E,oo} = \frac{\bar{t}_{E,oo}}{\bar{t}} = 1 + 2\left(\frac{D}{uL}\right) \quad \dots \text{or} \dots \quad t_{E,oo} = \frac{V}{v} \left[1 + 2\frac{D}{uL}\right] \quad (15)$$

open-open vessel

$$\sigma_{\theta,oo}^2 = \frac{\sigma_{t,oo}^2}{\bar{t}^2} = 2\frac{D}{uL} + 8\left(\frac{D}{uL}\right)^2$$

Comments

- For small D/uL the curves for the different boundary conditions all approach the “small deviation” curve of Eq. 8. At larger D/uL the curves differ more and more from each other.
- To evaluate D/uL either match the measured tracer curve or the measured σ^2 to theory. Matching σ^2 is simplest, though not necessarily best; however, it is often used. But be sure to use the right boundary conditions.
- If the flow deviates greatly from plug (D/uL large) chances are that the real vessel doesn't meet the assumption of the model (a lot of independent random fluctuations). Here it becomes questionable whether the model should even be used. I hesitate when $D/uL > 1$.
- You must always ask whether the model should be used. You can always match σ^2 values, but if the shape looks wrong, as shown in the accompanying sketches, don't use this model, use some other model.



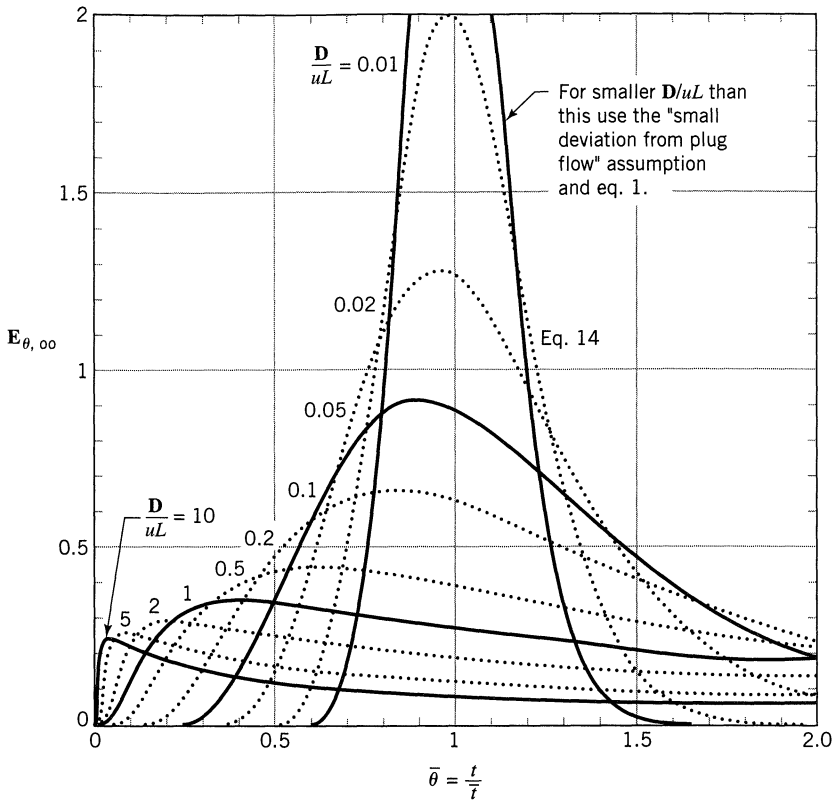


Figure 13.10 Tracer response curves for “open” vessels having large deviations from plug flow.

- (e) For large D/uL the literature is profuse and conflicting, primarily because of the unstated and unclear assumptions about what is happening at the vessel boundaries. The treatment of end conditions is full of mathematical subtleties as noted above, and the additivity of variances is questionable. Because of all this we should be very careful in using the dispersion model where backmixing is large, particularly if the system is not closed.
- (f) We will not discuss the equations and curves for the open-closed or closed-open boundary conditions. These can be found in Levenspiel (1996).

Step Input of Tracer

Here the output F curve is S-shaped and is obtained by integrating the corresponding E curve. Thus at any time t or θ

$$F = \int_0^{\theta} E_{\theta} d\theta = \int_0^t E dt \quad (16)$$

The shape of the F curve depends on D/uL and the boundary conditions for the vessel. Analytical expressions are not available for any of the F curves;

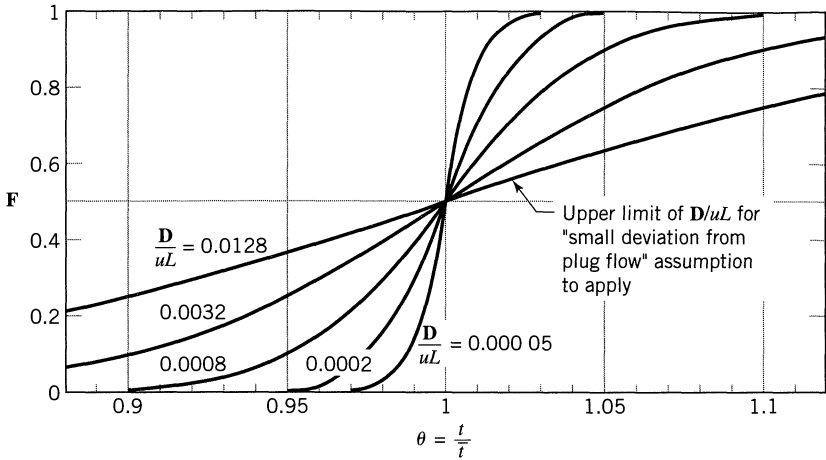


Figure 13.11 Step response curves for small deviations from plug flow.

however, their graphs can be constructed. Two typical cases are displayed below, in Figs. 13.11 and 13.13.

Small Deviation from Plug Flow, $D/uL < 0.01$ From Eqs. 8 and 16 we can find the curves of Fig. 13.11, as shown. For these small deviations from plug flow we can find D/uL directly by plotting the experimental data on probability graph paper as indicated in Fig. 13.12. Example 13.2 shows in detail how this is done.

Step Response for Large Dispersion, $D/uL > 0.01$. For large deviations from plug flow, the problem of boundary conditions must be considered, the resulting S-shaped response curves are not symmetrical, their equations are not available, and they are best analyzed by first differentiating them to give the corresponding C_{pulse} curve. Figure 13.13 shows an example of this family of curves.

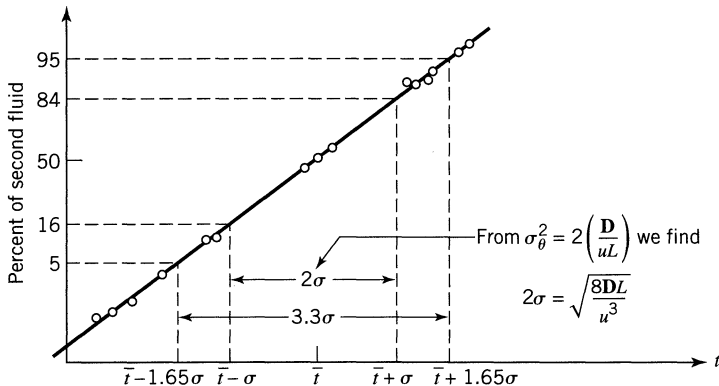


Figure 13.12 Probability plot of a step response signal. From this we find D/uL directly.

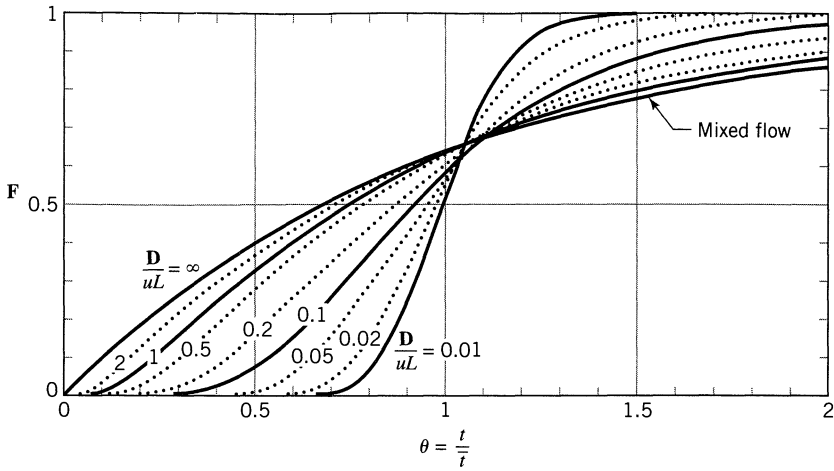


Figure 13.13 Step response curves for large deviations from plug flow in closed vessels.

Comments

- (a) One direct commercial application of the step experiment is to find the zone of intermixing—the contaminated width—between two fluids of somewhat similar properties flowing one after the other in a long pipeline. Given D/uL we find this from the probability plot of Fig. 13.12. Design charts to ease the calculation are given by Levenspiel (1958a).
- (b) Should you use a pulse or step injection experiment? Sometimes one type of experiment is naturally more convenient for one of many reasons. In such a situation this question does not arise. But when you do have a choice, then the pulse experiment is preferred because it gives a more “honest” result. The reason is that the F curve integrates effects; it gives a smooth good-looking curve which could well hide real effects. For example, Fig. 13.14 shows the corresponding E and F curves for a given vessel.

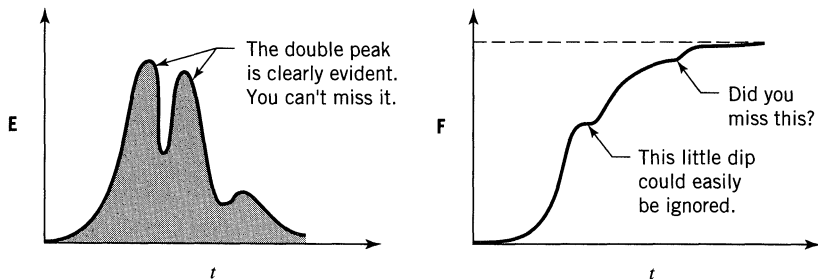


Figure 13.14 Sensitivity of the E and F curves for the same flow.

EXAMPLE 13.1 *D_uL FROM A C_{pulse} CURVE*

On the assumption that the closed vessel of Example 11.1, Chapter 11, is well represented by the dispersion model, calculate the vessel dispersion number D_{uL} . The C versus t tracer response of this vessel is

$t, \text{ min}$	0	5	10	15	20	25	30	35
$C_{\text{pulse}}, \text{ gm/liter}$	0	3	5	5	4	2	1	0

SOLUTION

Since the C curve for this vessel is broad and unsymmetrical, see Fig. 11.E1, let us guess that dispersion is too large to allow use of the simplification leading to Fig. 13.4. We thus start with the variance matching procedure of Eq. 18. The mean and variance of a continuous distribution measured at a finite number of equidistant locations is given by Eqs. 3 and 4 as

$$\bar{t} = \frac{\sum t_i C_i}{\sum C_i}$$

and

$$\sigma^2 = \frac{\sum t_i^2 C_i}{\sum C_i} - \bar{t}^2 = \frac{\sum t_i^2 C_i}{\sum C_i} - \left[\frac{\sum t_i C_i}{\sum C_i} \right]^2$$

Using the original tracer concentration-time data, we find

$$\sum C_i = 3 + 5 + 5 + 4 + 2 + 1 = 20$$

$$\sum t_i C_i = (5 \times 3) + (10 \times 5) + \dots + (30 \times 1) = 300 \text{ min}$$

$$\sum t_i^2 C_i = (25 \times 3) + (100 \times 5) + \dots + (900 \times 1) = 5450 \text{ min}^2$$

Therefore

$$\bar{t} = \frac{300}{20} = 15 \text{ min}$$

$$\sigma^2 = \frac{5450}{20} - \left(\frac{300}{20} \right)^2 = 47.5 \text{ min}^2$$

and

$$\sigma_{\theta}^2 = \frac{\sigma^2}{\bar{t}^2} = \frac{47.5}{(15)^2} = 0.211$$

Now for a closed vessel Eq. 13 relates the variance to \mathbf{D}/uL . Thus

$$\sigma_{\theta}^2 = 0.211 = 2 \frac{\mathbf{D}}{uL} - 2 \left(\frac{\mathbf{D}}{uL} \right)^2 (1 - e^{-uL/\mathbf{D}})$$

Ignoring the second term on the right, we have as a first approximation

$$\frac{\mathbf{D}}{uL} \cong 0.106$$

Correcting for the term ignored we find by trial and error that

$$\frac{\mathbf{D}}{uL} = \underline{\underline{0.120}}$$

Our original guess was correct: This value of \mathbf{D}/uL is much beyond the limit where the simple gaussian approximation should be used. ■

EXAMPLE 13.2 \mathbf{D}/uL FROM AN F CURVE

von Rosenberg (1956) studied the displacement of benzene by *n*-butyrate in a 38 mm diameter packed column 1219 mm long, measuring the fraction of *n*-butyrate in the exit stream by refractive index methods. When graphed, the fraction of *n*-butyrate versus time was found to be S-shaped. This is the **F** curve, and it is shown in Fig. E13.2a for von Rosenberg's run at the lowest flow rate, where $u = 0.0067$ mm/s, which is about 0.5 m/day.

Find the vessel dispersion number of this system.

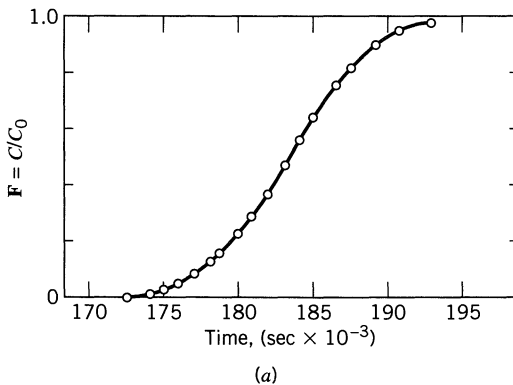
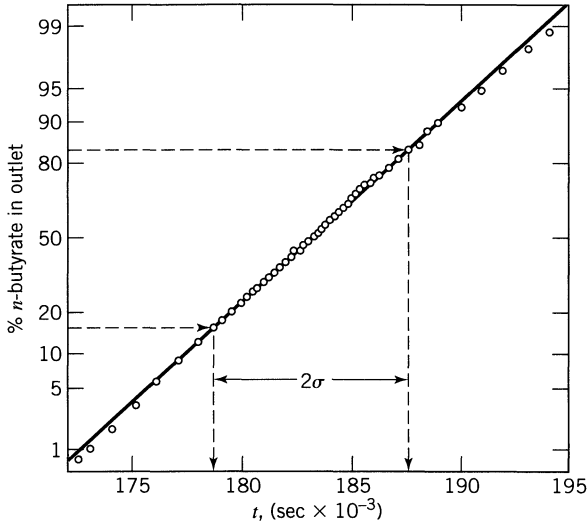


Figure E13.2a From von Rosenberg (1956).

SOLUTION

Instead of taking slopes of the **F** curve to give the **E** curve and then determining the spread of this curve, let us use the probability paper method. So, plotting the data on this paper does actually give close to a straight line, as shown in Fig. E13.2b.



(b)

Figure E13.2b From Levenspiel and Smith (1957).

To find the variance and \mathbf{D}/uL from a probability graph is a simple matter. Just follow the procedure illustrated in Fig. 13.12. Thus Fig. E13.2b shows that

the 16th percentile point falls at $t = 178\,550$ s

the 84th percentile point falls at $t = 187\,750$ s

and this time interval represents 2σ . Therefore the standard deviation is

$$\sigma = \frac{187\,750 - 178\,500}{2} = 4600 \text{ s}$$

We need this standard deviation in dimensionless time units if we are to find **D**. Therefore

$$\sigma_\theta = \frac{\sigma}{\bar{t}} = (4600 \text{ s}) \left(\frac{0.0067 \text{ mm/s}}{1219 \text{ mm}} \right) = 0.0252$$

Hence the variance

$$\sigma_{\theta}^2 = (0.0252)^2 = 0.00064$$

and from Eq. 8

$$\frac{D}{uL} = \frac{\sigma_{\theta}^2}{2} = \underline{\underline{0.00032}}$$

Note that the value of D/uL is well below 0.01, justifying the use of the gaussian approximation to the tracer curve and this whole procedure.

EXAMPLE 13.3 D/uL FROM A ONE-SHOT INPUT

Find the vessel dispersion number in a fixed-bed reactor packed with 0.625-cm catalyst pellets. For this purpose tracer experiments are run in equipment shown in Fig. E13.3.

The catalyst is laid down in a haphazard manner above a screen to a height of 120 cm, and fluid flows downward through this packing. A sloppy pulse of

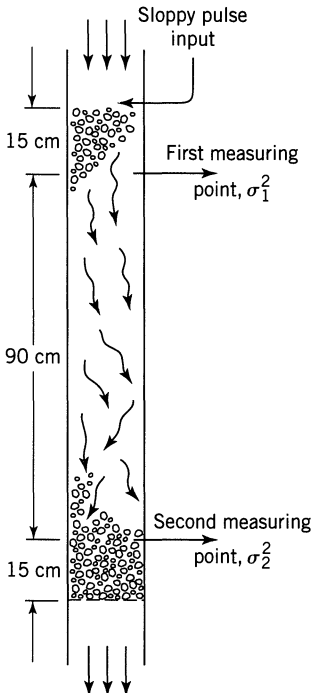


Figure E13.3

radioactive tracer is injected directly above the bed, and output signals are recorded by Geiger counters at two levels in the bed 90 cm apart.

The following data apply to a specific experimental run. Bed voidage = 0.4, superficial velocity of fluid (based on an empty tube) = 1.2 cm/sec, and variances of output signals are found to be $\sigma_1^2 = 39 \text{ sec}^2$ and $\sigma_2^2 = 64 \text{ sec}^2$. Find \mathbf{D}/uL .

SOLUTION

Bischoff and Levenspiel (1962) have shown that as long as the measurements are taken at least two or three particle diameters into the bed, then the open vessel boundary conditions hold closely. This is the case here because the measurements are made 15 cm into the bed. As a result this experiment corresponds to a one-shot input to an open vessel for which Eq. 12 holds. Thus

$$\Delta\sigma^2 = \sigma_2^2 - \sigma_1^2 = 64 - 39 = 25 \text{ sec}^2$$

or in dimensionless form

$$\Delta\sigma_\theta^2 = \Delta\sigma^2 \left(\frac{v}{V}\right)^2 = (25 \text{ sec}^2) \left[\frac{1.2 \text{ cm/sec}}{(90 \text{ cm})(0.4)}\right]^2 = \frac{1}{36}$$

from which the dispersion number is

$$\frac{\mathbf{D}}{uL} = \frac{\Delta\sigma_\theta^2}{2} = \underline{\underline{\frac{1}{72}}}$$

13.2 CORRELATIONS FOR AXIAL DISPERSION

The vessel dispersion number \mathbf{D}/uL is a product of two terms

$$\frac{\mathbf{D}}{uL} = \left(\begin{array}{c} \text{intensity of} \\ \text{dispersion} \end{array}\right) \left(\begin{array}{c} \text{geometric} \\ \text{factor} \end{array}\right) = \left(\frac{\mathbf{D}}{ud}\right) \left(\frac{d}{L}\right)$$

where

$$\frac{\mathbf{D}}{ud} = f \left(\begin{array}{c} \text{fluid} \\ \text{properties} \end{array}\right) \left(\begin{array}{c} \text{flow} \\ \text{dynamics} \end{array}\right) = f \left[\left(\begin{array}{c} \text{Schmidt} \\ \text{no.} \end{array}\right) \left(\begin{array}{c} \text{Reynolds} \\ \text{no.} \end{array}\right) \right]$$

and where

$$d \text{ is a characteristic length} = d_{\text{tube}} \text{ or } d_p$$

Experiments show that the dispersion model well represents flow in packed beds and in pipes. Thus theory and experiment give \mathbf{D}/ud for these vessels. We summarize them in the next three charts.

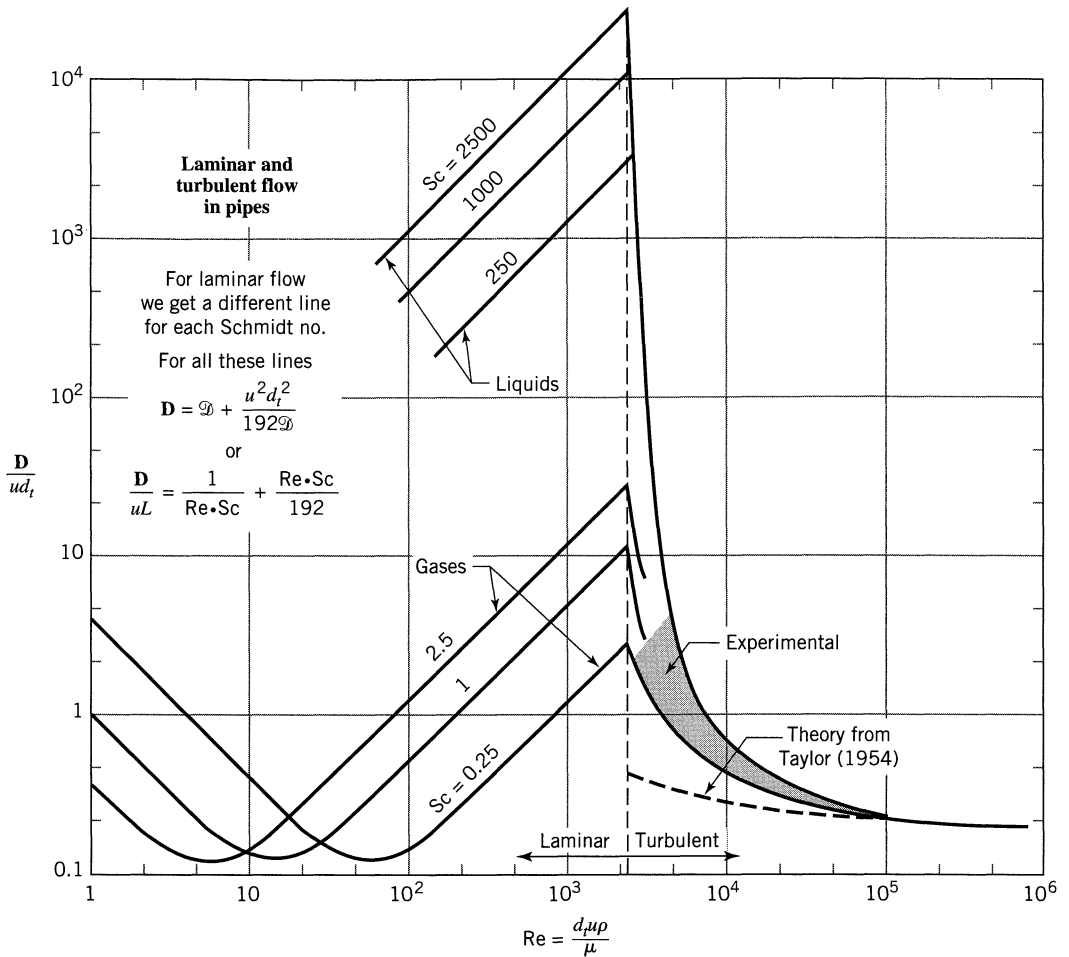


Figure 13.15 Correlation for the dispersion of fluids flowing in pipes, adapted from Levenspiel (1958b).

Figures 13.15 and 13.16 show the findings for flow in pipes. This model represents turbulent flow, but only represents streamline flow in pipes when the pipe is long enough to achieve radial uniformity of a pulse of tracer. For liquids this may require a rather long pipe, and Fig. 13.16 shows these results. Note that molecular diffusion strongly affects the rate of dispersion in laminar flow. At low flow rate it promotes dispersion; at higher flow rate it has the opposite effect.

Correlations similar to these are available or can be obtained for flow in beds of porous and/or adsorbing solids, in coiled tubes, in flexible channels, for pulsating flow, for non-Newtonians, and so on. These are given in Chapter 64 of Levenspiel (1996).

Figure 13.17 shows the findings for packed beds.

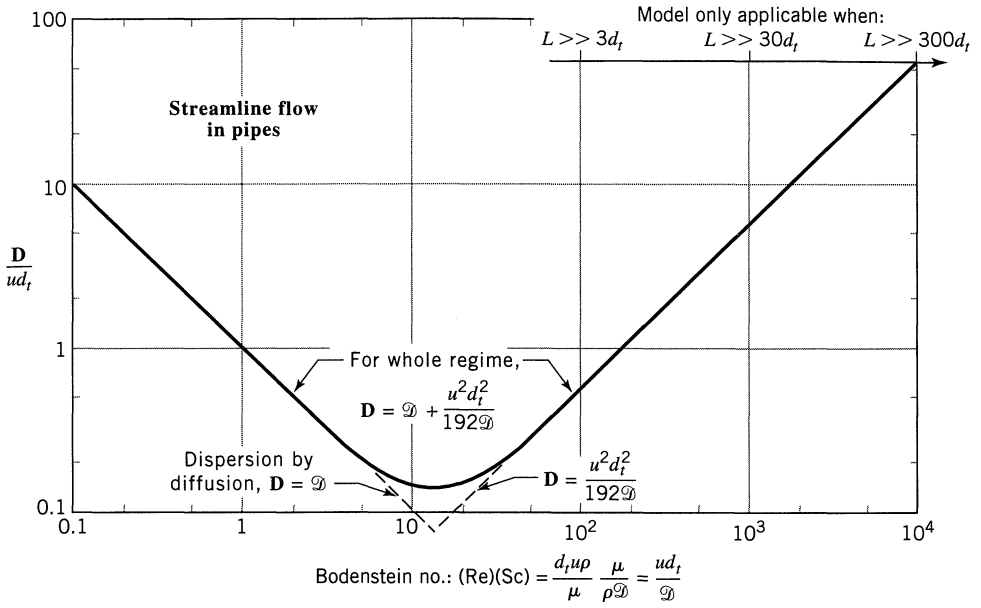


Figure 13.16 Correlation for dispersion for streamline flow in pipes; prepared from Taylor (1953, 1954a) and Aris (1956).

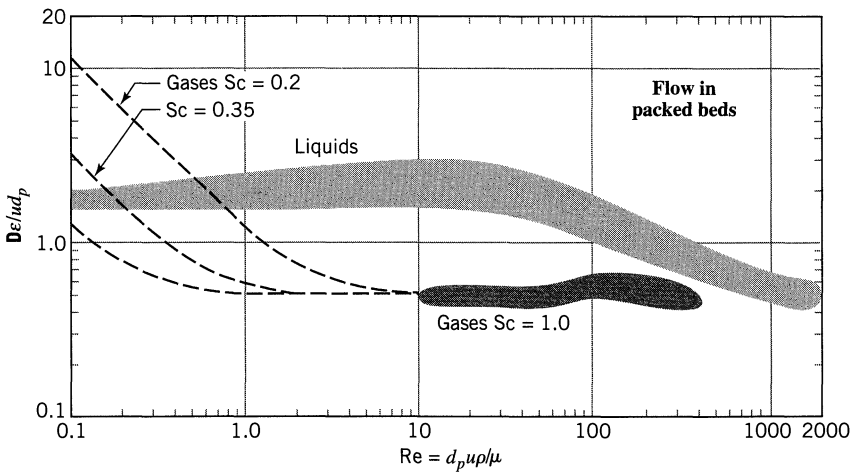
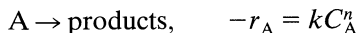


Figure 13.17 Experimental findings on dispersion of fluids flowing with mean axial velocity u in packed beds; prepared in part from Bischoff (1961).

13.3 CHEMICAL REACTION AND DISPERSION

Our discussion has led to the measure of dispersion by a dimensionless group D/ul . Let us now see how this affects conversion in reactors.

Consider a steady-flow chemical reactor of length L through which fluid is flowing at a constant velocity u , and in which material is mixing axially with a dispersion coefficient D . Let an n th-order reaction be occurring.



By referring to an elementary section of reactor as shown in Fig. 13.18, the basic material balance for any reaction component

$$\text{input} = \text{output} + \text{disappearance by reaction} + \text{accumulation} \quad (4.1)$$

becomes for component A, at steady state,

$$(\text{out-in})_{\text{bulk flow}} + (\text{out-in})_{\text{axial dispersion}} + \frac{\text{disappearance}}{\text{by reaction}} + \text{accumulation} = 0 \quad (17)$$

The individual terms (in moles A/time) are as follows:

$$\begin{aligned} \text{entering by bulk flow} &= \left(\frac{\text{moles A}}{\text{volume}} \right) \left(\frac{\text{flow}}{\text{velocity}} \right) \left(\frac{\text{cross-sectional}}{\text{area}} \right) \\ &= C_{A,l} u S, \quad [\text{mol/s}] \end{aligned}$$

$$\text{leaving by bulk flow} = C_{A,l+\Delta l} u S$$

$$\text{entering by axial dispersion} = \frac{dN_A}{dt} = - \left(DS \frac{dC_A}{dl} \right)_{l+\Delta l}$$

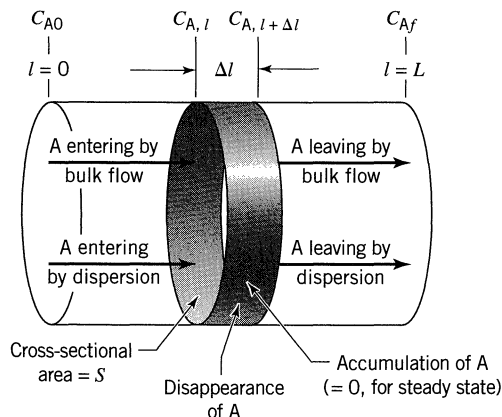


Figure 13.18 Variables for a closed vessel in which reaction and dispersion are occurring.

$$\text{leaving by axial dispersion} = \frac{dN_A}{dt} = - \left(\mathbf{D} S \frac{dC_A}{dl} \right)_{l+\Delta l}$$

$$\text{disappearance by reaction} = (-r_A) V = (-r_A) S \Delta l, \quad [\text{mol/s}]$$

Note that the difference between this material balance and that for the ideal plug flow reactors of Chapter 5 is the inclusion of the two dispersion terms, because material enters and leaves the differential section not only by bulk flow but by dispersion as well. Entering all these terms into Eq. 17 and dividing by $S \Delta l$ gives

$$u \frac{(C_{A,l+\Delta l} - C_{A,l})}{\Delta l} - \mathbf{D} \frac{\left[\left(\frac{dC_A}{dl} \right)_{l+\Delta l} - \left(\frac{dC_A}{dl} \right)_l \right]}{\Delta l} + (-r_A) = 0$$

Now the basic limiting process of calculus states that for any quantity Q which is a smooth continuous function of l

$$\lim_{l_2 \rightarrow l_1} \frac{Q_2 - Q_1}{l_2 - l_1} = \lim_{\Delta l \rightarrow 0} \frac{\Delta Q}{\Delta l} = \frac{dQ}{dl}$$

So taking limits as $\Delta l \rightarrow 0$ we obtain

$$u \frac{dC_A}{dl} - \mathbf{D} \frac{d^2 C_A}{dl^2} + k C_A^n = 0 \quad (18a)$$

In dimensionless form where $z = l/L$ and $\tau = \bar{t} = L/u = V/v$, this expression becomes

$$\frac{\mathbf{D}}{uL} \frac{d^2 C_A}{dz^2} - \frac{dC_A}{dz} - k\tau C_A^n = 0 \quad (18b)$$

or in terms of fractional conversion

$$\frac{\mathbf{D}}{uL} \frac{d^2 X_A}{dz^2} - \frac{dX_A}{dz} + k\tau C_{A0}^{n-1} (1 - X_A)^n = 0 \quad (18c)$$

This expression shows that the fractional conversion of reactant A in its passage through the reactor is governed by three dimensionless groups: a reaction rate group $k\tau C_{A0}^{n-1}$, the dispersion group \mathbf{D}/uL , and the reaction order n .

First-Order Reaction. Equation 18 has been solved analytically by Wehner and Wilhelm (1956) for first-order reactions. For vessels with any kind of entrance

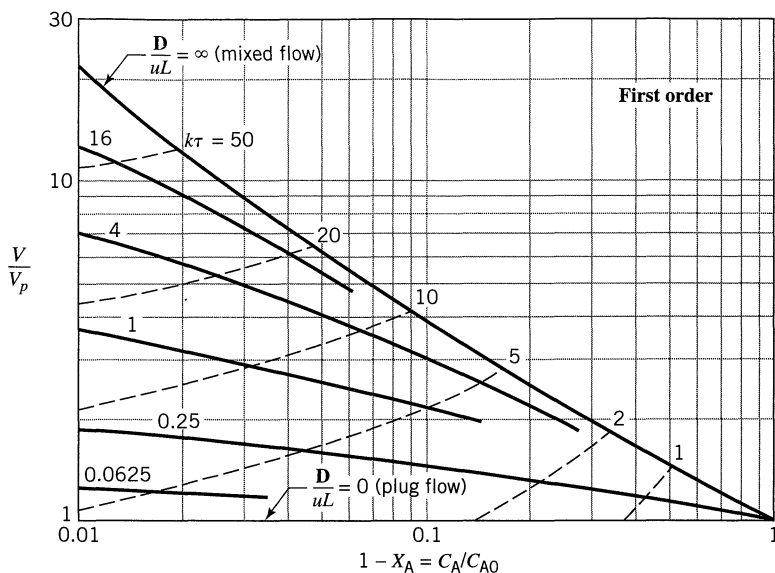


Figure 13.19 Comparison of real and plug flow reactors for the first-order $A \rightarrow$ products, assuming negligible expansion; from Levenspiel and Bischoff (1959, 1961).

and exit conditions the solution is

$$\frac{C_A}{C_{A0}} = 1 - X_A = \frac{4a \exp\left(\frac{1}{2} \frac{uL}{D}\right)}{(1+a)^2 \exp\left(\frac{a}{2} \frac{uL}{D}\right) - (1-a)^2 \exp\left(-\frac{a}{2} \frac{uL}{D}\right)} \quad (19)$$

where

$$a = \sqrt{1 + 4k\tau(D/uL)}$$

Figure 13.19 is a graphical representation of these results in useful form, prepared by combining Eq. 19 and Eq. 5.17, and allows comparison of reactor sizes for plug and dispersed plug flow.

For *small deviations from plug flow* D/uL becomes small, the E curve approaches gaussian; hence, on expanding the exponentials and dropping higher order terms Eq. 19 reduces to

$$\frac{C_A}{C_{A0}} = \exp\left[-k\tau + (k\tau)^2 \frac{D}{uL}\right] \quad (20)$$

$$= \exp\left[-k\tau + \frac{k^2 \sigma^2}{2}\right] \quad (21)^*$$

* It should be noted that Eq. 21 applies to any gaussian RTD with variance σ^2 .

Equation 20 with Eq. 5.17 compares the performance of real reactors which are close to plug flow with plug flow reactors. Thus the size ratio needed for identical conversion is given by

$$\frac{L}{L_p} = \frac{V}{V_p} = 1 + (k\tau) \frac{D}{uL} \quad \text{for same } C_{A,\text{out}} \quad (22)$$

while the exit concentration ratio for identical reactor size is given by

$$\frac{C_A}{C_{A,p}} = 1 + (k\tau)^2 \frac{D}{uL} \quad \text{for same } V \text{ or } \tau \quad (23)$$

***n*th-Order Reactions.** Figure 13.20 is the graphical representation of the solution of Eq. 18 for second-order reactions in closed vessels. It is used in a manner similar to the chart for first-order reactions. To estimate reactor performance for reactions of order different from one and two we may extrapolate or interpolate between Figs. 13.19 and 13.20.

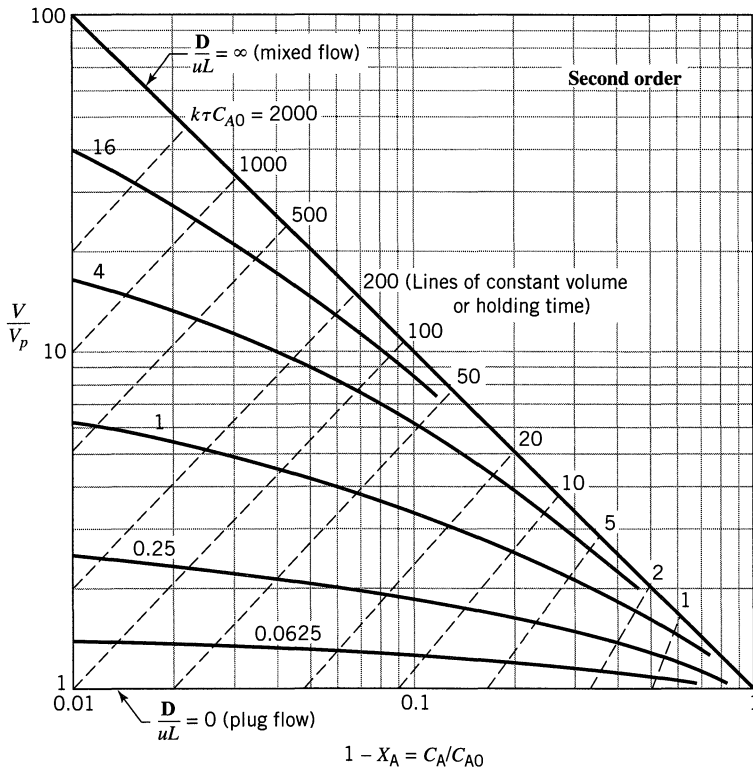
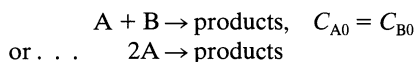


Figure 13.20 Comparison of real and plug flow reactors for the second-order reactions



assuming negligible expansion; from Levenspiel and Bischoff (1959, 1961).

EXAMPLE 13.4 CONVERSION FROM THE DISPERSION MODEL

Redo Example 11.3 of Chapter 11 assuming that the dispersion model is a good representation of flow in the reactor. Compare the calculated conversion by the two methods and comment.

SOLUTION

Matching the experimentally found variance with that of the dispersion model, we find from Example 13.1

$$\frac{D}{uL} = 0.12$$

Conversion in the real reactor is found from Fig. 13.19. Thus moving along the $k\tau = (0.307)(15) = 4.6$ line from $C/C_0 = 0.01$ to $D/uL = 0.12$, we find that the fraction of reactant unconverted is approximately

$$\frac{C}{C_0} = 0.035, \quad \text{or} \quad \underline{\underline{3.5\%}}$$

Comments. Figure E13.4 shows that except for a long tail the dispersion model curve has for the most part a greater central tendency than the actual curve. On the other hand, the actual curve has more short-lived material leaving the vessel.

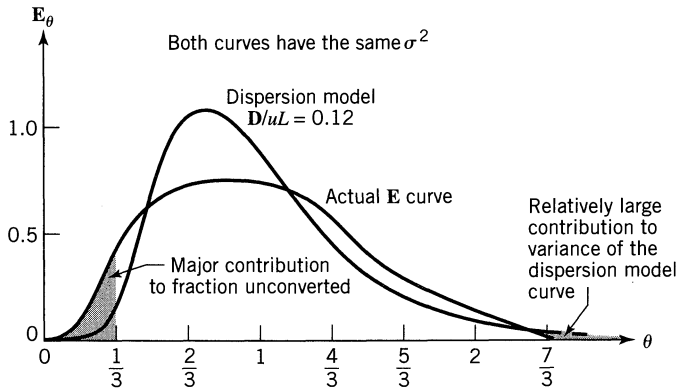


Figure E13.4

Because this contributes most to the reactant remaining unconverted, the finding

$$\left(\frac{C}{C_0}\right)_{\text{actual}} = 4.7\% > \left(\frac{C}{C_0}\right)_{\text{dispersion model}} = 3.5\%$$

is expected.

Extensions

Levenspiel (1996) Chapter 64 discusses and presents performance equations for various extensions to this treatment. A much more detailed exposition of this subject is given by Westerterp et al. (1984) Chapter 4.

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PROBLEMS

13.1. The flow pattern of gas through blast furnaces was studied by VDEh (Veren Deutscher Eisenhüttenleute Betriebsforschungsinstitut) by injecting Kr-85 into the air stream entering the tuyeres of the 688 m³ furnace. A sketch and listing of pertinent quantities for run 10.5 of 9.12.1969 is shown in Fig. P13.1. Assuming that the axial dispersion model applies to the flow of gas

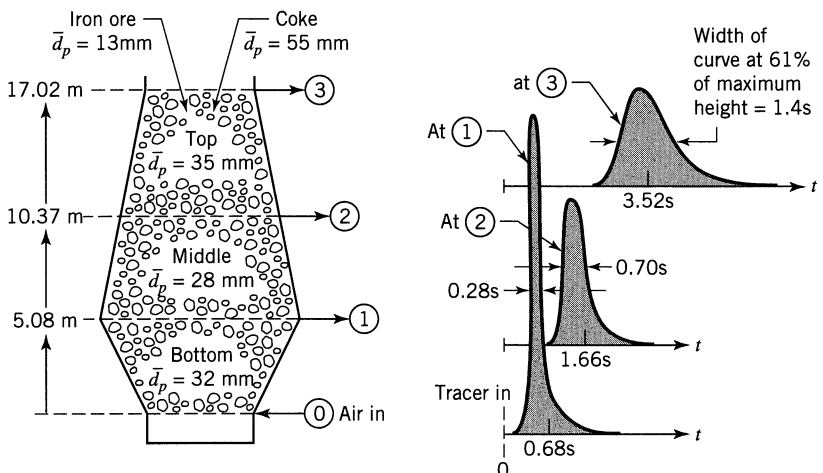


Figure P13.1

in the blast furnace, compare D/ud for the middle section of the blast furnace with that expected in an ordinary packed bed.

From Standish and Polthier, *Blast Furnace Aerodynamics*, p. 99, N. Standish, ed., Australian I. M. M. Symp., Wollongong, 1975.

- 13.2. Denmark's longest and greatest river, the Gudena, certainly deserves study, so pulse tracer tests were run on various stretches of the river using radioactive Br-82. Find the axial dispersion coefficient in the upper stretch of the river, between Tørring and Udum, 8.7 km apart, from the following reported measurements.

t , hr	C , arbitrary	t , hr	C , arbitrary
3.5	0	5.75	440
3.75	3	6	250
4	25	6.25	122
4.25	102	6.5	51
4.5	281	6.75	20
4.75	535	7	9
5	740	7.25	3
5.25	780	7.5	0
5.5	650		

Data from Danish Isotope Center, report of November 1976.

- 13.3. RTD studies were carried out by Jagadeesh and Satyanarayana (IEC/PDD 11 520, 1972) in a tubular reactor ($L = 1.21$ m, 35 mm ID). A squirt of NaCl solution (5 N) was rapidly injected at the reactor entrance, and mixing cup measurements were taken at the exit. From the following results calculate the vessel dispersion number; also the fraction of reactor volume taken up by the baffles.

t , sec	NaCl in sample	
0–20	0	
20–25	60	
25–30	210	
30–35	170	
35–40	75	$(v = 1300 \text{ ml/min})$
40–45	35	
45–50	10	
50–55	5	
55–70	0	

- 13.4. A pulse of radioactive Ba-140 was injected into a 10-in. pipeline (25.5 cm ID) 293 km long used for pumping petroleum products ($u = 81.7$ cm/s, $Re = 24\,000$) from Rangely, Colorado to Salt Lake City, Utah. Estimate the time of passage of fluid having more than $1/2 C_{\max}$ of tracer and compare the value you calculate with the reported time of passage of 895 sec averaged over five runs. From the table of values for the gaussian distribution $C > C_{\max}/2$ occurs between $\bar{\theta} \pm 1.18 \sigma_{\theta}$. This may be helpful information. Data from Hull and Kent, *Ind. Eng. Chem.*, **44**, 2745 (1952).

- 13.5.** An injected slug of tracer material flows with its carrier fluid down a long, straight pipe in dispersed plug flow. At point *A* in the pipe the spread of tracer is 16 m. At point *B*, 1 kilometer downstream from *A*, its spread is 32 m. What do you estimate its spread to be at a point *C*, which is 2 kilometers downstream from point *A*?
- 13.6.** A refinery pumps products *A* and *B* successively to receiving stations up to 100 km away through a 10-cm ID pipeline. The average properties of *A* and *B* are $\rho = 850 \text{ kg/m}^3$, $\mu = 1.7 \times 10^{-3} \text{ kg/m}\cdot\text{s}$, $\mathcal{D} = 10^{-9} \text{ m}^2/\text{s}$, the fluid flows at $u = 20 \text{ cm/s}$, and there are no reservoirs, holding tanks or pipe loops in the line; just a few bends. Estimate the 16%–84% contaminated width 100 km downstream. Adapted from *Petroleum Refiner*, **37**, 191 (March 1958); *Pipe Line Industry*, pg. 51 (May 1958).
- 13.7.** Kerosene and gasoline are pumped successively at 1.1 m/s through a 25.5-cm ID pipeline 1000 km long. Calculate the 5/95%–95/5% contaminated width at the exit of the pipe given that the kinematic viscosity for the 50/50% mixture is

$$\mu/\rho = 0.9 \times 10^{-6} \text{ m}^2/\text{s}$$

(Data and problem from Sjenitzer, *Pipeline Engineer*, December 1958).

- 13.8.** Water is drawn from a lake, flows through a pump and passes down a long pipe in turbulent flow. A slug of tracer (not an ideal pulse input) enters the intake line at the lake, and is recorded downstream at two locations in the pipe L meters apart. The mean residence time of fluid between recording points is 100 sec, and variance of the two recorded signals is

$$\sigma_1^2 = 800 \text{ sec}^2$$

$$\sigma_2^2 = 900 \text{ sec}^2$$

What would be the spread of an ideal pulse response for a section of this pipe, free from end effects and of length $L/5$?

- 13.9.** Last autumn our office received complaints of a large fish kill along the Ohio River, indicating that someone had discharged highly toxic material into the river. Our water monitoring stations at Cincinnati and Portsmouth, Ohio (119 miles apart) report that a large slug of phenol is moving down the river and we strongly suspect that this is the cause of the pollution. The slug took 9 hours to pass the Portsmouth monitoring station, and its concentration peaked at 8:00 A.M. Monday. About 24 hours later the slug peaked at Cincinnati, taking 12 hours to pass this monitoring station.

Phenol is used at a number of locations on the Ohio River, and their distance upriver from Cincinnati are as follows:

Ashland, KY—150 miles upstream	Marietta, OH—303
Huntington, WV—168	Wheeling, WV—385
Pomeroy, OH—222	Steubenville, OH—425
Parkersburg, WV—290	Pittsburgh, PA—500

What can you say about the probable pollution source?

- 13.10.** A 12-m length of pipe is packed with 1 m of 2-mm material, 9 m of 1-cm material, and 2 m of 4-mm material. Estimate the variance in the output C curve for a pulse input into this packed bed if the fluid takes 2 min to flow through the bed. Assume a constant bed voidage and a constant intensity of dispersion given by $\mathbf{D}/ud_p = 2$.
- 13.11.** The kinetics of a homogeneous liquid reaction are studied in a flow reactor, and to approximate plug flow the 48-cm long reactor is packed with 5-mm nonporous pellets. If the conversion is 99% for a mean residence time of 1 sec, calculate the rate constant for the first-order reaction
- assuming that the liquid passes in plug flow through the reactor
 - accounting for the deviation of the actual flow from plug flow
 - What is the error in calculated k if deviation from plug flow is not considered?

Data: Bed voidage $\varepsilon = 0.4$

Particle Reynolds number $Re_p = 200$

- 13.12.** Tubular reactors for thermal cracking are designed on the assumption of plug flow. On the suspicion that nonideal flow may be an important factor now being ignored, let us make a rough estimate of its role. For this assume isothermal operations in a 2.5-cm ID tubular reactor, using a Reynolds number of 10 000 for flowing fluid. The cracking reaction is approximately first order. If calculations show that 99% decomposition can be obtained in a plug flow reactor 3 m long, how much longer must the real reactor be if nonideal flow is taken into account?
- 13.13.** Calculations show that a plug flow reactor would give 99.9% conversion of reactant which is in aqueous solution. However, our reactor has an RTD somewhat as shown in Fig. P13.13. If $C_{A0} = 1000$, what outlet concentration can we expect in our reactor if reaction is first order? From mechanics $\sigma^2 = a^2/24$ for a symmetrical triangular distribution with base a , rotating about its center of gravity.

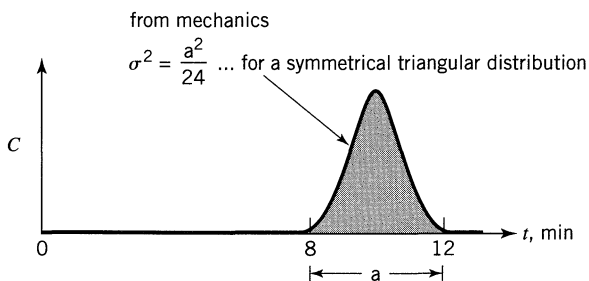


Figure P13.13

Chapter 14

The Tanks-In-Series Model

This model can be used whenever the dispersion model is used; and for not too large a deviation from plug flow both models give identical results, for all practical purposes. Which model you use depends on your mood and taste.

The dispersion model has the advantage in that all correlations for flow in real reactors invariably use that model. On the other hand the tanks-in-series model is simple, can be used with any kinetics, and it can be extended without too much difficulty to any arrangement of compartments, with or without recycle.

14.1 PULSE RESPONSE EXPERIMENTS AND THE RTD

Figure 14.1 shows the system we are considering. We also define

$$\theta_i = \frac{t}{\bar{t}_i} = \text{dimensionless time based on the mean residence time per tank } \bar{t}_i$$

$$\theta = \frac{t}{\bar{t}} = \text{dimensionless time based on the mean residence time in all } N \text{ tanks, } \bar{t}.$$

Then

$$\theta_i = N\theta \quad \dots \quad \text{and} \quad \dots \quad \bar{\theta}_i = 1, \quad \bar{\theta} = 1$$

and at any particular time, from Eq. 11 in Chapter 11

$$\mathbf{E}_\theta = \bar{t}\mathbf{E}$$

For the first tank. Consider a steady flow v m³/s of fluid into and out of the first of these ideal mixed flow units of volume V_1 . At time $t = 0$ inject a pulse of tracer into the vessel which when evenly distributed in the vessel (and it is) has a concentration C_0 .

At any time t after the tracer is introduced make a material balance, thus

$$\left(\begin{array}{c} \text{rate of disappearance} \\ \text{of tracer} \end{array} \right) = \left(\begin{array}{c} \text{input} \\ \text{rate} \end{array} \right) - \left(\begin{array}{c} \text{output} \\ \text{rate} \end{array} \right)$$

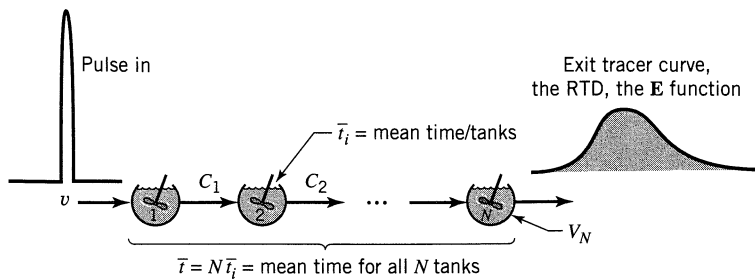


Figure 14.1 The tanks-in-series model.

In symbols this expression becomes

$$V_1 \frac{dC_1}{dt} = 0 - vC_1 \quad \left[\frac{\text{mol tracer}}{\text{s}} \right]$$

where C_1 is the concentration of tracer in tank “1.” Separating and integrating then gives

$$\int_{C_0}^{C_1} \frac{dC_1}{C_1} = -\frac{1}{t_1} \int_0^t dt$$

or

$$\frac{C_1}{C_0} = e^{-t/t_1}$$

Since the area under this C/C_0 versus t curve is t_1 (check this if you wish) it allows you to find the **E** curve; so one may write

$$t_1 \mathbf{E}_1 = e^{-t/t_1} \quad [-] \quad N = 1 \quad (1)$$

For the second tank where C_1 enters, C_2 leaves, a material balance gives

$$V_2 \frac{dC_2}{dt} = v \cdot \underbrace{\frac{C_0}{t_1}}_{C_1} e^{-t/t_1} - vC_2 \quad \left[\frac{\text{mol tracer}}{\text{s}} \right]$$

Separating gives a first-order differential equation, which when integrated gives

$$t_2 \mathbf{E}_2 = \frac{t}{t_2} e^{-t/t_2} \quad [-] \quad N = 2 \quad (2)$$

For the Nth tank. Integration for the 3rd, 4th, . . . , Nth tank becomes more complicated so it is simpler to do all of this by Laplace transforms.

The RTD's, means and variances, both in time and dimensionless time were first derived by MacMullin and Weber (1935) and are summarized by Eq. 3.

$$\begin{aligned}
 \bar{t} \mathbf{E} &= \left(\frac{t}{\bar{t}}\right)^{N-1} \frac{N^N}{(N-1)!} e^{-Nt/\bar{t}} \quad \dots \bar{t} = N\bar{t}_i \dots \sigma^2 = \frac{\bar{t}^2}{N} \\
 \bar{t}_i \mathbf{E} &= \left(\frac{t}{\bar{t}_i}\right)^{N-1} \frac{1}{(N-1)!} e^{-t/\bar{t}_i} \quad \dots \bar{t}_i = \frac{\bar{t}}{N} \dots \sigma^2 = N\bar{t}_i^2 \\
 \mathbf{E}_{\theta_i} &= \bar{t}_i \mathbf{E} = \frac{\theta_i^{N-1}}{(N-1)!} e^{-\theta_i} \quad \dots \sigma_{\theta_i}^2 = N \\
 \mathbf{E}_\theta &= (N\bar{t}_i) \mathbf{E} = N \frac{(N\theta)^{N-1}}{(N-1)!} e^{-N\theta} \dots \sigma_\theta^2 = \frac{1}{N}
 \end{aligned} \tag{3}$$

Graphically these equations are shown in Fig. 14.2. The properties of the RTD curves are sketched in Fig. 14.3.

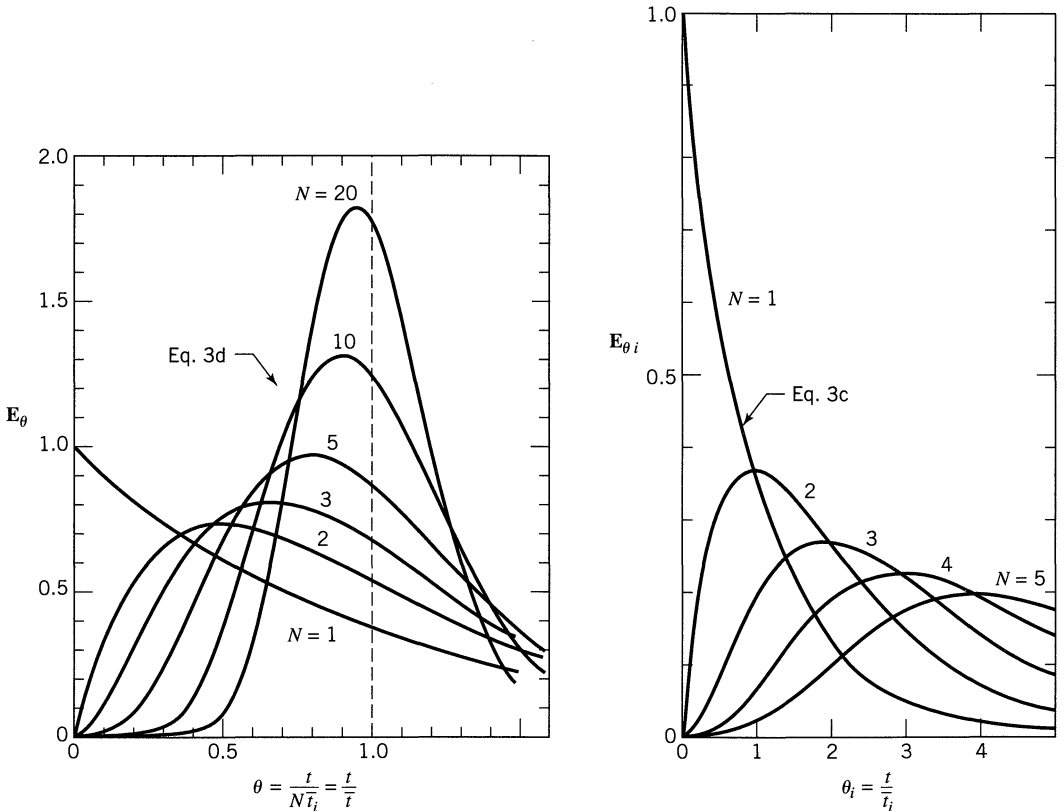


Figure 14.2 RTD curves for the tanks-in-series model, Eq. 3.

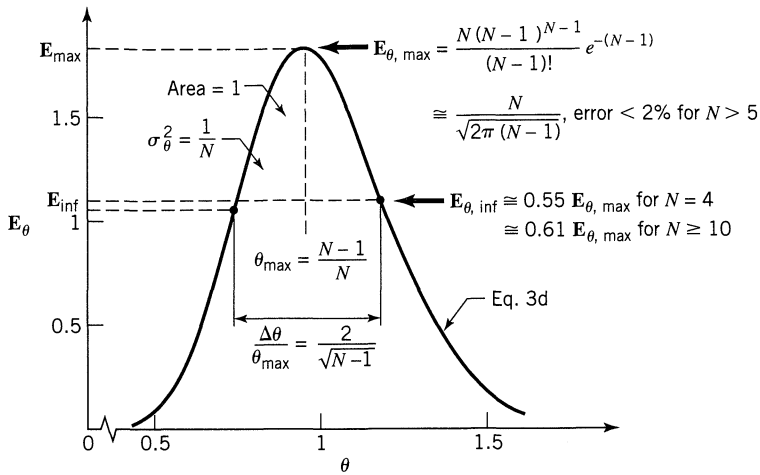


Figure 14.3 Properties of the RTD curve for the tanks-in-series model.

Comments and Extensions

Independence.¹ If M tanks are connected to N more tanks (all of the same size) then the individual means and variances (in ordinary time units) are additive, or

$$\bar{t}_{M+N} = \bar{t}_M + \bar{t}_N \dots \quad \text{and} \quad \dots \sigma_{M+N}^2 = \sigma_M^2 + \sigma_N^2 \quad (4)$$

Because of this property we can join incoming streams with recycle streams. Thus this model becomes useful for treating recirculating systems.

One-shot Tracer Input. If we introduce any one-shot tracer input into N tanks, as shown in Fig. 14.4, then from Eqs. 3 and 4 we can write

$$\Delta\sigma^2 = \sigma_{\text{out}}^2 - \sigma_{\text{in}}^2 = \frac{(\Delta\bar{t})^2}{N} \quad (5)$$

Because of the independence of stages it is easy to evaluate what happens to the C curve when tanks are added or subtracted. Thus this model becomes useful in treating recycle flow and closed recirculation systems. Let us briefly look at these applications.

¹ By independence we mean that the fluid loses its memory as it passes from vessel to vessel. Thus a faster moving fluid element in one vessel does not remember this fact in the next vessel and doesn't preferentially flow faster (or slower) there. Laminar flow often does not satisfy this requirement of independence; however, complete (or lateral) mixing of fluid between units satisfies this condition.

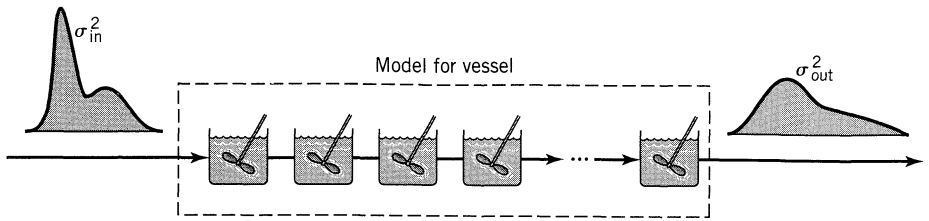


Figure 14.4 For any one-shot tracer input Eq. 4 relates input, output, and number of tanks.

Closed Recirculation System. If we introduce a δ signal into an N stage system, as shown in Fig. 14.5, the recorder will measure tracer as it flows by the first time, the second time, and so on. In other words it measures tracer which has passed through N tanks, $2N$ tanks, and so on. In fact it measures the superposition of all these signals.

To obtain the output signal for these systems simply sum up the contributions from the first, second, and succeeding passes. If m is the number of passes, we then have from Eq. 3

$$\bar{t}_i C_{\text{pulse}} = e^{-t/\bar{t}_i} \sum_{m=1}^{\infty} \frac{(t/\bar{t}_i)^{mN-1}}{(mN-1)!} \quad (6a)$$

$$C_{\theta_i, \text{pulse}} = e^{-\theta_i} \sum_{m=1}^{\infty} \frac{\theta_i^{mN-1}}{(mN-1)!} \quad (6b)$$

$$C_{\theta, \text{pulse}} = N e^{-N\theta} \sum_{m=1}^{\infty} \frac{(N\theta)^{mN-1}}{(mN-1)!} \quad (6c)$$

Figure 14.5 shows the resulting C curve. As an example of the expanded form of Eq. 5 we have for five tanks in series

$$C_{\text{pulse}} = \frac{5}{t} e^{-5t/\bar{t}_i} \left[\frac{(5t/\bar{t}_i)^4}{4!} + \frac{(5t/\bar{t}_i)^9}{9!} + \dots \right] \quad (7a)$$

$$C_{\theta_i, \text{pulse}} = e^{-\theta_i} \left[\frac{\theta_i^4}{4!} + \frac{\theta_i^9}{9!} + \frac{\theta_i^{14}}{14!} + \dots \right] \quad (7b)$$

$$C_{\theta, \text{pulse}} = 5e^{-5\theta} \left[\frac{(5\theta)^4}{4!} + \frac{(5\theta)^9}{9!} + \dots \right] \quad (7c)$$

where the terms in brackets represent the tracer signal from the first, second, and successive passes.

Recirculation systems can be represented equally well by the dispersion model [see van der Vusse (1962), Voncken et al. (1964), and Harrell and Perona (1968)]. Which approach one takes simply is a matter of taste, style, and mood.

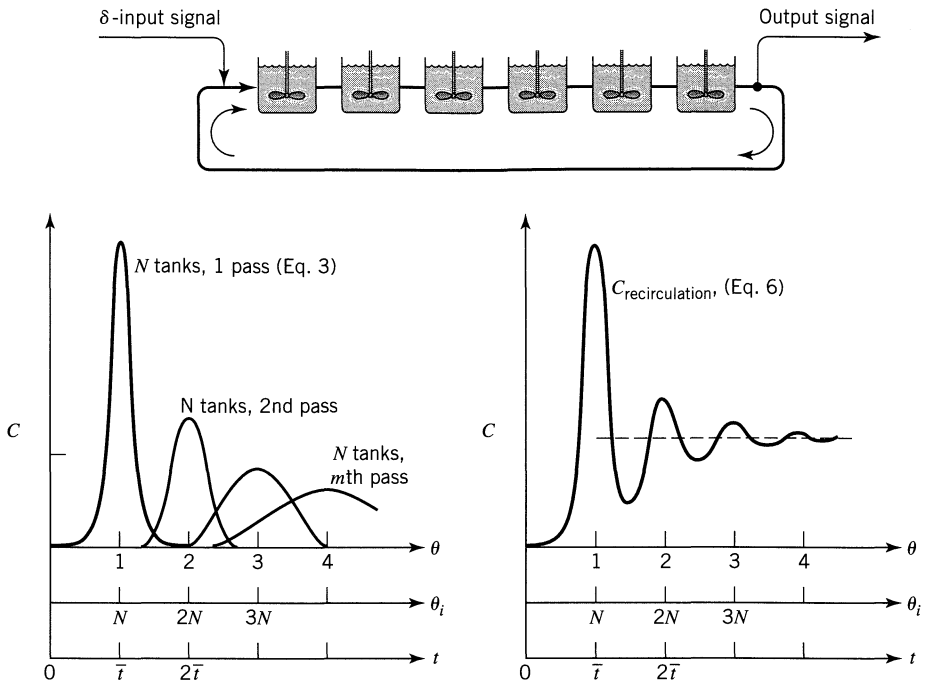


Figure 14.5 Tracer signal in a recirculating system.

Recirculation with Throughflow. For relatively rapid recirculation compared to throughflow, the system as a whole acts as one large stirred tank; hence, the observed tracer signal is simply the superposition of the recirculation pattern and the exponential decay of an ideal stirred tank. This is shown in Fig. 14.6 where C_0 is the concentration of tracer if it is evenly distributed in the system.

This form of curve is encountered in closed recirculation systems in which tracer is broken down and removed by a first-order process, or in systems using

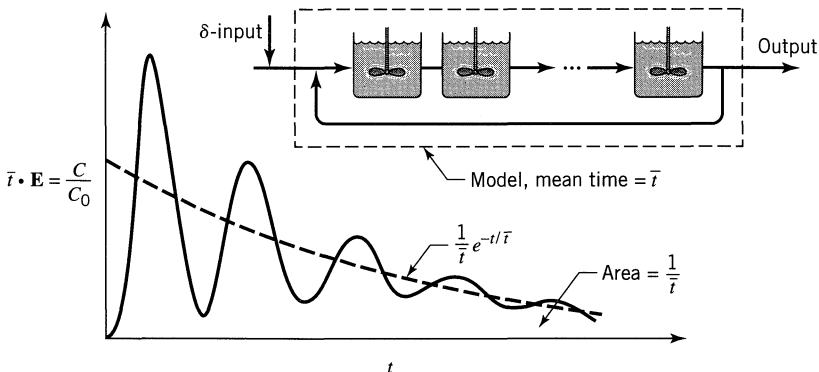


Figure 14.6 Recirculation with slow throughflow.

radioactive tracer. Drug injection on living organisms give this sort of superposition because the drug is constantly being eliminated by the organism.

Step Response Experiments and the F Curve The output **F** curve from a series of N ideal stirred tanks is, in its various forms, given by Eq. 8.

$$\begin{aligned}
 \mathbf{F} &= 1 - e^{-N\theta} \left[1 + N\theta + \frac{(N\theta)^2}{2!} + \dots + \frac{(N\theta)^{N-1}}{(N-1)!} + \dots \right] \\
 \mathbf{F} &= 1 - e^{-\theta_i} \left[1 + \theta_i + \frac{\theta_i^2}{2!} + \dots + \frac{\theta_i^{N-1}}{(N-1)!} + \dots \right]
 \end{aligned} \tag{8}$$

Number of tanks

- For one tank use the first term
- For $N = 2$
- For $N = 3$
- For N tanks

This is shown in graphical form in Fig. 14.7.

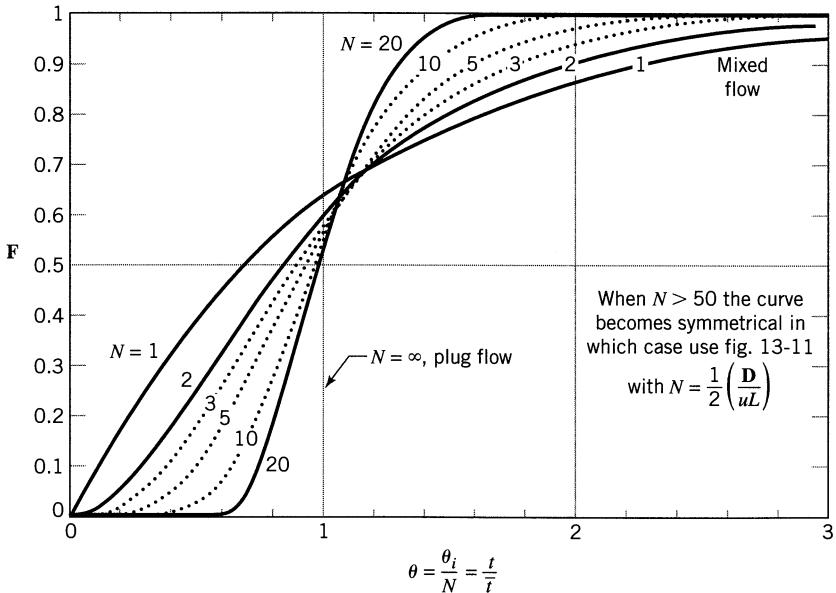


Figure 14.7 The **F** curve for the tanks-in-series model, from MacMullin and Weber (1935).

14.2 CHEMICAL CONVERSION

First-Order Reaction

Chapter 6 develops the conversion equation. Thus for first-order reactions in one tank

$$\frac{C_A}{C_{A0}} = \frac{1}{1 + k\bar{t}_i} = \frac{1}{1 + k\bar{t}}$$

for N tanks in series

$$\frac{C_A}{C_{A0}} = \frac{1}{(1 + k\bar{t}_i)^N} = \frac{1}{\left(1 + \frac{k\bar{t}}{N}\right)^N} \quad (9)$$

A comparison with plug flow performance is given in Fig. 6.5.

For small deviations from plug flow (large N) comparison with plug flow gives

$$\text{for same } C_{A \text{ final}}: \quad \frac{V_{N \text{ tanks}}}{V_p} = 1 + k\bar{t}_i = 1 + \frac{k\bar{t}}{2N}$$

$$\text{for same volume } V: \quad \frac{C_{A, N \text{ tanks}}}{C_{Ap}} = 1 + \frac{(k\bar{t})^2}{2N}$$

These equations apply to both micro- and macrofluids.

Second-Order Reaction of a Microfluid, $A \rightarrow R$ or $A + B \rightarrow R$ with $C_{A0} = C_{B0}$

For a microfluid flowing through N tanks in series Eq. 6.8 gives

$$C_N = \frac{1}{4k\tau_i} \left(-2 + 2 \sqrt{-1 \cdots + 2 \sqrt{-1 + 2 \sqrt{1 + 4C_0 k \tau_i}}} \right)^N \quad (10)$$

and Fig. 6.6 compares the performance to that for plug flow.

All Other Reaction Kinetics of Microfluids

Either solve the mixed flow equation for tank after tank

$$\bar{t}_i = \frac{C_{Ai-1} - C_{Ai}}{-r_i}$$

a rather tedious process, but no problem today with our handy slave, the computer. Or else we could use the graphical procedure shown in Fig. 14.8.

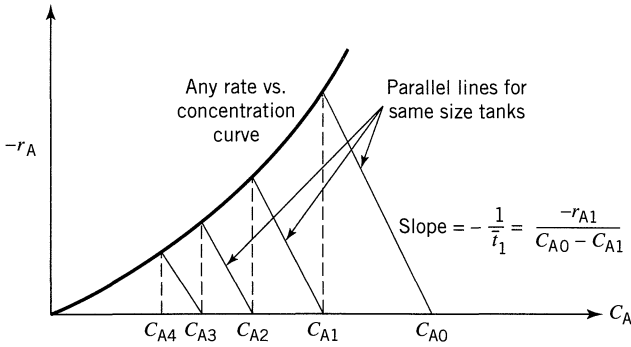


Figure 14.8 Graphical method of evaluating the performance of N tanks in series for any kinetics.

Chemical Conversion of Macrofluids

There is rare use for macrofluid equations for homogeneous reactions. However, if you do need them combine Eq. 11.3 with Eq. 3 for N tanks in series, to give

$$\frac{C_A}{C_{A0}} = \frac{N^N}{(N-1)! \cdot \bar{t}_N} \int_0^\infty \left(\frac{C_A}{C_{A0}} \right)_{\text{batch}} \cdot t^{N-1} e^{-tN/\bar{t}} dt \quad (11)$$

These equations may not be of practical use for homogeneous systems; however, they are of primary importance for heterogeneous systems, especially for G/S systems.

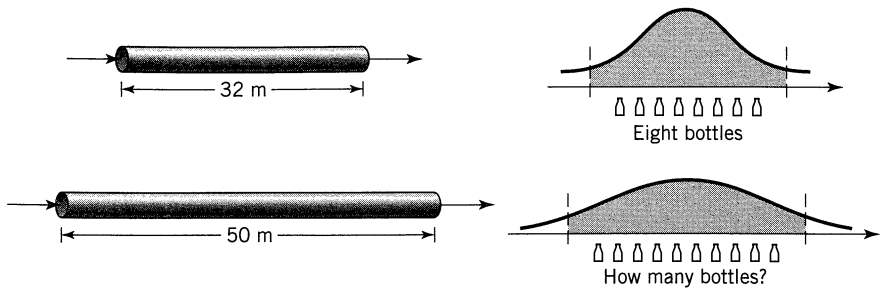
EXAMPLE 14.1 MODIFICATIONS TO A WINERY

A small diameter pipe 32 m long runs from the fermentation room of a winery to the bottle filling cellar. Sometimes red wine is pumped through the pipe, sometimes white, and whenever the switch is made from one to the other a small amount of “house blend” rosé is produced (8 bottles). Because of some construction in the winery the pipeline length will have to be increased to 50 m. For the same flow rate of wine, how many bottles of rosé may we now expect to get each time we switch the flow?

SOLUTION

Figure E14.1 sketches the problem. Let the number of bottles, the spread, be related to σ .

Original:	$L_1 = 32 \text{ m}$	$\sigma_1 = 8$	$\sigma_1^2 = 64$
Longer pipe:	$L_2 = 50 \text{ m}$	$\sigma_2 = ?$	$\sigma_2^2 = ?$


Figure E14.1

But for small deviations from plug flow, from Eq. 3 $\sigma^2 \propto N$ or $\sigma^2 \propto L$.

$$\therefore \frac{\sigma_2^2}{\sigma_1^2} = \frac{L_2}{L_1} = \frac{50}{32}$$

$$\therefore \sigma_2^2 = \frac{50}{32} (64) = 100$$

$$\therefore \sigma_2 = 10 \dots \text{or we can expect } \underline{\underline{10 \text{ bottles of vin rosé}}}$$

EXAMPLE 14.2 A FABLE ON RIVER POLLUTION

Last spring our office received complaints of a large fish kill along the Ohio River, indicating that someone had discharged highly toxic material into the river. Our water monitoring stations at Cincinnati and Portsmouth, Ohio (119 miles apart), report that a large slug of phenol is moving down the river, and we strongly suspect that this is the cause of the pollution. The slug took about 10.5 hours to pass the Portsmouth monitoring station, and its concentration peaked at 8:00 A.M. Monday. About 26 hours later the slug peaked at Cincinnati, taking 14 hours to pass this monitoring station.

Phenol is used at a number of locations on the Ohio River, and their distance upriver from Cincinnati are as follows:

Ashland, KY—150 miles upstream	Marietta, OH—303
Huntington, WV—168	Wheeling, WV—385
Pomeroy, OH—222	Steubenville, OH—425
Parkersburg, WV—290	Pittsburgh, PA—500

What can you say about the probable pollution source?

SOLUTION

Let us first sketch what is known, as shown in Fig. E14.2. To start, assume that a perfect pulse is injected. Then according to any reasonable flow model, either

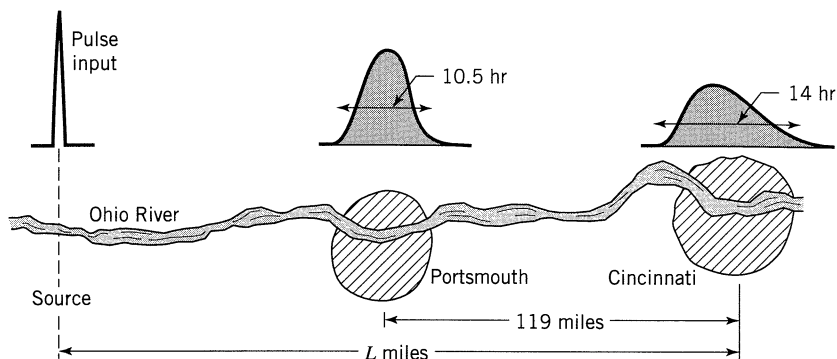


Figure E14.2

dispersion or tanks-in-series, we have

$$\sigma_{\text{tracer curve}}^2 \propto \left(\begin{array}{l} \text{distance from} \\ \text{point of origin} \end{array} \right)$$

or

$$\left(\begin{array}{l} \text{spread of} \\ \text{curve} \end{array} \right) \propto \sqrt{\begin{array}{l} \text{distance from} \\ \text{origin} \end{array}}$$

$$\left. \begin{array}{l} \therefore \text{from Cincinnati: } 14 = k L^{1/2} \\ \therefore \text{from Portsmouth: } 10.5 = k(L - 119)^{1/2} \end{array} \right\}$$

Dividing one by the other gives

$$\frac{14}{10.5} = \sqrt{\frac{L}{L - 119}} \quad \dots \text{from which } \underline{\underline{L = 272 \text{ miles}}}$$

Comment. Since the dumping of the toxic phenol may not have occurred instantaneously, any location where $L \leq 272$ miles is suspect, or

$$\left. \begin{array}{l} \underline{\text{Ashland}} \\ \underline{\text{Huntington}} \\ \underline{\text{Pomeroy}} \end{array} \right\} \leftarrow$$

This solution assumes that different stretches of the Ohio River have the same flow and dispersion characteristics (reasonable), and that no suspect tributary joins the Ohio within 272 miles of Cincinnati. This is a poor assumption . . . check a map for the location of Charleston, WV, on the Kanawah River.

EXAMPLE 14.3 FLOW MODELS FROM RTD CURVES

Let us develop a tanks-in-series model to fit the RTD shown in Fig. E14.3a.

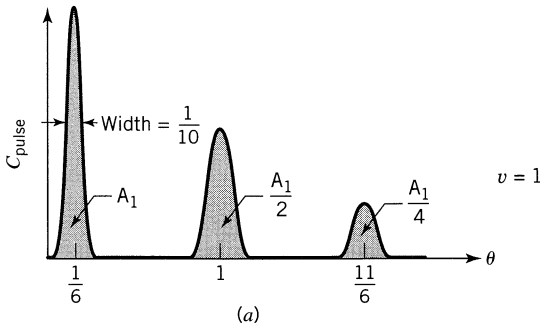


Figure E14.3a

SOLUTION

As a first approximation, assume that all the tracer curves are ideal pulses. We will later relax this assumption. Next notice that the first pulse appears early. This suggests a model as shown in Fig. E14.3b, where $v = 1$ and $V_1 + V_2 + V_d = 1$. In Chapter 12 we see the characteristics of this model, so let us fit it. Also it should be mentioned that we have a number of approaches. Here is one:

- Look at the ratio of areas of the first two peaks

$$\frac{A_2}{A_1} = \frac{1}{2} = \frac{R}{R+1} \quad \dots \cdot \underline{\underline{R=1}}$$

- From the location of the first peak

$$\frac{V_1}{(R+1)v} = \frac{V_1}{(1+1)} = \frac{1}{6} \quad \dots \cdot \underline{\underline{V_1 = \frac{1}{3}}}$$

- From the time between peaks

$$\Delta t = \frac{5}{6} = \frac{(1/3)}{(1+1)1} + \frac{V_2}{1(1)} \quad \dots \cdot \underline{\underline{V_2 = \frac{2}{3}}}$$

Since $V_1 + V_2$ add up to 1, there is no dead volume, so at this point our model reduces to Fig. E14.3c. Now relax the plug flow assumption and adopt the tanks-in-series model. From Fig. 14.3

$$\frac{\Delta\theta}{\theta_{\max}} = \frac{1/10}{1/6} = \frac{2}{\sqrt{N-1}} \quad \dots \cdot \underline{\underline{N=12}}$$

So our model finally is shown in Fig. E14.3d.

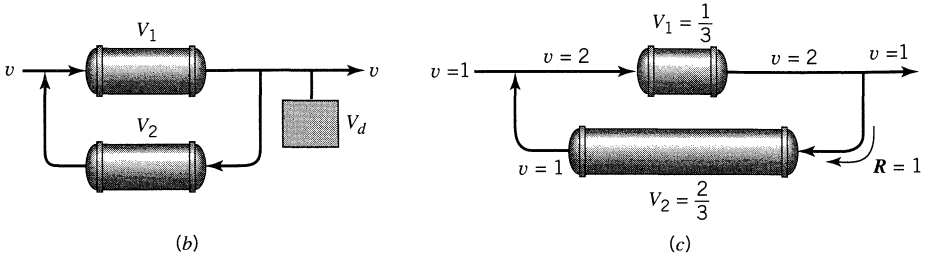


Figure E14.3b and c

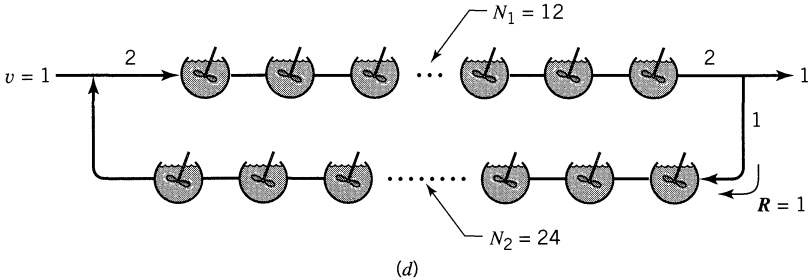


Figure E14.3d

Bypassing the Complex Process of Deconvolution

Suppose we measure the sloppy input and output tracer curves for a process vessel for the purpose of studying the flow through the vessel, thus to find the **E** curve for the vessel. In general this requires deconvolution (see Chapter 11); however, if we have a flow model in mind whose parameter has a one-to-one relationship with its variance, then we can use a very simple shortcut to find the **E** curve for the vessel.

Example 14.4 illustrates this method.

EXAMPLE 14.4 FINDING THE VESSEL **E** CURVE USING A SLOPPY TRACER INPUT

Given C_{in} and C_{out} as well as the location and spread of these tracer curves, as shown in Fig. E14.4a estimate the vessel **E** curve. We suspect that the tanks-in-series model reasonably represents the flow in the vessel.

SOLUTION

From Fig. E14.4a we have, for the vessel,

$$\Delta \bar{t} = 280 - 220 = 60 \text{ s}$$

$$\Delta(\sigma^2) = 1000 - 100 = 900 \text{ s}^2$$

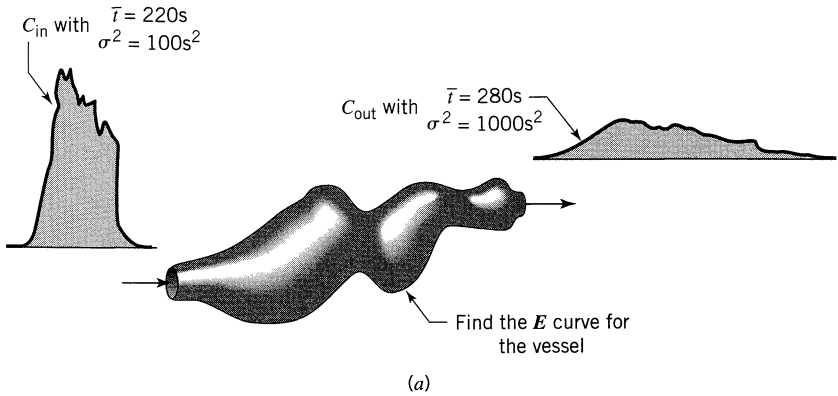


Figure E14.4a

Equation 3 represents the tanks-in-series model and gives

$$N = \frac{(\Delta\bar{t})^2}{\Delta(\sigma^2)} = \frac{60^2}{900} = 4 \text{ tanks}$$

So from Eq. 3a, for N tanks-in-series we have

$$E = \frac{t^{N-1}}{\bar{t}^N} \cdot \frac{N^N}{(N-1)!} e^{-tN/\bar{t}}$$

and for $N = 4$

$$E = \frac{t^3}{60^4} \cdot \frac{4^4}{3 \times 2} e^{-4t/60}$$

$$\underline{\underline{E = 3.2922 \times 10^{-6} t^3 e^{-0.0667t}}}$$

Figure E14.4b shows the shape of this E curve.

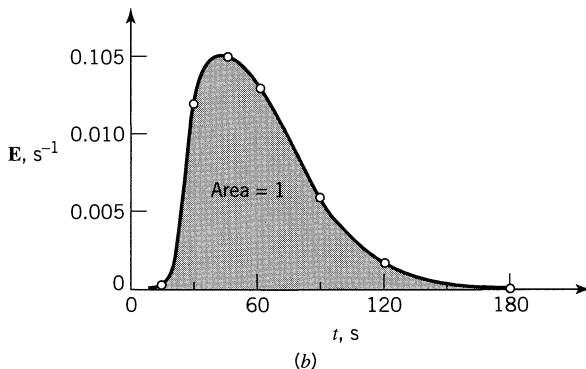


Figure E14.4b

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 MacMullin, R. B., and Weber, M., Jr., *Trans. AIChE*, **31**, 409 (1935).
 van der Vusse, J. G., *Chem. Eng. Sci.*, **17**, 507 (1962).
 Vonken, R. M., Holmes, D. B., and den Hartog, H. W., *Chem. Eng. Sci.*, **19**, 209 (1964).

PROBLEMS

- 14.1.** Fit the tanks-in-series model to the following mixing cup output data to a pulse input.

t	0-2	2-4	4-6	6-8	8-10	10-12
C	2	10	8	4	2	0

- 14.2.** Fluid flows at a steady rate through ten well-behaved tanks in series. A pulse of tracer is introduced into the first tank, and at the time this tracer leaves the system

$$\text{maximum concentration} = 100 \text{ mmol}$$

$$\text{tracer spread} = 1 \text{ min}$$

If ten more tanks are connected in series with the original ten tanks, what would be

- (a) the maximum concentration of leaving tracer?
 (b) the tracer spread?
 (c) How does the relative spread change with number of tanks?
- 14.3.** From the *New York Times Magazine*, December 25, 1955, we read: "The United States Treasury reported that it costs eight-tenths of a cent to print dollar bills, and that of the billion and a quarter now in circulation, a billion have to be replaced annually." Assume that the bills are put into circulation at a constant rate and continuously, and that they are withdrawn from circulation without regard to their condition, in a random manner.
- Suppose that a new series of dollar bills is put in circulation at a given instant in place of the original bills.
- (a) How many new bills will be in circulation at any time?
 (b) 21 years later, how many old bills will still be in circulation?
- 14.4.** Referring to the previous problem, suppose that during a working day a gang of counterfeiters put into circulation one million dollars in fake one-dollar bills.
- (a) If not detected, what will be the number in circulation as a function of time?
 (b) After 10 years, how many of these bills would still be in circulation?

- 14.5. Repeat Problem 13.13, but solve it using the tanks-in-series model instead of the dispersion model.
- 14.6. A stream of fully suspended fine solids ($v = 1 \text{ m}^3/\text{min}$) passes through two mixed flow reactors in series, each containing 1 m^3 of slurry. As soon as a particle enters the reactors, conversion to product begins and is complete after two minutes in the reactors. When a particle leaves the reactors, reaction stops. What fraction of particles is completely converted to product in this system?
- 14.7. Fit the RTD of Fig. P14.7 with the tanks-in-series model.

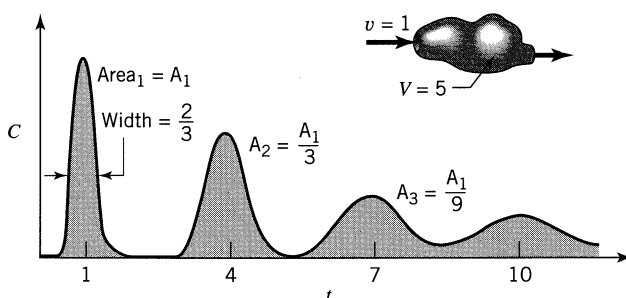


Figure P14.7

- 14.8. From a pulse input into a vessel we obtain the following output signal

Time, min	1	3	5	7	9	11	13	15
Concentration (arbitrary)	0	0	10	10	10	10	0	0

We want to represent the flow through the vessel with the tanks-in-series model. Determine the number of tanks to use.

- 14.9. Strongly radioactive waste fluids are stored in “safe-tanks” which are simply long, small-diameter (e.g., 20 m by 10 cm) slightly sloping pipes. To avoid sedimentation and development of “hot spots,” and also to insure uniformity before sampling the contents, fluid is recirculated in these pipes.

To model the flow in these tanks, a pulse of tracer is introduced and the curve of Fig. P14.9 is recorded. Develop a suitable model for this system and evaluate the parameters.

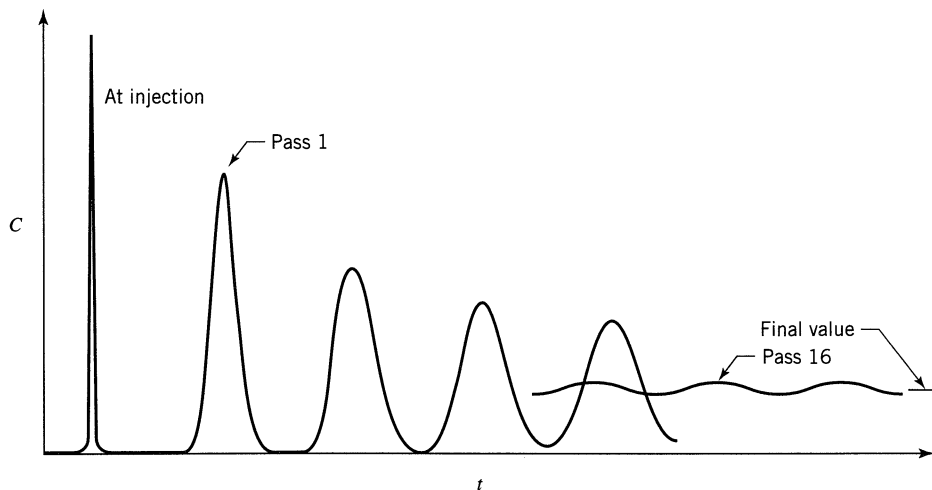
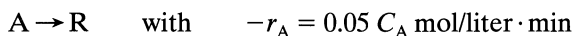


Figure P14.9 RTD for a closed recirculating system.

- 14.10.** A reactor with a number of dividing baffles is to be used to run the reaction



A pulse tracer test gives the following output curve:

Time, min	0	10	20	30	40	50	60	70
Concentration reading	35	38	40	40	39	37	36	35

- Find the area under the C versus t curve.
 - Find the E versus t curve.
 - Calculate the variance of the E curve.
 - How many tanks in series is this vessel equivalent to?
 - Calculate X_A assuming plug flow.
 - Calculate X_A assuming mixed flow.
 - Calculate X_A assuming the tanks-in-series model.
 - Calculate X_A directly from the data.
- 14.11.** A reactor has flow characteristics given by the nonnormalized C curve in Table P14.11, and by the shape of this curve we feel that the dispersion or tanks-in-series models should satisfactorily represent flow in the reactor.
- Find the conversion expected in this reactor, assuming that the dispersion model holds.
 - Find the number of tanks in series which will represent the reactor and the conversion expected, assuming that the tanks-in-series model holds.

Table P14.11.

Time	Tracer Concentration	Time	Tracer Concentration
0	0	10	67
1	9	15	47
2	57	20	32
3	81	30	15
4	90	41	7
5	90	52	3
6	86	67	1
8	77	70	0

- (c) Find the conversion by direct use of the tracer curve.
 (d) Comment on the difference in these results, and state which one you think is the most reliable.

Data. The elementary liquid-phase reaction taking place is $A + B \rightarrow$ products, with a large enough excess of B so that the reaction is essentially first order. In addition, if plug flow existed, conversion would be 99% in the reactor.

Chapter 15

The Convection Model for Laminar Flow

When a tube or pipe is long enough and the fluid is not very viscous, then the dispersion or tanks-in-series model can be used to represent the flow in these vessels. For a viscous fluid, one has laminar flow with its characteristic parabolic velocity profile. Also, because of the high viscosity there is but slight radial diffusion between faster and slower fluid elements. In the extreme we have the *pure convection model*. This assumes that each element of fluid slides past its neighbor with no interaction by molecular diffusion. Thus the spread in residence times is caused only by velocity variations. This flow is shown in Fig. 15.1. This chapter deals with this model.

15.1 THE CONVECTION MODEL AND ITS RTD

How to Tell from Theory Which Model to Use

The first question to ask is, “Which model should be used in a given situation?” The following chart, adapted from Ananthakrishnan et al. (1965), tells what regime you are in and which model to use. Just locate the point on Fig. 15.2 which corresponds to the fluid being used (Schmidt number), the flow conditions (Reynolds number), and vessel geometry (L/d_t). But be sure to check that your system is not in turbulent flow. Remember that this chart only has meaning if you have laminar flow. In this chart \mathcal{D}/ud_t is the reciprocal of the Bodenstein number. It measures the flow contribution made by molecular diffusion. It is NOT the axial dispersion number, \mathbf{D}/ud_t , except in the pure diffusion regime. The pure diffusion regime is not a very interesting regime because it represents very very slow flow.

Gases are likely to be in the dispersion regime, not the pure convection regime. Liquids can well be in one regime or another. Very viscous liquids such as polymers are likely to be in the pure convection regime. If your system falls in the no-man’s-land between regimes, calculate the reactor behavior based on

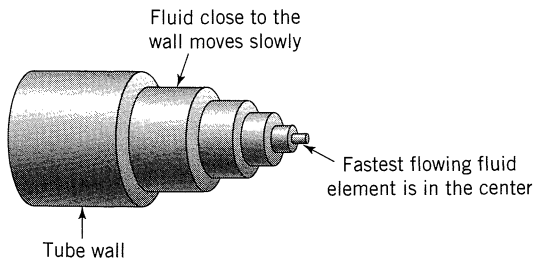


Figure 15.1 Flow of fluid according to the convection model.

the two bounding regimes and then try averaging. The numerical solution is impractically complex to use.

Finally, it is very important to use the correct type of model because the RTD curves are completely different for the different regimes. As an illustration, Fig. 15.3 shows RTD curves typical of these regimes.

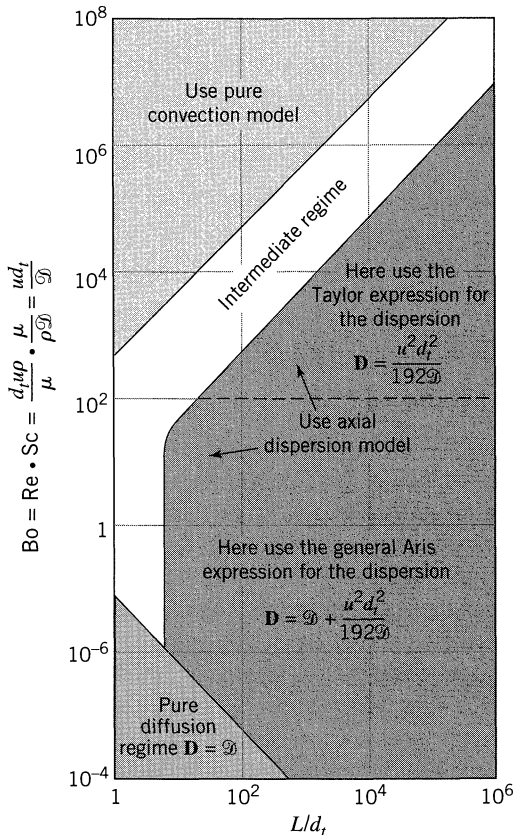


Figure 15.2 Map showing which flow models should be used in any situation.

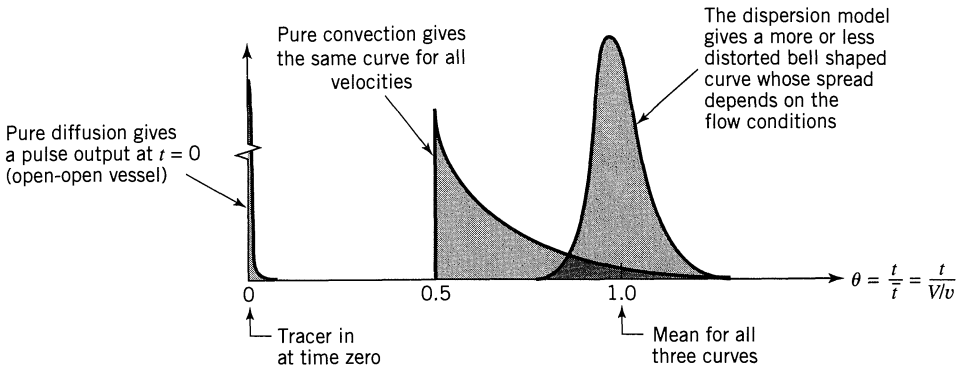


Figure 15.3 Comparison of the RTD of the three models.

How to Tell from Experiment Which Model to Use

The sharpest way of experimentally distinguishing between models comes by noting how a pulse or sloppy input pulse of tracer spreads as it moves downstream in a flow channel. For example, consider the flow, as shown in Fig. 15.4. The dispersion or tanks-in-series models are both stochastic models; thus, from Eq. 13.8 or Eq. 14.3 we see that the *variance grows linearly with distance* or

$$\sigma^2 \propto L \quad (1)$$

The convective model is a deterministic model; thus, the *spread of tracer grows linearly with distance*, or

$$\sigma \propto L \quad (2)$$

Whenever you have measurements of σ at 3 points use this test to tell which model to use. Just see if, in Fig. 15.4,

$$\frac{\Delta\sigma_{12}^2}{\Delta L_{12}} = \frac{\Delta\sigma_{23}^2}{\Delta L_{23}} \quad \text{or if} \quad \frac{\Delta\sigma_{12}}{\Delta L_{12}} = \frac{\Delta\sigma_{23}}{\Delta L_{12}} \quad (3)$$

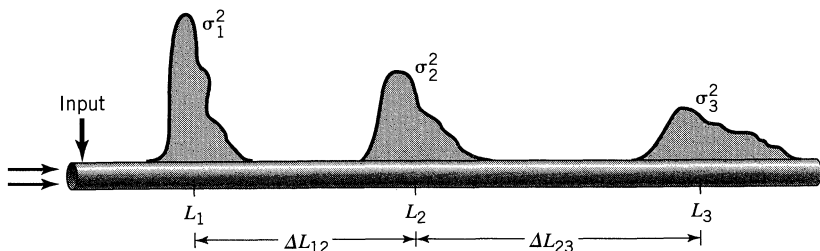


Figure 15.4 The changing spread of a tracer curve tells which model is the right one to use.

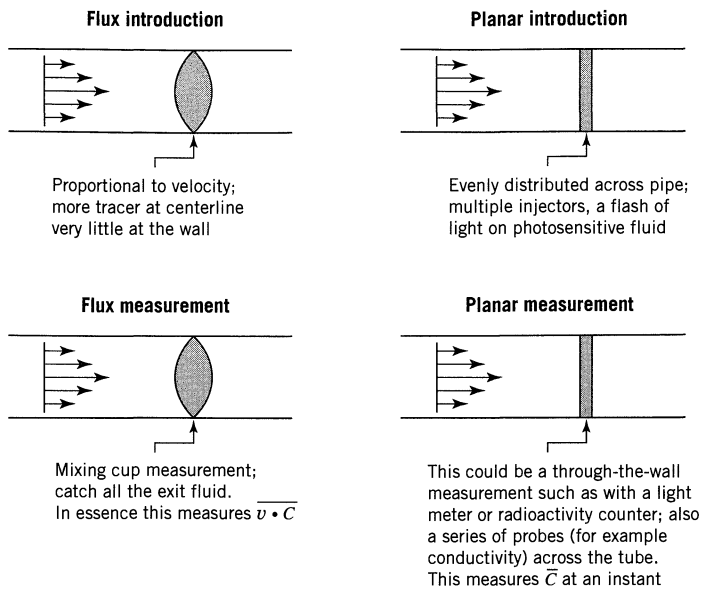


Figure 15.5 Various ways of introducing and measuring tracer.

Pulse Response Experiment and the E Curve for Laminar Flow in Pipes

The shape of the response curve is strongly influenced by the way tracer is introduced into the flowing fluid, and how it is measured. You may inject or measure the tracer in two main ways, as shown in Fig. 15.5. We therefore have four combinations of boundary conditions, as shown in Fig. 15.6, each with its own particular **E** curve. These **E** curves are shown in Fig. 15.7.

As may be seen in Fig. 15.7, the **E**, **E***, and **E**** curves are quite different, one from the other.

- **E** is the proper response curve for reactor purposes; it is the curve treated in Chapter 11, and it represents the RTD in the vessel.
- **E*** and ***E** are identical always, so we will call them **E*** from now on. One correction for the planar boundary condition will transform this curve to the proper RTD.
- **E**** requires two corrections—one for entrance, one for exit—to transform it to a proper RTD.

It may be simpler to determine **E*** or **E**** rather than **E**. This is perfectly all right. However, remember to transform these measured tracer curves to the **E** curve before calling it the RTD. Let us see how to make this transformation.

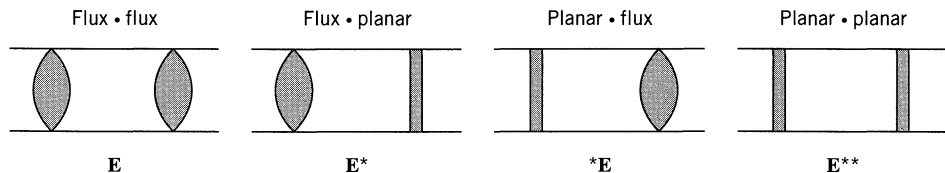


Figure 15.6 Various combinations of input-output methods.

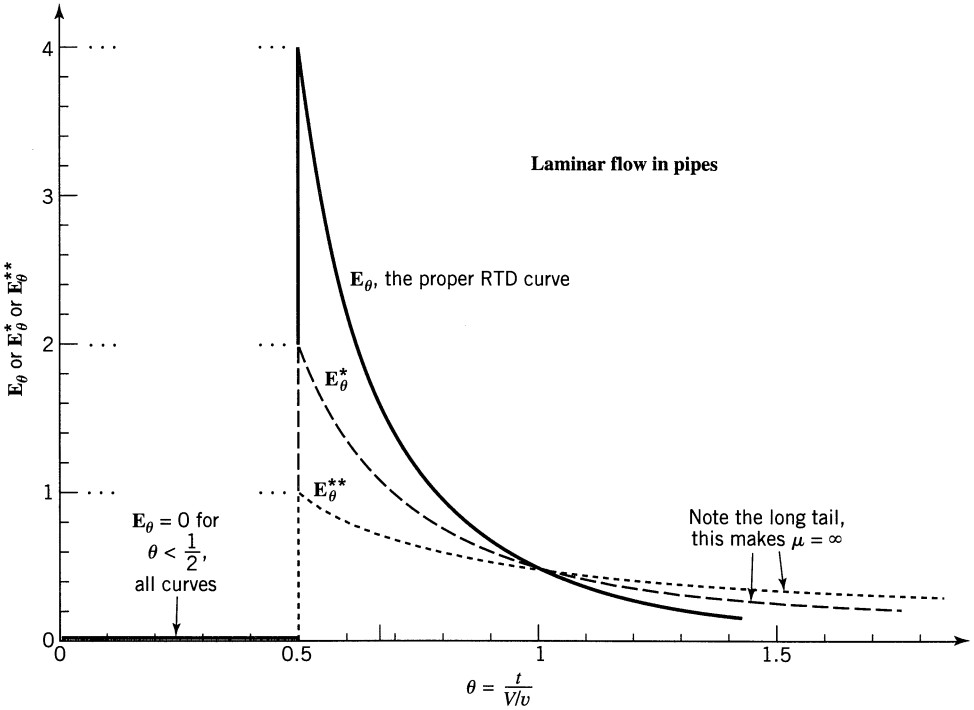


Figure 15.7 Note how different are the output curves depending on how you introduce and measure tracer.

For pipes and tubes with their parabolic velocity profile the various pulse response curves are found to be as follows:

$$\left. \begin{array}{l}
 \mathbf{E} = \frac{\bar{t}^2}{2t^3} \quad \text{for } t \geq \frac{\bar{t}}{2} \quad \left. \begin{array}{l} \mu_t = \bar{t} = \frac{V}{v} \\ \text{and} \\ \mu_\theta = 1 \end{array} \right\} \\
 \mathbf{E}_\theta = \frac{1}{2\theta^3} \quad \text{for } \theta \geq \frac{1}{2}
 \end{array} \right\} \\
 \\
 \left. \begin{array}{l}
 \mathbf{E}^* = \frac{\bar{t}}{2t^2} \quad \text{for } t \geq \frac{\bar{t}}{2} \quad \left. \begin{array}{l} \mu^* = \infty \\ \text{and} \\ \bar{t} = \frac{V}{v} \end{array} \right\} \\
 \mathbf{E}_\theta^* = \frac{1}{2\theta^2} \quad \text{for } \theta \geq \frac{1}{2} \quad \left. \begin{array}{l} \\ \text{and} \\ \theta = t / \frac{V}{v} \end{array} \right\}
 \end{array} \right\} \quad (4) \\
 \\
 \left. \begin{array}{l}
 \mathbf{E}^{**} = \frac{1}{2t} \quad \text{for } t \geq \frac{\bar{t}}{2} \quad \left. \begin{array}{l} \mu^{**} = \infty \\ \text{and} \\ \bar{t} = \frac{V}{v} \end{array} \right\} \\
 \mathbf{E}_\theta^{**} = \frac{1}{2\theta} \quad \text{for } \theta \geq \frac{1}{2} \quad \left. \begin{array}{l} \\ \text{and} \\ \theta = t / \frac{V}{v} \end{array} \right\}
 \end{array} \right\}$$

where μ , μ^* , and μ^{**} are the mean values of the measured curves.

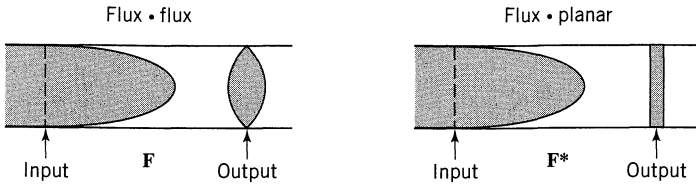


Figure 15.8 Two different ways of measuring the output curves.

Note the simple relationship between \mathbf{E} , \mathbf{E}^* , and \mathbf{E}^{**} . Thus at any time we can write

or

$$\left. \begin{aligned} \mathbf{E}_{\theta}^{**} &= \theta \mathbf{E}_{\theta}^* = \theta^2 \mathbf{E}_{\theta} \\ \mathbf{E}^{**} &= \frac{t}{\bar{t}} \mathbf{E}^* = \frac{t^2}{\bar{t}^2} \mathbf{E} \end{aligned} \right\} \text{ where } \bar{t} = \frac{V}{v} \quad (5)$$

Step Response Experiments and the F Curve for Laminar Flow in Pipes

When we do the step experiment by switching from one fluid to the other we obtain the C_{step} curve (see Chapter 11), from which we should be able to find the \mathbf{F} curve. However, this input always represents the flux input, while the output can be either planar or flux. Thus we only have two combinations, as shown in Fig. 15.8. With these two combinations of boundary conditions their equations and graphs are given in Eq. 6 and Fig. 15.9.

$$\left. \begin{aligned} \mathbf{F} &= 1 - \frac{1}{4\theta^2} \quad \text{for } \theta \geq \frac{1}{2} \\ \mathbf{F}^* &= 1 - \frac{1}{2\theta} \quad \text{for } \theta \geq \frac{1}{2} \end{aligned} \right\} \text{ where } \theta = t / \frac{V}{v} \quad (6)$$

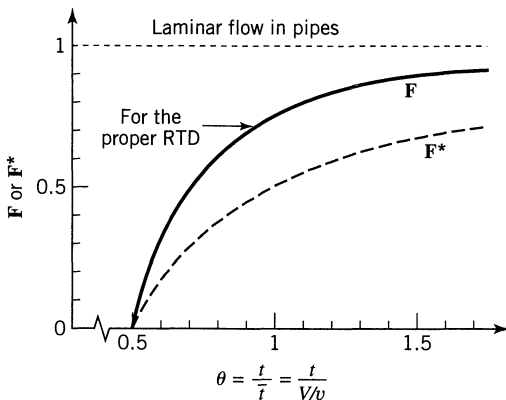


Figure 15.9 Different ways of measuring the output gives different \mathbf{F} curves.

Also each **F** curve is related to its corresponding **E** curve. Thus at any time t_1 or θ_1

$$\mathbf{F}^* = \int_0^{t_1} \mathbf{E}_t^* dt = \int_0^{\theta_1} \mathbf{E}_\theta^* d\theta \quad \text{and} \quad \mathbf{E}_t^* = \left. \frac{d\mathbf{F}^*}{dt} \right|_{t_1} \quad \text{or} \quad \mathbf{E}_\theta^* = \left. \frac{d\mathbf{F}^*}{d\theta} \right|_{\theta_1} \quad (7)$$

The relationship is similar between **E** and **F**.

E Curves for Non-newtonians and for Non-circular Channels

Since plastics and nonnewtonians are often very viscous they usually should be treated by the convective model of this chapter. The **E**, **E***, and **E**** curves for various situations besides newtonian fluids in circular pipes have been developed, for example,

- for power law fluids
- for Bingham plastics

E curves have also been developed

- for falling films
- for flow between parallel plates
- where line measurements are made rather than across the whole vessel cross section.

These **E** equations and corresponding charts plus sources to various other analyses can be found in Levenspiel, (1996).

15.2 CHEMICAL CONVERSION IN LAMINAR FLOW REACTORS

Single n -th Order Reactions

In the pure convection regime (negligible molecular diffusion) each element of fluid follows its own streamline with no intermixing with neighboring elements. In essence this gives macrofluid behavior. From Chapter 11 the conversion expression is then

$$\frac{C_A}{C_{A0}} = \int_0^\infty \left(\frac{C_A}{C_{A0}} \right)_{\text{element of fluid}} \cdot \mathbf{E} dt$$

for zero reaction order	$\frac{C_A}{C_{A0}} = 1 - \frac{kt}{C_{A0}}$ for $t \leq \frac{C_{A0}}{k}$
for first order reaction	$\frac{C_A}{C_{A0}} = e^{-kt}$
for second order reaction	$\frac{C_A}{C_{A0}} = \frac{1}{1 + kC_{A0}t}$

For zero-order reaction of a newtonian in laminar flow in a pipe, integration of Eq. 8 gives

$$\frac{C_A}{C_{A0}} = \left(1 - \frac{k\bar{t}}{2C_{A0}}\right)^2 \quad (9)$$

For first-order reaction of a newtonian in laminar flow in a pipe,

$$\frac{C_A}{C_{A0}} = \frac{\bar{t}^2}{2} \int_{\bar{t}/2}^{\infty} \frac{e^{-kt}}{t^3} dt = y^2 \text{ei}(y) + (1-y)e^{-y}, \quad y = \frac{k\bar{t}}{2} \quad (10)$$

where $\text{ei}(y)$ is the exponential integral, see Chapter 16.

For second-order reaction of a newtonian in laminar flow in a pipe:

$$\frac{C_A}{C_{A0}} = 1 - kC_{A0}\bar{t} \left[1 - \frac{kC_{A0}\bar{t}}{2} \ln \left(1 + \frac{2}{kC_{A0}\bar{t}} \right) \right] \quad (11)$$

These performance expressions were first developed by Bosworth (1948) for zero order, by Denbigh (1951) for second order, and by Cleland and Wilhelm (1956) for first order reactions. For other kinetics, channel shapes, or types of fluids insert the proper terms in the general performance expression and integrate.

Comments

- (a) *Test for the RTD curve.* Proper RTD curves must satisfy the material balance checks (calculated zero and first moments should agree with measured values)

$$\int_0^{\infty} \mathbf{E}_\theta d\theta = 1 \quad \text{and} \quad \int_0^{\infty} \theta \mathbf{E}_\theta d\theta = 1 \quad (12)$$

The \mathbf{E} curves of this chapter, for non-newtonians and all shapes of channels, all meet this requirement. All the \mathbf{E}^* and \mathbf{E}^{**} curves of this chapter do not; however, their transforms to \mathbf{E} do.

- (b) *The variance and other RTD descriptors.* The variance of all the \mathbf{E} curves of this chapter is finite; but it is infinite for all the \mathbf{E}^* and \mathbf{E}^{**} curves. So be sure you know which curve you are dealing with.

In general the convection model \mathbf{E} curve has a long tail. This makes the measurement of its variance unreliable. Thus σ^2 is not a useful parameter for convection models and is not presented here.

The breakthrough time θ_0 is probably the most reliably measured and most useful descriptive parameter for convection models, so it is widely used.

- (c) Comparison with plug flow for n th-order reaction is shown in Fig. 15.10.

This graph shows that even at high X_A convective flow does not drastically lower reactor performance. This result differs from the dispersion and tanks-in-series models (see Chapters 13 and 14).

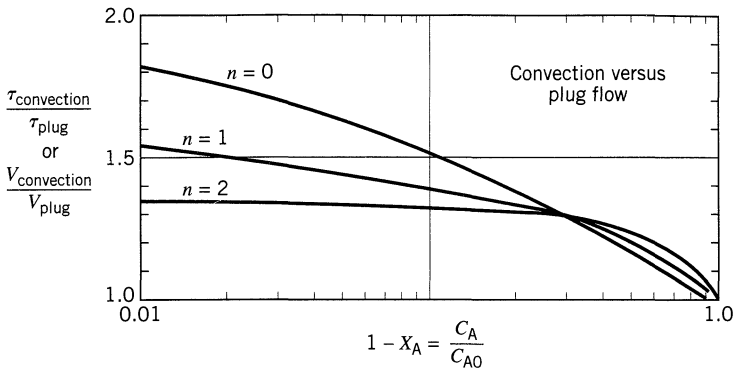
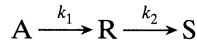


Figure 15.10 Convective flow lowers conversion compared to plug flow.

Multiple Reaction in Laminar Flow

Consider a two-step first-order irreversible reactions in series



Because laminar flow represents a deviation from plug flow, the amount of intermediate formed will be somewhat less than for plug flow. Let us examine this situation.

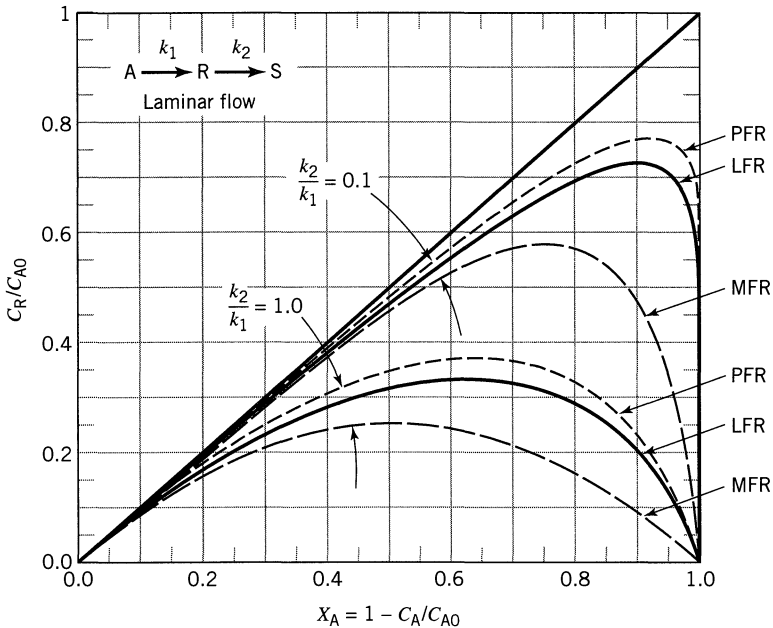


Figure 15.11 Typical product distribution curves for laminar flow compared with the curves for plug flow (Fig. 8.13) and mixed flow (Fig. 8.14).

The disappearance of A is given by the complicated Eq. 10, and the formation and disappearance of R is given by an even more complicated equation. Developing the product distribution relationship, solving numerically, and comparing the results with those for plug flow and for mixed flow gives Fig. 15.11; see Johnson (1970) and Levien and Levenspiel (1998).

This graph shows that the LFR gives a little less intermediate than does the PFR, about 20% of the way from the PFR to the MFR.

We should be able to generalize these findings to other more complex reaction systems, such as for two component multistep reactions; to polymerizations; and to non-Newtonian power law fluids.

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PROBLEMS

A viscous liquid is to react while passing through a tubular reactor in which flow is expected to follow the convection model. What conversion can we expect in this reactor if plug flow in the reactor will give 80% conversion?

15.1. Reaction follows zero-order kinetics.

15.2. Reaction is second order.

15.3. Assuming plug flow we calculate that a tubular reactor 12 m long would give 96% conversion of A for the second-order reaction $A \rightarrow R$. However, the fluid is very viscous, and flow will be strongly laminar, thus we expect the convection model, not the plug flow model, to closely represent the flow. How long should we make the reactor to insure 96% conversion of A?

15.4. Aqueous A ($C_{A0} = 1$ mol/liter) with physical properties close to water ($\rho = 1000$ kg/m³, $\mathcal{D} = 10^{-9}$ m²/s) reacts by a first-order homogeneous reaction ($A \rightarrow R$, $k = 0.2$ s⁻¹) as it flows at 100 mm/s through a tubular reactor ($d_t = 50$ mm, $L = 5$ m). Find the conversion of A in the fluid leaving this reactor.

- 15.5.** Aqueous A ($C_{A0} = 50 \text{ mol/m}^3$) with physical properties close to water ($\rho = 1000 \text{ kg/m}^3$, $\mathcal{D} = 10^{-9} \text{ m}^2/\text{s}$) reacts by a second-order reaction ($k = 10^{-3} \text{ m}^3/\text{mol}\cdot\text{s}$) as it flows at 10 mm/s through a tubular reactor ($d_t = 10 \text{ mm}$, $L = 20 \text{ m}$). Find the conversion of reactant A from this reactor.
- 15.6.** We want to model the flow of fluid in a flow channel. For this we locate three measuring points *A*, *B*, and *C*, 100 m apart along the flow channel. We inject tracer upstream of point *A*, fluid flows past points *A*, *B*, and *C* with the following results:
- At *A* the tracer width is 2 m
 - At *B* the tracer width is 10 m
 - At *C* the tracer width is 14 m
- What type of flow model would you try to use to represent this flow: dispersion, convective, tanks-in-series, or none of these? Give a reason for your answer.

Earliness of Mixing, Segregation, and RTD

The problem associated with the mixing of fluids during reaction is important for extremely fast reactions in homogeneous systems, as well as for all heterogeneous systems. This problem has two overlapping aspects: first, the *degree of segregation* of the fluid, or whether mixing occurs on the microscopic level (mixing of individual molecules) or the macroscopic level (mixing of clumps, groups, or aggregates of molecules); and second, the *earliness of mixing*, or whether fluid mixes early or late as it flows through the vessel.

These two concepts are intertwined with the concept of RTD, so it becomes rather difficult to understand their interaction. Please reread the first few pages of Chapter 11 where these concepts are introduced and discussed.

In this chapter we first treat systems in which a single fluid is reacting. Then we treat systems in which two fluids are contacted and reacted.

16.1 SELF-MIXING OF A SINGLE FLUID

Degree of Segregation

The normally accepted state of a liquid or gas is that of a microfluid, and all previous discussions on homogeneous reactions have been based on the assumption. Let us now consider a single reacting macrofluid being processed in turn in batch, plug flow, and mixed flow reactors, and let us see how this state of aggregation can result in behavior different from that of a microfluid.

Batch Reactor. Let the batch reactor be filled with a macrofluid containing reactant A. Since each aggregate or packet of macrofluid acts as its own little batch reactor, conversion is the same in all aggregates and is in fact identical to what would be obtained with a microfluid. Thus for batch operations the degree of segregation does not affect conversion or product distribution.

Plug Flow Reactor. Since plug flow can be visualized as a flow of small batch reactors passing in succession through the vessel, macro- and microfluids act

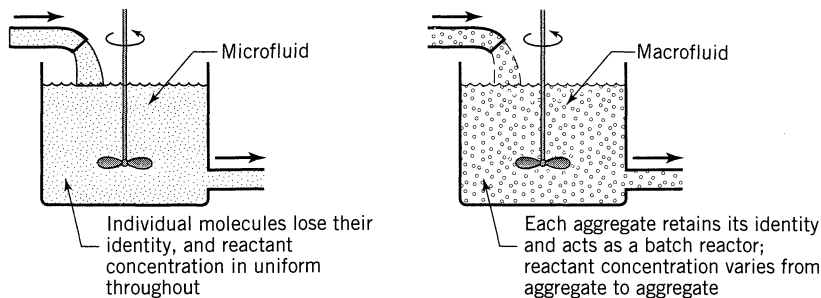


Figure 16.1 Difference in behavior of microfluids and macrofluids in mixed flow reactors.

alike. Consequently the degree of segregation does not influence conversion or product distribution.

Mixed Flow Reactor–Microfluid. When a microfluid containing reactant A is treated as in Fig. 16.1, the reactant concentration everywhere drops to the low value prevailing in the reactor. No clump of molecules retains its high initial concentration of A. We may characterize this by saying that each molecule loses its identity and has no determinable past history. In other words, by examining its neighbors we cannot tell whether a molecule is a newcomer or an old-timer in the reactor.

For this system the conversion of reactant is found by the usual methods for homogeneous reactions, or

$$X_A = \frac{(-r_A)V}{F_{A0}} \quad (5.11)$$

or, with no density changes,

$$\frac{C_A}{C_{A0}} = 1 - \frac{(-r_A)\bar{t}}{C_{A0}} \quad (1)$$

where \bar{t} is the mean residence time of fluid in the reactor.

Mixed Flow Reactor–Macrofluid. When a macrofluid enters a mixed flow reactor, the reactant concentration in an aggregate does not drop immediately to a low value but decreases in the same way as it would in a batch reactor. Thus a molecule in a macrofluid does not lose its identity, its past history is not unknown, and its age can be estimated by examining its neighboring molecules.

The performance equation for a macrofluid in a mixed flow reactor is given by Eq. 11.13 as

$$1 - \bar{X}_A = \frac{\bar{C}_A}{C_{A0}} = \int_0^\infty \left(\frac{C_A}{C_{A0}} \right)_{\text{batch}} \mathbf{E} dt \quad (11.13) \text{ or } (2)$$

where

$$\mathbf{E} dt = \frac{v}{V} e^{-vt/V} dt = \frac{e^{-t/\bar{t}}}{\bar{t}} dt \quad (3)$$

Replacing Eq. 3 in Eq. 2 gives

$$1 - \bar{X}_A = \frac{\bar{C}_A}{C_{A0}} = \int_0^\infty \left(\frac{C_A}{C_{A0}} \right)_{\text{batch}} \frac{e^{-t/\bar{t}}}{\bar{t}} dt \quad (4)$$

This is the general equation for determining conversion of macrofluids in mixed flow reactors, and it may be solved once the kinetics of the reaction is given. Consider various reaction orders.

For a *zero-order reaction* in a batch reactor, Chapter 3 gives

$$\left(\frac{C_A}{C_{A0}} \right)_{\text{batch}} = 1 - \frac{kt}{C_{A0}} \quad (3.31)$$

Inserting into Eq. 4 and integrating gives

$$\boxed{\frac{\bar{C}_A}{C_{A0}} = 1 - \frac{kt}{C_{A0}} (1 - e^{-C_{A0}/kt})} \quad (5)$$

For a *first-order reaction* in a batch, reactor Chapter 3 gives

$$\left(\frac{C_A}{C_{A0}} \right)_{\text{batch}} = e^{-kt} \quad (3.11)$$

On replacing into Eq. 4 we obtain

$$\frac{\bar{C}_A}{C_{A0}} = \frac{1}{\bar{t}} \int_0^\infty e^{-kt} e^{-t/\bar{t}} dt$$

which on integration gives the expression for conversion of a macrofluid in a mixed flow reactor

$$\boxed{\frac{\bar{C}_A}{C_{A0}} = \frac{1}{1 + k\bar{t}}} \quad (6)$$

This equation is identical to that obtained for a microfluid; for example, see Eq. 5.14a. Thus we conclude that the degree of segregation has no effect on conversion for first-order reactions.

For a *second-order reaction* of a single reactant in a batch reactor Eq. 3.16 gives

$$\left(\frac{C_A}{C_{A0}}\right)_{\text{batch}} = \frac{1}{1 + C_{A0}kt} \quad (7)$$

On replacing into Eq. 4 we find

$$\frac{\bar{C}_A}{C_{A0}} = \frac{1}{\bar{t}} \int_0^\infty \frac{e^{-t/\bar{t}}}{1 + C_{A0}kt} dt$$

and by letting $\alpha = 1/C_{A0}k\bar{t}$ and converting into reduced time units $\theta = t/\bar{t}$, this expression becomes

$$\frac{\bar{C}_A}{C_{A0}} = \alpha e^\alpha \int_\alpha^\infty \frac{e^{-(\alpha+\theta)}}{\alpha + \theta} d(\alpha + \theta) = \alpha e^\alpha \text{ei}(\alpha) \quad (8)$$

This is the conversion expression for second-order reaction of a macrofluid in a mixed flow reactor. The integral, represented by $\text{ei}(\alpha)$ is called an *exponential integral*. It is a function alone of α , and its value is tabulated in a number of tables of integrals. Table 16.1 presents a very abbreviated set of values for both $\text{ei}(x)$ and $\text{Ei}(x)$. We will refer to this table later in the book.

Table 16.1 Two of the Family of Exponential Integrals

x	$\text{Ei}(x)$	$\text{ei}(x)$	x	$\text{Ei}(x)$	$\text{ei}(x)$	x	$\text{Ei}(x)$	$\text{ei}(x)$
0	$-\infty$	$+\infty$	0.2	-0.8218	1.2227	2.0	4.9542	0.048 90
0.01	-4.0179	4.0379	0.3	-0.3027	0.9057	2.5	7.0738	0.024 91
0.02	-3.3147	3.3547	0.5	0.4542	0.5598	3.0	9.9338	0.013 05
0.05	-2.3679	2.4679	1.0	1.8951	0.2194	5.0	40.185	0.001 15
0.1	-1.6228	1.8229	1.4	3.0072	0.1162	7.0	191.50	0.000 12

Here are two useful exponential integrals

$$\left\{ \begin{array}{l} \text{Ei}(x) = \int_{-\infty}^x \frac{e^u}{u} du = 0.577 21 + \ln x + x + \frac{x^2}{2 \cdot 2!} + \frac{x^3}{3 \cdot 3} + \dots \\ \text{ei}(x) = \int_x^\infty \frac{e^{-u}}{u} du = -0.577 21 - \ln x + x - \frac{x^2}{2 \cdot 2!} + \frac{x^3}{3 \cdot 3!} - \dots \end{array} \right.$$

$$\text{for } x \geq 10 \left\{ \begin{array}{l} \text{Ei}(x) = e^x \left[\frac{1}{x} + \frac{1}{x^2} + \frac{2!}{x^3} + \frac{3!}{x^4} + \dots \right] \\ \text{ei}(x) = e^{-x} \left[\frac{1}{x} - \frac{1}{x^2} + \frac{2!}{x^3} - \frac{3!}{x^4} + \dots \right] \end{array} \right.$$

Equation 8 may be compared with the corresponding expression for microfluids, Eq. 5.14

$$\frac{C_A}{C_{A0}} = \frac{-1 + \sqrt{1 + 4C_{A0}k\bar{t}}}{2C_{A0}k\bar{t}} \quad (9)$$

For an n th-order reaction the conversion in a batch reactor can be found by the methods of Chapter 3 to be

$$\left(\frac{C_A}{C_{A0}}\right)_{\text{batch}} = [1 - (n-1)C_{A0}^{n-1}kt]^{1/(1-n)} \quad (10)$$

Insertion into Eq. 4 gives the conversion for an n th-order reaction of a macrofluid.

Difference in Performance: Early or Late Mixing, Macro- or Microfluids, PFR or MFR

Figure 16.2 illustrates the difference in performance of macrofluids and microfluids in mixed flow reactors, and they show clearly that a rise in segregation improves reactor performance for reaction orders greater than unity but lowers performance for reaction orders smaller than unity. Table 16.2 was used in preparing these charts.

Early and Late Mixing of Fluids

Each flow pattern of fluid through a vessel has associated with it a definite clearly defined residence time distribution (RTD), or exit age distribution function E . The converse is not true, however. Each RTD does not define a specific flow pattern; hence, a number of flow patterns—some with earlier mixing, others with later mixing of fluids—may be able to give the same RTD.

Idealized Pulse RTD. Reflection shows that the only pattern of flow consistent with this RTD is one with no intermixing of fluid of different ages, hence, that of plug flow. Consequently it is immaterial whether we have a micro- or macrofluid. In addition the question of early or late mixing of fluid is of no concern since there is no mixing of fluid of different ages.

Exponential Decay RTD. The mixed flow reactor can give this RTD. However, other flow patterns can also give this RTD, for example, a set of parallel plug flow reactors of proper length, a plug flow reactor with sidestreams, or a combination of these. Figure 16.3 shows a number of these patterns. Note that in patterns a and b entering fluid elements mix immediately with material of different ages, while in patterns c and d no such mixing occurs. Thus patterns a and b represent the microfluid, while patterns c and d represent the macrofluid.

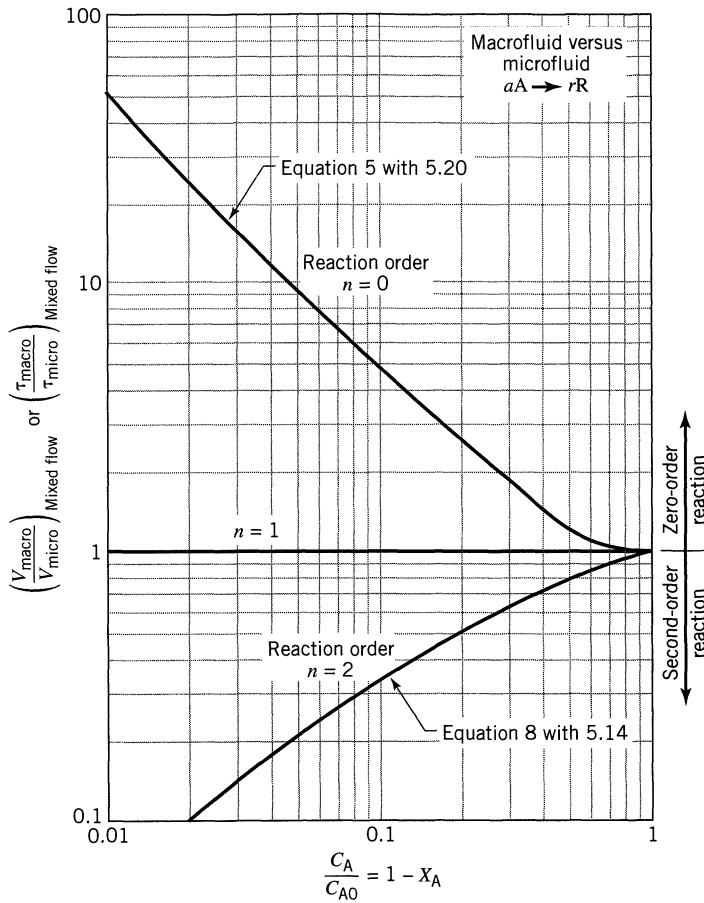


Figure 16.2 Comparison of performance of mixed flow reactors treating micro- and macrofluids; for zero- and second-order reactions with $\varepsilon_A = 0$.

Arbitrary RTD. In extending this argument we see that when the RTD is close to that of plug flow, then the state of segregation of fluid as well as early or late mixing of fluid has little effect on conversion. However, when the RTD approaches the exponential decay of mixed flow, then the state of segregation and earliness of mixing become increasingly important.

For any RTD one extreme in behavior is represented by the macrofluid and the latest mixing microfluid, and Eq. 2 gives the performance expression for this case. The other extreme is represented by the earliest mixing microfluid. The performance expression for this case has been developed by Zwietering (1959) but is difficult to use. Although these extremes give the upper and lower bound to the expected conversion for real vessels, it is usually simpler and preferable to develop a model to reasonably approximate the real vessel and then calculate conversions from this model. This is what actually was done in developing Fig. 13.20 for second-order reaction with axial dispersion. There we assumed that the same extent of mixing occurs along the whole vessel.

Table 16.2 Conversion Equations for Macrofluids and Microfluids with $\varepsilon = 0$ in Ideal Reactors

	Plug Flow		Mixed Flow	
	Microfluid or Macrofluid	Microfluid	Microfluid	Macrofluid
General kinetics	$\tau = \int_{C_0}^C \frac{dC}{-r}$	$\tau = \frac{C_0 - C}{-r}$	$\frac{\bar{C}}{C_0} = \frac{1}{\tau} \int_0^\infty \left(\frac{C}{C_0}\right)_{\text{batch}} e^{-t/\tau} dt$	
n th-order reaction ($R = C_0^{n-1}k\tau$)	$\frac{C}{C_0} = [1 + (n-1)R]^{1/(1-n)}$ $R = \frac{1}{n-1} \left[\left(\frac{C}{C_0}\right)^{1-n} - 1 \right]$	$\left(\frac{C}{C_0}\right)^n R + \frac{C}{C_0} - 1 = 0$ $R = \left(1 - \frac{C}{C_0}\right) \left(\frac{C_0}{C}\right)^n$	$\frac{\bar{C}}{C_0} = \frac{1}{\tau} \int_0^\infty [1 + (n-1)C_0^{n-1}kt]^{1/(1-n)} e^{-t/\tau} dt$	
Zero-order reaction ($R = \frac{k\tau}{C_0}$)	$\frac{C}{C_0} = 1 - R, \quad R \leq 1$ $C = 0, \quad R \geq 1$	$\frac{C}{C_0} = 1 - R, \quad R \leq 1$ $C = 0, \quad R \geq 1$	$\frac{\bar{C}}{C_0} = 1 - R + Re^{-1/R}$	
First-order reaction ($R = k\tau$)	$\frac{C}{C_0} = e^{-R}$ $R = \ln \frac{C_0}{C}$	$\frac{C}{C_0} = \frac{1}{1+R}$ $R = \frac{C_0}{C} - 1$	$\frac{\bar{C}}{C_0} = \frac{1}{1+R}$ $R = \frac{C_0}{C} - 1$	
Second-order reaction ($R = C_0k\tau$)	$\frac{C}{C_0} = \frac{1}{1+R}$ $R = \frac{C_0}{C} - 1$	$\frac{C}{C_0} = \frac{-1 + \sqrt{1+4R}}{2R}$ $R = \left(\frac{C_0}{C} - 1\right) \frac{C_0}{C}$	$\frac{\bar{C}}{C_0} = \frac{e^{1/R}}{R} \text{ei} \left(\frac{1}{R}\right)$	

$R = C_0^{n-1}k\tau$, reaction rate group for n th-order reaction, a time or capacity factor. $\tau = \bar{t}$ since $\varepsilon = 0$ throughout.

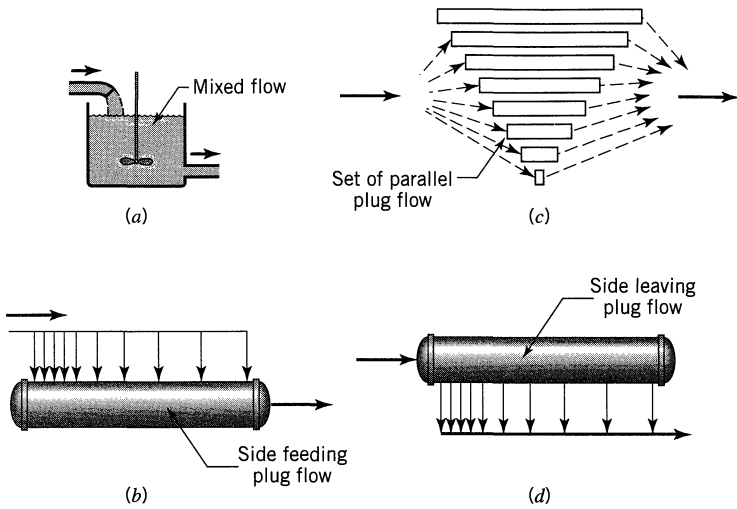


Figure 16.3 Four contacting patterns which can all give the same exponential decay RTD. Cases *a* and *b* represent the earliest possible mixing while cases *c* and *d* represent the latest possible mixing of fluid elements of different ages.

Summary of Findings for a Single Fluid

1. *Factors affecting the performance of a reactor.* In general we may write

$$\text{Performance: } X_A \text{ or } \varphi \left(\frac{R}{A} \right) = f \left(\begin{array}{l} \text{kinetics, RTD, degree of segregation,} \\ \text{earliness of mixing} \end{array} \right) \quad (11)$$

2. *Effect of kinetics, or reaction order.* Segregation and earliness of mixing affect the conversion of reactant as follows

$$\text{For } n > 1 \dots X_{\text{macro}} \text{ and } X_{\text{micro, late}} > X_{\text{micro, early}}$$

For $n < 1$ the inequality is reversed, and for $n = 1$ conversion is unaffected by these factors. This result shows that segregation and late mixing improves conversion for $n > 1$, and decreases conversion for $n < 1$.

3. *Effect of mixing factors for nonfirst-order reactions.* Segregation plays no role in plug flow; however, it increasingly affects the reactor performance as the RTD shifts from plug to mixed flow.
4. *Effect of conversion level.* At low conversion levels X_A is insensitive to RTD, earliness of mixing, and segregation. At intermediate conversion levels, the RTD begins to influence X_A ; however, earliness and segregation still have little effect. This is the case of Example 16.1. Finally, at high conversion levels all these factors may play important roles.
5. *Effect on product distribution.* Although segregation and earliness of mixing can usually be ignored when treating single reactions, this often is not so with multiple reactions where the effect of these factors on product distribution can be of dominating importance, even at low conversion levels.

As an example consider free-radical polymerization. When an occasional free radical is formed here and there in the reactor it triggers an extremely rapid chain of reactions, often thousands of steps in a fraction of a second. The local reaction rate and conversion can thus be very high. In this situation the immediate surroundings of the reacting and growing molecules—and hence the state of segregation of the fluid—can greatly affect the type of polymer formed.

EXAMPLE 16.1 EFFECT OF SEGREGATION AND EARLINESS OF MIXING ON CONVERSION

A second-order reaction occurs in a reactor whose RTD is given in Fig. E16.1. Calculate the conversion for the flow schemes shown in this figure. For simplicity take $C_0 = 1$, $k = 1$, and $\tau = 1$ for each unit.

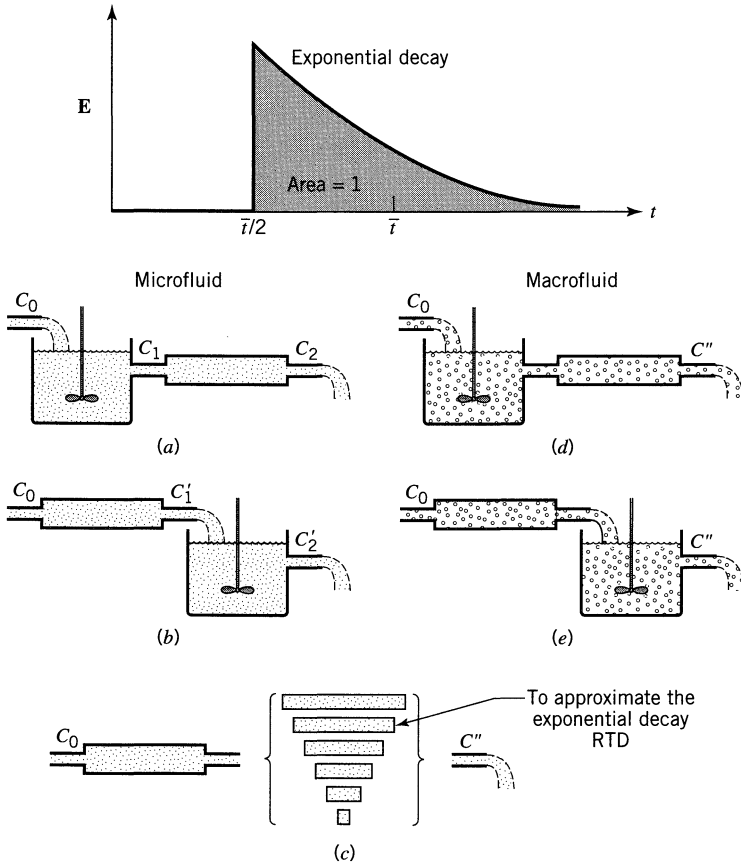


Figure E16.1 (a) Microfluid, early mixing at molecular level; (b) Microfluid, fairly late mixing at molecular level; (c) Microfluid, late mixing at molecular level; (d) Macrofluid, early mixing of elements; (e) Macrofluid, late mixing of elements.

SOLUTION

Scheme A. Referring to Fig. E16.1a we have for the mixed flow reactor

$$\tau = 1 = \frac{C_0 - C_1}{kC_1^2} = \frac{1 - C_1}{C_1^2}$$

or

$$C_1 = \frac{-1 + \sqrt{1 + 4}}{2} = 0.618$$

For the plug flow reactor

$$\tau = 1 = -\int_{C_1}^{C_2} \frac{dC}{kC^2} = \frac{1}{k} \left(\frac{1}{C_2} - \frac{1}{C_1} \right)$$

or

$$\underline{\underline{\text{Micro-early: } C_2 = \frac{C_1}{C_1 + 1} = \frac{0.618}{1.168} = 0.382}}$$

Scheme B. Referring to Fig. E16.1b, we have for the plug flow reactor

$$\tau = 1 = -\int_{C_0}^{C_1'} \frac{dC}{kC^2} = \frac{1}{C_1'} - 1$$

or

$$C_1' = 0.5$$

For the mixed reactor

$$\tau = 1 = \frac{C_1' - C_2'}{kC_2'^2} = \frac{0.5 - C_2'}{C_2'^2}$$

or

$$\underline{\underline{\text{Micro-fairly late: } C_2' = 0.366}}$$

Scheme C, D, and E. From Fig. 12.1 the exit age distribution function for the two equal-size plug-mixed flow reactor system is

$$\mathbf{E} = \frac{2}{t} e^{1-2/t}, \quad \text{when } \frac{t}{\bar{t}} > \frac{1}{2}$$

$$= 0, \quad \text{when } \frac{t}{\bar{t}} < \frac{1}{2}$$

Thus Eq. 3 becomes

$$C'' = \int_{\bar{t}/2}^{\infty} \frac{1}{1 + C_0 k t} \cdot \frac{2}{\bar{t}} e^{1-2t/\bar{t}} dt$$

With the mean residence time in the two-vessel system $\bar{t} = 2$ min, this becomes

$$C'' = \int_1^{\infty} \frac{e^{1-t}}{1+t} dt$$

and replacing $1 + t$ by x we obtain the exponential integral

$$C'' = \int_2^{\infty} \frac{e^{2-x}}{x} dx = e^2 \int_2^{\infty} \frac{e^{-x}}{x} dx = e^2 \text{ei}(2)$$

From the table of integrals in Table 16.1 we find $\text{ei}(2) = 0.04890$ from which

$$\underline{\underline{\text{Micro-late, and macro-late or early: } C'' = 0.362}}$$

The results of this example confirm the statements made above: that macrofluids and late mixing microfluids give higher conversions than early mixing microfluids for reaction orders greater than unity. The difference is small here because the conversion levels are low; however, this difference becomes more important as conversion approaches unity.

Extensions for a Single Fluid

Partial Segregation. There are various ways of treating intermediate extents of segregation, for example,

Intensity of segregation model—Danckwerts (1958)

Coalescence model—Curl (1963), Spielman and Levenspiel (1965)

Two environment and melting ice cube models—Ng and Rippin (1965) and Suzuki (1970)

These approaches are discussed in Levenspiel (1972).

The Life of an Element of Fluid. Let us estimate how long a fluid element retains its identity. First, all large elements are broken into smaller elements by stretching or folding (laminar behavior) or by turbulence generated by baffles, stirrers, etc., and mixing theory estimates the time needed for this breakup.

Small elements lose their identity by the action of molecular diffusion, and the Einstein random walk analysis estimates this time as

$$t = \frac{(\text{size of element})^2}{\left(\begin{array}{c} \text{diffusion} \\ \text{coefficient} \end{array} \right)} = \frac{d_{\text{element}}^2}{\mathcal{D}} \quad (12)$$

Thus an element of water 1 micron in size would lose its identity in a very short time, approximately

$$t = \frac{(10^{-4} \text{ cm})^2}{10^{-5} \text{ cm}^2/\text{sec}} = 10^{-3} \text{ sec} \quad (13a)$$

while an element of viscous polymer 1.0 mm in size and 100 times as viscous as water (10–30 W motor oil at room temperature) would retain its identity for a long time, roughly

$$t = \frac{(10^{-1} \text{ cm})^2}{10^{-7} \text{ cm}^2/\text{sec}} = 10^5 \text{ sec} \approx 30 \text{ hr} \quad (13b)$$

In general, then, ordinary fluids behave as microfluids except for very viscous materials and for systems in which very fast reactions are taking place.

The concept of micro- and macrofluids is of particular importance in heterogeneous systems because one of the two phases of such systems usually approximates a macrofluid. For example, the solid phase of fluid-solid systems can be treated exactly as a macrofluid because each particle of solid is a distinct aggregate of molecules. For such systems, then, Eq. 2 with the appropriate kinetic expression is the starting point for design.

In the chapters to follow we apply these concepts of micro- and macrofluids to heterogeneous systems of various kinds.

16.2 MIXING OF TWO MISCIBLE FLUIDS

Here we consider one topic, the role of the mixing process when two completely miscible reactant fluids A and B are brought together. When two miscible fluids A and B are mixed, we normally assume that they first form a homogeneous mixture which then reacts. However, when the time required for A and B to become homogeneous is not short with respect to the time for reaction to take place, reaction occurs during the mixing process, and the problem of mixing becomes important. Such is the case for very fast reactions or with very viscous reacting fluids.

To help understand what occurs, imagine that we have A and B available, each first as a microfluid, and then as a macrofluid. In one beaker mix micro A with micro B, and in another beaker mix macro A with macro B and let them react. What do we find? Micro A and B behave in the expected manner, and reaction occurs. However, on mixing the macrofluids no reaction takes place because molecules of A cannot contact molecules of B. These two situations are illustrated in Fig. 16.4. So much for the treatment of the two extremes in behavior.

Now a real system acts as shown in Fig. 16.5 with regions of A-rich fluid and regions of B-rich fluid.

Though partial segregation requires an increase in reactor size, this is not the only consequence. For example, when reactants are viscous fluids, their mixing in a stirred tank or batch reactor often places layers or “streaks” of one fluid next to the other. As a result reaction occurs at different rates from point to

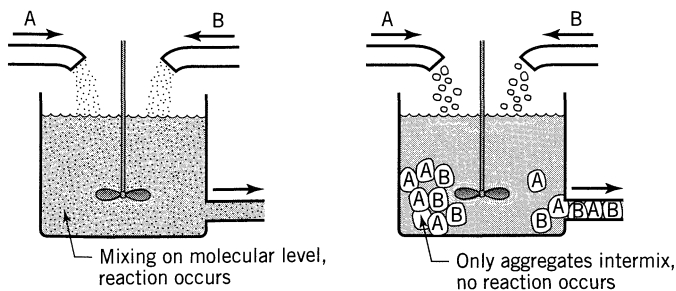


Figure 16.4 Difference in behavior of microfluids and macrofluids in the reaction of A and B.

point in the reactor, giving a nonuniform product which may be commercially unacceptable. Such is the case in polymerization reactions in which monomer must be intimately mixed with a catalyst. For reactions such as this, proper mixing is of primary importance and often the rate of reaction and product uniformity correlate well with the mixing energy input to the fluid.

For fast reactions the increase in reactor size needed because of segregation is of secondary importance while other effects become important. For example, if the product of reaction is a solid precipitate, the size of the precipitate particles may be influenced by the rate of intermixing of reactants, a fact that is well known from the analytical laboratory. As another example, hot gaseous reaction mixtures may contain appreciable quantities of a desirable compound because of favorable thermodynamic equilibrium at such temperatures. To reclaim this component the gas may have to be cooled. But, as is often the case, a drop in temperature causes an unfavorable shift in equilibrium with essentially complete disappearance of desired material. To avoid this and to "freeze" the composition of hot gases, cooling must be very rapid. When the method of quenching used involves mixing the hot gases with an inert cold gas, the success of such a procedure is primarily dependent on the rate at which segregation can be destroyed. Finally the length, type, and temperature of a burning flame, the combustion products obtained, the noise levels of jet engines, and the physical properties of polymers as they are affected by the molecular weight distribution of the

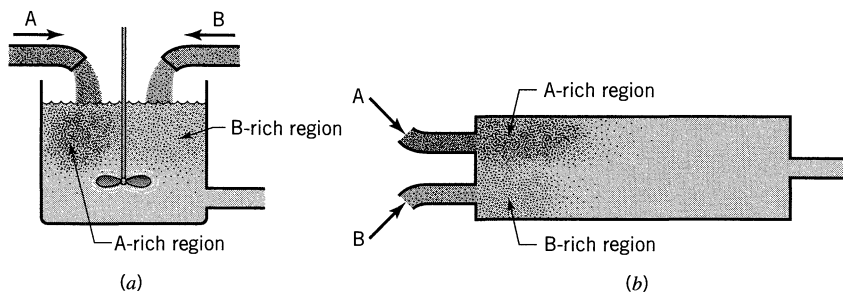


Figure 16.5 Partial segregation in the mixing of two miscible fluids in a reactor.

material are some of the many phenomena that are closely influenced by the rate and intimacy of fluid mixing.

Product Distribution in Multiple Reactions

When multiple reactions take place on mixing two reactant fluids and when these reactions proceed to an appreciable extent before homogeneity is attained, segregation is important and can affect product distribution.

Consider the homogeneous-phase competitive consecutive reactions



occurring when A and B are poured into a batch reactor. If the reactions are slow enough so that the contents of the vessel are uniform before reaction takes place, the maximum amount of R formed is governed by the k_2/k_1 ratio. This situation, treated in Chapter 8, is one in which we may assume microfluid behavior. If, however, the fluids are very viscous or if the reactions are fast enough, they will occur in the narrow zones between regions of high A concentration and high B concentration. This is shown in Fig. 16.6. The zone of high reaction rate will contain a higher concentration of R than the surrounding fluid. But from the qualitative treatment of this reaction in Chapter 8 we know that any nonhomogeneity in A and R will depress formation of R. Thus partial segregation of reactants will depress the formation of intermediate.

For increased reaction rate, the zone of reaction narrows, and in the limit, for an infinitely fast reaction, becomes a boundary surface between the A-rich and

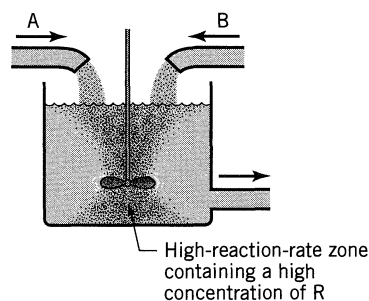
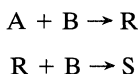


Figure 16.6 When reaction rate is very high, zones of nonhomogeneity exist in a reactor. This condition is detrimental to obtaining high yields of intermediate R from the reactions



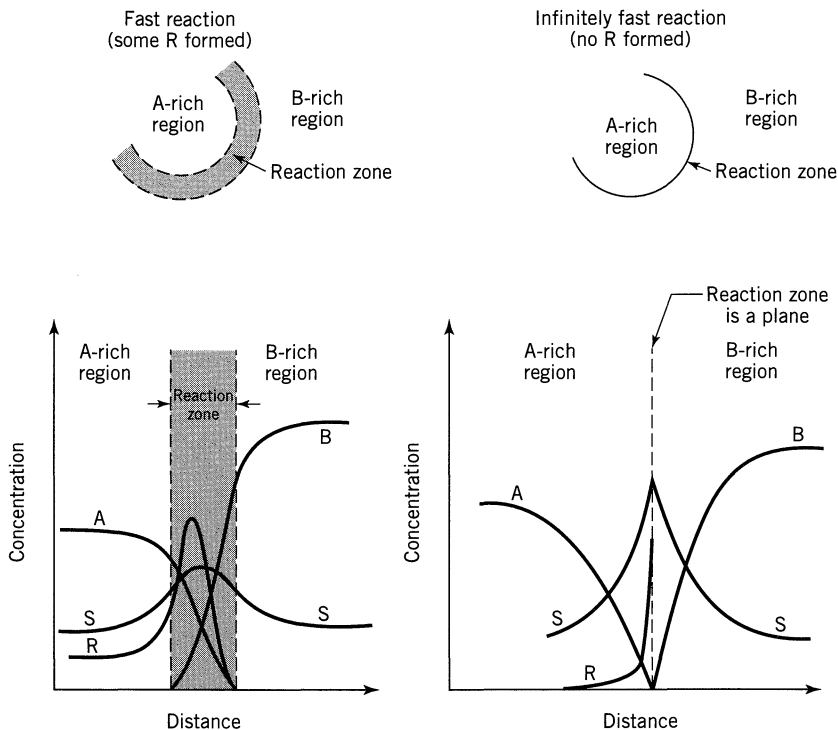


Figure 16.7 Concentration profiles of the components of the reactions



at a representative spot in the reactor between A-rich and B-rich fluid for a very fast and for an infinitely fast reaction.

B-rich regions. Now R will only be formed at this plane. What will happen to it? Consider a single molecule of R formed at the reaction plane. If it starts its random wanderings (diffusion) into the A zone and never moves back into the B zone, it will not react further and will be saved. However, if it starts off into the B zone or if at any time during its wanderings it moves through the reaction plane into the B zone, it will be attacked by B to form S. Interestingly enough, from probabilities associated with a betting game treated by Feller (1957), we can show that the odds in favor of a molecule of R never entering the B zone become smaller and smaller as the number of diffusion steps taken by a molecule gets larger and larger. This finding holds, no matter what pattern of wanderings is chosen for the molecules of R. Thus we conclude that no R is formed. Looked at from the point of view of Chapter 8, an infinitely fast reaction gives a maximum nonhomogeneity of A and R in the mixture, resulting in no R being formed. Figure 16.7 shows the concentration of materials at a typical reaction interface and illustrates these points.

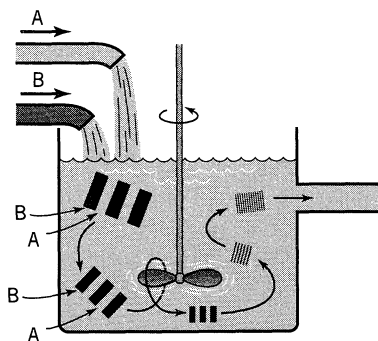


Figure 16.8 Stretching, folding, and thinning of sheets of very viscous A and B.

This behavior of multiple reaction could provide a powerful tool in the study of partial segregation in homogeneous systems. It has been used by Paul and Treybal (1971) who simply poured reactant B into a beaker of A and measured the amount of R formed for a very fast reaction of Eq. 14.

Ottino (1989, 1994) discuss the whole problem of intermixing of fluids A and B in terms of stretching, folding, thinning, and finally diffusional mixing of fluid elements. Figure 16.8 tries to illustrate this mechanism; however, we must now leave this fascinating subject.

These observations serve as a guide to the selection and design of equipment favoring the formation of intermediate when reaction is very fast. The important point is to achieve homogeneity in A and R throughout the reaction mixture before reaction has proceeded to any significant extent. This is done by:

- (a) making the reaction zone as large as possible by vigorous mixing.
- (b) dispersing B in A in as fine a form as possible, rather than A in B.
- (c) slowing the reaction.

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Part III

Reactions Catalyzed by Solids

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Chapter 17

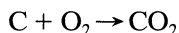
Heterogeneous Reactions—Introduction

The second half of this book treats the kinetics and design of chemical reactors for heterogeneous systems of various kinds, each chapter considering a different system (see Chapter 1 for discussions of heterogeneous and homogeneous systems). For these systems there are two complicating factors that must be accounted for beyond what is normally considered in homogeneous systems. First, we have the complication of the rate expression, and second the complication of the contacting patterns for two-phase systems. Let us briefly discuss these in turn.

The Complications of the Rate Equation. Since more than one phase is present, the movement of material from phase to phase must be considered in the rate equation. Thus the rate expression in general will incorporate mass transfer terms in addition to the usual chemical kinetics term. These mass transfer terms are different in type and numbers in the different kinds of heterogeneous systems; hence, no single rate expression has general application. Here are some simple examples.

EXAMPLE 17.1 *THE BURNING OF A CARBON PARTICLE IN AIR*

Tell how many rate steps are involved. The kinetics is given by



and ignore the possible formation of CO.

SOLUTION

From Fig. E17.1 we see that two steps in series are involved—mass transfer of oxygen to the surface followed by reaction at the surface of the particle.

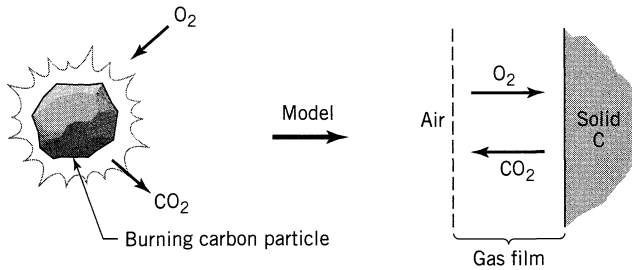


Fig. E17.1

EXAMPLE 17.2 AEROBIC FERMENTATION

Tell how many rate steps are involved when air bubbles through a tank of liquid which contains dispersed microbes and is taken up by the microbes to produce product material.

SOLUTION

From Fig. E17.2 we see that there are up to seven possible resistance steps, only one involving the reaction. How many you choose to consider depends on you and on the situation.

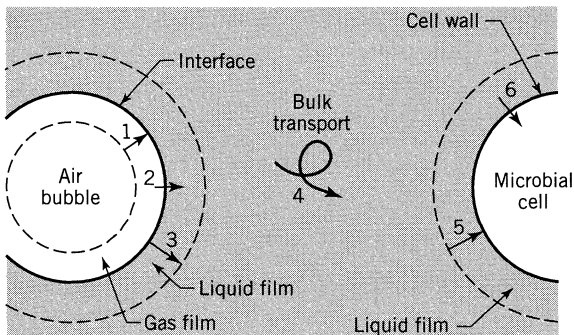


Fig. E17.2

To get an overall rate expression, write the individual rate steps on the same basis (unit surface of burning particle, unit volume of fermenter, unit volume of cells, etc.).

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt} = \frac{\text{mol A reacted}}{\text{volume of reactor fluid} \cdot \text{time}}$$

or

$$-r'_A = -\frac{1}{W} \frac{dN_A}{dt} = \frac{\text{mol A reacted}}{\text{mass of solid} \cdot \text{time}}$$

or

$$-r''_A = -\frac{1}{S} \frac{dN_A}{dt} = \frac{\text{mol A reacted}}{\text{interfacial surface} \cdot \text{time}}$$

Now put all the mass transfer and reaction steps into the same rate form and then combine. Thus

$$\frac{\text{mol A reacted}}{\text{time}} = (-r_A)V = (-r'_A)W = (-r''_A)S$$

or

$$r_A = \frac{W}{V} r'_A, \quad r''_A = \frac{V}{S} r_A, \quad r'_A = \frac{S}{W} r''_A$$

and if the steps are in series, as in Examples 17.1 and 17.2

$$r_{\text{overall}} = r_1 = r_2 = r_3$$

If they are in parallel

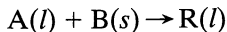
$$r_{\text{overall}} = r_1 + r_2$$

Consider steps in series. In general, if all the steps are linear in concentration, then it is easy to combine them. However, if any of the steps are nonlinear, then you will get a messy overall expression. Therefore, you may try to bypass this nonlinear step in one of various ways. Approximating the r_A versus C_A curve by a first-order expression is probably the most useful procedure.

Another point: in combining rates we normally do not know the concentration of materials at intermediate conditions, so these are the concentrations that we eliminate in combining rates. Example 17.3 shows this.

EXAMPLE 17.3 OVERALL RATE FOR A LINEAR PROCESS

Dilute A diffuses through a stagnant liquid film onto a plane surface consisting of B, reacts there to produce R which diffuses back into the mainstream. Develop the overall rate expression for the L/S reaction



which takes place on this flat surface, see Fig. E17.3.

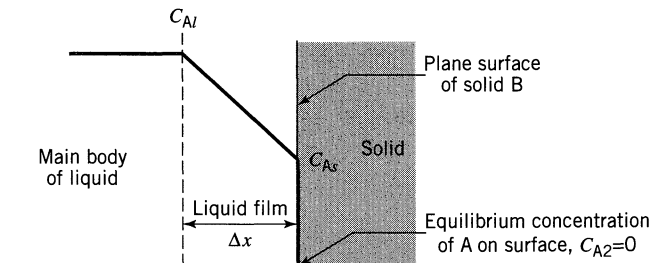


Figure E17.3.

SOLUTION

By diffusion, the flux of A to the surface is

$$r''_{A1} = \frac{1}{S} \frac{dN_A}{dt} = -\frac{\mathcal{D}}{\Delta x} (C_{Al} - C_{As}) = k_l (C_{Al} - C_{As}) \quad \text{(i)}$$

Reaction is first order with respect to A, so based on unit surface

$$r''_{A2} = \frac{1}{S} \frac{dN_A}{dt} = k'' C_{As} \quad \text{(ii)}$$

At steady state the flow rate to the surface is equal to the reaction rate at the surface (steps in series). So

$$r''_{A1} = r''_{A2}$$

and from Eqs. (i) and (ii)

$$k_l (C_{Al} - C_{As}) = k'' C_{As}$$

from which

$$C_{A_s} = \frac{k_l}{k_l + k''} C_{A_l} \quad (\text{iii})$$

Replacing Eq. (iii) into either Eq. (i) or Eq. (ii) then eliminates C_{A_s} which cannot be measured, giving

$$r''_{A1} = r''_{A2} = r''_A = -\frac{1}{\frac{1}{k_l} + \frac{1}{k''}} C_{A_l} = -k_{\text{overall}} C_{A_l}, \quad \left[\frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \right]$$

Comment This result shows that $1/k_l$ and $1/k''$ are additive resistances. It so happens that the addition of resistances to obtain an overall resistance is permissible only when the rate is a linear function of the driving force and when the processes occur in series.

EXAMPLE 17.4 OVERALL RATE FOR A NONLINEAR PROCESS

Repeat Example 17.3 with just one change: let the reaction step be second order with respect to A, or

$$r''_{A2} = -k'' C_A^2$$

SOLUTION

Combining the reaction steps to eliminate C_{A_s} , as was done in Example 17.3, is now not so simple, and gives

$$-r''_A = -r''_{A1} = -r''_{A2} = \frac{k_l}{2k''} (2k'' C_{A_l} + k_l - \sqrt{k_l^2 + 4k''k_l C_{A_l}}), \quad \left[\frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \right]$$

Contacting Patterns for Two-Phase Systems

There are many ways that two phases can be contacted, and for each the design equation will be unique. Design equations for these ideal flow patterns may be developed without too much difficulty. However, when real flow deviates considerably from these, we can do one of two things: we may develop models to mirror actual flow closely, or we may calculate performance with ideal patterns which “bracket” actual flow. Fortunately, most real reactors for heterogeneous systems can be satisfactorily approximated by one of the five ideal flow patterns of Fig. 17.1. Notable exceptions are the reactions which take place in fluidized beds. There special models must be developed.

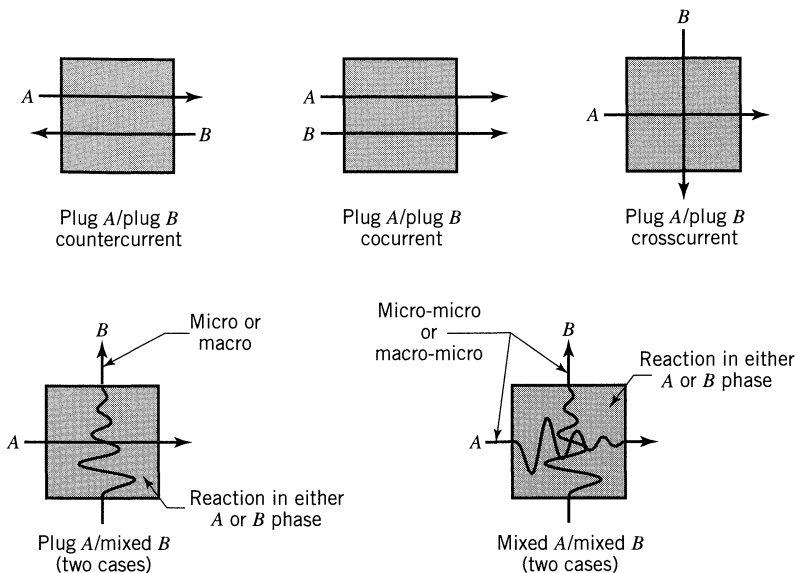


Figure 17.1. Ideal contacting patterns for two flowing fluids.

Final Thoughts on Flow Modeling

In reactor design and scale-up, it is essential to select a flow model which reasonably represents our setup. Too often we put too little thought here, carelessly picking a nonrepresentative model and then doing computer calculations to the n th degree of accuracy. And then we are surprised when design and scale-up do not agree with our predictions. A simple reasonable model is much better than a precise and detailed model which does not represent the contacting. Often the choice of a good flow model and the knowledge of how the flow pattern changes with scale-up spells the difference between success and failure.

The preceding thoughts guide us in our approach to heterogeneous reaction, which we will consider in the rest of the book.

PROBLEMS

- 17.1. Gaseous reactant A diffuses through a gas film and reacts on the surface of a solid according to a reversible first-order rate,

$$-r''_A = k''(C_{As} - C_{Ae})$$

where C_{Ae} is the concentration of A in equilibrium with the solid surface. Develop an expression for the rate of reaction of A accounting for both the mass transfer and reaction steps.

- 17.2. Example 17.4 gives the final rate expression for film mass transfer followed by a second-order rate expression for reaction on a plane surface. Please derive this expression and show that it is correct.
- 17.3. In slurry reactors, pure reactant gas is bubbled through liquid containing suspended catalyst particles. Let us view these kinetics in terms of the film theory, as shown in Fig. P17.3. Thus, to reach the surface of the solid, the

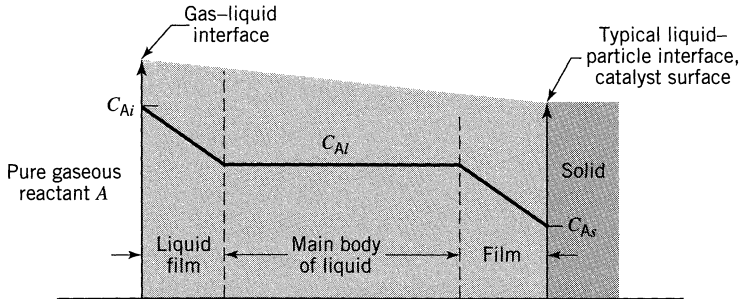


Figure P17.3

reactant which enters the liquid must diffuse through the liquid film into the main body of liquid, and then through the film surrounding the catalyst particle. At the surface of the particle, reactant yields product according to first-order kinetics. Derive an expression for the rate of reaction in terms of these resistances.

Chapter 18

Solid Catalyzed Reactions

With many reactions, the rates are affected by materials which are neither reactants nor products. Such materials called *catalysts* can speed a reaction by a factor of a million or much more, or they may slow a reaction (negative catalyst).

There are two broad classes of catalysts: those that operate at close to ambient temperature with biochemical systems, and the man-made catalysts that operate at high temperature.

The biochemical catalysts, called *enzymes*, are found everywhere in the biochemical world and in living creatures, and without their action I doubt that life could exist at all. In addition, in our bodies hundreds of different enzymes and other catalysts are busily at work all the time, keeping us alive. We treat these catalysts in Chapter 27.

The man-made catalysts, mostly solids, usually aim to cause the high-temperature rupture or synthesis of materials. These reactions play an important role in many industrial processes, such as the production of methanol, sulfuric acid, ammonia, and various petrochemicals, polymers, paints, and plastics. It is estimated that well over 50% of all the chemical products produced today are made with the use of catalysts. These materials, their reaction rates, and the reactors that use them are the concern of this chapter and Chapters 19–22.

Consider petroleum. Since this consists of a mixture of many compounds, primarily hydrocarbons, its treatment under extreme conditions will cause a variety of changes to occur simultaneously, producing a spectrum of compounds, some desirable, others undesirable. Although a catalyst can easily speed the rate of reactions a thousandfold or a millionfold, still, when a variety of reactions are encountered, the most important characteristic of a catalyst is its *selectivity*. By this we mean that it only changes the rates of certain reactions, often a single reaction, leaving the rest unaffected. Thus, in the presence of an appropriate catalyst, products containing predominantly the materials desired can be obtained from a given feed.

The following are some general observations.

1. The selection of a catalyst to promote a reaction is not well understood; therefore, in practice extensive trial and error may be needed to produce a satisfactory catalyst.

2. Duplication of the chemical constitution of a good catalyst is no guarantee that the solid produced will have any catalytic activity. This observation suggests that it is the physical or crystalline structure which somehow imparts catalytic activity to a material. This view is strengthened by the fact that heating a catalyst above a certain critical temperature may cause it to lose its activity, often permanently. Thus present research on catalysts is strongly centered on the surface structure of solids.
3. To explain the action of catalysts, it is thought that reactant molecules are somehow changed, energized, or affected to form intermediates in the regions close to the catalyst surface. Various theories have been proposed to explain the details of this action. In one theory, the intermediate is viewed as an association of a reactant molecule with a region of the surface; in other words, the molecules are somehow attached to the surface. In another theory, molecules are thought to move down into the atmosphere close to the surface and be under the influence of surface forces. In this view the molecules are still mobile but are nevertheless modified. In still a third theory, it is thought that an active complex, a free radical, is formed at the surface of the catalyst. This free radical then moves back into the main gas stream, triggering a chain of reactions with fresh molecules before being finally destroyed. In contrast with the first two theories, which consider the reaction to occur in the vicinity of the surface, this theory views the catalyst surface simply as a generator of free radicals, with the reaction occurring in the main body of the gas.
4. In terms of the transition-state theory, the catalyst reduces the potential energy barrier over which the reactants must pass to form products. This lowering in energy barrier is shown in Fig. 18.1.
5. Though a catalyst may speed up a reaction, it never determines the equilibrium or endpoint of a reaction. This is governed by thermodynamics alone. Thus with or without a catalyst the equilibrium constant for the reaction is always the same.

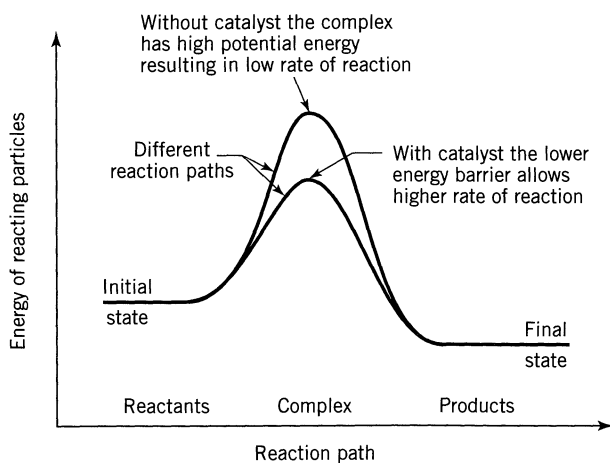


Figure 18.1 Representation of the action of a catalyst.

6. Since the solid surface is responsible for catalytic activity, a large readily accessible surface in easily handled materials is desirable. By a variety of methods, active surface areas the size of football fields can be obtained per cubic centimeter of catalyst.

Though there are many problems related to solid catalysts, we consider only those which are related to the development of kinetic rate equations needed in design. We simply assume that we have a catalyst available to promote a specific reaction. We wish to evaluate the kinetic behavior of reactants in the presence of this material and then use this information for design.

The Spectrum of Kinetic Regimes

Consider a porous catalyst particle bathed by reactant A. The rate of reaction of A for the particle as a whole may depend on:

- ① Surface kinetics, or what happens at the surfaces, interior or exterior of the particle. This may involve the adsorption of reactant A onto the surface, reaction on the surface, or desorption of product back into the gas stream.
- ② Pore diffusion resistance which may cause the interior of the particle to be starved for reactant.
- ③ Particle ΔT or temperature gradients within the particle. This is caused by large heat release or absorption during reaction.
- ④ Film ΔT between the outer surface of the particle and the main gas stream. For example, the particle may be uniform in temperature throughout but hotter than the surrounding gas.
- ⑤ Film diffusion resistance or concentration gradients across the gas film surrounding the particle.

For gas/porous catalyst systems slow reactions are influenced by ① alone, in faster reactions ② intrudes to slow the rate, then ③ and/or ④ enter the picture, ⑤ unlikely limits the overall rate. In liquid systems the order in which these effects intrude is ①, ②, ⑤, and rarely ③ and/or ④.

In different areas of application (outside of catalytic kinetics too) different combinations of these five factors enter the picture. Table 18.1 shows what we normally encounter.

Table 18.1 Factors which Influence the Rate of Reaction of Particles

Rate Influencing Factor	Porous Catalyst Particle	Catalyst Coated Surface	Burning of a Droplet of Fuel	Cells and Simple Living Creatures
① Surface reaction	Yes	Yes	No	Yes
② Pore diffusion	Yes	No	No	Maybe
③ Particle ΔT	Not too likely	No	No	No
④ Film ΔT	Sometimes	Rare	All important	No
⑤ Film mass transfer	No	Yes	All important	Could be

Although here we introduce all the phenomena which affect the rate, the real world is never so exciting that we have to concern ourselves with all five factors at any one time. In fact, in the majority of situations with porous catalyst particles we only have to consider factors ① and ②.

Here let us treat factors ① and ②; then ③ and ④ briefly.

18.1 THE RATE EQUATION FOR SURFACE KINETICS

Because of the great industrial importance of catalytic reactions, considerable effort has been spent in developing theories from which kinetic equations can rationally be developed. The most useful for our purposes supposes that the reaction takes place on an active site on the surface of the catalyst. Thus three steps are viewed to occur successively at the surface.

Step 1. A molecule is adsorbed onto the surface and is attached to an active site.

Step 2. It then reacts either with another molecule on an adjacent site (dual-site mechanism), with one coming from the main gas stream (single-site mechanism), or it simply decomposes while on the site (single-site mechanism).

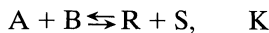
Step 3. Products are desorbed from the surface, which then frees the site.

In addition, all species of molecules, free reactants, and free products as well as site-attached reactants, intermediates, and products taking part in these three processes are assumed to be in equilibrium.

Rate expressions derived from various postulated mechanisms are all of the form

$$\text{rate of reaction} = \frac{(\text{kinetic term})(\text{driving force or displacement from equilibrium})}{(\text{resistance term})} \quad (1)$$

For example, for the reaction



occurring in the presence of inert carrier material U, the rate expression when adsorption of A controls is

$$-r_A'' = \frac{k(p_A - p_R p_S / K p_B)}{(1 + K_A p_R p_S / K p_B + K_B p_B + K_R p_R + K_S p_S + K_U p_U)^2}$$

When reaction between adjacent site-attached molecules of A and B controls, the rate expression is

$$-r_A'' = \frac{k(p_A p_B - p_R p_S / K)}{(1 + K_A p_A + K_B p_B + K_R p_R + K_S p_S + K_U p_U)^2}$$

whereas for desorption of R, controlling it becomes

$$-r_A'' = \frac{k(p_A p_B / p_S - p_R / K)}{1 + K_A p_A + K_B p_B + K K_R p_A p_B / p_S + K_S p_S + K_U p_U}$$

Each detailed mechanism of reaction with its controlling factor has its corresponding rate equation, involving anywhere from three to seven arbitrary constants, the K values. For reasons to be made clear, we do not intend to use equations such as these. Consequently, we do not go into their derivations. These are given by Hougen and Watson (1947), Corrigan (1954, 1955), Walas (1959), and elsewhere.

Now, in terms of the contact time or space time, most catalytic conversion data can be fitted adequately by relatively simple first- or n th-order rate expressions (see Prater and Lago, 1956). Since this is so, why should we concern ourselves with selecting one of a host of rather complicated rate expressions which satisfactorily fits the data?

The following discussion summarizes the arguments for and against the use of simple empirical kinetic equations.

Truth and Predictability. The strongest argument in favor of searching for the actual mechanism is that if we find one which we think represents what truly occurs, extrapolation to new and more favorable operating conditions is much more safely done. This is a powerful argument. Other arguments, such as augmenting knowledge of the mechanism of catalysis with the final goal of producing better catalysts in the future, do not concern a design engineer who has a specific catalyst at hand.

Problems of Finding the Mechanism. To prove that we have such a mechanism we must show that the family of curves representing the rate equation type of the favored mechanism fits the data *so much better than the other families that all the others can be rejected*. With the large number of parameters (three to seven) that can be chosen arbitrarily for each rate-controlling mechanism, a very extensive experimental program is required, using very precise and reproducible data, which in itself is quite a problem. We should bear in mind that it is not good enough to select the mechanism that well fits—or even best fits—the data. Difference in fit may be explainable entirely in terms of experimental error. In statistical terms these differences may not be “significant.” Unfortunately, if a number of alternative mechanisms fit the data equally well, we must recognize that the equation selected can only be considered to be one of good fit, not one that represents reality. With this admitted, there is no reason why we should not use the simplest and easiest-to-handle equation of satisfactory fit. In fact, unless there are good positive reasons for using the more complicated of two equations, we should always select the simpler of the two if both fit the data equally well. The statistical analyses and comments by Chou (1958) on the codimer example in Hougen and Watson (1947) in which 18 mechanisms were examined illustrate the difficulty in finding the correct mechanism from kinetic data, and show that even in the most carefully conducted programs of experimentation the magnitude of the experimental error will very likely mask the differences predicted by the various mechanisms.

Thus it is hardly ever possible to determine with reasonable confidence which is the correct mechanism.

Problems of Combining Resistances. Suppose that we have found the correct mechanism and resultant rate equation for the surface phenomenon. Combining this step with any of the other resistance steps, such as pore or film diffusion, becomes rather impractical. When this has to be done, it is best to replace the multiconstant rate equation by an equivalent first-order expression, which can then be combined with other reaction steps to yield an overall rate expression.

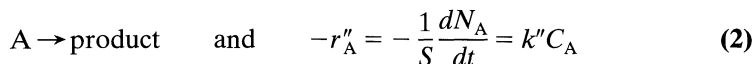
Summary on Surface Kinetics. From this discussion we conclude that it is good enough to use the simplest available correlating rate expression, hence first-order or n th-order kinetics, to represent the surface reaction.

For additional comments questioning the validity of the active-site approach, suggesting forms of kinetic equations to be used in reactor design, and suggesting what is the real utility of the active site theory, see the opposing points of view presented by Weller (1956) and Boudart (1956).

18.2 PORE DIFFUSION RESISTANCE COMBINED WITH SURFACE KINETICS

Single Cylindrical Pore, First-Order Reaction

First consider a single cylindrical pore of length L , with reactant A diffusing into the pore, and reacting on the surface by a first-order reaction



taking place at the walls of the pore, and product diffusing out of the pore, as shown in Fig. 18.2. This simple model will later be extended.

The flow of materials into and out of any section of pore is shown in detail in Fig. 18.3. At steady state a material balance for reactant A for this elementary section gives

$$\text{output} - \text{input} + \text{disappearance by reaction} = 0 \quad (4.1)$$

or with the quantities shown in Fig. 18.3,

$$-\pi r^2 \mathcal{D} \left(\frac{dC_A}{dx} \right)_{\text{out}} + \pi r^2 \mathcal{D} \left(\frac{dC_A}{dx} \right)_{\text{in}} + k''C_A(2\pi r\Delta x) = 0$$

Rearranging gives

$$\frac{\left(\frac{dC_A}{dx} \right)_{\text{out}} - \left(\frac{dC_A}{dx} \right)_{\text{in}}}{\Delta x} - \frac{2k''}{\mathcal{D}r} C_A = 0$$

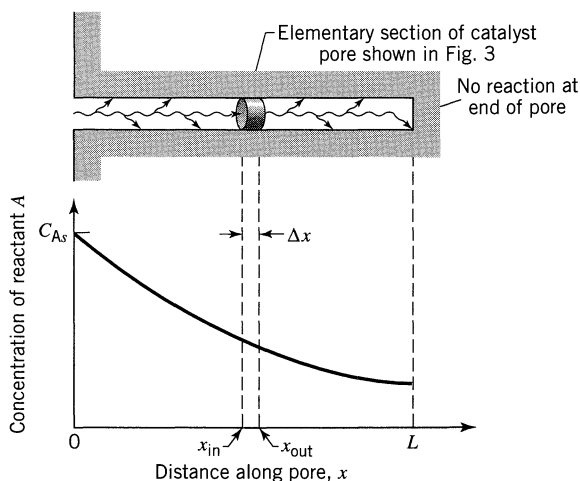


Figure 18.2 Representation of a cylindrical catalyst pore.

and taking the limit as Δx approaches zero (see the equation above Eq. 13.18a), we obtain

$$\frac{d^2 C_A}{dx^2} - \frac{2k''}{\mathcal{D}r} C_A = 0 \quad (3)$$

Note that the first-order chemical reaction is expressed in terms of unit surface area of the wall of the catalyst pore; hence k'' has unit of length per time (see

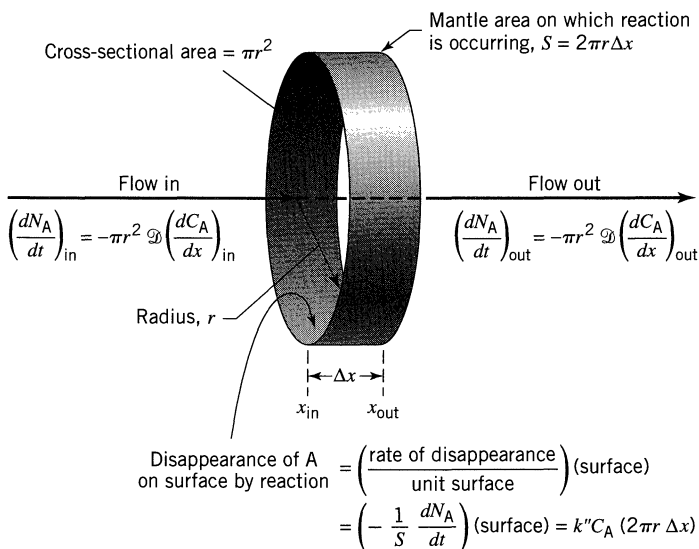


Figure 18.3 Setting up the material balance for the elementary slice of catalyst pore.

Eq. 1.4). In general, the interrelation between rate constants on different bases is given by

$$kV = k'W = k''S \quad (4)$$

Hence for the cylindrical catalyst pore

$$k = k'' \left(\frac{\text{surface}}{\text{volume}} \right) = k'' \left(\frac{2\pi rL}{\pi r^2 L} \right) = \frac{2k''}{r} \quad (5)$$

Thus in terms of volumetric units Eq. 3 becomes

$$\frac{d^2 C_A}{dx^2} - \frac{k}{\mathcal{D}} C_A = 0 \quad (6)$$

This is a frequently met linear differential equation whose general solution is

$$C_A = M_1 e^{mx} + M_2 e^{-mx} \quad (7)$$

where

$$m = \sqrt{\frac{k}{\mathcal{D}}} = \sqrt{\frac{2k''}{\mathcal{D}r}}$$

and where M_1 and M_2 are constants. It is in the evaluation of these constants that we restrict the solution to this system alone. We do this by specifying what is particular about the model selected, a procedure which requires a clear picture of what the model is supposed to represent. These specifications are called the boundary conditions of the problem. Since two constants are to be evaluated, we must find and specify two boundary conditions. Examining the physical limits of the conceptual pore, we find that the following statements can always be made. First, at the pore entrance

$$C_A = C_{As}, \quad \text{at} \quad x = 0 \quad (8a)$$

Second, because there is no flux or movement of material through the interior end of the pore

$$\frac{dC_A}{dx} = 0, \quad \text{at} \quad x = L \quad (8b)$$

With the appropriate mathematical manipulations of Eqs. 7 and 8 we then obtain

$$M_1 = \frac{C_{As} e^{-mL}}{e^{mL} + e^{-mL}}, \quad M_2 = \frac{C_{As} e^{mL}}{e^{mL} + e^{-mL}} \quad (9)$$

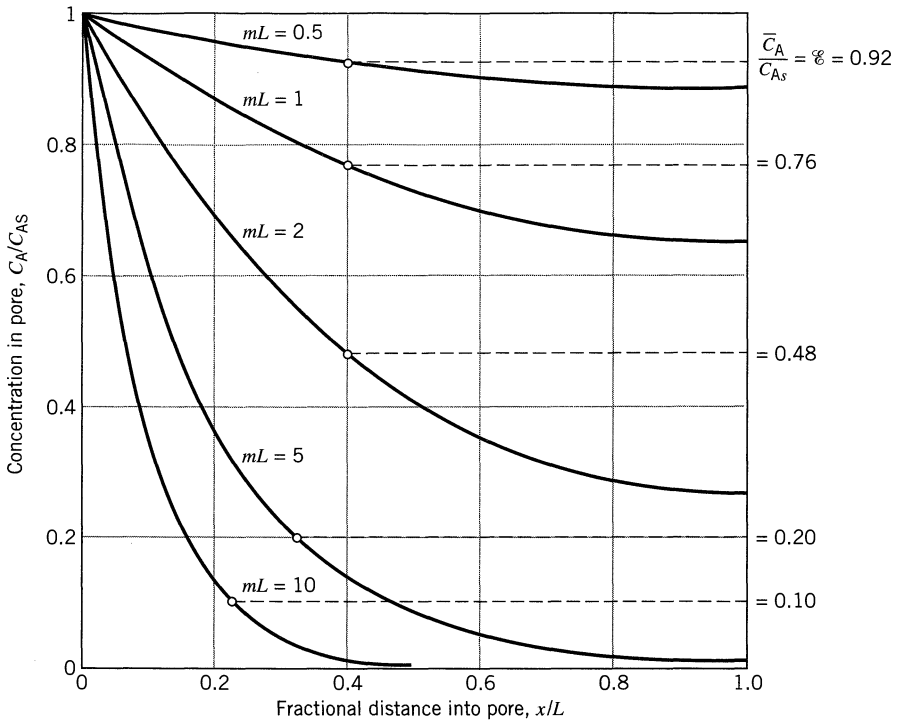


Figure 18.4 Distribution and average value of reactant concentration within a catalyst pore as a function of the parameter $mL = L\sqrt{k/\mathcal{D}}$

Hence the concentration of reactant within the pore is

$$\frac{C_A}{C_{As}} = \frac{e^{m(L-x)} + e^{-m(L-x)}}{e^{mL} + e^{-mL}} = \frac{\cosh m(L-x)}{\cosh mL} \quad (10)$$

This progressive drop in concentration on moving into the pore is shown in Fig. 18.4, and this is seen to be dependent on the dimensionless quantity mL , or M_T , called the *Thiele modulus*.

To measure how much the reaction rate is lowered because of the resistance to pore diffusion, define the quantity \mathcal{E} called the effectiveness factor as follows:

$$\begin{aligned} \text{Effectiveness factor, } \mathcal{E} &= \frac{\text{(actual mean reaction rate within pore)}}{\text{(rate if not slowed by pore diffusion)}} \quad (11) \\ &= \frac{\bar{r}_A, \text{ with diffusion}}{r_A, \text{ without diffusion resistance}} \end{aligned}$$

In particular, for first-order reactions $\mathcal{E} = C_A/C_{As}$, because the rate is proportional to the concentration. Evaluating the average rate in the pore from Eq. 10 gives

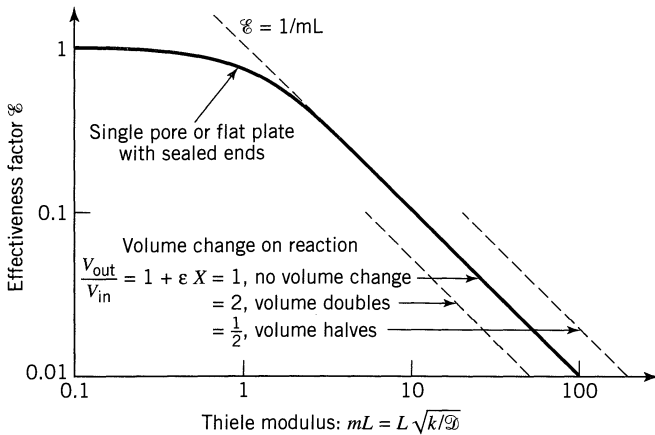


Figure 18.5 The effectiveness factor as a function of the parameter mL or M_T , called the Thiele modulus, prepared from Aris (1957) and Thiele (1939).

the relationship

$$\mathcal{E}_{\text{first order}} = \frac{\bar{C}_A}{C_{A_s}} = \frac{\tanh mL}{mL} \quad (12)$$

which is shown by the solid line in Fig. 5. With this figure we can tell whether pore diffusion modifies the rate of reaction, and inspection shows that this depends on whether mL is large or small.

For small mL , or $mL < 0.4$, we see that $\mathcal{E} \cong 1$, the concentration of reactant does not drop appreciably within the pore; thus pore diffusion offers negligible resistance. This can also be verified by noting that a small value for $mL = L \sqrt{k/\mathcal{D}}$ means either a short pore, slow reaction, or rapid diffusion, all three factors tending to lower the resistance to diffusion.

For large mL , or $mL > 4$, we find that $\mathcal{E} = 1/mL$, the reactant concentration drops rapidly to zero on moving into the pore, hence diffusion strongly influences the rate of reaction. We call this the regime of *strong pore resistance*.

18.3 POROUS CATALYST PARTICLES

The results for a single pore can approximate the behavior of particles of various shapes—spheres, cylinders, etc. For these systems the following apply.

- 1. Use of the proper diffusion coefficient.** Replace the molecular diffusion coefficient \mathcal{D} by the effective diffusion coefficient of fluid in the porous structure. Representative \mathcal{D}_e values for gases and liquids in porous solids are given by Weisz (1959).
- 2. Proper measure of particle size.** To find the effective distance penetrated

by gas to get to all the interior surfaces we define a characteristic size of particle

$$L \left\{ \begin{array}{l} = \left(\frac{\text{volume of particle}}{\text{exterior surface available for reactant penetration}} \right), \text{ any particle shape} \\ = \frac{\text{thickness}}{2}, \text{ for flat plates} \\ = \frac{R}{2}, \text{ for cylinders} \\ = \frac{R}{3}, \text{ for spheres} \end{array} \right. \quad (13)$$

3. Measures of reactions rates. In catalytic systems the rate of reaction can be expressed in one of many equivalent ways. For example, for first-order kinetics

$$\begin{array}{l} \text{Based on volume of} \\ \text{voids in the reactor} \end{array} \quad -r_A = -\frac{1}{V} \frac{dN_A}{dt} = kC_A, \left[\frac{\text{mols reacted}}{\text{m}^3 \text{ voids} \cdot \text{s}} \right] \quad (14)$$

$$\begin{array}{l} \text{Based on weight of} \\ \text{catalyst pellets} \end{array} \quad -r'_A = -\frac{1}{W} \frac{dN_A}{dt} = k'C_A, \left[\frac{\text{mol reacted}}{\text{kg cat} \cdot \text{s}} \right] \quad (15)$$

$$\begin{array}{l} \text{Based on catalyst surface} \end{array} \quad -r''_A = -\frac{1}{S} \frac{dN_A}{dt} = k''C_A, \left[\frac{\text{mol reacted}}{\text{m}^2 \text{ cat. surf.} \cdot \text{s}} \right] \quad (16)$$

$$\begin{array}{l} \text{Based on volume of} \\ \text{catalyst pellets} \end{array} \quad -r'''_A = -\frac{1}{V_p} \frac{dN_A}{dt} = k'''C_A, \left[\frac{\text{mol reacted}}{\text{m}^3 \text{ solid} \cdot \text{s}} \right] \quad (17)$$


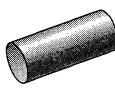

$$\begin{array}{l} \text{Based on total reactor} \\ \text{volume} \end{array} \quad -r'''_A = -\frac{1}{V_r} \frac{dN_A}{dt} = k'''C_A, \left[\frac{\text{mol reacted}}{\text{m}^3 \text{ reactor} \cdot \text{s}} \right] \quad (18)$$

Use whichever definition is convenient. However, for porous catalyst particles rates based on unit mass and on unit volume of particles, r' and r''' are the useful measures. Hence for n th order reactions

$$\begin{array}{l} -r'_A \left[\frac{\text{mol A}}{(\text{kg cat}) \cdot \text{s}} \right] = k' C_A^n \quad \text{where} \quad k' = \left[\frac{(\text{m}^3 \text{ gas})^n}{(\text{mol A})^{n-1} (\text{kg cat}) \cdot \text{s}} \right] \\ -r'''_A \left[\frac{\text{mol A}}{(\text{m}^3 \text{ cat}) \cdot \text{s}} \right] = k''' C_A^n \quad \text{where} \quad k''' = \left[\frac{(\text{m}^3 \text{ gas})^n}{(\text{mol A})^{n-1} (\text{m}^3 \text{ cat}) \cdot \text{s}} \right] \end{array} \quad (19)$$

4. In a manner similar to what was done for a single cylindrical pore, Thiele

(1939) and Aris (1957) related \mathcal{E} with M_T for the various particle shapes as follows:

$A \rightarrow R$ $-r_A''' = k''' C_A \mathcal{E}$ <p style="text-align: center; margin-left: 20px;">mol/m³ cat · s</p>	<p>... where</p>	\mathcal{E}	$= \frac{1}{M_T} \cdot \tanh M_T$		<p>(20)</p>
			$= \frac{1}{M_T} \cdot \frac{I_1(2M_T)}{I_0(2M_T)}$	<p>Bessel function</p> 	<p>(21)</p>
			$= \frac{1}{M_T} \cdot \left(\frac{1}{\tanh 3M_T} - \frac{1}{3M_T} \right)$		<p>(22)</p>

where

$$M_T = L \sqrt{k''' / \mathcal{D}_e} \tag{23}$$

These relationships are shown in Fig. 18.6. If you know \mathcal{D}_e , k''' , and L you can find the reaction rate from M_T and Fig. 18.6. However, what if you want to evaluate k''' from an experiment in which you measure a rate which could have been slowed by diffusional resistance, but which you are unsure of?

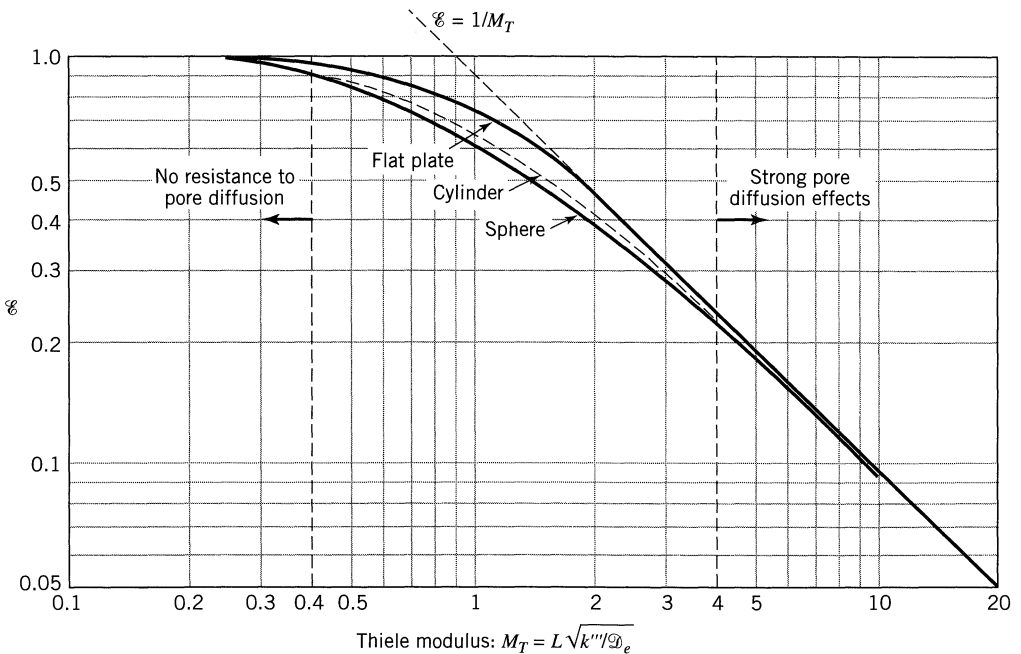


Figure 18.6 Effectiveness factor versus M_T for porous particles of various shapes.

5. **Finding pore resistance effects from experiment.** Here we have a simple trick to help us. Define another modulus which only includes observable and measurable quantities. This is known as the Wagner-Weisz-Wheeler modulus M_W (lucky for us that the three researchers who first dealt with this problem had last names all starting with the same letter).

$$M_W = M_T^2 \mathcal{E} = L^2 \frac{(-r_A'''/C_A)_{\text{obs}}}{\mathcal{D}_e} \quad (24)$$

We shall call this the Wagner modulus.

6. **Pore resistance limits.** When reactant fully penetrates the particle and bathes all its surfaces, then the particle is in the diffusion free regime. This occurs when $M_T < 0.4$ or $M_W < 0.15$.

At the other extreme when the center of the particle is starved for reactant and is unused then the particle is in the strong pore resistance regime. This occurs when $M_T > 4$ or $M_W > 4$.

Figures 18.6 and 18.7 show these limits.

7. **Particles of Different Sizes.** Comparing the behavior of particles of size R_1 and R_2 we find in the diffusion-free regime

$$\frac{r'_{A1}}{r'_{A2}} = \frac{\mathcal{E}_1 k' C_A}{\mathcal{E}_2 k' C_A} = \frac{\mathcal{E}_1}{\mathcal{E}_2} = 1$$

In the regime of strong diffusion resistance

$$\frac{r'_{A1}}{r'_{A2}} = \frac{\mathcal{E}_1}{\mathcal{E}_2} = \frac{M_{T2}}{M_{T1}} = \frac{R_2}{R_1} \quad (25)$$

Thus the rate varies inversely proportional to the particle size.

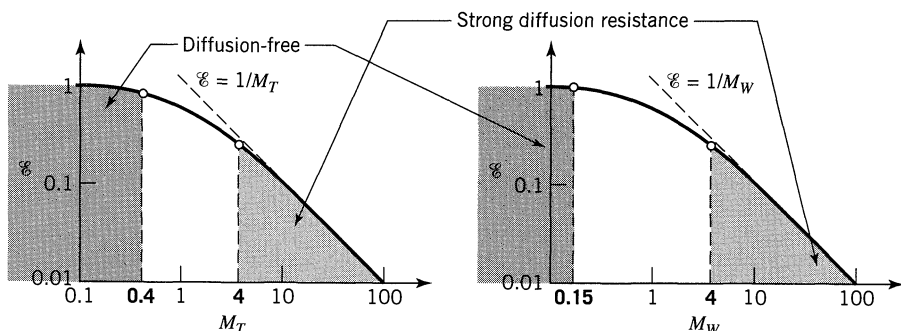


Figure 18.7 Shows the limits for negligible and for strong pore diffusion resistance.

Extensions

There are many extensions to this basic treatment. Here we just mention a few.

Mixture of Particles of Various Shapes and Sizes. For a catalyst bed consisting of a mixture of particles of various shapes and sizes Aris (1957) showed that the correct mean effectiveness factor is

$$\bar{\mathcal{E}} = \mathcal{E}_1 f'_1 + \mathcal{E}_2 f'_2 + \dots$$

where f'_1, f'_2, \dots are the volume fractions of particles of sizes 1, 2, . . . in the mixture.

Molar Volume Change. With decrease in fluid density (expansion) during reaction the increased outflow of molecules from the pores makes it harder for reactants to diffuse into the pore, hence lowering \mathcal{E} . On the other hand, volumetric contraction results in a net molar flow into the pore, hence increasing \mathcal{E} . For a first-order reaction Thiele (1939) found that this flow simply shifted the \mathcal{E} versus M_T curve as shown in Fig. 18.5.

Arbitrary Reaction Kinetics. If the Thiele modulus is generalized as follows [see Froment and Bischoff (1962)]

$$M_T = \frac{(-r''_{As})L}{\left[2\mathcal{D}_e \int_{C_{Ae}}^{C_{As}} (-r''_A) dC_A\right]^{1/2}}, \quad C_{Ae} = \left(\begin{array}{l} \text{equilibrium} \\ \text{concentration} \end{array}\right) \quad (26)$$

then the \mathcal{E} versus M_T curves for all forms of rate equation closely follow the curve for the first-order reaction. This generalized modulus becomes

for first-order reversible reactions

$$M_T = L \sqrt{\frac{k'''}{\mathcal{D}_e X_{Ae}}} \quad (27)$$

for n th-order irreversible reactions

$$M_T = L \sqrt{\frac{(n+1)k''' C_{As}^{n-1}}{2\mathcal{D}_e}} \quad (28)$$

n th-order reactions behave in an unexpected way in the region of strong pore resistance. Combining the n th-order rate with the generalized modulus of Eq.

28 we obtain

$$\begin{aligned}
 -r_A''' &= k''' C_{As}^n \mathcal{C} = k''' C_{As}^n \cdot \frac{1}{M_T} = k''' C_{As}^n \cdot \frac{1}{L} \sqrt{\frac{2\mathcal{D}_e}{(n+1)k''' C_{As}^{n-1}}} \\
 &= \left(\frac{2}{n+1} \cdot \frac{k''' \mathcal{D}_e}{L^2} \right)^{1/2} C_{As}^{(n+1)/2}
 \end{aligned} \tag{29}$$

Thus, in the regime of strong pore diffusion, an n th-order reaction behaves like a reaction of order $(n+1)/2$ or

0 order becomes $1/2$ order

1st order remains 1st order

2nd order becomes 1.5 order

3rd order becomes 2nd order

(30)

In addition the temperature dependency of reactions is affected by strong pore resistance. From Eq. 29 the observed rate constant for n th-order reactions is

$$k'''_{\text{obs}} = \left(\frac{2}{n+1} \cdot \frac{k''' \mathcal{D}_e}{L^2} \right)^{1/2}$$

Taking logarithms and differentiating with respect to temperature and noting that both the reaction rate and to a lesser extent the diffusional process are temperature-dependent gives

$$\frac{d(\ln k'''_{\text{obs}})}{dT} = \frac{1}{2} \left[\frac{d(\ln k''')}{dT} + \frac{d(\ln \mathcal{D}_e)}{dT} \right] \tag{31}$$

With Arrhenius temperature dependencies for both reaction and diffusion we have

$$k''' = k'''_0 e^{-E_{\text{true}}/RT} \quad \text{and} \quad \mathcal{D}_e = \mathcal{D}_{e0} e^{-E_{\text{diff}}/RT}$$

and replacing in Eq. 31 gives

$$\mathbf{E}_{\text{obs}} = \frac{\mathbf{E}_{\text{true}} + \mathbf{E}_{\text{diff}}}{2} \tag{32}$$

Since the activation energy for gas-phase reactions is normally rather high, say 80 ~ 240 kJ, while that for diffusion is small (about 5 kJ at room temperature or 15 kJ at 1000°C), we can write approximately

$$\mathbf{E}_{\text{obs}} \cong \frac{\mathbf{E}_{\text{true}}}{2} \tag{33}$$

These results show that the observed activation energy for reactions influenced by strong pore resistance is approximately one-half the true activation energy.

Summary—Diffusion Resistance in Pores

For first-order surface reaction we summarize our finding in compact form in Eq. 34.

rate without any diffusion effects = 1 for no diffusion resistance

... with ... $\mathcal{E} = \frac{\tanh M_T}{M_T}$

this flat plate expression is a good approximation for all particle shapes

$-r_A''' = k''' C_{As} \mathcal{E}$

characteristic length

effective diffusion coefficient in porous solids; $m^3 \text{ gas}/m \text{ solid}\cdot s$

where $M_T = L \sqrt{\frac{k'''}{\mathcal{D}_e}}$... and also ... $M_W = M_T^2 \mathcal{E} = \frac{L^2 (-r_{A,obs}''')}{C_{A,obs} \mathcal{D}_e}$

\mathcal{E} = effectiveness factor, a fudge factor which varies between 0 and 1, and which accounts for the resistance to pore diffusion

M_T = Thiele modulus, useful for predicting reactor behavior from known kinetic information, thus known k'''

M_W = Weisz modulus, useful for interpreting experiments since it only includes observables

(34)

To find how pore resistance influences the rate evaluate M_T or M_W , then find \mathcal{E} from the above equations or figures, and insert \mathcal{E} into the rate equation.

Desirable processing range: Fine solids are free of pore diffusion resistance but are difficult to use (imagine the pressure drop of a packed bed of face powder). On the other hand a bed of large particles have a small Δp but are liable to be in the regime of strong pore diffusion where much of the pellets' interior is unused.

For most effective operations what we want is to use the largest particle size which is still free of diffusional resistance or

$$M_T \cong 0.4 \quad \text{or} \quad M_W \cong 0.15 \quad (35)$$

18.4 HEAT EFFECTS DURING REACTION

When reaction is so fast that the heat released (or absorbed) in the pellet cannot be removed rapidly enough to keep the pellet close to the temperature of the fluid, then nonisothermal effects intrude. In such a situation two different kinds of temperature effects may be encountered:

Within-particle ΔT . There may be a temperature variation within the pellet.

Film ΔT . The pellet may be hotter (or colder) than the surrounding fluid.

For exothermic reaction, heat is released and particles are hotter than the surrounding fluid, hence the nonisothermal rate is always higher than the isothermal rate as measured by the bulk stream conditions. However, for endothermic reactions the nonisothermal rate is lower than the isothermal rate because the particle is cooler than the surrounding fluid.

Thus our first conclusion: if the harmful effects of thermal shock, or sintering of the catalyst surface, or drop in selectivity, do not occur with hot particles, then we would encourage nonisothermal behavior in exothermic reactions. On the other hand, we would like to depress such behavior for endothermic reactions.

We next ask which form of nonisothermal effect, if any, may be present. The following simple calculations tell.

For *film* ΔT we equate the rate of heat removal through the film with the rate of heat generation by reaction within the pellet. Thus

$$\begin{aligned} Q_{\text{generated}} &= (V_{\text{pellet}})(-r''_{\text{A, obs}})(-\Delta H_r) \\ Q_{\text{removed}} &= hS_{\text{pellet}}(T_g - T_s) \end{aligned}$$

and on combining we find

$$\Delta T_{\text{film}} = (T_g - T_s) = \frac{L(-r''_{\text{A, obs}})(-\Delta H_r)}{h} \quad (36)$$

where L is the characteristic size of the pellet.

For *within-particle* ΔT the simple analysis by Prater (1958) for any particle geometry and kinetics gives the desired expression. Since the temperature and concentration within the particle are represented by the same form of differential equation (Laplace equation) Prater showed that the T and C_A distributions must have the same shape; thus at any point in the pellet x

$$-k_{\text{eff}} \frac{dT}{dx} = \mathcal{D}_e \frac{dC_A}{dx} (-\Delta H_r) \quad (37)$$

and for the pellet as a whole

$$\Delta T_{\text{particle}} = (T_{\text{center}} - T_s) = \frac{\mathcal{D}_e(C_{\text{As}} - C_{\text{A, center}})(-\Delta H_r)}{k_{\text{eff}}} \quad (38)$$

where k_{eff} is the effective thermal conductivity within the pellet.

For temperature gradients within particles the corresponding nonisothermal effective factor curves have been calculated by Carberry (1961), Weisz and Hicks (1962), and others [see Bischoff (1967) for references]. Figure 18.8 illustrates these curves in dimensionless form, and shows that the shape is very similar to the isothermal curve of Fig. 18.6 with the following exception. For exothermic reactions only, where pore resistance just begins to intrude, the effectiveness factor can become greater than unity. This finding is not unexpected in light of the above discussion.

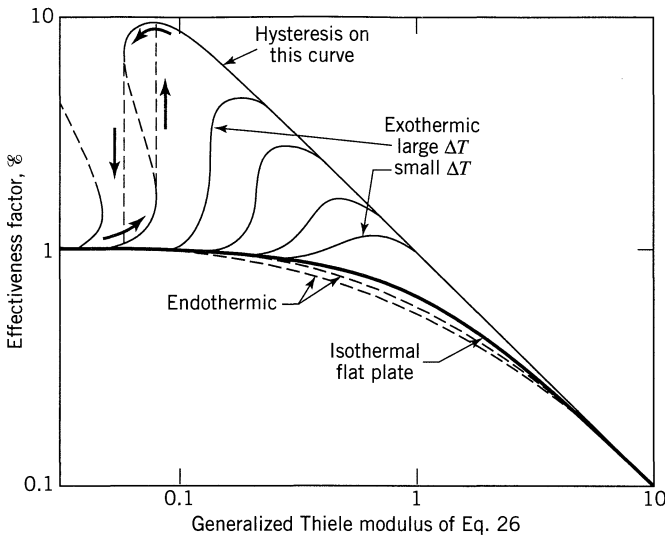


Figure 18.8 Nonisothermal effectiveness factor curve for temperature variation within the particle. Adapted from Bischoff (1967).

However, for gas-solid systems Hutchings and Carberry (1966) and McGreavy and coworkers (1969, 1970) show that if reaction is fast enough to introduce nonisothermal effects, then the temperature gradient occurs primarily across the gas film, not within the particle. Thus we may expect to find a significant film ΔT , before any within-particle ΔT becomes evident.

For detailed versions of Fig. 18.8 which show \mathcal{E} versus M_T and \mathcal{E} versus M_W plus discussion and problems dealing with nonisothermal reactors, see Chapter 22 in Levenspiel (1996).

18.5 PERFORMANCE EQUATIONS FOR REACTORS CONTAINING POROUS CATALYST PARTICLES

For Plug Flow. Take a thin slice of the PFR. Then following the analysis of Chapter 5 for homogeneous reactions we have the situation shown in Fig. 18.9.

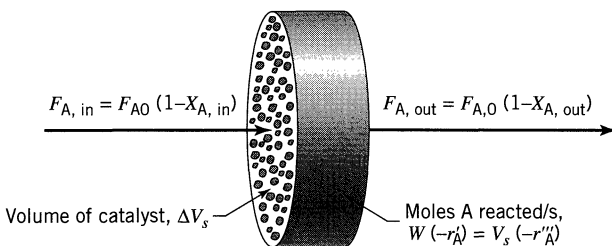


Figure 18.9 Elementary slice of solid catalyzed plug flow reactor.

At steady state a material balance for reactant A gives

$$\text{input} = \text{output} + \text{accumulation} \cdots \left[\frac{\text{mol A}}{\text{s}} \right] \quad (39)$$

in symbols

$$F_{A0} - F_{A0}X_{A\text{in}} = F_{A0} - F_{A0}X_{A\text{out}} + (-r'_A) \Delta W$$

In differential form

$$F_{A0} dX_A = (-r'_A) dW = (-r''_A) dV_s \quad (40)$$

Integrating over the whole reactor gives

$$\boxed{\frac{W}{F_{A0}} = \int_0^{X_{A\text{out}}} \frac{dX_A}{-r'_A} \quad \text{or} \quad \frac{V_s}{F_{A0}} = \int_0^{X_{A\text{out}}} \frac{dX_A}{-r''_A}} \quad (41)$$

Note the similarity of this equation with Eq. 5.13 for homogeneous reactions. To bring this analogy closer let

$$\frac{WC_{A0}}{F_{A0}} = \tau' \quad \left[\frac{\text{kg} \cdot \text{s}}{\text{m}^3} \right] \quad (42)$$

$$\frac{V_s C_{A0}}{F_{A0}} = \tau'' \quad \left[\frac{\text{m}^3 \cdot \text{s}}{\text{m}^3} \right] \quad (43)$$

We have no name for these two measures but if we wanted to we could call them by the ugly terms *weight-time*, and *volume-time*, respectively. So for first-order catalytic reactions Eq. 41 becomes

$$k' \tau' = k'' \tau'' = (1 + \varepsilon_A) \ln \frac{1}{1 - X_{A\text{out}}} - \varepsilon_A X_{A\text{out}} \quad [-] \quad (44)$$

For Mixed Flow. Here we have, following the analysis of Chapter 5, for any ε_A value

$$\boxed{\frac{W}{F_{A0}} = \frac{X_{A\text{out}} - X_{A\text{in}}}{(-r'_{A\text{out}})} \quad \text{or} \quad \frac{V_s}{F_{A0}} = \frac{X_{A\text{out}} - X_{A\text{in}}}{(-r''_{A\text{out}})}} \quad (45)$$

For first-order reactions with $C_{A\text{in}} = C_{A0}$, and $\varepsilon_A \neq 0$

$$k' \tau' = k'' \tau'' = \frac{X_{A\text{out}}(1 + \varepsilon_A X_{A\text{out}})}{1 - X_{A\text{out}}} \quad (46)$$

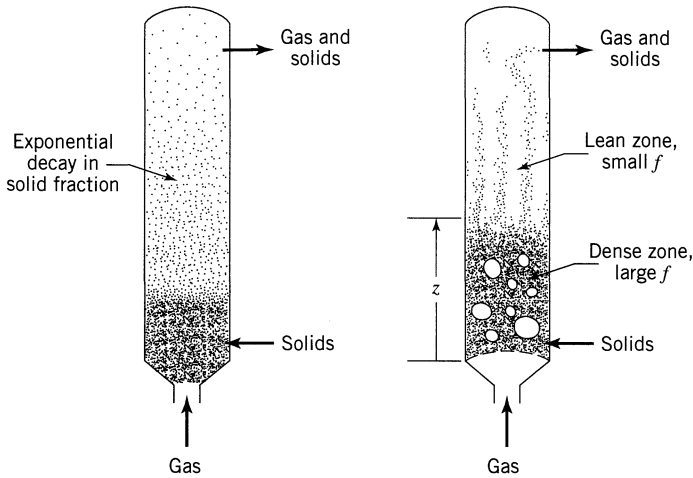


Figure 18.10 Catalytic reactors where solid fraction f varies with height.

For a Reactor Containing a Batch of Catalyst and a Batch of Gas

$$\frac{t}{C_{A0}} = \frac{V}{W_s} \int \frac{dX_A}{-r'_A} \quad \text{or} \quad \frac{t}{C_{A0}} = \frac{V}{V_s} \int \frac{dX_A}{-r''_A} \quad \left[\frac{\text{m}^3 \cdot \text{s}}{\text{mol}} \right] \quad (47)$$

Extensions of the Simple Performance Equations. There are numerous applications of catalytic reactions where the fraction of solids f varies with height z in the reactor (see Fig. 18.10).

For these situations the performance equations could more usefully be written differently. With u_0 as the superficial gas velocity (velocity if solids are absent) through the vertical reactor, Fig. 18.11 shows what happens in a thin slice through the reactor. A steady-state material balance gives

Input of A = output of A + disappearance of A

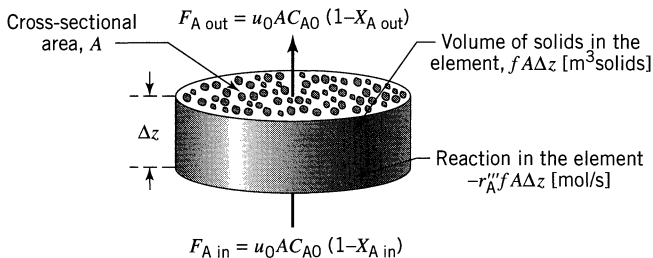


Figure 18.11 Section of catalytic reactor which has a solid fraction f .

In symbols

$$u_0 A C_{A0} (1 - X_{Ain}) = u_0 A C_{A0} (1 - X_{Aout}) + (-r_A''') f A \Delta z$$

In differential form

$$\frac{C_{A0} dX_A}{-r_A'''} = \frac{f dz}{u_0} \quad (48)$$

Integrating

$$\boxed{C_{A0} \int_0^{X_A} \frac{dX_A}{(-r_A''')} = \frac{1}{u_0} \int_0^H f dz} \quad (49)$$

For first-order reactions this expression reduces to

$$(1 + \varepsilon_A) \ln \frac{1}{1 - X_A} - \varepsilon_A X_A = \frac{k'''}{u_0} \int_0^H f dz \quad (50)$$

For the special case where $\varepsilon_A = 0$, f is constant, and the height of catalyst bed is H , we have

$$-\frac{dC_A}{dz} = f \frac{k''' C_A}{u_0} \quad \text{or} \quad \ln \frac{C_{A0}}{C_A} = \frac{k''' f H}{u_0} \quad (51)$$

The original derivation leading to Eqs. 40 to 47 is used in the next chapter on packed beds. The extension leading to Eqs. 48 to 51 is used in Chapter 20, when dealing with suspended solids reactors.

18.6 EXPERIMENTAL METHODS FOR FINDING RATES

Any type of reactor with known contacting pattern may be used to explore the kinetics of catalytic reactions. Since only one fluid phase is present in these reactions, the rates can be found as with homogeneous reactions. The only special precaution to observe is to make sure that the performance equation used is dimensionally correct and that its terms are carefully and precisely defined.

The experimental strategy in studying catalytic kinetics usually involves measuring the extent of conversion of gas passing in steady flow through a batch of solids. Any flow pattern can be used, as long as the pattern selected is known; if it is not known then the kinetics *cannot be found*. A batch reactor can also be used. In turn we discuss the following experimental devices:

- Differential (flow) reactor
- Integral (plug flow) reactor
- Mixed flow reactor
- Batch reactor for both gas and solid

Differential Reactor. We have a differential flow reactor when we choose to consider the rate to be constant at all points within the reactor. Since rates are concentration-dependent this assumption is usually reasonable only for small conversions or for shallow small reactors. But this is not necessarily so, e.g., for slow reactions where the reactor can be large, or for zero-order kinetics where the composition change can be large.

For each run in a differential reactor the plug flow performance equation becomes

$$\frac{W}{F_{A0}} = \int_{X_{Ain}}^{X_{Aout}} \frac{dX_A}{-r'_A} = \frac{1}{(-r'_A)_{ave}} \int_{X_{Ain}}^{X_{Aout}} dX_A = \frac{X_{Aout} - X_{Ain}}{(-r'_A)_{ave}} \quad (52)$$

from which the average rate for each run is found. Thus each run gives directly a value for the rate at the average concentration in the reactor, and a series of runs gives a set of rate-concentration data which can then be analyzed for a rate equation.

Example 18.2 illustrates the suggested procedure.

Integral Reactor. When the variation in reaction rate within a reactor is so large that we choose to account for these variations in the method of analysis, then we have an integral reactor. Since rates are concentration-dependent, such large variations in rate may be expected to occur when the composition of reactant fluid changes significantly in passing through the reactor. We may follow one of two procedures in searching for a rate equation.

Integral Analysis. Here a specific mechanism with its corresponding rate equation is put to the test by integrating the basic performance equation to give, similar to Eq. 5.17,

$$\frac{W}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{-r'_A} \quad (53)$$

Equations 5.20 and 5.23 are the integrated forms of Eq. 5.17 for simple kinetic equations, and Example 18.3a illustrates this procedure.

Differential Analysis. Integral analysis provides a straightforward rapid procedure for testing some of the simpler rate expressions. However, the integrated forms of these expressions become unwieldy with more complicated rate expressions. In these situations, the differential method of analysis becomes more convenient. The procedure is closely analogous to the differential method described in Chapter 3. So, by differentiating Eq. 53 we obtain

$$-r'_A = \frac{dX_A}{dW/F_{A0}} = \frac{dX_A}{d(W/F_{A0})} \quad (54)$$

Example 18.3b illustrates this procedure.

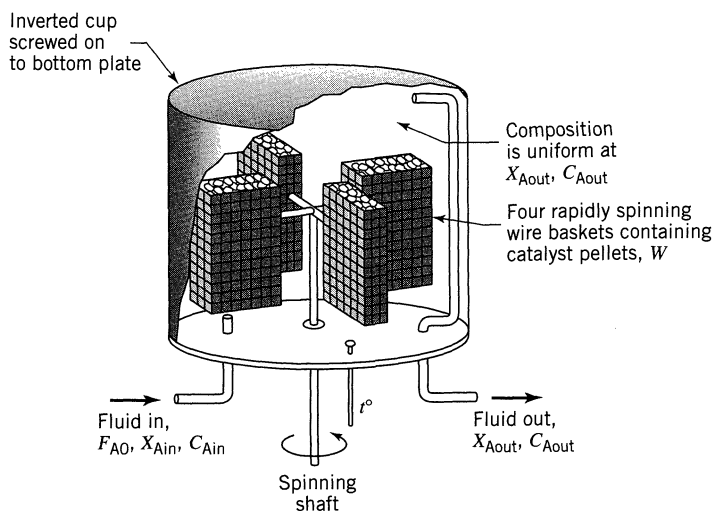


Figure 18.12 Sketch of a Carberry basket-type experimental mixed flow reactor.

Mixed Flow Reactor. A mixed flow reactor requires a uniform composition of fluid throughout, and although it may seem difficult at first thought to approach this ideal with gas-solid systems (except for differential contacting), such contacting is in fact practical. One simple experimental device which closely approaches this ideal has been devised by Carberry (1964). It is called the *basket-type mixed flow reactor*, and it is illustrated in Fig. 18.12. References to design variations and uses of basket reactors are given by Carberry (1969). Another device for approaching mixed flow is the design developed by Berty (1974), and illustrated in Fig. 18.13. Still another design is that of a recycle reactor with $R = \infty$. This is considered in the next section.

For the mixed flow reactor the performance equation becomes

$$\frac{W}{F_{A0}} = \frac{X_{Aout}}{-r'_{Aout}}$$

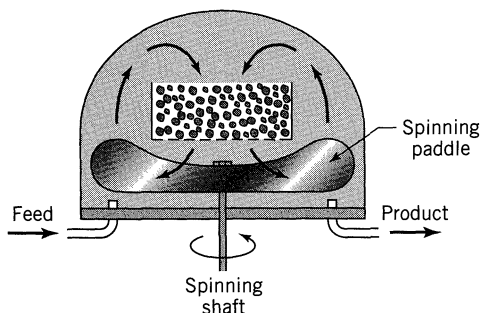


Figure 18.13 Principle of the Berty experimental mixed flow reactor.

from which the rate is

$$-r'_{Aout} = \frac{F_{A0} X_{Aout}}{W} \quad (55)$$

Thus each run gives directly a value for the rate at the composition of the exit fluid.

Examples 5.1, 5.2, and 5.3 and 18.6 show how to treat such data.

Recycle Reactor. As with integral analysis of an integral reactor, when we use a recycle reactor we must put a specific kinetic equation to the test. The procedure requires inserting the kinetic equation into the performance equation for recycle reactors

$$\frac{W}{F_{A0}} = (R + 1) \int_{X_{Af}}^{X_{A0}} \frac{dX_A}{(R/R+1)X_{Af} - r'_A} \quad (6.21)$$

and integrating. Then a plot of the left- versus right-hand side of the equation tests for linearity. Figure 18.14 sketches an experimental recycle reactor.

Unfortunately such data would be difficult to interpret when done using a low or intermediate recycle ratio. So we ignore this regime. But with a large enough recycle ratio mixed flow is approached, in which case the methods of the mixed flow reactor (direct evaluation of rate from each run) can be used. Thus a high recycle ratio provides a way of approximating mixed flow with what is essentially a plug flow device. But be warned, the problems of deciding how large a recycle ratio is large enough can be serious. Wedel and Villadsen (1983) and Broucek (1983) discuss the limitation of this reactor.

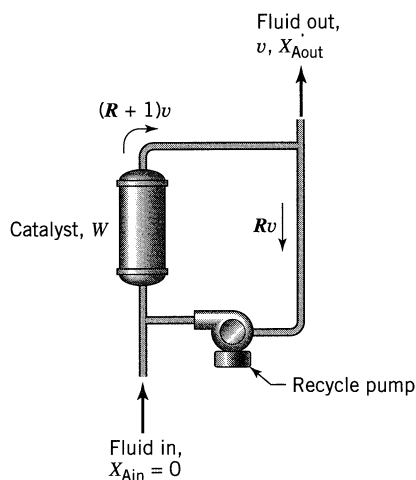


Figure 18.14 Experimental recycle reactor. When the recycle ratio is large enough mixed flow is closely approximated.

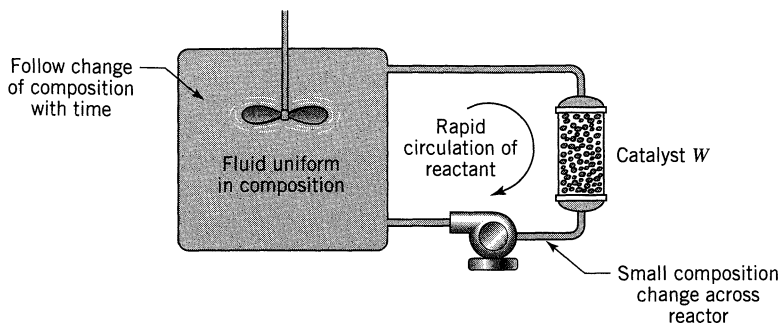


Figure 18.15 Batch reactor (batch of catalyst and batch of fluid) for catalytic reactions.

Batch Reactor. Figure 18.15 sketches the main features of an experimental reactor which uses a batch of catalyst and a batch of fluid. In this system we follow the changing composition with time and interpret the results with the batch reactor performance equation.

$$\frac{t}{C_{A0}} = \int_0^{X_A} \frac{dX_A}{-r_A} = \frac{V}{W} \int \frac{dX_A}{-r'_A} \quad V = \begin{pmatrix} \text{volume} \\ \text{of gas} \end{pmatrix} \quad (56)$$

The procedure is analogous with the homogeneous batch reactor. To ensure meaningful results, the composition of fluid must be uniform throughout the system at any instant. This requires that the conversion per pass across the catalyst be small.

A recycle reactor without through-flow becomes a batch reactor. This type of batch reactor was used by Butt et al. (1962).

Comparison of Experimental Reactors

1. The integral reactor can have significant temperature variations from point to point, especially with gas-solid systems, even with cooling at the walls. This could well make kinetic measurements from such a reactor completely worthless when searching for rate expressions. The basket reactor is best in this respect.
2. The integral reactor is useful for modeling the operations of larger packed bed units with all their heat and mass transfer effects, particularly for systems where the feed and product consist of a variety of materials.
3. Since the differential and mixed flow reactors give the rate directly they are more useful in analyzing complex reacting systems. The test for anything but a simple kinetic form can become awkward and impractical with the integral reactor.
4. The small conversions needed in differential reactors require more accurate measurements of composition than the other reactor types.
5. The recycle reactor with large recycle acts as a mixed flow reactor and shares its advantages. Actually, to minimize heat effects the catalyst need not be all at one location, but can be distributed throughout the recycle loop.

6. In exploring the physical factors of heat and mass transfer, the integral reactor most closely models the larger fixed bed; however, the basket, recycle, and batch G/S reactors are more suited for finding the limits for such heat effects, for avoiding the regime where these effects intrude, and for studying the kinetics of the reaction unhindered by these phenomena.
7. The batch G/S reactor, like the integral reactor, gives cumulative effects, thus is useful for following the progress of multiple reactions. In these reactors it is easier to study reactions free from heat and mass transfer resistances (simply increase the circulation rate), and it is also simple to slow down the progress of reactions (use a larger batch of fluid, or less catalyst); however, direct modeling of the packed bed with all its complexities is best done with the integral flow reactor.
8. Because of the ease in interpreting its results the mixed flow reactor is probably the most attractive device for studying the kinetics of solid catalyzed reactions.

Determining Controlling Resistances and the Rate Equation

Interpretation of experiments becomes difficult when more than one resistance affects the rate. To avoid this problem we should like, with preliminary runs, to first find the limits of operations where the various resistances become important. This will allow us to select conditions of operations in which the resistances can be studied separately.

Film Resistance. First of all, it is best to see whether film resistance of any kind (for mass or heat transfer) need be considered. This can be done in a number of ways.

1. Experiments can be devised to see whether the conversion changes at different gas velocities but at identical weight-time. This is done by using different amounts of catalyst in integral or differential reactors for identical values for weight-time, by changing the spinning rate in basket reactors, or by changing the circulation rate in recycle or batch reactors.
2. If data are available we can calculate whether film resistance to heat transfer is important by the estimate of Eq. 36., and whether film resistance to mass transport is important by comparing the observed first-order rate constant based on the volume of particle with the mass transfer coefficient for that type of flow.

For fluid moving past a single particle at relative velocity u Froessling (1938) gives

$$\frac{k_g d_p}{\mathcal{D}} = 2 + 0.6 \text{Re}^{1/2} \text{Sc}^{1/3} = 2 + 0.6 \left(\frac{d_p u \rho}{\mu} \right)^{1/2} \left(\frac{\mu}{\rho \mathcal{D}} \right)^{1/3}$$

while for fluid passing through a packed bed of particles Ranz (1952) gives

$$\frac{k_g d_p}{\mathcal{D}} = 2 + 1.8 \text{Re}^{1/2} \text{Sc}^{1/3}, \quad \text{Re} > 80$$

Thus we have roughly

$$\left. \begin{aligned} k_g &\sim \frac{1}{d_p} && \text{for small } d_p \text{ and } u \\ k_g &\sim \frac{u^{1/2}}{d_p^{1/2}} && \text{for large } d_p \text{ and } u \end{aligned} \right\} \quad (57)$$

Thus to see whether film mass transfer resistance is important compare

$$k''_{\text{obs}} V_p \text{ versus } k_g S_{\text{ex}} \quad (58)$$

If the two terms are of the same order of magnitude we may suspect that the gas film resistance affects the rate. On the other hand, if $k_{\text{obs}} V_p$ is much smaller than $k_g S_{\text{ex}}$ we may ignore the resistance to mass transport through the film. Example 18.1 illustrate this type of calculation. The results of that example confirm our earlier statement that film mass transfer resistance is unlikely to play a role with porous catalyst.

Nonisothermal Effects. We may expect temperature gradients to occur either across the gas film or within the particle. However, the previous discussion indicates that for gas-solid systems the most likely effect to intrude on the rate will be the temperature gradient across the gas film. Consequently, if experiment shows that gas film resistance is absent then we may expect the particle to be at the temperature of its surrounding fluid; hence, isothermal conditions may be assumed to prevail. Again see Example 18.1.

Pore Resistance. The effectiveness factor accounts for this resistance. Thus, based on unit mass of catalyst we have

$$-r''_A = k'' C_A^n \mathcal{E} \quad \text{where} \quad \mathcal{E} = \frac{1}{M_T}$$

The existence of pore resistance can be determined by

1. Calculation if \mathcal{D}_e is known.
2. Comparing rates for different pellet sizes.
3. Noting the drop in activation energy of the reaction with rise in temperature, coupled with a possible change in reaction order.

18.7 PRODUCT DISTRIBUTION IN MULTIPLE REACTIONS

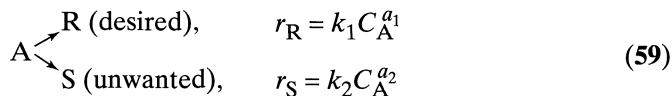
More often than not, solid-catalyzed reactions are multiple reactions. Of the variety of products formed, usually only one is desired, and it is the yield of this material which is to be maximized. In cases such as these the question of product distribution is of primary importance.

Here we examine how strong pore diffusion modifies the true instantaneous fractional yield for various types of reactions; however, we leave to Chapter 7

the calculation of the overall fractional yield in reactors with their particular flow patterns of fluid. In addition, we will not consider film resistance to mass transfer since this effect is unlikely to influence the rate.

Decomposition of a Single Reactant by Two Paths

No resistance to pore diffusion. Consider the parallel-path decomposition



Here the instantaneous fractional yield at any element of catalyst surface is given by

$$\varphi_{\text{true}} \left(\frac{\text{R}}{\text{R} + \text{S}} \right) = \frac{r_{\text{R}}}{r_{\text{R}} + r_{\text{S}}} = \frac{1}{1 + (k_2/k_1) C_{\text{A}}^{a_2 - a_1}} \quad (60)$$

or for first-order reactions

$$\varphi_{\text{true}} = \frac{1}{1 + (k_2/k_1)} \quad (61)$$

Strong resistance to pore diffusion. Under these conditions we have

$$r_{\text{R}} = k_1 C_{\text{A}_g}^{a_1} \cdot \mathcal{E}_1 = k_1 C_{\text{A}_g}^{a_1} \cdot \frac{1}{M_T}$$

and with Eq. 29

$$r_{\text{R}} \cong k_1 C_{\text{A}_g}^{a_1} \cdot \frac{1}{L} \left[\frac{4\mathcal{D}_e}{(a_1 + a_2 + 2)(k_1 + k_2) C_{\text{A}_g}^{a_1 - 1}} \right]^{1/2}$$

Using a similar expression for r_{S} and replacing both of these into the defining equation for φ gives

$$\varphi_{\text{obs}} = \frac{r_{\text{R}}}{r_{\text{R}} + r_{\text{S}}} \cong \frac{1}{1 + (k_2/k_1) C_{\text{A}_g}^{(a_2 - a_1)/2}} \quad (62)$$

and for equal-order or for first-order reactions

$$\varphi_{\text{obs}} = \frac{1}{1 + (k_2/k_1)} \quad (63)$$

This result is expected since the rules in Chapter 7 suggest that the product distribution for competing reactions of same order should be unaffected by changing concentration of A in the pores or in the reactor.

Reactions in Series

As characteristic of reactions in which the desired product can decompose further, consider the successive first-order decompositions



When C_A does not drop in the interior of catalyst particles, true rates are observed, thus

$$\varphi_{\text{obs}} = \varphi_{\text{true}} \quad \text{or} \quad \left(\frac{k_2}{k_1}\right)_{\text{obs}} = \left(\frac{k_2}{k_1}\right)_{\text{true}} \quad (64)$$

Strong resistance to pore diffusion. An analysis similar to that starting with Eq. 2 using the appropriate kinetic rate expressions gives the concentration ratio of materials in the main gas stream (or pore mouths) at any point in the reactor. Thus the differential expression (see Wheeler, 1951 for details) is

$$\frac{dC_{Rg}}{dC_{Ag}} = -\frac{1}{1+\gamma} + \gamma \frac{C_{Rg}}{C_{Ag}}, \quad \gamma = \left(\frac{k_2}{k_1}\right)^{1/2} \quad (65)$$

For mixed flow with C_A going from C_{A0} to C_{Ag} Eq. 65 with $C_{R0} = 0$ gives

$$C_{Rg} = \frac{1}{1+\gamma} \cdot \frac{C_{Ag}(C_{A0} - C_{Ag})}{C_{Ag} + \gamma(C_{A0} - C_{Ag})} \quad (66)$$

For plug flow, integration with $C_{R0} = 0$ gives

$$\frac{C_{Rg}}{C_{A0}} = \frac{1}{1+\gamma} \cdot \frac{1}{1-\gamma} \left[\left(\frac{C_{Ag}}{C_{A0}}\right)^\gamma - \frac{C_{Ag}}{C_{A0}} \right] \quad (67)$$

Comparing Eqs. 66 and 67 with the corresponding expressions for no resistance in pores, Eqs. 8.41 and 8.37, shows that here the distributions of A and R are given by a reaction having the square root of the true k ratio, with the added modification that C_{Rg} is divided by $1 + \gamma$. The maximum yield of R is likewise affected. Thus for plug flow Eq. 8.8 or 8.38 is modified to give

$$\frac{C_{Rg, \text{max}}}{C_{A0}} = \frac{\gamma^{\gamma/(1-\gamma)}}{1+\gamma}, \quad \gamma = \left(\frac{k_2}{k_1}\right)^{1/2} \quad (68)$$

and for mixed flow Eq. 8.15 or 8.41 is modified to give

$$\frac{C_{Rg, \text{max}}}{C_{A0}} = \frac{1}{(1+\gamma)(\gamma^{1/2} + 1)^2} \quad (69)$$

Table 18.2 shows that the yield of R is about halved in the presence of strong resistance to diffusion in the pores.

Table 18.2 The Role of Diffusion in Pores for First-Order Reactions in Series

k_2/k_1	$C_{Rg,max}/C_{A0}$ for Plug Flow			$C_{Rg,max}/C_{A0}$ for Mixed Flow		
	No Resistance	Strong Resistance	Percent Decrease	No Resistance	Strong Resistance	Percent Decrease
1/64	0.936	0.650	30.6	0.790	0.486	38.5
1/16	0.831	0.504	39.3	0.640	0.356	44.5
1/4	0.630	0.333	47.6	0.444	0.229	48.5
1	0.368	0.184	50.0	0.250	0.125	50.0
4	0.157	0.083	47.2	0.111	0.057	48.5
16	0.051	0.031	38.2	0.040	0.022	44.5

For more on the whole subject of the shift in product distribution caused by diffusional effects, see Wheeler (1951).

Extensions to Real Catalysts

So far we have considered catalyst pellets having only one size of pore. Real catalysts, however, have pores of various sizes. A good example of this are the pellets prepared by compressing a porous powder. Here there are large openings between the agglomerated particles and small pores within each particle. As a first approximation we may represent this structure by two pore sizes as shown in Fig. 18.16. If we define the degree of branching of a porous structure by α where

$\alpha = 0$ represents a nonporous particle

$\alpha = 1$ represents a particle with one size of pore

$\alpha = 2$ represents a particle with two pore sizes

then every real porous pellet can be characterized by some value of α .

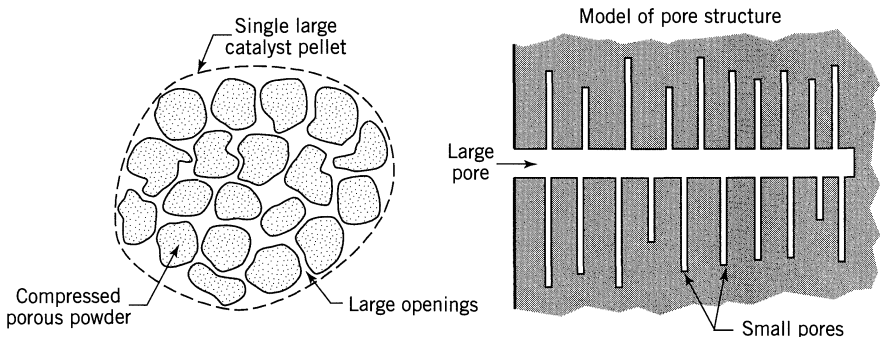


Figure 18.16 Porous structure with two sizes of pores as a model for a pellet of compressed porous powder.

Now for strong pore diffusion in one size of pore we already know that the observed order of reaction, activation energy, and k ratio for multiple reactions will differ from the true value. Thus from Eqs. 30 and 32

$$\text{for } \alpha = 1 \left\{ \begin{array}{l} \mathbf{E}_{\text{obs}} = \frac{1}{2} \mathbf{E}_{\text{diff}} + \frac{1}{2} \mathbf{E} \\ n_{\text{obs}} = 1 + \frac{n-1}{2} \\ \left(\frac{k_2}{k_1} \right)_{\text{obs}} = \left(\frac{k_2}{k_1} \right)^{1/2} \cdots \text{for side-by-side reactions} \end{array} \right. \quad (70)$$

Carberry (1962a, b), Tartarelli (1968), and others have extended this type of analysis to other values of α and to reversible reactions. Thus for two sizes of pores, where reaction occurs primarily in the smaller pores (because of much more area there), while both sizes of pores offer strong pore diffusional resistance, we find

$$\text{for } \alpha = 2 \left\{ \begin{array}{l} \mathbf{E}_{\text{obs}} = \frac{3}{4} \mathbf{E}_{\text{diff}} + \frac{1}{4} \mathbf{E} \\ n_{\text{obs}} = 1 + \frac{n-1}{4} \\ \left(\frac{k_2}{k_1} \right)_{\text{obs}} = \left(\frac{k_2}{k_1} \right)^{1/4} \cdots \text{for side-by-side reactions} \end{array} \right. \quad (71)$$

More generally for an arbitrary porous structure

$$\text{for any } \alpha \left\{ \begin{array}{l} \mathbf{E}_{\text{obs}} = \left(1 - \frac{1}{2^\alpha} \right) \mathbf{E}_{\text{diff}} + \frac{1}{2^\alpha} \mathbf{E} \\ n_{\text{obs}} = 1 + \frac{n-1}{2^\alpha} \\ \left(\frac{k_2}{k_1} \right)_{\text{obs}} = \left(\frac{k_2}{k_1} \right)^{1/2^\alpha} \cdots \text{for side-by-side reactions} \end{array} \right. \quad (72)$$

These findings show that for large α , diffusion plays an increasingly important role, in that the observed activation energy decreases to that of diffusion, and the reaction order approaches unity. So, for a given porous structure with unknown α , the only reliable estimate of the true k ratio would be from experiments under conditions where pore diffusion is unimportant. On the other hand, finding the experimental ratio of k values under both strong and negligible pore resistance should yield the value of α . This in turn should shed light on the pore structure geometry of the catalyst.

EXAMPLE 18.1 SEARCH OF THE RATE-CONTROLLING MECHANISM

An experimental rate measurement on the decomposition of A is made with a particular catalyst (see pertinent data listed below).

- Is it likely that film resistance to mass transfer influences the rate?
- Could this run have been made in the regime of strong pore diffusion?
- Would you expect to have temperature variations within the pellet or across the gas film?

Data

For the spherical particle:

$$d_p = 2.4 \text{ mm or } L = R/3 = 0.4 \text{ mm} = 4 \times 10^{-4} \text{ m cat}$$

$$\mathcal{D}_e = 5 \times 10^{-5} \text{ m}^2/\text{hr} \cdot \text{m cat (effective mass conductivity)}$$

$$k_{\text{eff}} = 1.6 \text{ kJ/hr} \cdot \text{m cat} \cdot \text{K (effective thermal conductivity)}$$

For the gas film surrounding the pellet (from correlations in the literature):

$$h = 160 \text{ kJ/hr} \cdot \text{m}^2 \text{ cat} \cdot \text{K (heat transfer coefficient)}$$

$$k_g = 300 \text{ m}^3/\text{hr} \cdot \text{m}^2 \text{ cat (mass transfer coefficient)}$$

For the reaction:

$$\Delta H_r = -160 \text{ kJ/mol A (exothermic)}$$

$$C_{A_g} = 20 \text{ mol/m}^3 \text{ (at 1 atm and 336}^\circ\text{C)}$$

$$-r''_{A, \text{obs}} = 10^5 \text{ mol/hr} \cdot \text{m}^3 \text{ cat}$$

Assume that the reaction is first order.

SOLUTION

- Film mass transfer.** From Eq. 58, and introducing numerical values, we obtain

$$\begin{aligned} \frac{\text{observed rate}}{\text{rate if film resistance controls}} &= \frac{k''_{\text{obs}} V_p}{k_g S_{\text{ex}}} = \frac{(-r''_{A, \text{obs}}/C_{A_g})(\pi d_p^3/6)}{k_g(\pi d_p^2)} = \frac{-r''_{A, \text{obs}}}{C_{A_g} k_g} \cdot \frac{d_p}{6} \\ &= \frac{10^5 \text{ mol/hr} \cdot \text{m}^3 \text{ cat}}{(20 \text{ mol/m}^3)(300 \text{ m}^3/\text{hr} \cdot \text{m}^2 \text{ cat})} \cdot \frac{2.4 \times 10^{-3} \text{ m cat}}{6} \\ &= \frac{1}{150} \end{aligned}$$

The observed rate is very much lower than the limiting film mass transfer rate.

Thus the resistance to film mass transfer certainly should not influence the rate of reaction.

(b) **Strong pore diffusion.** Equations 24 and Fig. 18.7 test for strong pore diffusion. Thus

$$M_W = \frac{(-r_A''')_{\text{obs}} L^2}{\mathcal{D}_e C_{A_g}} = \frac{(10^5 \text{ mol/hr} \cdot \text{m}^3 \text{ cat})(4 \times 10^{-4} \text{ m cat})^2}{(5 \times 10^{-5} \text{ m}^3/\text{hr} \cdot \text{m cat})(20 \text{ mol/m}^3)} = 16$$

This quantity M_W is greater than 4, hence pore diffusion is influencing and slowing the rate of reaction.

(c) **Nonisothermal operations.** The estimate for the upper limit to temperature variations is given by Eqs. 38 and 36. Thus within the pellet

$$\begin{aligned} \Delta T_{\text{max, pellet}} &= \frac{\mathcal{D}_e (C_{A_g} - 0)(-\Delta H_r)}{k_{\text{eff}}} \\ &= \frac{(5 \times 10^{-5} \text{ m}^3/\text{hr} \cdot \text{m cat})(20 \text{ mol/m}^3)(160 \text{ kJ/mol})}{(1.6 \text{ kJ/hr} \cdot \text{m cat} \cdot \text{K})} \\ &= 0.1^\circ\text{C} \end{aligned}$$

Across the gas film

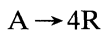
$$\begin{aligned} \Delta T_{\text{max, film}} &= \frac{L(-r_A''')_{\text{obs}}(-\Delta H_r)}{h} \\ &= \frac{(4 \times 10^{-4} \text{ m})(10^5 \text{ mol/hr} \cdot \text{m}^3)(160 \text{ kJ/mol})}{(160 \text{ kJ/hr} \cdot \text{m}^2 \cdot \text{K})} \\ &= 40^\circ\text{C} \end{aligned}$$

These estimates show that the pellet is close to uniform in temperature, but could well be hotter than the surrounding fluid.

The findings of this example use coefficients close to those observed in real gas-solid systems (see the appendix), and the conclusions verify the discussion of this chapter.

EXAMPLE 18.2 THE RATE EQUATION FROM A DIFFERENTIAL REACTOR

The catalytic reaction



is run at 3.2 atm and 117°C in a plug flow reactor which contains 0.01 kg of catalyst and uses a feed consisting of the partially converted product of 20 liters/hr of pure unreacted A. The results are as follows:

Run	1	2	3	4
C_{Ain} , mol/liter	0.100	0.080	0.060	0.040
C_{Aout} , mol/liter	0.084	0.070	0.055	0.038

Find a rate equation to represent this reaction.

SOLUTION

Since the maximum variation about the mean concentration is 8% (run 1), we may consider this to be a differential reactor and we may apply Eq. 52 to find the reaction rate.

Basing conversion for all runs on pure A at 3.2 atm and 117°C, we have

$$C_{A0} = \frac{N_{A0}}{V} = \frac{p_{A0}}{RT} = \frac{3.2 \text{ atm}}{(0.082 \text{ liter} \cdot \text{atm/mol} \cdot \text{K})(390 \text{ K})} = 0.1 \frac{\text{mol}}{\text{liter}}$$

and

$$F_{A0} = C_{A0} v = \left(0.1 \frac{\text{mol A}}{\text{liter}}\right) \left(20 \frac{\text{liters}}{\text{hr}}\right) = 2 \frac{\text{mol}}{\text{hr}}$$

Because the density changes during reaction, concentrations and conversions are related by

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

where $\varepsilon_A = 3$ for the basis selected (pure A).

Table E18.2 shows the details of the calculations. Plotting $-r'_A$ versus C_A as shown in Fig. E18.2 gives a straight line through the origin, indicating a first-

Table E18.2

$\frac{C_{Ain}}{C_{A0}}$	$\frac{C_{Aout}}{C_{A0}}$	C_{Aav} mol/liter	$X_{Ain} =$ $\frac{1 - \frac{C_{Ain}}{C_{A0}}}{1 + \varepsilon_A \frac{C_{Ain}}{C_{A0}}}$	$X_{Aout} =$ $\frac{1 - \frac{C_{Aout}}{C_{A0}}}{1 + \varepsilon_A \frac{C_{Aout}}{C_{A0}}}$	$\frac{\Delta X_A}{X_{Aout} - X_{Ain}}$	$-r'_A = \frac{\Delta X_A}{W/F_{A0}}$
1	0.84	0.092	$\frac{1 - 1}{1 + 3} = 0$	$\frac{1 - 0.84}{1 + 3(0.84)} = 0.0455$	0.0455	$\frac{0.0455}{0.01/2} = 9.1$
0.8	0.70	0.075	0.0588	0.0968	0.0380	7.6
0.6	0.55	0.0575	0.1429	0.1698	0.0269	5.4
0.4	0.38	0.039	0.2727	0.2897	0.0171	3.4

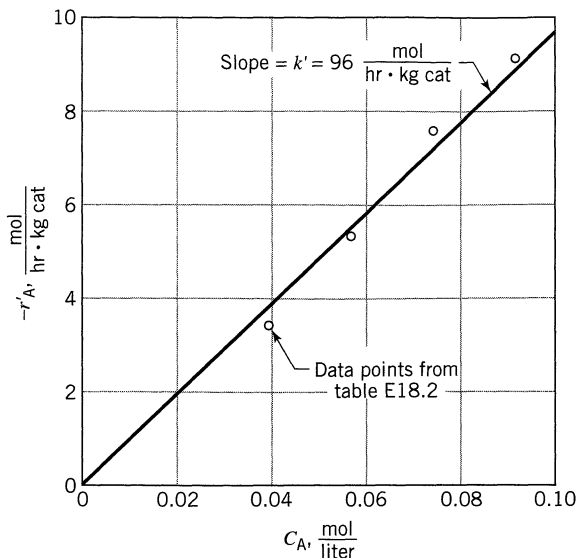


Figure E18.2

order decomposition. The rate in terms of moles A reacted/hr·kg cat is then found from this figure to be

$$\underline{\underline{-r'_A}} = -\frac{1}{W} \frac{dN_A}{dt} = \left(96 \frac{\text{liters}}{\text{hr} \cdot \text{kg cat}} \right) \left(C_A \frac{\text{mol}}{\text{liter}} \right)$$

EXAMPLE 18.3 THE RATE EQUATION FROM AN INTEGRAL REACTOR

The catalytic reaction



is studied in a plug flow reactor using various amounts of catalyst and 20 liters/hr of pure A feed at 3.2 atm and 117°C. The concentrations of A in the effluent stream is recorded for the various runs as follows.

Run	1	2	3	4
Catalyst used, kg	0.020	0.040	0.080	0.160
C_{Aout} , mol/liter	0.074	0.060	0.044	0.029

- Find the rate equation for this reaction, using the integral method of analysis
- Repeat part (a), using the differential method of analysis.

SOLUTION

(a) **Integral Analysis.** From Example 18.2 we have for all experimental runs

$$C_{A0} = 0.1 \text{ mol/liter}, \quad F_{A0} = 2 \text{ mol/hr}, \quad \varepsilon_A = 3$$

Since the concentration varies significantly during the runs, the experimental reactor should be considered to be an integral reactor.

As a first guess try a first-order rate expression. Then for plug flow Eq. 44 gives

$$k' \frac{C_{A0}W}{F_{A0}} = (1 + \varepsilon_A) \ln \frac{1}{1 - X_A} - \varepsilon_A X_A$$

and with ε_A , C_{A0} , and F_{A0} replaced by numerical values this becomes

$$\left(4 \ln \frac{1}{1 - X_A} - 3X_A\right) = k' \left(\frac{W}{20}\right) \quad (\text{i})$$

The two terms in parentheses should be proportional to each other with k' as the constant of proportionality. Evaluating these terms in Table E18.3a for

Table E18.3a Calculations Needed to Test the Fit of Eq. (i); Integral Analysis

$X_A = \frac{C_{A0} - C_A}{C_{A0} + 3C_A}$	$4 \ln \frac{1}{1 - X_A}$	$3X_A$	$\left(4 \ln \frac{1}{1 - X_A} - 3X_A\right)$	$W, \text{ kg}$	$\frac{W}{20}$
0.0808	0.3372	0.2424	0.0748	0.02	0.001
0.1429	0.6160	0.4287	0.1873	0.04	0.002
0.2415	1.1080	0.7245	0.3835	0.08	0.004
0.379	1.908	1.137	0.771	0.16	0.008

the data points and plotting as in Fig. 18.3a, we see that there is no reason to suspect that we do not have a linear relationship. Hence we may conclude that the first-order rate equation satisfactorily fits the data. With k' evaluated from Fig. 18.3a, we then have

$$\underline{\underline{-r'_A = \left(95 \frac{\text{liters}}{\text{hr} \cdot \text{kg cat}}\right) \left(C_A, \frac{\text{mol}}{\text{liter}}\right)}}$$

(b) **Differential Analysis.** Equation 54 shows that the rate of reaction is given by the slope of the X_A versus W/F_{A0} curve. The tabulation (Table E18.3b) based on the measured slopes in Fig. E18.3b shows how the rate of reaction

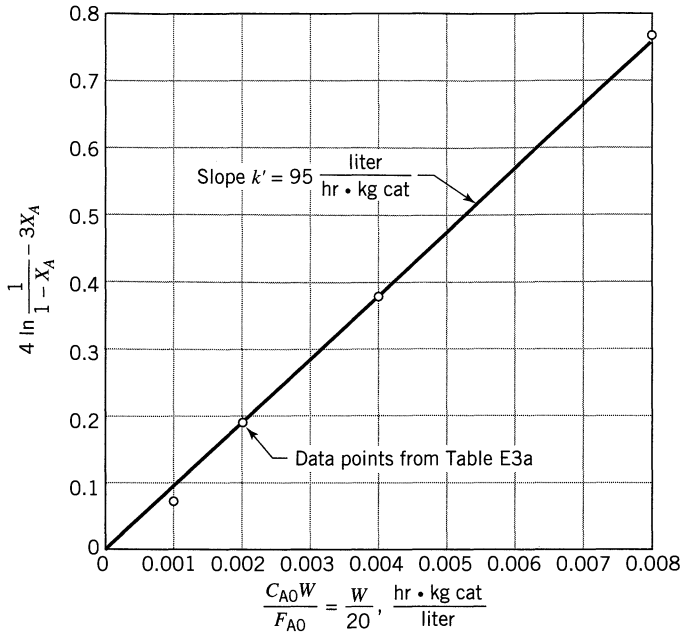


Figure E18.3a

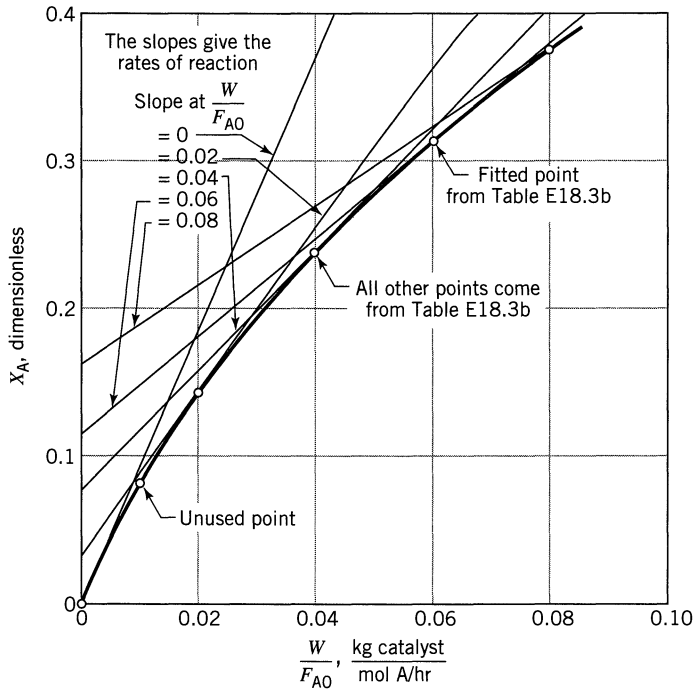
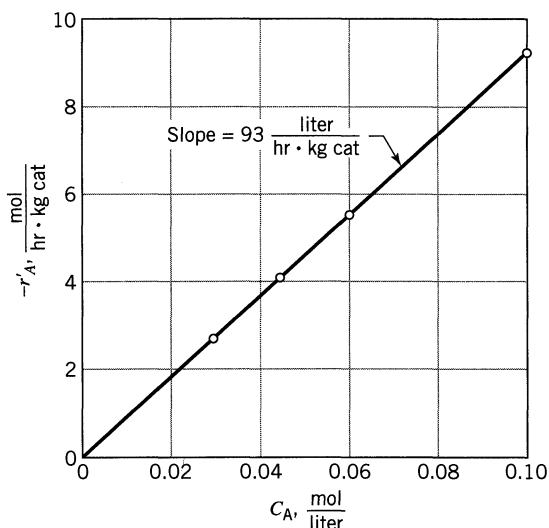


Figure E18.3b

Table E18.3b Calculations Used for the Differential Analysis

W	$\frac{W}{F_{A0}}$	$\frac{C_{Aout}}{C_{A0}}$	$X_A = \frac{1 - \frac{C_A}{C_{A0}}}{1 + \varepsilon_A \frac{C_A}{C_{A0}}}$	$-r'_A = \frac{dX_A}{d\left(\frac{W}{F_{A0}}\right)}$ (from Fig. E18.3b)
0	0	1	0	$\frac{0.4}{0.043} = 9.3$
0.02	0.01	0.74	0.0808	unused
0.04	0.02	0.60	0.1429	5.62
0.08	0.04	0.44	0.2415	4.13
0.16	0.08	0.29	0.379	2.715

**Figure E18.3c**

is found at various C_A . The linear relation between $-r'_A$ and C_A in Fig. E18.3c then gives for the rate equation:

$$\underline{\underline{-r'_A = \left(93 \frac{\text{liters}}{\text{hr} \cdot \text{kg cat}}\right) \left(C_A, \frac{\text{mol}}{\text{liter}}\right)}}$$

EXAMPLE 18.4 PLUG FLOW REACTOR SIZE FROM A RATE EQUATION

Consider the catalytic reaction of Example 18.2. Using the rate equation found for this reaction determine the amount of catalyst needed in a packed bed reactor (assume plug flow) for 35% conversion of A to R for a feed of 2000 mol/hr of pure A at 3.2 atm and 117°C.

SOLUTION

The amount of catalyst needed is given by the first-order rate expression for plug flow, Eq. 44. Thus

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

Replacing all the known values from Example 18.2 into this expression gives the final result, or

$$\begin{aligned} W &= \frac{2000 \frac{\text{mol A}}{\text{hr}}}{\left(96 \frac{\text{liter}}{\text{hr} \cdot \text{kg cat}}\right) \left(0.1 \frac{\text{mol A}}{\text{liter}}\right)} \left(4 \ln \frac{1}{0.65} - 1.05\right) \\ &= \underline{\underline{140 \text{ kg catalyst}}} \end{aligned}$$

EXAMPLE 18.5 PLUG FLOW REACTOR SIZE FROM RATE CONCENTRATION DATA

For the reaction of Example 18.2 suppose the following rate concentration data are available:

C_A , mol/liter	0.039	0.0575	0.075	0.092
$-r'_A$, mol A/hr · kg cat	3.4	5.4	7.6	9.1

Directly from this data, and without using a rate equation, find the size of packed bed needed to treat 2000 mol/hr of pure A at 117°C (or $C_{A0} = 0.1$ mol/liter, $\varepsilon_A = 3$) to 35% conversion, all at 3.2 atm.

Note: Rate information such as this can be obtained from a differential reactor (see Table E18.2), or from other types of experimental reactors.

SOLUTION

To find the amount of catalyst needed without using an analytic expression for the rate concentration relationship requires graphical integration of the plug flow performance equation, or

$$\frac{W}{F_{A0}} = \int_0^{0.35} \frac{dX_A}{-r'_A}$$

Table E18.5

$-r'_A$ (given)	$\frac{1}{-r'_A}$	C_A (given)	$X_A = \frac{1 - C_A/0.1}{1 + 3C_A/0.1}$
3.4	0.294	0.039	0.2812
5.4	0.186	0.0575	0.1563
7.6	0.1316	0.075	0.0778
9.1	0.110	0.092	0.02275

The needed $1/-r'_A$ versus X_A data are determined in Table E18.5 and are plotted in Fig. E18.5. Integrating graphically then gives

$$\int_0^{0.35} \frac{dX_A}{-r'_A} = 0.0735$$

Hence

$$\underline{W} = \left(2000 \frac{\text{mol A}}{\text{hr}} \right) \left(0.0735 \frac{\text{hr} \cdot \text{kg cat}}{\text{mol A}} \right) = \underline{\underline{147 \text{ kg cat}}}$$

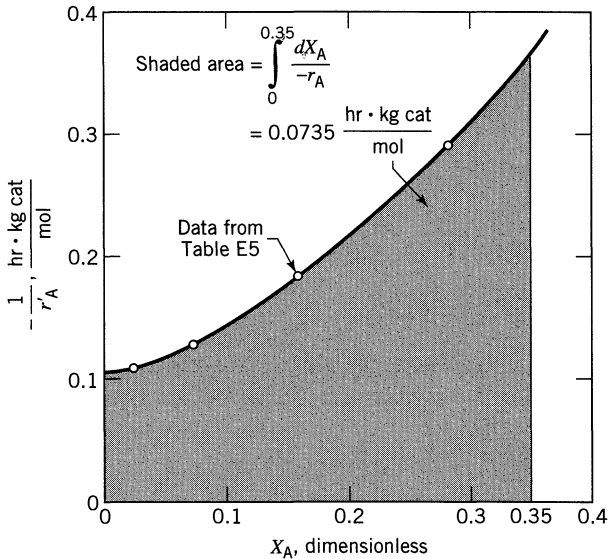


Figure E18.5

EXAMPLE 18.6 MIXED FLOW REACTOR SIZE

For the reaction of Example 18.2 determine the amount of catalyst needed in a packed bed reactor with a very large recycle rate (assume mixed flow) for 35% conversion of A to R for a feed rate of 2000 mol/hr of pure A at 3.2 atm and 117°C. For the reaction at this temperature



From Example 18.2, $C_{A0} = 0.1$ mol/liter and $\varepsilon_A = 3$.

SOLUTION

At 35% conversion the concentration of reactant is

$$C_A = C_{A0} \left(\frac{1 - X_A}{1 + \varepsilon_A X_A} \right) = 0.1 \left(\frac{1 - 0.35}{1 + 3(0.35)} \right) = 0.0317$$

Now for mixed flow Eq. 45 gives

$$\frac{W}{F_{A0}} = \frac{X_{Aout} - X_{Ain}}{-r'_{Aout}} = \frac{X_{Aout} - X_{Ain}}{k' C_{Aout}}$$

or

$$\underline{\underline{W}} = 2000 \left(\frac{0.35 - 0}{96(0.0317)} \right) = \underline{\underline{230 \text{ kg}}}$$

Note: A mixed flow reactor requires more catalyst than does a plug flow reactor, as expected.

EXAMPLE 18.7 MASS TRANSFER RESISTANCES

What is the most reasonable interpretation, in terms of controlling resistances, of the kinetic data of Table E18.7 obtained in a basket type mixed flow reactor if we know that the catalyst is porous? Assume isothermal behavior.

Table E18.7

Pellet Diameter	Leaving Concentration of Reactant	Spinning Rate of Baskets	Measured Reaction Rate, $-r'_A$
1	1	high	3
3	1	low	1
3	1	high	1

SOLUTION

Let us see whether film resistance or pore resistance could be slowing the rate of reaction.

Runs 2 and 3 use different spinning rates but have the same reaction rate. Therefore film diffusion is ruled out for the larger pellets. But Eq. 57 shows that if film resistance is not important for large pellets it will not be important for small pellets. Therefore film resistance does not influence the rate.

Next, comparing run 1 and either run 2 or 3 shows that

$$-r'_A \propto \frac{1}{R}$$

Eq. 25 then tells us that we are in the regime of strong pore resistance. Thus our final conclusion is

- negligible film resistance
- strong pore diffusion resistance

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PROBLEMS

These problems are loosely grouped as follows:

Problems 1–19: Direct application of performance equations. These problems should be tried first.

Problems 20–30: Pore diffusion kinetics.

Problems 31–40: Reactor size + pore diffusion

- 18.1.** While being shown around Lumphead Laboratories, you stop to view a reactor used to obtain kinetic data. It consists of a 5-cm ID glass column packed with a 30-cm height of active catalyst. Is this a differential or integral reactor?
- 18.2.** A solid catalyzed first-order reaction, $\varepsilon = 0$, takes place with 50% conversion in a basket type mixed reactor. What will be the conversion if the reactor size is trebled and all else—temperature, amount of catalyst, feed composition, and flow rate—remains unchanged?
- 18.3.** The following kinetic data on the reaction $A \rightarrow R$ are obtained in an experimental packed bed reactor using various amounts of catalyst and a fixed feed rate $F_{A0} = 10$ kmol/hr.
- | | | | | | | | |
|--------------|------|------|------|------|------|------|------|
| W , kg cat | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| X_A | 0.12 | 0.20 | 0.27 | 0.33 | 0.37 | 0.41 | 0.44 |
- (a) Find the reaction rate at 40% conversion.
 (b) In designing a large packed bed reactor with feed rate $F_{A0} = 400$ kmol/hr how much catalyst would be needed for 40% conversion.
 (c) How much catalyst would be needed in part (b) if the reactor employed a very large recycle of product stream.

A gas containing A (2 mol/m^3) is fed ($1 \text{ m}^3/\text{hr}$) to a plug flow reactor with recycle loop (0.02 m^3 loop volume, 3 kg of catalyst), and the output composition from the reactor system is measured (0.5 mol A/m^3). Find the rate equation for the decomposition of A for the following cases. Be sure to give the units of $-r'_A$, C_A , and k' in your final expression.

18.4. Very large recycle, $A \rightarrow R$, $n = 1/2$

18.5. Very large recycle, $A \rightarrow 3R$, $n = 1$, 50% A–50% inerts in feed

18.6. No recycle, $A \rightarrow 3R$, $n = 2$, 25% A–75% inerts in feed

Gaseous A reacts ($A \rightarrow R$) in an experimental reactor. From the following conversion data at various conditions find a rate equation to represent the reaction

18.7. $v_0, \text{m}^3/\text{hr}$ | 3 2 1.2 Mixed flow
 X_A | 0.2 0.3 0.5 $C_{A0} = 10 \text{ mol/m}^3$
 $W = 4 \text{ gm}$

18.8. W, gm | 0.5 1.0 2.5 Plug flow
 C_A | 30 20 10 $C_{A0} = 60 \text{ mol/m}^3$
 $v = 3 \text{ liter/min}$

The following kinetic data are obtained in an experimental Carberry type basket reactor using 100 gm of catalyst in the paddles and different flow rates from run to run:

$A \rightarrow R$	$F_{A0}, \text{mol/min}$	0.14	0.42	1.67	2.5	1.25
$C_{A0} = 10 \text{ mol/m}^3$	$C_A, \text{mol/m}^3$	8	6	4	2	1

18.9. Determine the amount of catalyst needed in a packed bed reactor for 75% conversion of 1000 mol A/min of a $C_{A0} = 8 \text{ mol/m}^3$ feed.

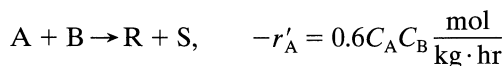
18.10. Find W for mixed flow, $X_A = 0.90$, $C_{A0} = 10 \text{ mol/m}^3$, $F_{A0} = 1000 \text{ mol/min}$.

How much catalyst is needed in a packed bed reactor for 80% conversion of 1000 m^3/hr of pure gaseous A ($C_{A0} = 100 \text{ mol/m}^3$) if the stoichiometry and rate are given by

18.11. $A \rightarrow R, -r'_A = \frac{50C_A}{1 + 0.02C_A} \frac{\text{mol}}{\text{kg} \cdot \text{hr}}$

18.12. $A \rightarrow R, -r'_A = 8C_A^2 \frac{\text{mol}}{\text{kg} \cdot \text{hr}}$

18.13. Gaseous feed with A and B ($v_0 = 10 \text{ m}^3/\text{hr}$) pass through an experimental reactor packed with catalyst ($W = 4 \text{ kg}$). Reaction occurs as follows:



Find the conversion of reactants if the feed contains $C_{A0} = 0.1 \text{ mol/m}^3$ and $C_{B0} = 10 \text{ mol/m}^3$.

- 18.14.** A West Texas gas oil is cracked in a tubular reactor packed with silica-alumina cracking catalyst. The liquid feed ($m_w = 0.255$) is vaporized, heated, enters the reactor at 630°C and 1 atm, and with adequate temperature control stays close to this temperature within the reactor. The cracking reaction follows first-order kinetics and gives a variety of products with mean molecular weight $m_w = 0.070$. Half the feed is cracked for a feed rate of $60 \text{ m}^3 \text{ liquid/m}^3 \text{ reactor} \cdot \text{hr}$. In the industry this measure of feed rate is called the *liquid hourly space velocity*. Thus $\text{LHSV} = 60 \text{ hr}^{-1}$. Find the first-order rate constants k' and k'' for this cracking reaction.

Data: Density of liquid feed: $\rho_l = 869 \text{ kg/m}^3$
 Bulk density of packed bed: $\rho_b = 700 \text{ kg/m}^3$
 Density of catalyst particles: $\rho_s = 950 \text{ kg/m}^3$

This problem is prepared from Satterfield (1970).

- 18.15.** Kinetic experiments on the solid catalyzed reaction $A \rightarrow 3R$ are conducted at 8 atm and 700°C in a basket type mixed reactor 960 cm^3 in volume and containing 1 gm of catalyst of diameter $d_p = 3 \text{ mm}$. Feed consisting of pure A is introduced at various rates into the reactor and the partial pressure of A in the exit stream is measured for each feed rate. The results are as follows:

Feed rate, liters/hr	100	22	4	1	0.6
$p_{A\text{out}}/p_{A\text{in}}$	0.8	0.5	0.2	0.1	0.05

Find a rate equation to represent the rate of reaction on catalyst of this size.

- 18.16.** “El jefe” (the chief) decided to do something to improve the low conversion ($X_A = 0.80$) of our first-order solid-catalyzed liquid-phase reaction. Instead of ordering more of the expensive catalyst to fill the half-empty reactor, he decided to save money by adding some tricky piping to the present vertical packed bed reactor. When I saw what the mechanics were putting together for him, (see Fig. P18.16), I told “el jefe” that it didn’t seem right. I could sense right away that my saying this annoyed him, but all he said was, “All right, young lady. Why don’t you tell me what conversion to expect with this arrangement?” Please do this.

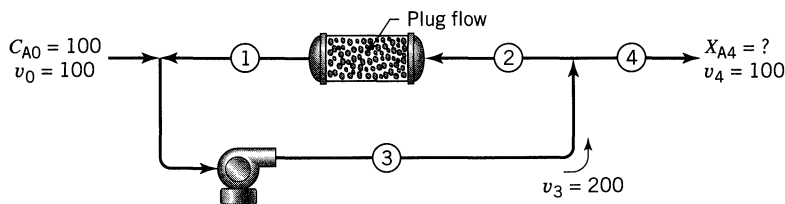


Figure P18.16

- 18.17.** The second-order reaction $A \rightarrow R$ is studied in a recycle reactor with very large recycle ratio, and the following data are recorded:

Void volume of reactor: 1 liter

Weight of catalyst used: 3 gm

Feed to the reactor: $C_{A0} = 2$ mol/liter

$v_0 = 1$ liter/hr

Exit stream condition: $C_{Aout} = 0.5$ mol/liter

- (a) Find the rate constant for this reaction (give units).
 (b) How much catalyst is needed in a packed bed reactor for 80% conversion of 1000 liter/hr of feed of concentration $C_{A0} = 1$ mol/liter. No recycle.
 (c) Repeat part (b) if the reactor is packed with 1 part catalyst to 4 parts inert solid. This addition of inerts helps maintain isothermal conditions and reduce possible hot spots.

Note: Assume isothermal conditions throughout.

- 18.18.** A small experimental packed bed reactor ($W = 1$ kg) using very large recycle of product stream gives the following kinetic data:

$A \rightarrow R,$	$C_A, \text{ mol/m}^3$	1	2	3	6	9
$C_{A0} = 10 \text{ mol/m}^3$	$v_0, \text{ liter/hr}$	5	20	65	133	540

Find the amount of catalyst needed for 75% conversion for a flow rate of 1000 mol A/hr of a $C_{A0} = 8$ mol/m³ feed stream

- (a) in a packed bed reactor with no recycle of exit fluid
 (b) in a packed bed reactor with very high recycle
- 18.19.** A closed loop batch G/S reactor (see Fig. P18.19) is used for catalytic rate studies. For this purpose feed gas with reactant is introduced into the system and is rapidly circulated through the catalyst loop. From the following composition-time data find a kinetic equation in units of mol/gm · min to represent this reaction.

$t, \text{ min}$	0	4	8	16	36	Pure A at 609 K
$\pi_0, \text{ atm}$	1	0.75	0.67	0.6	0.55	$2A \rightarrow R$

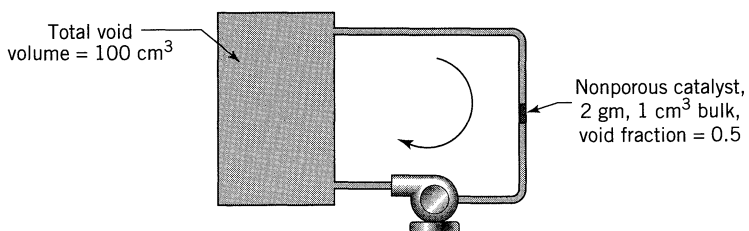


Figure P18.19

- 18.20.** Our packed bed reactor runs the gas phase reaction $A \rightarrow R$ at 10 atm and 336°C , and gives 90% conversion of a pure A feed. However, the catalyst salesman guarantees that in the absence of any pore diffusion resistance our reaction will proceed on his new improved porous catalyst ($\mathcal{D}_e = 2 \times 10^{-6} \text{ m}^3/\text{m cat} \cdot \text{s}$) with a rate given by

$$-r_A''' = 0.88C_A \frac{\text{mol}}{\text{m}^3 \text{ cat} \cdot \text{s}}$$

which is much better than what we now can do. The catalyst is rather expensive, since it is formulated of compressed kookaburra droppings and it is sold by weight. Still, we'll try it when we next replace our catalyst. What diameter of catalyst balls should we order?

- 18.21.** A reaction $A \rightarrow R$ is to take place on a porous catalyst pellet ($d_p = 6 \text{ mm}$, $\mathcal{D}_e = 10^{-6} \text{ m}^3/\text{m cat} \cdot \text{s}$). How much is the rate slowed by pore diffusional resistance if the concentration of reactant bathing the particle is $100 \text{ mol}/\text{m}^3$ and the diffusion-free kinetics are given by

$$-r_A''' = 0.1C_A^2 \frac{\text{mol}}{\text{m}^3 \text{ cat} \cdot \text{s}}$$

- 18.22.** In the absence of pore diffusion resistance a particular first-order gas-phase reaction proceeds as reported below.

$$-r_A''' = 10^{-6} \text{ mol}/\text{cm}^3 \text{ cat} \cdot \text{s}$$

at

$$C_A = 10^{-5} \text{ mol}/\text{cm}^3, \quad \text{at 1 atm and } 400^\circ\text{C}$$

What size of spherical catalyst pellets ($\mathcal{D}_e = 10^{-3} \text{ cm}^3/\text{cm cat} \cdot \text{s}$) would ensure that pore resistance effects do not intrude to slow the rate of reaction?

The first-order decomposition of A is run in an experimental mixed flow reactor. Find the role played by pore diffusion in these runs; in effect determine whether the runs were made under diffusion-free, strong resistance, or intermediate conditions.

18.23.

d_p	W	C_{A0}	v	X_A	
3	1	100	9	0.4	A \rightarrow R
12	4	300	8	0.6	

18.24.

d_p	W	C_{A0}	v	X_A	
4	1	300	60	0.8	A \rightarrow R
8	3	100	160	0.6	

18.25.

d_p	W	C_{A0}	v	X_A	
2	4	75	10	0.2	$A \rightarrow R$
1	6	100	5	0.6	

18.26. Find the activation energy of the first-order reaction from the following data:

d_p	C_A	$-r'_A$	T, K	
1	20	1	480	$A \rightarrow R$ $C_{A0} = 50$
2	40	1	480	
2	40	3	500	

18.27. What can you tell about the influencing resistances for the porous catalyst from the data of Table P18.27 obtained in a recycle type mixed flow reactor. In all runs the leaving stream has the same composition, and conditions are isothermal throughout.

Table P18.27

Quantity of Catalyst	Pellet Diameter	Flow Rate of Given Feed	Recycle Rate	Measured Reaction Rate, $-r'_A$
1	1	1	High	4
4	1	4	Higher still	4
1	2	1	Higher still	3
4	2	4	High	3

18.28. Experiments at 300°C in a packed bed reactor with very large recycle stream give the results shown below for the first order catalytic decomposition $A \rightarrow R \rightarrow S$. Under the best possible conditions (always at 300°C) what $C_{R, \max}/C_{A0}$ may we expect, and how do you suggest we get this (what flow pattern and particle size, large or small)?

d_p	W/F_{A0}	$C_{R, \max}/C_{A0}$	
4	1	0.5	No recycle
8	2	0.5	

18.29. Experiments with a basket type mixed flow reactor on the solid catalyzed decomposition $A \rightarrow R \rightarrow S$ give the results of Table P18.29. Under the best possible reaction conditions (always at 300°C) what is the maximum concentration of R we may expect? How do you suggest that this be obtained?

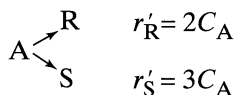
Table P18.29

Size of Porous Pellets	Temperature	W/F_{A0}	C_{Rmax}/C_{A0}
6 mm	300°C	25	23%
12 mm	300°C	50	23%

18.30. Reactant A at $C_{A0} = 10 \text{ mol/m}^3$ is to be passed through a packed bed catalytic reactor where it will decompose into either R or S. To maximize the formation of R and for 90% decomposition of A determine

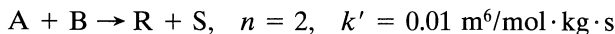
- whether to operate in the strong pore diffusion regime or in the diffusion-free regime
- whether to use plug flow or mixed flow (high recycle)
- C_R expected in the exit stream.

The kinetics of the decomposition, when free of pore diffusion resistance, is given by



18.31. A packed bed reactor converts A to R by a first-order catalytic reaction, $A \rightarrow R$. With 9-mm pellets the reactor operates in the strong pore diffusion resistance regime and gives 63.2% conversion. If these pellets were replaced by 18-mm pellets (to reduce pressure drop) how would this affect the conversion?

18.32. We want to build a packed bed reactor filled with 1.2-cm porous catalyst particles ($\rho_s = 2000 \text{ kg/m}^3$, $\mathcal{D}_c = 2 \times 10^{-6} \text{ m}^3/\text{m cat} \cdot \text{s}$) to treat $1 \text{ m}^3/\text{s}$ of feed gas (1/3 A, 1/3 B, 1/3 inert) at 336°C and 1 atm to 80% conversion of A. Experiments with fine catalyst particles which are free from diffusional resistance show that



How much catalyst must we use?

18.33. In an experimental mixed flow reactor with 10 gm of 1.2-mm catalyst particles and a feed of $4 \text{ cm}^3/\text{s}$ of pure A at 1 atm and 336°C we get 80% conversion for the first-order reaction



We want to design a commercial-sized reactor to treat large amounts of feed to 80% conversion at the above temperature and pressure. Our choice

is between a fluidized bed of 1-mm particles (assume mixed flow of gas) and a packed bed of 1.5-cm particles. Which should we choose so as to minimize the amount of catalyst needed? How much advantage is there in this choice?

Additional Data: For the catalyst particles:

$$\rho_s = 2000 \text{ kg/m}^3 \quad \mathcal{D}_e = 10^{-6} \text{ m}^2/\text{m cat} \cdot \text{s}$$

In aqueous solution, and in contact with the right catalyst, reactant A is converted to product R by the elementary reaction $A \rightarrow 2R$. Find the mass of catalyst needed in a packed bed reactor for 90% conversion of 10^4 mol A/hr of feed having $C_{A0} = 10^3 \text{ mol/m}^3$. For this reaction

18.34. $k''' = 8 \times 10^{-4} \text{ m}^3/\text{m}^3 \text{ bed} \cdot \text{s}$

18.35. $k''' = 2 \text{ m}^3/\text{m}^3 \text{ bed} \cdot \text{s}$

Additional data:

Diameter of porous catalyst pellets = 6 mm

Effective diffusion coefficient of A in the pellet = $4 \times 10^{-8} \text{ m}^2/\text{m cat} \cdot \text{s}$

Voidage of packed bed = 0.5

Bulk density of packed bed = 2000 kg/m^3 of bed

- 18.36.** A first-order catalytic reaction $A(l) \rightarrow R(l)$ is run in a long, narrow vertical reactor with upflow of liquid through a fluidized bed of catalyst particles. Conversion is 95% at the start of operations when the catalyst particles are 5 mm in diameter. The catalyst is friable and slowly wears away, particles shrink and the fine powder produced washes out of the reactor. After a few months each of the 5-mm spheres has shrunk to 3-mm spheres. What should be the conversion at this time? Assume plug flow of liquid.
- (a) Particles are porous and allow easy access for reactants (no resistance to pore diffusion).
- (b) Particles are porous and at all sizes provide a strong resistance to pore diffusion.
- 18.37.** At present we are running our catalytic first-order reaction in the strong pore diffusion regime in a packed bed reactor filled with platinum impregnated 6-mm particles of uniform size. A catalyst manufacturer suggests that we replace our catalyst with 6-mm pellets consisting of fused 0.06-mm grains. The voidage between grains in the pellet would be about 25%. If these new pellets were free of pore diffusion resistance in their large voids (between grains), but if the grains were still in the strong diffusional resistance regime, how would this change affect the weight of catalyst needed and the reactor volume?
- 18.38.** Instead of impregnating the whole porous particle uniformly with platinum (see Problem 18.37), suppose we only impregnate the outer layer of the

spherical particle to a thickness of 0.3 mm. How much platinum do we save by this change? Assume that we are in the strong pore diffusion regime throughout.

- 18.39.** Because the catalytic reaction $A \rightarrow R$ is highly exothermic with rate highly temperature-dependent, a long tubular flow reactor immersed in a trough of water, as shown in Fig. P18.39, is used to obtain essentially isothermal kinetic data. Pure A at 0°C and 1 atm flows through this tube at $10\text{ cm}^3/\text{sec}$, and the stream composition is analyzed at various locations.

Distance from feed input, meters	0	12	24	36	48	60	72	84	(∞)
Partial pressure of A, mm Hg	760	600	475	390	320	275	240	215	150

Determine what size of plug flow reactor operating at 0°C and 1 atm would give 50% conversion of A to R for a feed rate of 100 kmol/hr of pure A.

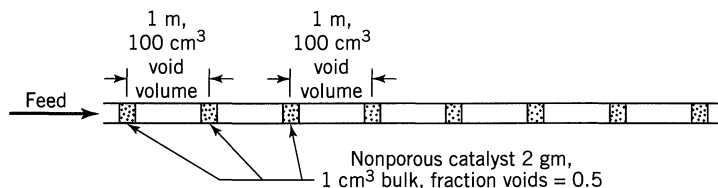


Figure P18.39

- 18.40.** A closed-loop experimental G/S batch system as sketched in Fig. P18.19 is used to study the kinetics of a catalytic reaction $A \rightarrow 2R$. Pure A is introduced into the systems and is circulated at 0°C and 1 atm at $10\text{ cm}^3/\text{sec}$. The stream is analyzed from time to time with the following results:

Time, min	0	2	4	6	8	10	12	14	(∞)
Partial pressure of A, mm Hg	760	600	475	290	320	275	240	215	150

- Determine the size of a plug flow reactor operating at 0°C and 1 atm required to effect a 50% conversion of A to R for a feed rate of 100 kmol A/hr .
- Repeat part a with the modification that an inert at a partial pressure of 1 atm is present in the closed loop so that the total pressure at the start is 2 atm.

Chapter 19

The Packed Bed Catalytic Reactor

Reactant gas can be made to contact solid catalyst in many ways, and each has its specific advantages and disadvantages. Figure 19.1 illustrates a number of these contacting patterns. These may be divided into two broad types, the fixed-bed reactors of Fig. 19.1*a*, *b*, and *c* and the fluidized-bed reactors of Figs. 19.1*d*, *e*, and *f*. The moving-bed reactor of Fig. 19.1*g* is an intermediate case which embodies some of the advantages and some of the disadvantages of fixed-bed and fluidized-bed reactors. Let us compare the merits of these reactor types.

1. In passing through fixed beds, gases approximate plug flow. It is quite different with bubbling fluidized beds where the flow is complex and not well known, but certainly far from plug flow, and with considerable bypassing. This behavior is unsatisfactory from the standpoint of effective contacting and requires much more catalyst for high gas conversion, and greatly depresses the amount of intermediate which can be formed in series reactions. Hence, if efficient contacting in a reactor is of primary importance, then the fixed bed is favored.
2. Effective temperature control of large fixed beds can be difficult because such systems are characterized by a low heat conductivity. Thus in highly exothermic reactions hot spots or moving hot fronts are likely to develop which may ruin the catalyst. In contrast with this, the rapid mixing of solids in fluidized beds allows easily and reliably controlled, practically isothermal, operations. So if operations are to be restricted within a narrow temperature range, either because of the explosive nature of the reaction or because of product distribution considerations, then the fluidized bed is favored.
3. Fixed beds cannot use very small sizes of catalyst because of plugging and high-pressure drop, whereas fluidized beds are well able to use small-size particles. Thus for very fast reactions in which pore and film diffusion may influence the rate, the fluidized bed with its vigorous gas-solid contacting and small particles will allow a much more effective use of the catalyst.
4. If the catalyst has to be treated (regenerated) frequently because it deactivates rapidly, then the liquid-like fluidized state allows it to be pumped easily from unit to unit. This feature of fluidized contacting offers overwhelming advantages over fixed bed operations for such solids.

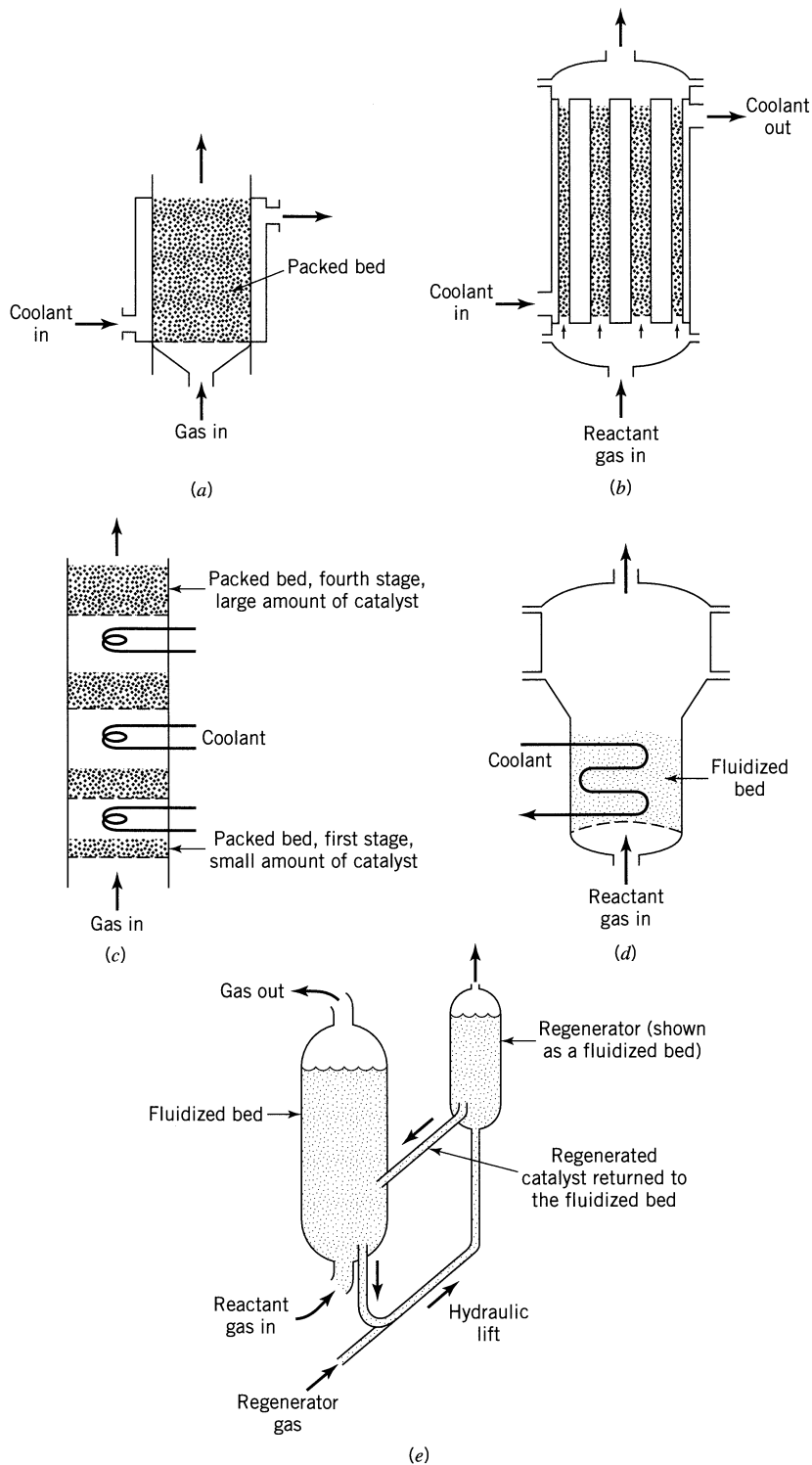


Figure 19.1 Various types of catalytic reactors.

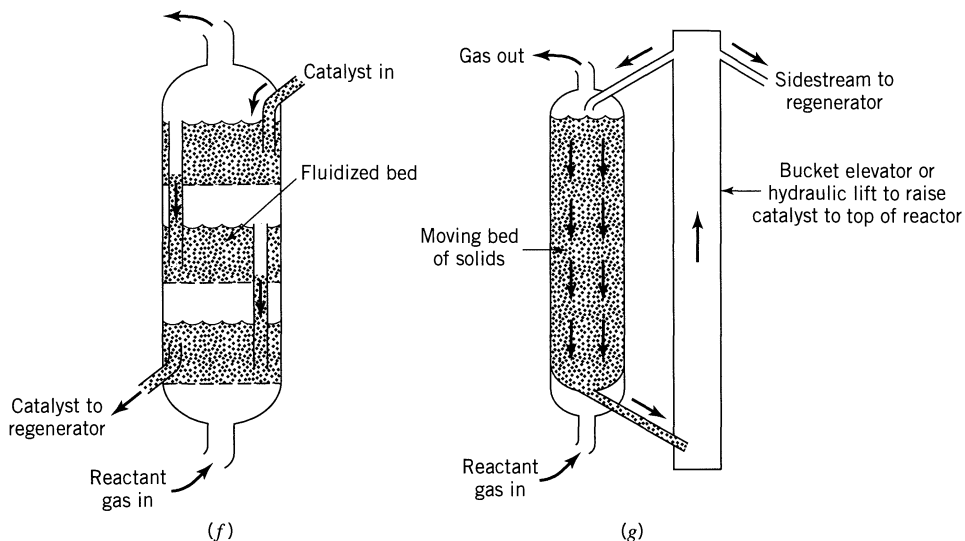


Figure 19.1 (Continued.)

With these points in mind, let us proceed to Fig. 19.1. Figure 19.1*a* is a typical packed bed reactor embodying all its advantages and disadvantages. Figure 19.1*b* shows how the problem of hot spots can be substantially reduced by increasing the cooling surface. Figure 19.1*c* shows how intercooling can still further control the temperature. Note that in the first stage where reaction is fastest, conversion is kept low by having less catalyst present than in the other stages. Units such as these can all be incorporated in a single shell or can be kept separate with heat exchanges between stages.

Figure 19.1*d* shows a fluidized reactor for a stable catalyst which need not be regenerated. The heat exchanger tubes are immersed in the bed to remove or add heat and to control the temperature. Figure 19.1*e* shows operations with a deactivating catalyst which must be continually removed and regenerated. Figure 19.1*f* shows a three-stage countercurrent unit which is designed to overcome the shortcomings of fluidized beds with regard to poor contacting. Figure 19.1*g* shows a moving-bed reactor. Such units share with fixed beds the advantages of plug flow and disadvantages of large particle size, but they also share with fluidized beds the advantages of low catalyst-handling costs.

Many factors must be weighed to obtain optimum design, and it may be that the best design is one that uses two different reactor types in series. For example, for high conversion of a very exothermic reaction we may well look into the use of a fluidized bed followed by a fixed bed.

The main difficulties of design of catalytic reactors reduce to the following two questions: (1) How do we account for the nonisothermal behavior of packed beds? and (2) How do we account for the nonideal flow of gas in fluidized beds.

Consider a packed bed with heat exchange (Figs. 19.1*a* and 19.1*b*). For an exothermic reaction Fig. 19.2 shows the types of heat and mass movement that will occur when the packed bed is cooled at the walls. The centerline will be hotter than the walls, reaction will be faster, and reactants will be more rapidly consumed there; hence, radial gradients of all sorts will be set up.

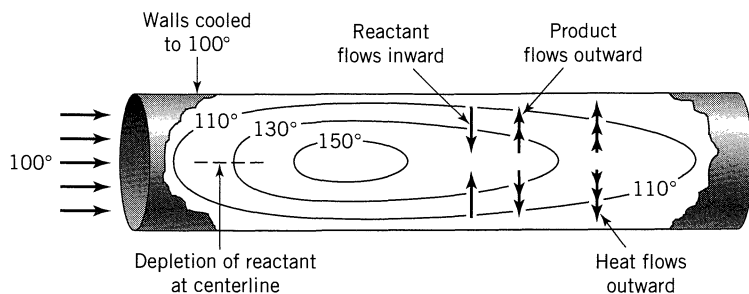


Figure 19.2 The temperature field in a packed bed reactor for an exothermic reaction creates radial movement of heat and matter.

The detailed analysis of this situation should include the simultaneous radial dispersion of heat and matter, and maybe axial dispersion too. In setting up the mathematical model, what simplifications are reasonable, would the results properly model the real situation, would the solution indicate unstable behavior and hot spots? These questions have been considered by scores of researchers, numerous precise solutions have been claimed; however, from the point of view of prediction and design the situation today still is not as we would wish. The treatment of this problem is quite difficult, and we will not consider it here. A good review of the state-of-the-art is given by Froment (1970), and Froment and Bischoff (1990).

The staged adiabatic packed bed reactor of Fig. 19.1c presents a different situation. Since there is no heat transfer in the zone of reaction the temperature and conversion are related simply, hence the methods of Chapter 9 can be applied directly. We will examine numerous variations of staging and heat transfer to show that this is a versatile setup which can closely approximate the optimum.

The fluidized bed and other suspended solid reactor types are considered in the next chapter.

Staged Adiabatic Packed Bed Reactors

With proper interchange of heat and proper gas flow, staged adiabatic packed beds become a versatile system, which is able to approximate practically any desired temperature progression. Calculation and design of such a system is simple, and we can expect that real operations will closely follow these predictions.

We illustrate the design procedure with the single reaction $A \rightarrow R$ with any kinetics. This procedure can be extended to other reaction types without difficulty. We first consider different ways of operating these reactors, and then compare these and point out when one or other is favored.

Staged Packed Beds (Plug Flow) with Intercooling.¹ The reasoning in Chapter 9 shows that we would like the reacting conditions to follow the optimal tempera-

¹ This section follows directly from pp. 215–235 of Chapter 9. Hence it is suggested that the reader familiarize himself with that section before proceeding here.

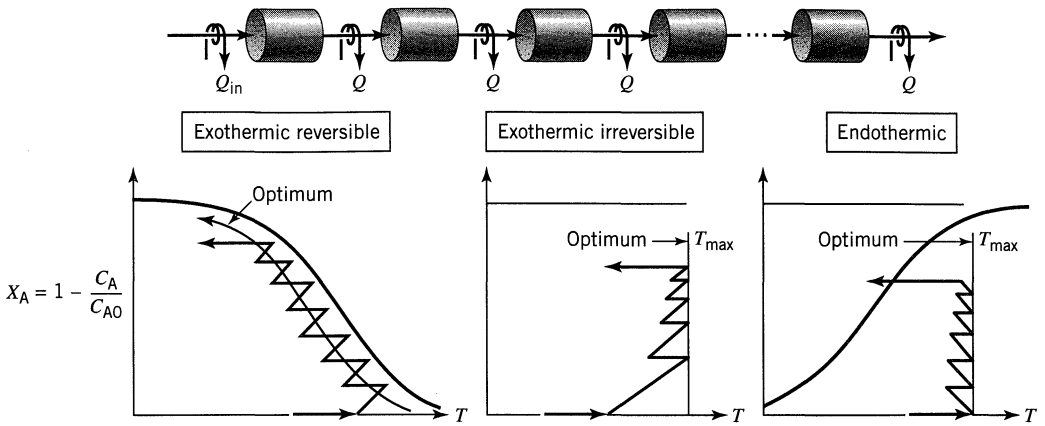


Figure 19.3 Sketch showing how staged packed beds can closely approach the optimal temperature progression.

ture progression. With many stages available this can be closely approximated, as shown in Fig. 19.3.

For any preset number of stages the optimization of operations reduces to minimizing the total amount of catalyst needed to achieve a given conversion. Let us illustrate the procedure for two-stage operations with *reversible exothermic reactions*. The method of attack is shown in Fig. 19.4. In this figure we wish to minimize the total area under the $1/-r'_A$ versus X_A curve in going from $X_A = 0$ to $X_{A2} =$ some fixed or required conversion. In searching for this optimum we have three variables which we can set at will: the incoming temperature (point T_a), the amount of catalyst used in the first stage (locates point b along the adiabatic), and the amount of intercooling (locates point c along the bc line). Fortunately, we are able to reduce this 3-dimensional search (5-dimensional for

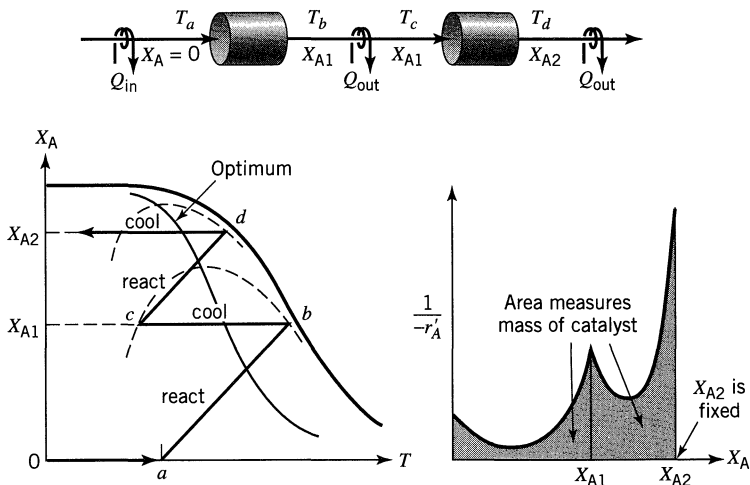


Figure 19.4 Optimum two-stage packed bed reactor.

three stages, etc.) to a one-dimensional search where T_a alone is guessed. The procedure is as follows:

1. Guess T_a .
2. Move along the adiabatic line until the following condition is satisfied:

$$\int_{\text{in}}^{\text{out}} \frac{\partial}{\partial T} \left(\frac{1}{-r'_A} \right) dX_A = 0 \quad (1)$$

This gives point b in Fig. 19.4, thus the amount of catalyst needed in the first stage as well as the outlet temperature from that stage. Especially in preliminary design it may not be convenient to use the criterion of Eq. 1. A simple alternative is a trial-and-error search. Usually two or three carefully chosen trials keeping away from low rate conditions will yield a good design, close to the optimum.

3. Cool to point c which has the same rate of reaction as point b ; thus

$$(-r'_A)_{\text{leaving a reactor}} = (-r'_A)_{\text{entering the next reactor}} \quad (2)$$

4. Move along the adiabatic from point c until the criterion of Eq. 1 is satisfied, giving point d .
- 5a. If point d is at the desired final conversion then we have guessed T_a correctly.
- 5b. If point d is not at the desired final conversion try a different incoming temperature T_a . Usually three trials will very closely approach the optimum.

For three or more stages the procedure is a direct extension of that presented here, and it still remains a one-dimensional search. This procedure was first developed by Konoki (1956a) and later, independently, by Horn (1961a).

Overall cost considerations will determine the number of stages to be used, so in practice we examine 1, then 2, etc., stages until a minimum cost is obtained.

Let us next consider the two other cases of Fig. 19.3. For *irreversible exothermic reactions* the criterion for optimal operations has also been presented by Konoki (1956b). For *endothermic reactions* the optimal criterion has yet to be developed. In all these cases a trial-and-error search keeping far from the regions of low rates is recommended.

Staged Mixed Flow Reactors. For very high recycle the staged recycle reactors approach mixed flow. As shown in Fig. 19.5, in this case the reactors should operate on the line of optimum temperature progression, the best distribution of catalyst among the stages being found by the maximization of rectangles (see Figs. 6.9–6.11). In effect we need to choose the distribution of catalyst so as to maximize area KLMN which then minimizes the shaded area in Fig. 19.5.

Staged Packed Beds with Recycle. Here we have a flexible system which can approach mixed flow and as such is able to avoid regions of low rates. Figure

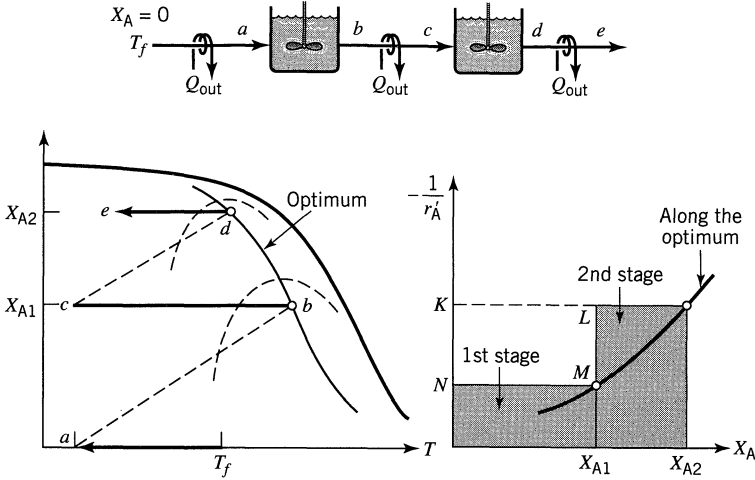


Figure 19.5 Optimum two-stage mixed flow reactor set up (infinite recycle for staged packed beds).

19.6 illustrates two-stage operations with a recycle ratio $R = 1$, and a feed temperature T_f . Extension to three or more stages follows directly.

Konoki (1961) presents the criterion for optimal operations; however, in preliminary design a few good guesses will suffice to closely approach optimal operations.

In recycle operations the heat exchangers can be located in a number of places without affecting what goes on in the reactor. Figure 19.6 illustrates one of these; other alternatives are shown in Fig. 19.7. The best location will depend on

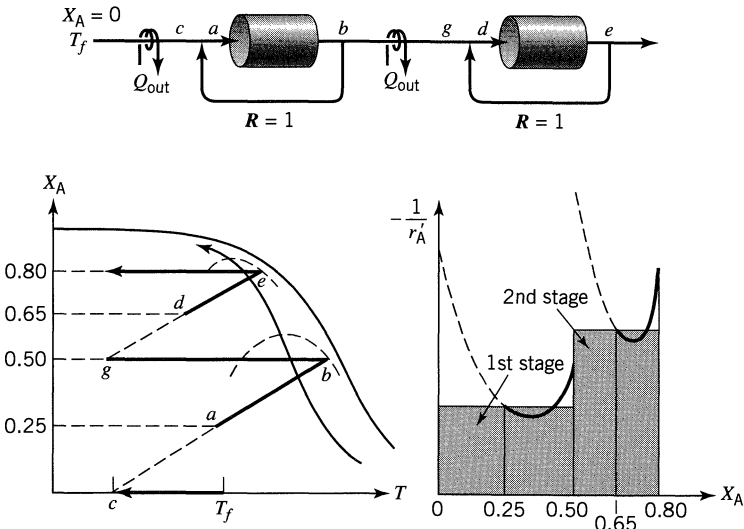


Figure 19.6 Optimum two-stage packed bed reactor with recycle. The conversions shown represent a recycle ratio $R = 1$ in both stages.

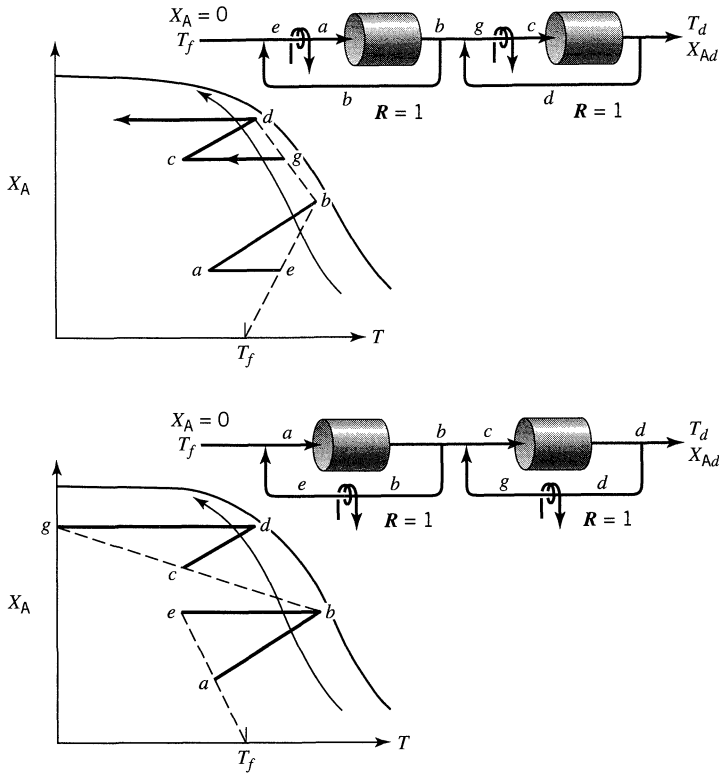


Figure 19.7 Different location for the heat exchangers while keeping the same reactor conditions as in Fig. 19.6.

convenience for startup, and on which location gives a higher heat transfer coefficient (note that the exchanger arrangement of Fig. 19.7a has a higher through-flow of fluid than the arrangement of Fig. 19.7b).

Cold Shot Cooling. One way of eliminating the interstage heat exchangers is by properly adding cold feed directly into the second and succeeding stages of the reactor. The procedure is shown in Fig. 19.8. The criterion for optimal operations of such an arrangement is given by Konoki (1960), and, in somewhat different form, by Horn (1961b). They found that the extent of interstage cooling is given by Eq. 2, and this is shown in Fig. 19.8.

With cold shot cooling the calculation of reactor volumes by the $1/-r'_A$ versus X_A curve becomes more complicated because different amounts of feed are involved in each stage. We can also cold shot cool with inert fluid. This will affect both the $1/-r'_A$ versus X_A and T versus X_A curves.

Choice of Contacting System. With so many contacting alternatives let us suggest when one or other is favored.

1. For endothermic reactions the rate always decreases with conversion; hence we should always use plug flow with no recycle (see Chapter 9). For exother-

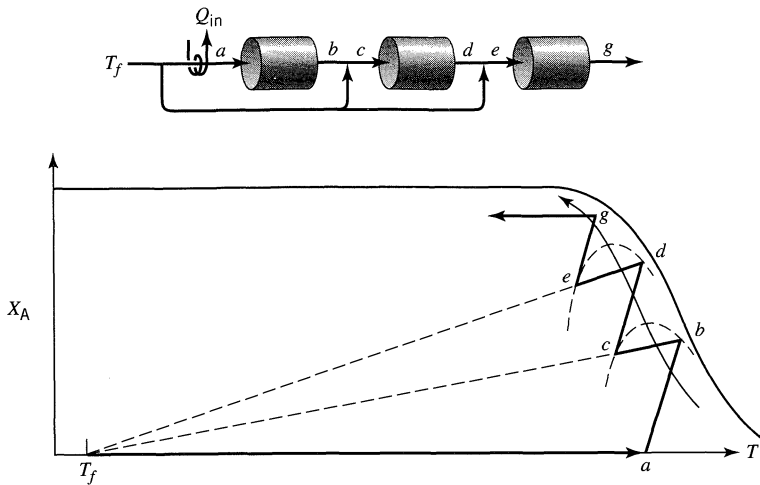


Figure 19.8 Cold shot cooling eliminates interstage heat exchangers.

mic reactions the slope of the adiabatic line determines which contacting scheme is best. The rest of these comments concern this case of exothermic reactions.

2. All else being equal, cold shot cooling has the advantage of lower cost because interstage heat exchangers are not needed. However, cold shot cooling is only practical when the feed temperature is very much below the reaction temperature, and, in addition, when the temperature does not change much during reaction. These conditions can be summarized as follows:

Cold shot cooling is practical when

$$T_{\text{reaction}} - T_f > \frac{-\Delta H_r}{C_p}$$

Two situations, one when cold shot cooling is practical, the other when it is not, are shown in Fig. 19.9.

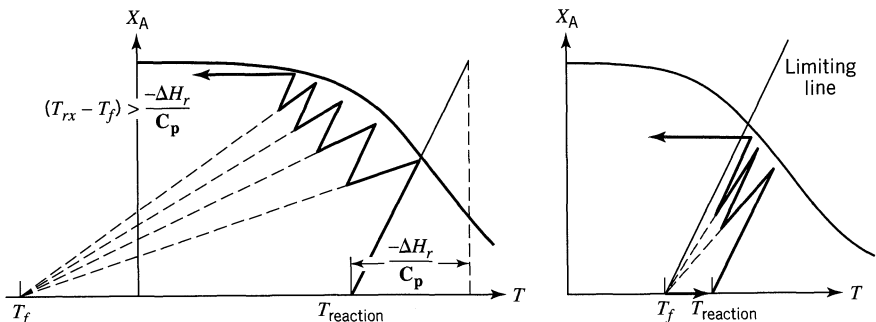


Figure 19.9 Situations where cold shot cooling could be helpful and where it should not be used.

3. For exothermic reactions if the slope of the adiabatic line is low (large temperature rise during reaction) it is advantageous to avoid the low temperature regime where the rate is very low. Thus use high recycle approaching mixed flow. On the other hand, if the slope is high (small temperature rise during reaction) the rate decreases with conversion and plug flow is to be used. Typically, for pure gaseous reactant the slope of the adiabatic is small; for a dilute gas or for a liquid it is large. As an example, consider a reactant having $C_p = 40 \text{ J/mol} \cdot \text{K}$ and $\Delta H_r = -120\,000 \text{ J/mol}$ and inerts with $C_p = 40 \text{ J/mol} \cdot \text{K}$:

For a pure reactant gas stream

$$\text{slope} = \frac{C_p}{-\Delta H_r} = \frac{40}{120\,000} = \frac{1}{3000}$$

For a dilute 1% reactant gas stream

$$\text{slope} = \frac{C_p}{-\Delta H_r} = \frac{4000}{120\,000} = \frac{1}{30}$$

For a 1-molar liquid solution

$$\text{slope} = \frac{C_p}{-\Delta H_r} = \frac{4000}{120\,000} = \frac{1}{30}$$

The adiabatic lines for these cases are sketched in Fig. 19.10 and illustrate this point.

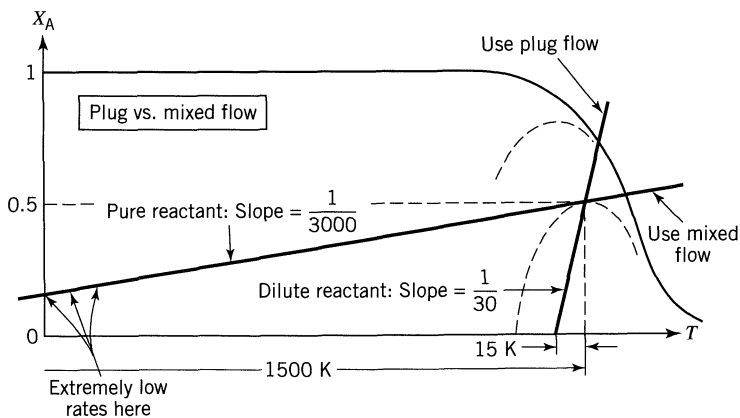


Figure 19.10 Sketch showing why plug flow is used for steep adiabatic lines, and mixed flow (packed beds with large recycle) for lines with small slope.

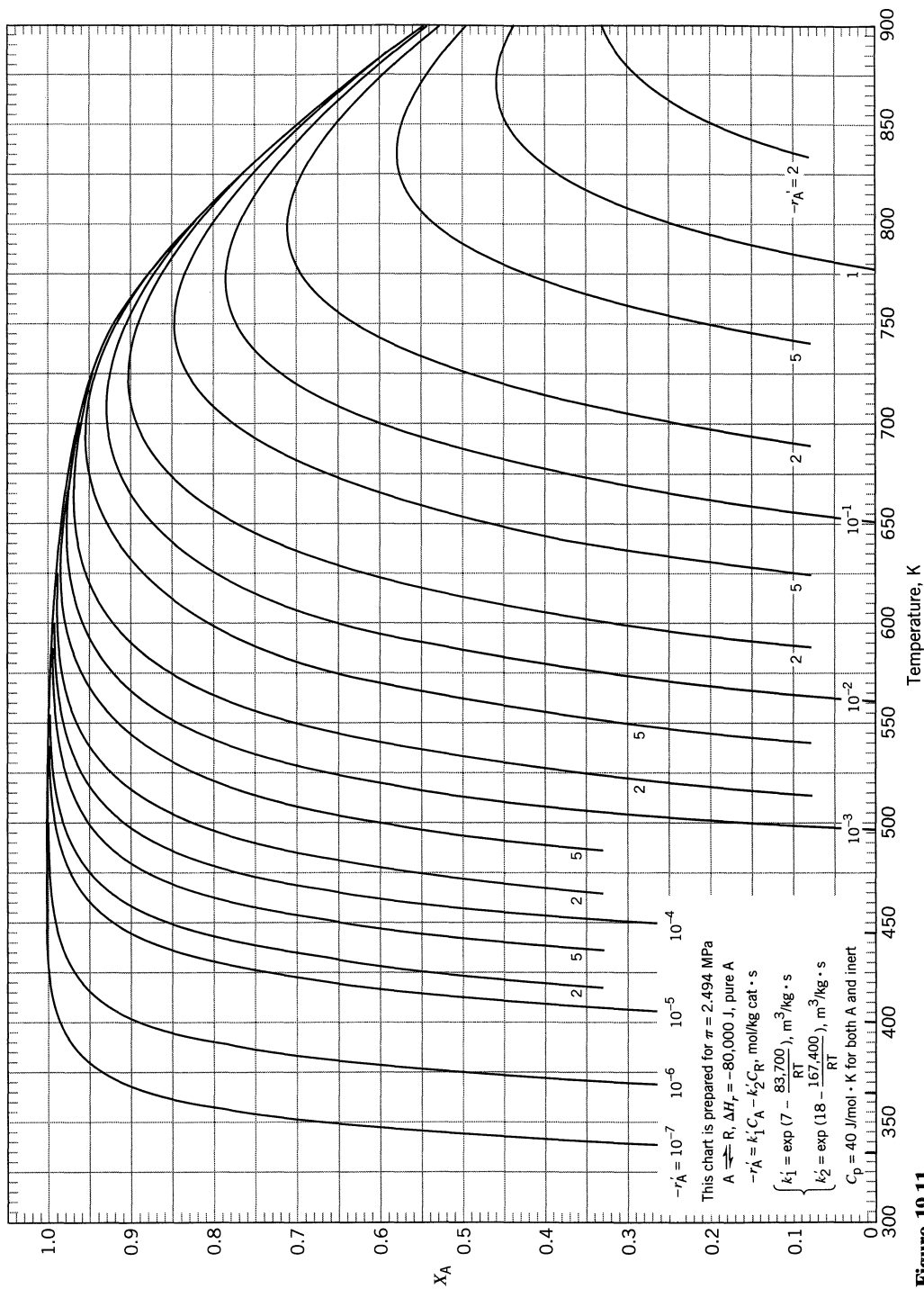


Figure 19.11

4. For exothermic reactions in staged reactors the above discussion can be summarized as follows:

For pure gas use high recycle approaching mixed flow.
 For dilute gas (or a liquid) requiring no large preheating of feed use plug flow.
 For a dilute gas (or a solution) requiring large preheating to bring the stream up to reaction temperature use cold shot operations.

(3)

Preliminaries for a Set of Problems Dealing with a Single Packed Bed Reactor

A single catalytic packed bed reactor is to be designed to treat 100 mol/s of reactant A and produce product R. Feed gas enters at 2.49 MPa and 300 K, the maximum allowable temperature is 900 K unless otherwise noted, the product stream is wanted at 300 K, and the thermodynamics and kinetics of the exothermic reaction are given to us in Fig. 19.11. Prepare a sketch showing the details of the system you plan to use:

- type of reactor: plug, recycle, or mixed (∞ recycle)
- amount of catalyst needed
- heat duty ahead of the reactor, at the reactor itself, and after the reactor
- the temperature of all flowing streams

Example 19.1 treats one case, Problems 19.13 to 19.16 treat four other cases. In all these problems assume that

- we are dealing with ideal gases.
- $C_p = 40 \text{ J/mol} \cdot \text{K}$ for all materials, and at all temperatures. This means (from Example 9.1) that ΔH_r has the same value at all temperatures.

EXAMPLE 19.1 DESIGN OF A SINGLE ADIABATIC PACKED BED SYSTEM

Work out a good design for 80% conversion of a feed consisting of 1 mol A and 7 mol inert.

SOLUTION

First determine the slope of the adiabatic line. For this note that 8 moles enter/mole of A. Thus

$$C_p = (40 \text{ J/mol} \cdot \text{K}) (8) = 320 \text{ J}/(\text{mol of A} + \text{inerts}) \cdot \text{K}$$

Thus the slope of the adiabatic is

$$\frac{C_p}{-\Delta H_r} = \frac{320}{80\,000} = 0.004 = \frac{1}{250}$$

Drawing various adiabatics in Fig. 19.11 it seems that the one shown on Fig. E19.1a looks best. So now tabulate X_A versus $1/(-r'_A)$ from Fig. 19.11. This gives

X_A	$-r'_A$	$1/(-r'_A)$
0.8	0.05	20
0.78	0.1	10
0.70	0.2	5
0.60	0.225	4.4
0.50	0.2	5
0.26	0.1	10
0.10	0.05	20
0	0.03	33

$\left. \begin{array}{l} \left. \begin{array}{l} \left. \begin{array}{l} 20 \\ 10 \\ 5 \\ 4.4 \\ 5 \\ 10 \\ 20 \\ 33 \end{array} \right\} \div 8 \\ \left. \begin{array}{l} 0.8 \\ 0.78 \\ 0.70 \\ 0.60 \\ 0.50 \\ 0.26 \\ 0.10 \\ 0 \end{array} \right\} \times 8 \end{array} \right\} \end{array} \right\}$

Plotting $1/(-r'_A)$ versus X_A gives Fig. E19.1b. This tells right away that a recycle reactor should be used. Thus

$$\frac{W}{F_{A0}} = \frac{X_A}{-r'_A} = 0.8(6 \times 8) = 38.4 \text{ kg} \cdot \text{s/mol}$$

or

$$W = F_{A0}(38.4) = (100)(38.4) = \underline{\underline{3840 \text{ kg}}}$$

The recycle ratio, from Fig. E19.1b is $R = 1$.

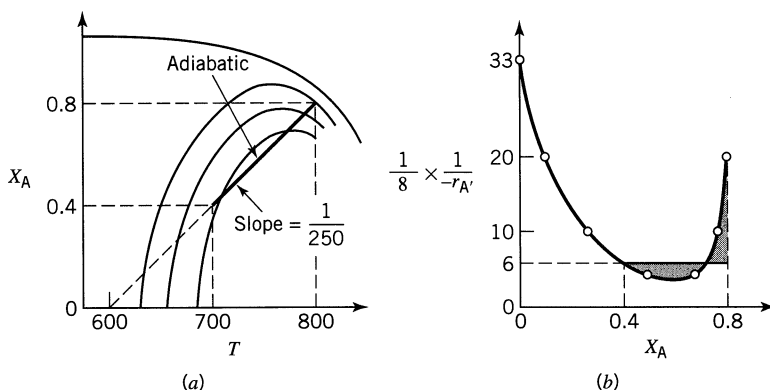


Figure E19.1a,b

The feed is available at 300 K, but enters the reactor at 600 K (from Fig. E19.1a), so it must be heated. Thus

$$\begin{aligned}
 Q_1 &= n C_p \Delta T = (800 \text{ mol/s})(40 \text{ J/mol} \cdot \text{K})(600 - 300 \text{ K}) = 9.6 \times 10^6 \text{ J/s} \\
 &= \underline{\underline{9.6 \text{ MW}}}
 \end{aligned}$$

The product stream leaves the reactor at 800 K and must be cooled to 300 K, thus

$$\begin{aligned} Q_2 &= n C_p \Delta T = (800 \text{ mol/s})(40 \text{ J/mol} \cdot \text{K})(300 - 800 \text{ K}) = -16 \times 10^6 \text{ J/s} \\ &= \underline{\underline{-16 \text{ MW}}} \end{aligned}$$

We show our recommended design in Fig. E19.1c.

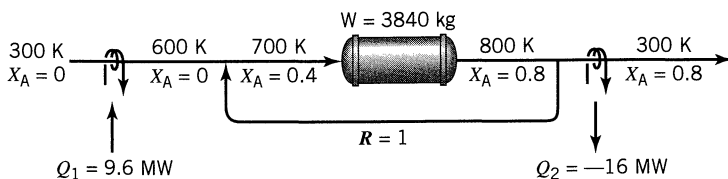


Figure E19.1c

Preliminaries for a Set of Problems Dealing with Two Packed Bed Reactors in Series

Two catalyst filled packed bed reactors are to be designed to process 100 mol/s of reactant A so as to produce product R. Feed gas enters at 2.49 MPa and 300 K, the allowable $T_{\max} = 900 \text{ K}$, unless otherwise noted, $T_{\min} = 300 \text{ K}$, the product stream is wanted at 300 K, and the thermodynamics and kinetics of the exothermic reaction are given to us in Fig. 19.11. Prepare a sketch of your recommended design and on it show

- the flow arrangement selected: plug, recycle (give R value), or mixed (when ever $R > 5$). Do not consider injection of cold fluid between stages unless the problem states that you are permitted to do so.
- weight of catalyst needed in each stage.
- location and duty of heat exchangers.
- temperature of the flowing streams.

EXAMPLE 19.2 DESIGN OF A TWO ADIABATIC PACKED BED SYSTEM

Work out a good design for 85% conversion of a pure A feed to two packed beds.

SOLUTION

First determine the slope of the adiabatic line and draw it lightly on Fig. 18.11.

$$\text{slope} = \frac{C_p}{-\Delta H_r} = \frac{40}{80\,000} = \frac{1}{2000}$$

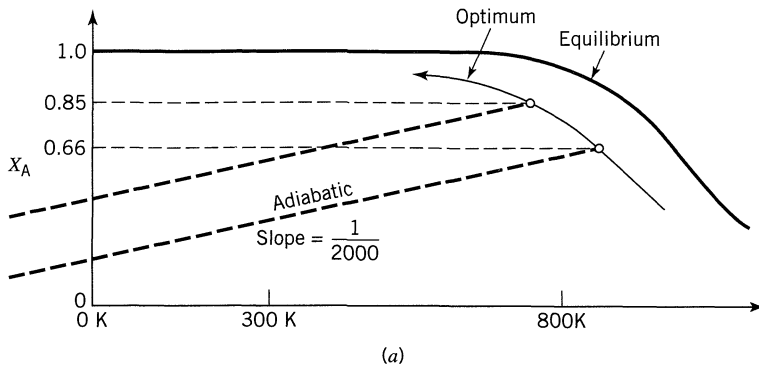


Figure E19.2a

This gives a very shallow adiabatic, as sketched in Fig. E19.2a. The rate continually increases as you move along this adiabatic, thus use a mixed flow reactor operating at the optimum.

To minimize the amount of catalyst needed Chapter 6 says use the method of maximization of rectangles, so tabulate X_A versus $1/(-r'_A)_{\text{opt}}$

X_A	$(-r'_A)_{\text{opt}}$	$1/(-r'_A)_{\text{opt}}$
0.85	0.05	20
0.785	0.1	10
0.715	0.2	5
0.66	0.28	3.6
0.58	0.5	2
0.46	1.0	1

And use the method of maximization of rectangles as shown in Fig. E19.2b. Then from the performance equation

$$\frac{W}{F_0} = (X_A) \frac{1}{(-r_A)_{\text{opt}}} = \left(\begin{array}{l} \text{shaded area} \\ \text{in Fig. E19.2b} \end{array} \right)$$

we have

$$W_1 = F_{A0} (\text{area})_1 = 100 (2.376) = \underline{\underline{237.6 \text{ kg}}}$$

and

$$W_2 = F_{A0} (\text{area})_2 = 100 (3.819) = \underline{\underline{381.9 \text{ kg}}}$$

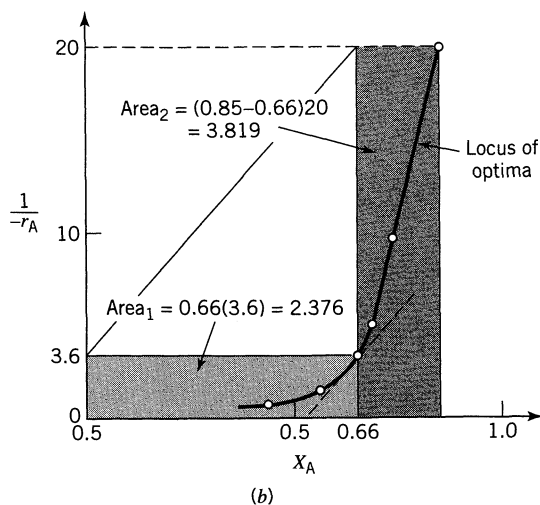


Figure E19.2b

Now to heat exchange:

For the first reactor. If we want to cool the feed before introducing it into the first reactor we'd have to cool it to

$$820 - 2000(0.6) = -380 \text{ K}$$

which is well below absolute zero. This is impossible. So we have to cool it somewhere inside the recycle reactor loop as shown in Fig. E19.2c. But wherever you put the exchanger the amount of heating or cooling needed is the same.

So to go to 66% conversion at 820°C the amount of heat needed per mole of A is

$$(820 - 300)40 + 0.66(-80000) = -32\,000 \text{ J/mol}$$

heat in heat out

But for 100 mol/s of feed

$$Q_1 = (32\,000 \text{ J/mol})(100 \text{ mol/s}) = \underline{\underline{-3.2 \text{ MW}}} \text{ (cooling)}$$

For the second reactor. To go from $X_A = 0.66$ at 820 K to $X_A = 0.85$ at 750 K requires, per mole

$$(750-820)40 + (0.85 - 0.66)(-80\,000) = -18\,000 \text{ J/mol}$$

So for 100 mol/s

$$Q_2 = (-18\,000)(100) = \underline{\underline{-1.8 \text{ MW}}} \text{ (cooling)}$$

Similarly for the exchanger needed to cool the exit stream from 750 K to 300 K

$$Q_3 = 100(40)(300 - 750) = \underline{\underline{-1.8 \text{ MW}}}$$

So our recommended design is shown in Fig. E19.2c.

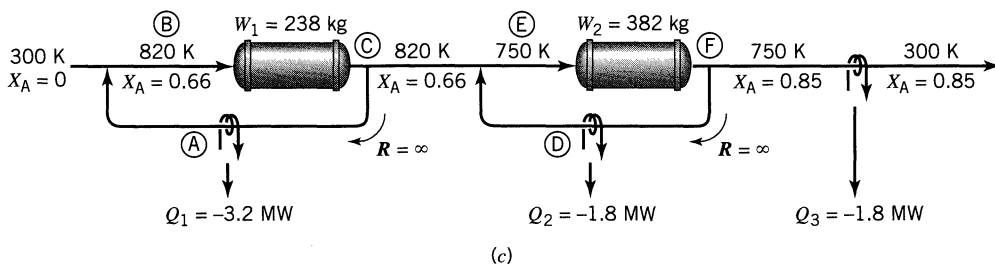


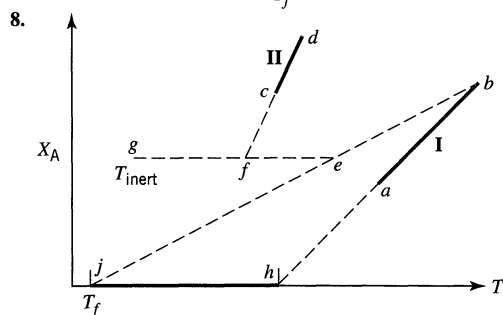
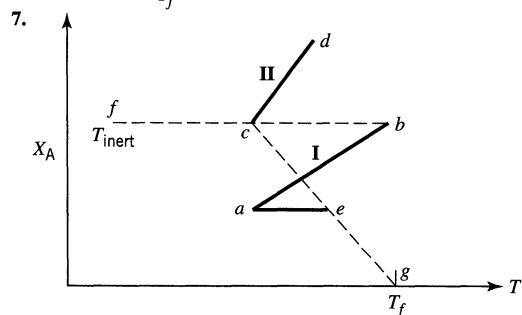
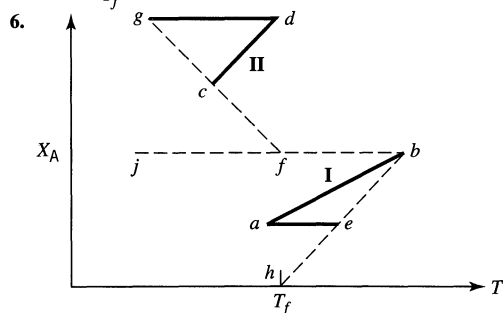
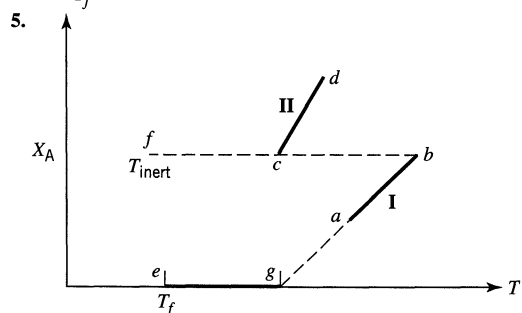
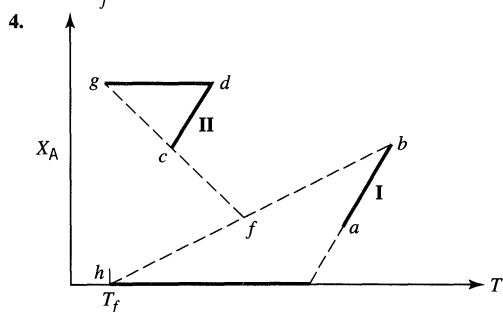
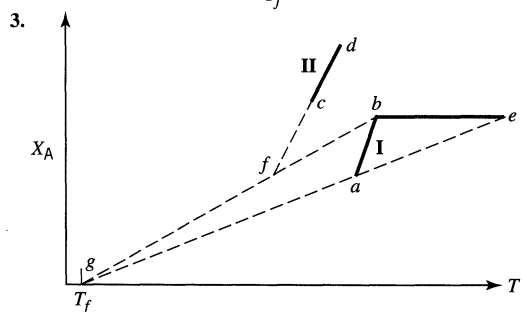
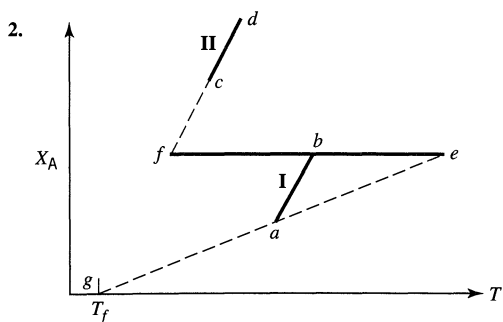
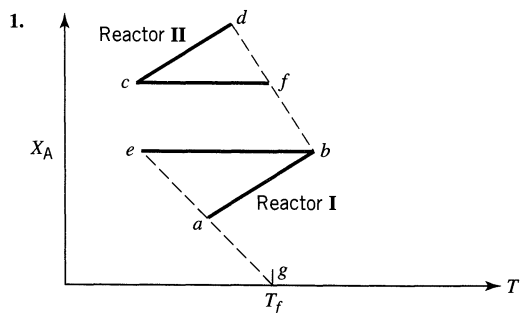
Figure E19.2c Note: exchanger Q_1 can be placed at A, B, or C and exchanger Q_2 can be placed at D, E, or F.

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PROBLEMS

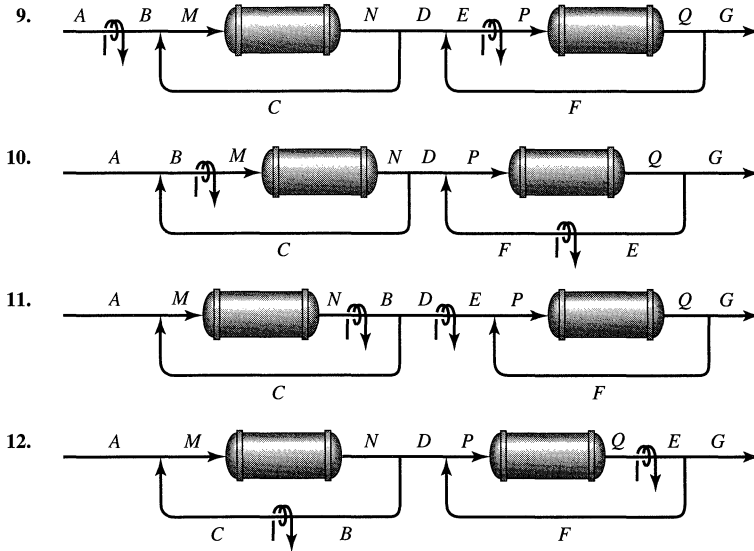
- 19.1–19.8.** Sketch the flow sheet for the two reactor system represented by the X_A versus T diagrams Figs. P.19.1 to Fig. P19.8, and on the sketch show
- the flow rate of all streams for each 100 mol of entering fluid, and where pertinent give the recycle ratios.
 - the location of the heat exchangers and indicate whether they cool or heat.



Figures P19.1 to P19.8

19.9–19.12. Sketch the X_A versus T diagram for the two packed bed reactor system shown in Figs. P19.9 to P19.12 for an exothermic reaction where

- conversion: $X_{A1} = 0.6$, $X_{A2} = 0.9$.
- recycle ratio: $R_1 = 2$, $R_2 = 1$.
- heat exchangers all cool the reacting fluid.



Figures P19.9 to p19.12

For the single reactor situation outlined in the text and followed by Example 19.1 let us here consider four alternatives. We plan to use

- 19.13.** . . . pure A feed, $X_A = 0.85$, in a reactor which follows the optimal temperature progression.
- 19.14.** . . . a 50% A–50% inert feed, $X_A = 0.70$, in an adiabatic reactor of your choice.
- 19.15.** . . . a 20% A–80% inert feed to an adiabatic reactor of your choice whose outlet is at $X_A = 0.75$ and $T = 825$ K.
- 19.16.** . . . a 5% A–95% inert feed, $X_A = 0.5$, in an adiabatic reactor of your choice.
-

For the two-reactor situation outlined in the text and followed by Example 19.2 let us consider five alternatives, thus

19.17. . . . a pure A feed, $X_A = 0.85$.

19.18. . . . a pure A feed, $X_A = 0.85$ and $T_{\max} = 550$ K. In this problem, do not worry about the possibility of an unstable operating point. But before you build such a unit, you'd better check for this—otherwise you'll be in trouble.

19.19. . . . a 20% A–80% inert feed, $X_A = 0.85$

19.20. . . . a 40% A–60% inert feed, $X_A = 0.95$

19.21. . . . a 5% A–95% inert feed, $X_A = 0.95$ (try cold feed injection)

Chapter 20

Reactors with Suspended Solid Catalyst, Fluidized Reactors of Various Types

The formation of phthalic anhydride is highly exothermic, and even with the most careful design the heat removal from packed bed reactors can become uncheckable, leading to temperature runaways, meltdowns, and even explosions. If the chief engineer of those reactors had been required to sit on the reactor during start up, there would be fewer chief engineers about.¹

The invention of the fluidized bed with its suspended and rapidly mixing solids completely overcame this dangerous situation. This is because the rapid mixing of solids, and the large heat sink (the solids) will only allow the bed temperature to change very slowly, and it can be easily controlled.

Another problem—catalyst formulators (those magicians) have been very successful in creating better and better catalysts, those that give higher and higher rates of reaction. But to use the whole of the catalyst volume effectively we must keep the Thiele modulus

$$M_T = L \sqrt{\frac{k'''}{\mathcal{D}_e}} < 0.4$$

This means using smaller and smaller particles as k''' is made larger and larger.

This leads us to use suspended solids. Also note that with these very effective catalysts the required residence time of reactant gas becomes very small, say a few seconds for a large 30-m high reactor.

Figure 20.1 shows the transition from fixed to BFB to TF to FF to PC reactors.

20.1 BACKGROUND INFORMATION ABOUT SUSPENDED SOLIDS REACTORS

This is a vast subject, but we must be brief and can only touch on the highlights. See Kunii and Levenspiel (1991) for a much more complete presentation.

¹ “They ought to give medals for making phthalic,” *Chem. Week*, **70**, 40 (1952).

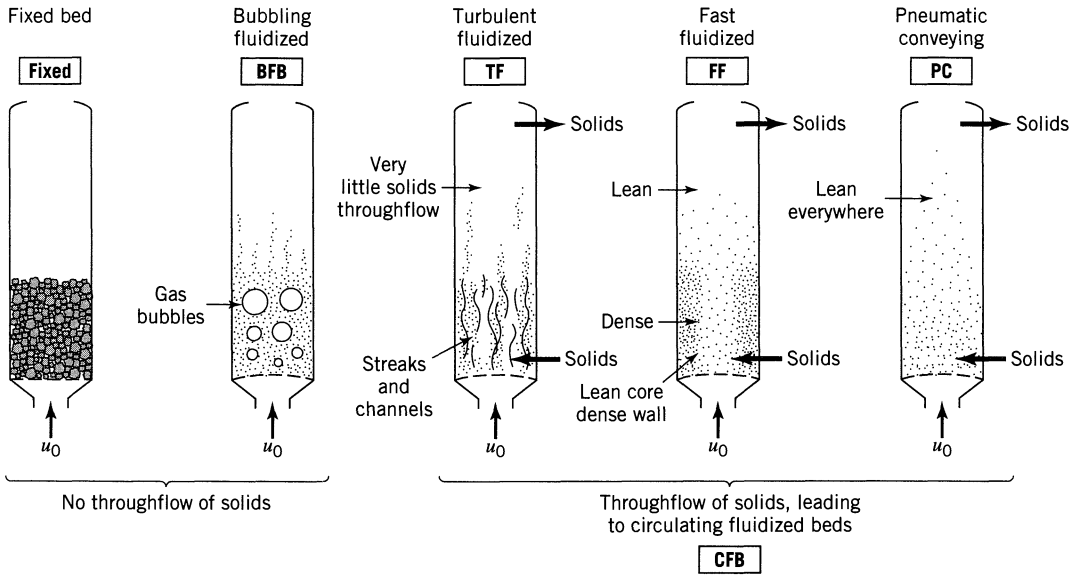


Figure 20.1 G/S contacting regimes, from low to very high gas velocity.

First, Geldart (1973) and Geldart and Abrahamson (1978) looked at how different kinds of solids behaved when fluidized, and came up with the following simple classification of solids which we now call the Geldart classification, thus Geldart A, B, C, D. These are shown and described in Fig. 20.2.

Next consider the distribution of solids in the vertical vessel. Let f be the volume fraction of solids at height z of the vessel. Then as shown in Fig. 20.3 when we go to higher and higher gas velocities the solids spread throughout the vessel.

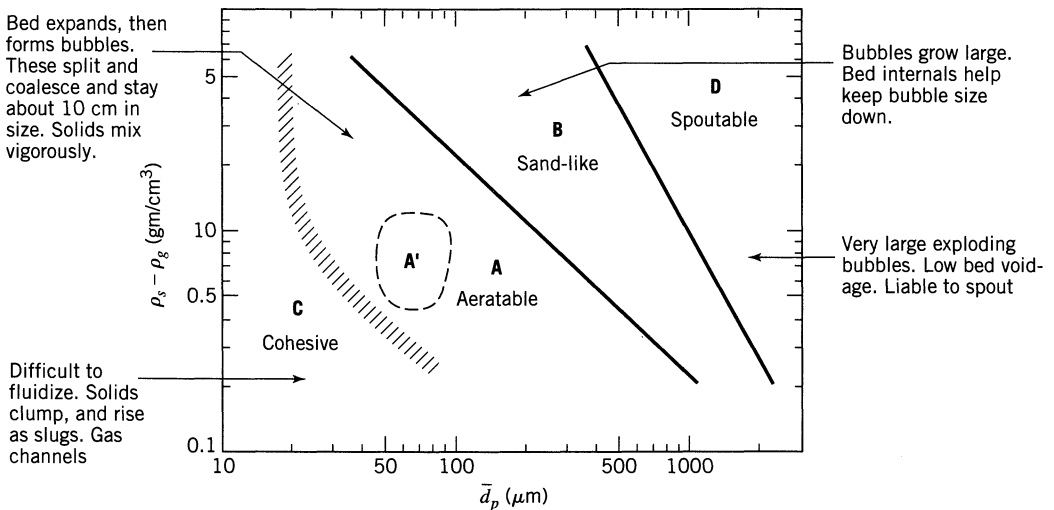


Figure 20.2 Geldart classification of solids in BFB.

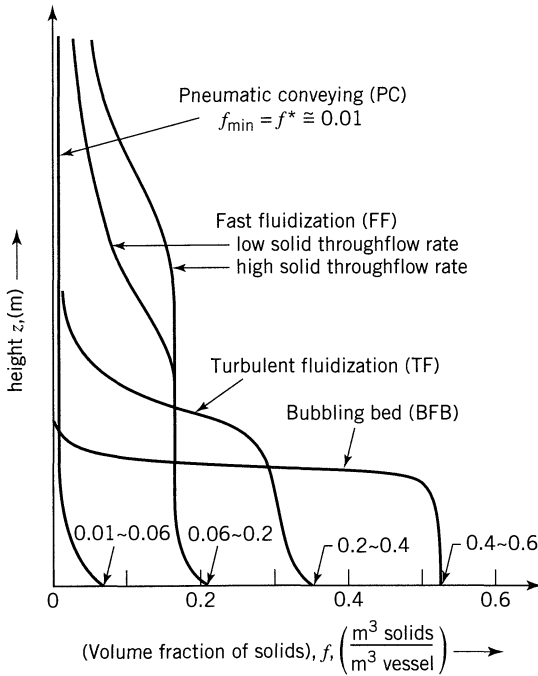


Figure 20.3 Distribution of solids in the various contacting regimes.

***G/S* Contacting Regimes.** To develop the language that tells what contacting regime we have at hand consider solids of size d_p in a bed of cross-sectional area A which is fed gas at a superficial gas velocity u_0 , as shown in Fig. 20.4.

To simplify the equations let us start by defining two dimensionless quantities

$$\left. \begin{aligned} d_p^* &= d_p \left[\frac{\rho_g(\rho_s - \rho_g)g}{\mu^2} \right]^{1/3} \\ u^* &= u \left[\frac{\rho_g^2}{\mu(\rho_s - \rho_g)g} \right]^{1/3} = \frac{(\text{Re}_p)}{d_p^*} \end{aligned} \right\} \text{Re}_p = u^* d_p^* \quad (1)$$

$$(2)$$

Minimum Fluidizing Velocity. The solids will be suspended when the pressure drop exceeds the weight of solids. This happens when the gas velocity exceeds the minimum fluidizing velocity u_{mf} . This velocity is given by Ergun (1952), and in dimensionless form is

$$150(1 - \epsilon_{mf})u_{mf}^* + 1.75(u_{mf}^*)^2 d_p^* = \epsilon_{mf}^3 (d_p^*)^2 \quad (3)$$

Terminal Velocity, u_t . Individual particles are blown out of the bed when the gas velocity exceeds what is called the terminal velocity, u_t . Haider and Levens-

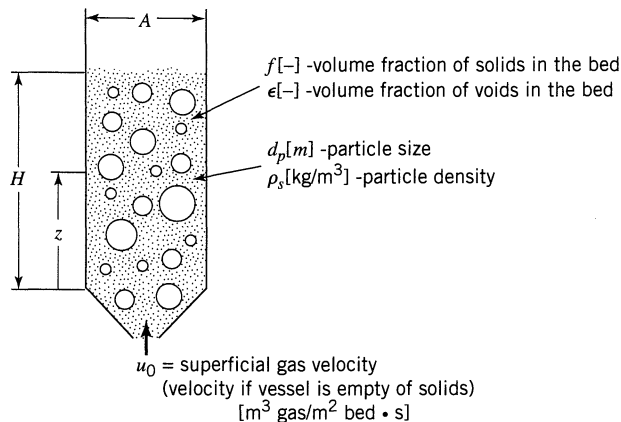


Figure 20.4 Notation for a bed of suspended solids.

piel (1989) give this velocity for *spherical particles* as

$$u_i^* = \left[\frac{18}{(d_p^*)^2} + \frac{0.591}{(d_p^*)^{1/2}} \right]^{-1} \quad (4)$$

and for *irregularly shaped particles* of sphericity ϕ_s

$$u_i^* = \left[\frac{18}{(d_p^*)^2} + \frac{2.335 - 1.744 \phi_s}{(d_p^*)^{1/2}} \right]^{-1} \quad (5)$$

where the particle sphericity ϕ_s is defined as

$$\phi_s = \left(\frac{\text{surface of a sphere}}{\text{surface of a particle}} \right)_{\text{same volume}} \quad (6)$$

For fine particles we evaluate the size by screen analysis, which gives d_{scr} . Unfortunately, there is no general relationship between d_{scr} and d_p . The best we can say for pressure drop considerations is

- $d_p = \phi_s d_{scr}$ for irregular particles with no seeming longer or shorter dimension
- $d_p \cong d_{scr}$ for irregular particles with one somewhat longer dimension but with length ratio not greater than 2:1 (eggs, for example)
- $d_p \cong \phi_s^2 d_{scr}$ for irregular particles with one shorter dimension but with length ratio not less than 1:2 (pillows, for example)

Although a single particle will be entrained by a stream of gas flowing faster than u_t , this finding does not extend to a fluidized bed of particles. In the BFB the gas velocity can be many times greater than u_t with very little carryover of solids. Thus the single particle terminal velocity is not very useful in estimating when entrainment of solids will become appreciable.

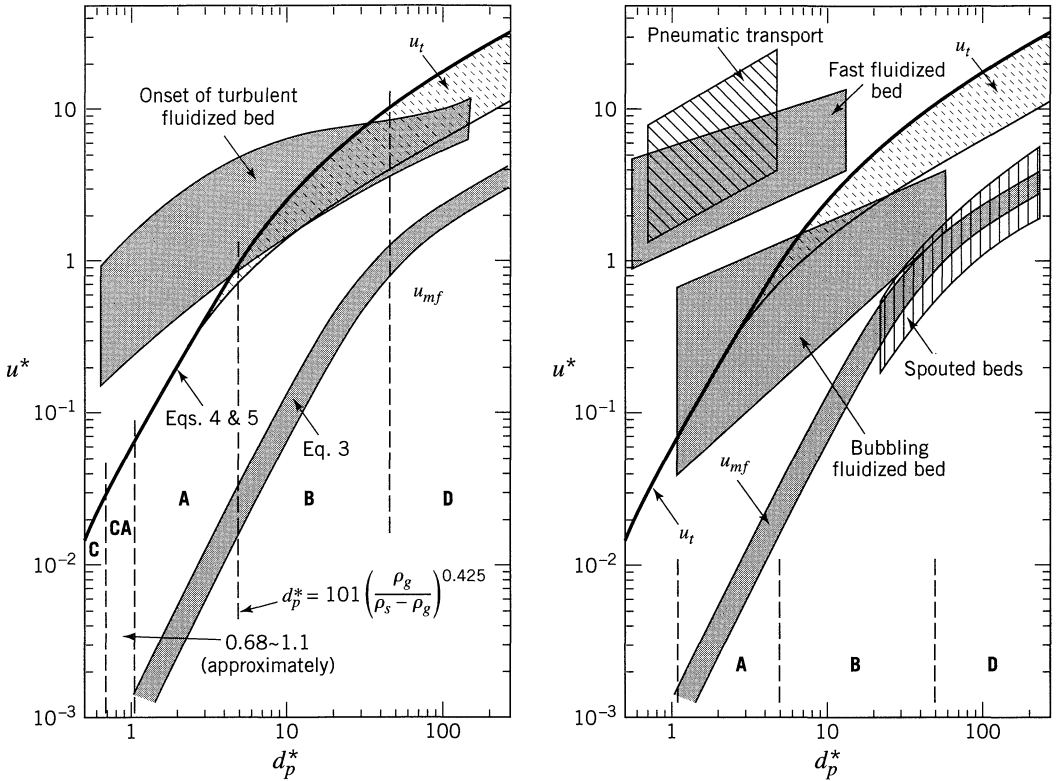


Figure 20.5 General flow regime diagram for the whole range of G/S contacting.

General Chart Showing G/S Contacting Regimes. Grace (1986) prepared a graph to show the expected behavior of G/S systems all the way from BFB to CFB. Figure 20.5 shows a somewhat modified version of this chart. In it you will see Eqs. 3, 4, and 5, which tell when the bed will fluidize and when solids will begin to entrain from the vessel.

We now look at the various contacting regimes in detail and see what predictions are available for each regarding reactor behavior.

20.2 THE BUBBLING FLUIDIZED BED—BFB

Pass gas upward through a bed of fine particles. For superficial (or inlet) gas velocities u_0 much in excess of this minimum the bed takes on the appearance of a boiling liquid with large bubbles rising rapidly through the bed. In this state we have the *bubbling fluidized bed*, BFB. Industrial reactors particularly for solid catalyzed gas-phase reactions often operate as bubbling beds with gas velocities $u_0 = 5 \sim 30 u_{mf}$.

Calculations show that the conversion in bubbling beds may vary from plug flow to well below mixed flow, see Fig. 20.6, and for many years the perplexing and embarrassing thing about this was that often we could not reliably estimate

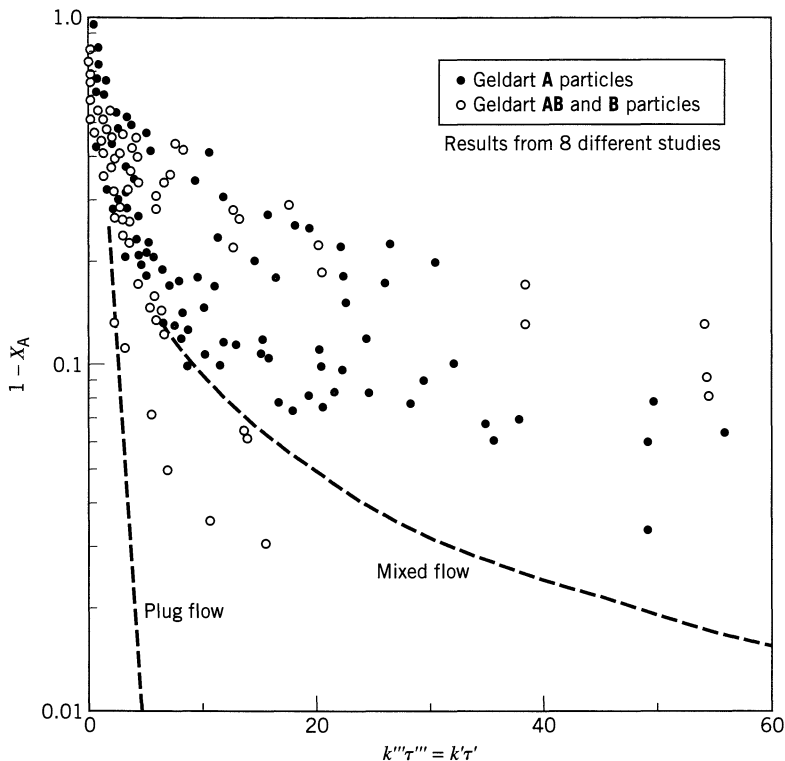


Figure 20.6 Conversion of reactant in BFB is usually poorer than for both plug flow and mixed flow. Adapted from Kunii and Levenspiel (1991).

or guess what it would be for any new situation. Because of this, scale-up was cautious and uncertain, and preferably left to others.

It was soon recognized that this difficulty stemmed from lack of knowledge of the contacting and flow pattern in the bed: in effect, the bypassing of much of the solids by the rising bubble gas. This led to the realization that adequate prediction of bed behavior had to await a reasonable flow model for the bed.

Since the bubbling bed represents such severe deviations from ideal contacting, not just minor ones as with other single-fluid reactors (packed beds, tubes, etc.), it would be instructive to see how this problem of flow characterization has been attacked. A wide variety of approaches have been tried. We consider these in turn.

Dispersion and Tanks in Series Model. The first attempts at modeling naturally tried the simple one-parameter models; however, observed conversion well below mixed flow cannot be accounted for by these models so this approach has been dropped by most workers.

RTD Models. The next class of models relied on the RTD to calculate conversions. But since the rate of catalytic reaction of an element of gas depends on the amount of solid in its vicinity, the effective rate constant is low for bubble gas, high for emulsion gas. Thus any model that simply tries to calculate conver-

sion from the RTD and the fixed rate constant in effect assumes that all elements of gas, both slow and fast moving, spend the same fraction of time in each of the phases. As we will show when we treat the details of gas contacting in fluidized beds this assumption is a shaky one, hence the direct use of the RTD to predict conversions, as developed for linear systems in Chapter 11, is quite inadequate.

Contact Time Distribution Models. To overcome this difficulty and still use the information given by the RTD, models were proposed which assumed that faster gas stayed mainly in the bubble phase, the slower in the emulsion. Gilliland and Knudsen (1971) used this approach and proposed that the effective rate constant depends on the length of stay of the element of gas in the bed, thus

$$\left. \begin{array}{l} \text{short stay means small } k \\ \text{long stay means large } k \end{array} \right\} \quad \text{or } k = k_0 t^m$$

where m is a fitted parameter. Thus combining with Eq. 11.13 we find for the conversion

$$\frac{\bar{C}_A}{C_{A0}} = \int_0^\infty e^{-kt} \mathbf{E} dt = \int_0^\infty e^{-k_0 t^{m+1}} \mathbf{E} dt \quad (7)$$

The problem with this approach involves obtaining a meaningful \mathbf{E} function to use in Eq. 7 from a measured C-curve. This approach has also been discarded.

Two-Region Models. Recognizing that the bubbling bed consists of two rather distinct zones, the bubble phase and the emulsion phase, experimenters spent much effort in developing models based on this fact. Since such models contain six parameters, see Fig. 20.7, many simplifications and special cases have been explored (eight by 1962, 15 by 1972, and over two dozen to date), and even the complete six-parameter model of Fig. 20.7 has been used. The users of this model,

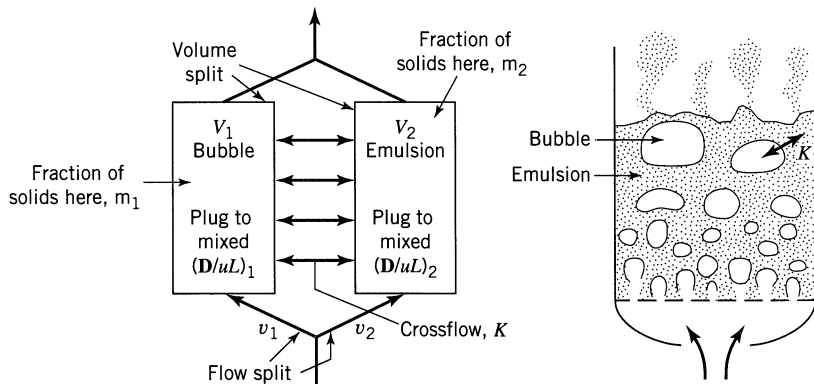


Figure 20.7 Two-phase model to represent the bubbling fluidized bed, with its six adjustable parameters, v_1 , V_1 , $(D/uL)_1$, $(D/uL)_2$, m_1 , K .

those dealing with FCC reactors, claim that this model fits their data beautifully. However, they had to choose different sets of parameter values for each crude oil feed, in each of their FCC reactors. Also some of the values for their parameters made no physical sense, for example, a negative value for V_1 or v_2 .

With this as the situation we should also discard this type of model which gives a perfect fit but predicts nothing, and brings no understanding with it. The reason is that we have no idea how to assign values to the parameters for new conditions. Thus this is just a curve-fitting model, and we should be able to do better.

Hydrodynamic Flow Models. The discouraging result with the previous approaches lead us reluctantly to the conclusion that we must know more about what goes on in the bed if we hope to develop a reasonable predictive flow model. In particular we must learn more about the behavior of rising gas bubbles, since they probably cause much of the difficulty.

Two developments are of particular importance in this regard. The first is Davidson's remarkable theoretical development and experimental verification [see Davidson and Harrison (1963) for details] of the flow in the vicinity of a single rising bubble in a fluidized bed which is otherwise at minimum fluidizing conditions. What he found was that the rise velocity of the bubble u_{br} depends only on the bubble size, and that the gas behavior in the vicinity of the bubble depends only on the relative velocity of rising bubble and of gas rising in the emulsion u_e . In the extremes he found completely different behavior, as shown in Fig. 20.8. For catalytic reactions we are only interested in fine particle beds, so let us ignore the large particle extreme from now on.

Now, for the fine particle bed gas circulates within the bubble plus a thin cloud surrounding the bubble. Thus the bubble gas forms a vortex ring and stays segregated from the rest of the gas in the bed. Theory says that

$$\left(\frac{\text{thickness of cloud}}{\text{diameter of bubble}} \right) \cong \frac{u_e}{u_{br}} \quad (8)$$

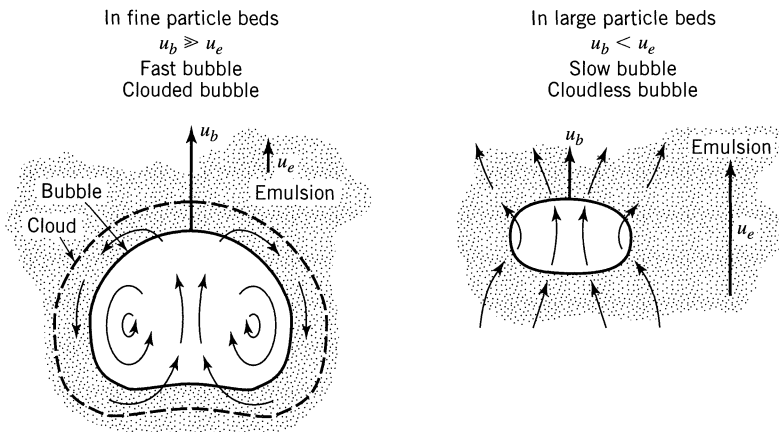


Figure 20.8 Extremes of gas flow in the vicinity of rising gas bubbles in BFBs.

As an example if the bubble rises 25 times as fast as the emulsion gas (not all that uncommon because this ratio is 100 or more in some industrial operations), then the cloud thickness is just 2% of the bubble diameter. This is the regime which interests us.

The second finding on single bubbles is that every rising gas bubble drags behind it a wake of solids. We designate this wake by α , where

$$\alpha = \left(\frac{\text{volume of wake}}{\text{volume of bubble}} \right) \cdot \cdot \cdot \begin{cases} \alpha \text{ varies between 0.2 and 2.0} \\ \text{depending on the research study} \end{cases} \quad (9)$$

See Rowe and Partridge (1962, 1965) for the original study which discovered this.

20.3 THE K-L MODEL FOR BFB

Hydrodynamic type flow models can be developed to represent the BFB, based on the above two seemingly simple findings. Let us consider and develop the simplest of these, the K-L BFB model.

Pass an excess of gas upward through a bed of fine particles. With a large enough bed diameter we get a freely bubbling bed of fast bubbles. As simplifications, assume the following:

- The bubbles are all spherical, all of the same size d_b , and all follow the Davidson model. Thus the bed contains bubbles surrounded by thin clouds rising through an emulsion. We ignore the upflow of gas through the cloud because the cloud volume is small compared to that of the bubble. This is the regime where $u_b \gg u_e$ (see Fig. 20.8).
- The emulsion stays at minimum fluidization conditions, thus the relative G/S velocity stays constant in the emulsion.
- Each bubble drags up a wake of solids behind it. This generates a circulation of solids in the bed, upflow behind the bubbles, and downflow everywhere else in the bed. If this downflow of solids is rapid enough then gas upflow in the emulsion is impeded, can actually stop, and even reverse itself. Such downflow of gas has been observed and recorded, and occurs when

$$u_0 > (3 \text{ to } 11) u_{mf}$$

We ignore any upflow or downflow of gas in the emulsion. We show this model in Fig. 20.9.

Let

u_0 = superficial gas velocity in the bed, $\text{m}^3 \text{ gas}/\text{m}^2 \text{ bed} \cdot \text{s}$

d = diameter, m

ϵ = fraction of voids in the bed

subscripts b, c, e, w refer to bubble, cloud, emulsion, and wake, respectively.

subscripts m, mf, f refer to packed bed, minimum fluidization, and bubbling fluidized bed conditions, respectively.

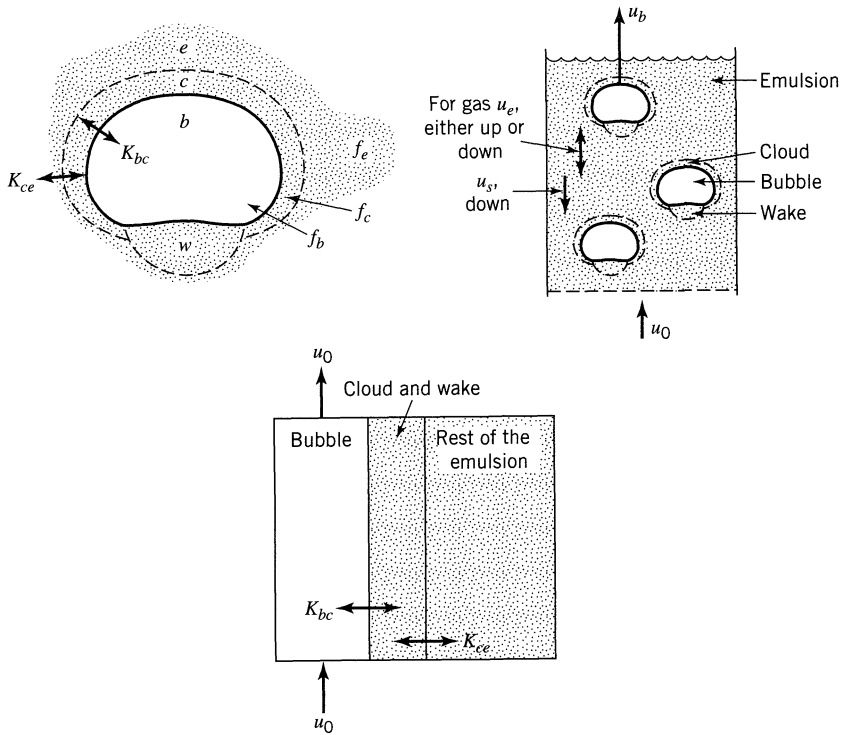


Figure 20.9 Model and symbols used to describe the K-L bubbling gas fluidized bed.

In essence, given u_{mf} , ϵ_{mf} , u_0 , α , and the effective bubble size in the bed d_b , this model tells you all the other properties of the bed—flows, region volumes, interchange rates, and consequently reactor behavior.

Material Balance for Gas and for Solids

From Kunii and Levenspiel (1991) a material balance for the bed material gives

$$u_{br} = 0.711(gd_b)^{1/2} \quad \text{m/s ... rise velocity of a single bubble in a bed otherwise at } u_{mf} \quad (10)$$

acceleration of gravity = 9.8m/s²

$$u_b = u_0 - u_{mf} + u_{br}, \text{ m/s} \quad \text{rise velocity of bubbles in a bubbling bed} \quad (11)$$

$$\delta = \text{bed fraction in bubbles, } \frac{\text{m}^3 \text{ bubbles}}{\text{m}^3 \text{ bed}} \quad (12)$$

$$\delta = \frac{u_0 - u_{mf}}{u_b} = 1 - \frac{u_{br}}{u_b}, \quad \text{and for } u_b \gg u_{mf} \text{ we can use } \delta \cong \frac{u_0}{u_b}$$

Useful relationships:

$$H_m(1 - \epsilon_m) = H_{mf}(1 - \epsilon_{mf}) = H_f(1 - \epsilon_f)$$

$$1 - \delta = \frac{1 - \epsilon_f}{1 - \epsilon_{mf}} = \frac{H_{mf}}{H_f} \dots H = \text{height}$$

$$u_s = \frac{\alpha \delta u_b}{1 - \delta - \alpha \delta}, \text{ m/s} \quad \dots \text{downflow of emulsion solids}$$

$$u_e = \frac{u_{mf}}{\epsilon_{mf}} - u_s, \text{ m/s} \quad \dots \text{rise velocity of emulsion gas (can be + or -)}$$

Using Davidson's theoretical expression for bubble-cloud circulation and the Higbie theory for cloud-emulsion diffusion the interchange of gas between bubble and cloud is then found to be

$$K_{bc} = 4.50 \left(\frac{u_{mf}}{d_b} \right) + 5.85 \left(\frac{\mathcal{D}^{1/2} g^{1/4}}{d_b^{5/4}} \right) = \frac{\text{(interchange volume between } b \text{ and } c, \text{ or } c \text{ and } b)/s}{\text{volume of bubble}}, \text{ s}^{-1} \quad (13)$$

and between cloud-wake and emulsion

$$K_{ce} = 6.77 \left(\frac{\epsilon_{mf} \mathcal{D} u_{br}}{d_b^3} \right)^{1/2} = \frac{\text{interchange volume/s}}{\text{volume of bubble}}, \text{ s}^{-1} \quad (14)$$

volume of solids

$$f_b = 0.001 \sim 0.01 = \frac{\text{in bubble}}{\text{volume of bed}} \dots \text{rough estimate from experiment} \quad (15)$$

$$f_c = \delta(1 - \epsilon_{mf}) \left[\frac{3u_{mf}/\epsilon_{mf}}{u_{br} - u_{mf}/\epsilon_{mf}} + \alpha \right] = \frac{\text{volume of solids in cloud and wake}}{\text{volume of bed}} \quad (16)$$

$$f_e = \overbrace{(1 - \epsilon_{mf})(1 - \delta)}^{(1 - \epsilon_f)} - f_c - f_b = \frac{\text{volume of solids in the rest of the emulsion}}{\text{volume of bed}} \quad (17)$$

$$f_b + f_c + f_e = f_{\text{total}} = 1 - \epsilon_f \quad (18)$$

$$H_{\text{BFB}} = H_f = W/\rho_s A(1 - \epsilon_f) \quad (19)$$

Application to Catalytic Reactions

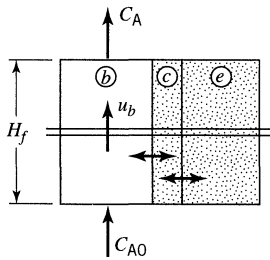
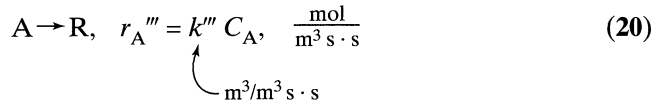
In our development we make two questionable assumptions:

- We ignore the flow of gas through the cloud since the cloud volume is very small for fast bubbles.
- We ignore the flow of gas, either up or down, through the emulsion since this flow is much smaller than the flow through the bubbles.

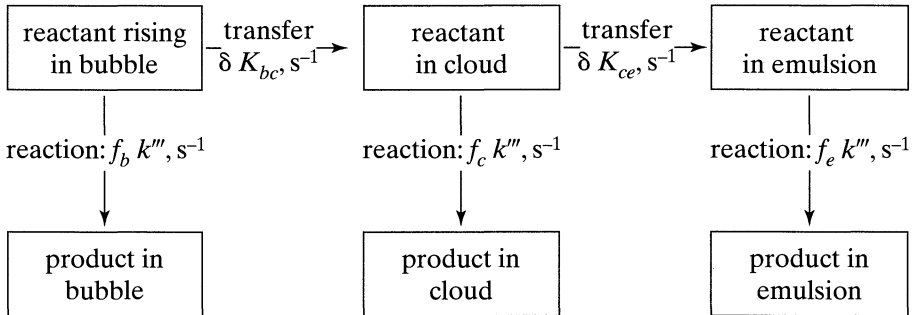
In effect, we consider the emulsion gas as stagnant. Of course more general expressions can be developed for beds where bubbles have thick clouds (not too large and fast bubbles), or where flow through the emulsion is significant (u_0 close to u_{mf} , thus where $u_0 \cong 1-2 u_{mf}$). However, for fast bubble, vigorously bubbling fine particle beds the above assumptions are reasonable.

We next see how to calculate performance in such a bed.

First-Order Reaction. Let the reaction be



Then for any slice of bed we have



Accounting for these five resistances in series—parallel, eliminating cloud and emulsion concentrations, and integrating from the bottom to the top of the

bed gives

$$\ln \frac{C_{A0}}{C_A} = K''' \tau''' = \underbrace{\left[f_b k''' + \frac{1}{\delta \cdot K_{bc}} + \frac{1}{f_c k''' + \frac{1}{\delta \cdot K_{ce}} + \frac{1}{f_e k'''} \right]}_{f_{\text{total}}} \cdot \underbrace{\frac{f_{\text{total}} H_{\text{BFB}}}{u_0}}_{\tau'''} \quad (21)$$

K''' , effective rate constant for the fluidized bed, $\text{m}^3/\text{m}^3 \cdot \text{s}$ τ''' , $\text{m}^3 \cdot \text{s} / \text{m}^3$

We also find that the average gas composition seen by the solids is approximately (from S. Kimura, personal communication)

$$\bar{C}_A, \text{ bathing the solids} = \frac{C_{A0} - C_A}{K''' \tau'''} = \frac{C_{A0} X_A v_0}{K''' V_s} = \frac{C_{A0} X_A v_0}{K' W} \quad (22)$$

of solids alone, W/ρ_s

This quantity is important for noncatalytic G/S reactions because it is this C_A that the solids see and react with.

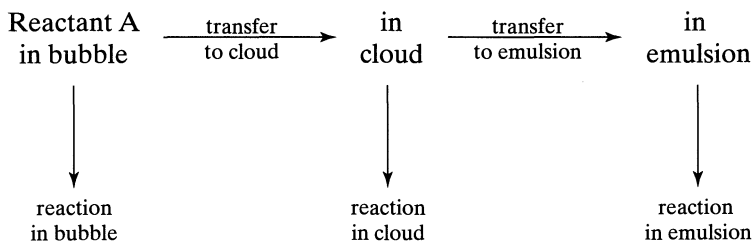
Let us now look at packed bed reactors. Assuming plug flow $K_{bc} \rightarrow \infty$, $K_{ce} \rightarrow \infty$, so Eq. 21 reduces to

$$\text{for plug flow} \begin{cases} \ln \frac{C_{A0}}{C_{Ap}} = k''' \tau''' = \frac{k'' H_p (1 - \epsilon_p)}{u_0} = k' \tau' = \frac{k' W}{u_0 A_t} & (23) \\ \bar{C}_A = \frac{C_{A0} - C_{Ap}}{k''' \tau'''} & (24) \end{cases}$$

Comparing Eq. 21 with 23, and Eq. 22 with 24 shows that a fluidized bed can be treated as a plug flow reactor if

K''' is replaced by k'''

Comments. The five terms in brackets of the performance equation, Eq. 21, represent the complex series-parallel resistances to mass transfer and reaction or



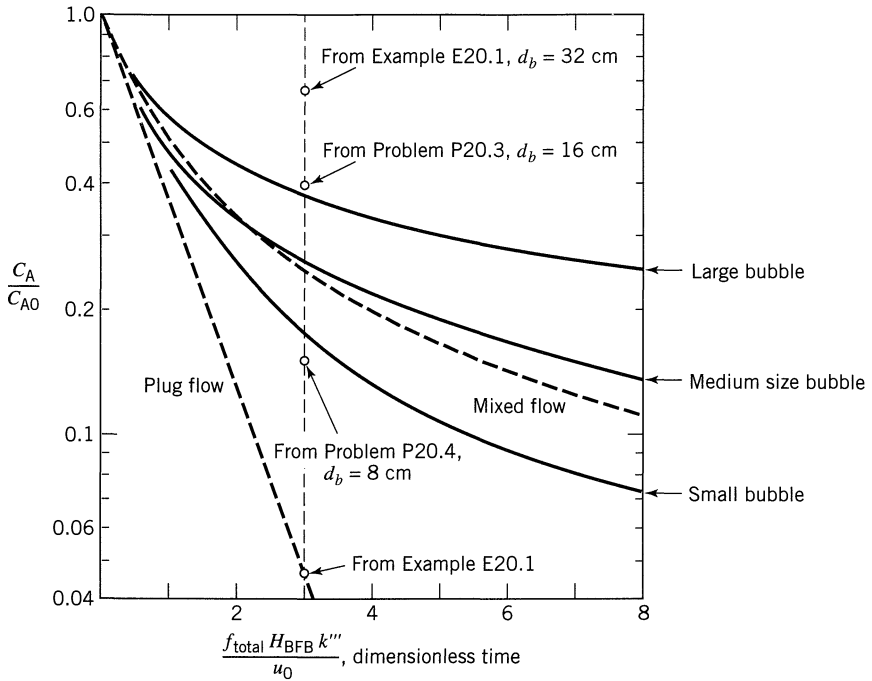


Figure 20.10 Performance of a fluidized bed as a function of bubble size, as determined by Eq. 21. Compare with the plug flow and mixed flow predictions.

For very fast reaction (large k''' value) very little A gets as far as the emulsion and the first two terms dominate. For slow reaction the latter terms become increasingly important.

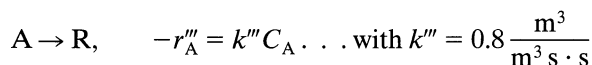
Since the bubble size is the one quantity which governs all the rate quantities with the exception of k''' , we can plot the performance of a fluidized bed as a function of d_b , as shown in Fig. 20.10. Note that large d_b gives poor performance because of extensive bypassing of bubble gas, and that the performance of the bed can drop considerably below mixed flow.

For multiple reactions the effect of this flow is much more serious still. Thus for reactions in series the lowering in amount of intermediate formed can be and usually is quite drastic.

Finally we have kept this presentation very brief. To help understand how to use it please look at the following illustrative example.

EXAMPLE 20.1 First-Order Catalytic Reaction in a BFB

Reactant gas ($u_0 = 0.3$ m/s, $v_0 = 0.3 \pi$ m³/s) passes upward through a 2-m diameter fluidized bed ($u_{mf} = 0.03$ m/s, $\epsilon_{mf} = 0.5$) containing 7 tons of catalyst ($W = 7000$ kg, $\rho_s = 2000$ kg/m³). Reaction proceeds as follows:



- (a) Calculate the conversion of reactant.
 (b) Find the proper mean concentration of A seen by the solids.
 (c) If gas were made to flow downward through the solids we would have a packed bed. Assuming plug flow of gas find the conversion of reactant for this situation.

Additional Data

$C_{A0} = 100 \text{ mol/m}^3$, $\mathcal{D} = 20 \times 10^{-6} \text{ m}^2/\text{s}$, $\alpha = 0.33$
 Estimated bubble size in the bed: $d_b = 0.32 \text{ m}$
 See Fig. E20.1 which represents this system.

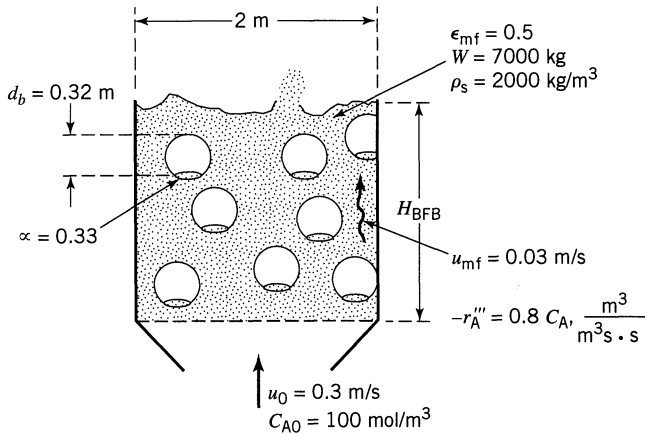


Figure E20.1

SOLUTION

Preliminary Determine the rise velocity of bubbles

$$u_{br} = 0.711 (9.8 \times 0.32)^{1/2} = 1.26 \text{ m/s}$$

$$u_b = 0.30 - 0.03 + 1.26 = 1.53 \text{ m/s}$$

Now see whether the fast bubble model of this chapter applies.

- Check for slugging: The bubble size (32 cm) is small compared to the bed size (200 cm), hence no slugging.
- Check the fast bubble assumption: Take the velocity ratio

$$\frac{u_b}{u_f} = \frac{u_b}{u_{mf} \epsilon_{mf}} = \frac{1.53}{0.03/0.5} = 25.5$$

Since the bubble rises ~ 25 times as fast as the emulsion gas we have a fast bubble with thin cloud—less than 1 cm thick.

Thus we can safely use the **bubbling bed model** of this chapter.

(a) **Calculate X_A .** Replacing numbers into the expressions for this model gives, in turn,

$$\delta = \frac{0.30}{1.53} = 0.196$$

$$\epsilon_f = 1 - (1 - \epsilon_{mf})(1 - \delta) = 1 - 0.5(1 - 0.196) = 0.60$$

$$K_{bc} = 4.50 \left(\frac{0.03}{0.32} \right) + 5.85 \left(\frac{(20 \times 10^{-6})^{1/2} (9.8)^{1/4}}{(0.32)^{5/4}} \right) = 0.614 \text{ s}^{-1}$$

$$K_{ce} = 6.77 \left(\frac{0.5(20 \times 10^{-6}) 1.26}{(0.32)^3} \right)^{1/2} = 0.133 \text{ s}^{-1}$$

$$\left. \begin{aligned} f_b &= 0.001 \sim 0.01, \text{ choose it to be } 0.001 \\ f_c &= 0.196(1 - 0.5) \left(\frac{3 \times 0.03/0.5}{1.26 - 0.03/0.5} + 0.33 \right) = 0.047 \\ f_e &= (1 - 0.6) - 0.047 - 0.001 = 0.352 \end{aligned} \right\} f_b + f_c + f_e = (1 - \epsilon_f) = 0.4$$

$$H_{\text{BFB}} = \frac{7000}{2000(\pi)(1 - 0.6)} = 2.785 \text{ m}$$

$$\ln \frac{C_{A0}}{C_A} = \frac{\left[\frac{0.001(0.8) + \frac{1}{\frac{1}{0.196(0.614)} + \frac{1}{0.047(0.8) + \frac{1}{\frac{1}{\frac{1}{0.196(0.133)} + \frac{1}{0.354(0.8)}}}}}}{(0.001 + 0.047 + 0.352)} \right] \cdot 2.785(0.4)}{0.3}$$

$$= [0.0415] \cdot (9.284) = 0.385$$

Therefore

$$\frac{C_A}{C_{A0}} = 0.68 \dots \text{ or } \underline{\underline{X_A = 32\%}} \text{ (see Fig. 20.10)}$$

(b) **Find \bar{C}_A seen by the solids.** Since every particle samples all the gas in the bed, $\tau''' = (C_{A0} - C_A)/-r_A''$, or

$$\bar{C}_A = \frac{(C_{A0} - C_A) v_0}{k''' V_s} = \frac{(100 - 68) 0.3 \pi}{(0.8)(3.5)} = \underline{\underline{11 \text{ mol/m}^3}}$$

(c) **Calculate X_A for a fixed bed.** From Eq. 11.44 or 11.51, for plug flow,

$$\ln \frac{C_{A0}}{C_{Ap}} = k''' \tau''' = k''' \frac{f_{\text{total}} H_{\text{BFB}}}{u_0} = k''' \frac{V_s}{v_0} = (0.8) \left(\frac{3.5}{0.3 \pi} \right) = 2.97$$

Therefore

$$\frac{C_{Ap}}{C_{A0}} = 0.05 \quad \dots \text{or} \quad \underline{\underline{X_A = 95\%}}$$

This point is shown in Fig. 20.10.

Comments

- The conversion in the fluidized bed is drastically lower than in the packed bed (32% vs. 95%), and is even much below mixed flow (75%). This comes from the severe bypassing of reactant gas in the large gas bubbles. Reduce the size of bubbles in the bed and the conversion will rise spectacularly.
- Gas enters at $C_{A0} = 100$, leaves at $C_A = 68$; however, the solids see a much lower concentration of A, or $C_A = 11$. Thus the solids, mostly in the emulsion, are starved for gaseous reactant. This sort of finding, quite general for fast bubble beds, is of great importance in G/S reactions. Thus in combustion and roasting of fine solids these solids may be starved for O_2 even though the off gas from the bed may contain a significant amount of oxygen.
- Example 20.1 and the solutions to Problems 20.1 and 20.2 at the end of this chapter tell how conversion is affected by bubble size according to the K-L model. This is shown in Fig. 20.11. In all four cases the rate constant is the same and the catalyst is fixed at 7 tons, so $k''' \tau''' = f_{\text{total}} H_{\text{BFB}} k'''/u_0 = 2.97$.

Multiple Reactions and Product Distribution in Fluidized Beds

A derivation similar to that for single first-order reactions can be developed for the Denbigh reaction system

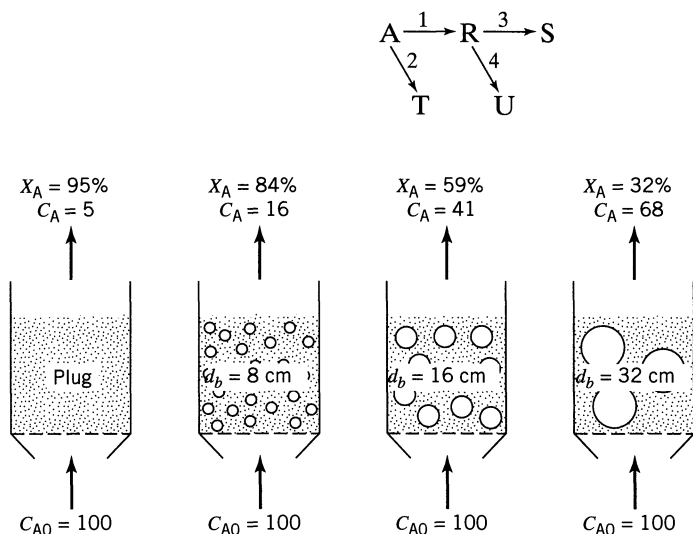
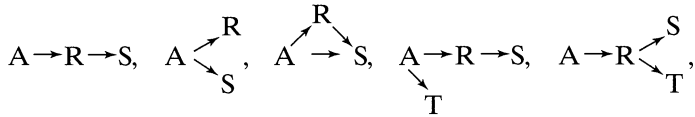
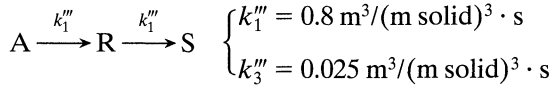


Figure 20.11 Different bubble size gives different reactor performance. Data from Example 20.1 and Problems 20.3 and 20.4.

and its special cases



These derivations are rather tedious, we will not give them here, but we refer the reader to Levenspiel (1996) Chapter 25 for them. However, to illustrate the general findings let us take one example:



Let us suppose that these reactions take place in a BFB reactor having a gas flow rate similar to that of Example 20.1.

Let us see how much catalyst is needed to achieve $C_{R, \max}$ for different sizes of bubbles in the BFB. The results are shown in Fig. 20.12.

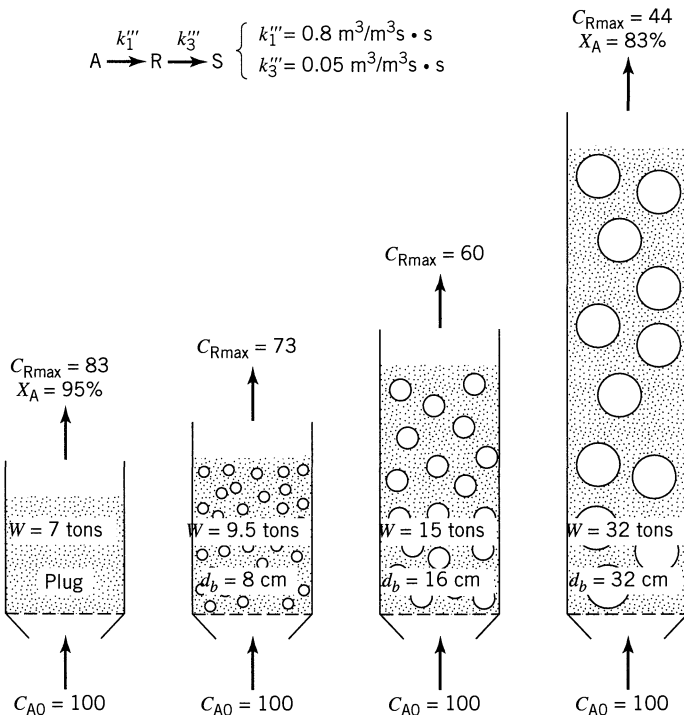


Figure 20.12 Different bubble sizes give different bed sizes for maximum production of intermediate.

The results of the calculations verify the general findings on bubbling fluidized beds.

- The BFB always needs more catalyst than a fixed bed to achieve a given conversion of reactant, or to reach $C_{R, \max}$.
- For reactions in series the BFB always gives a lower yield of intermediate compared to a fixed bed.
- For reactions in parallel of the same reaction order the product distribution is the same in fixed and BFBs.

Final Remarks About BFB

The expressions developed in this chapter show that if we know ϵ_{mf} , estimate α , and measure u_{mf} and u_0 , then all flow quantities and regional volumes can be determined in terms of one parameter, the bubble size. Figure 20.9 then represents the model as visualized. The use of this model to calculate chemical reactor behavior is straightforward and direct. The special feature of this model is that its one parameter can be tested against what is measured and what is observed.

Various other hydrodynamic models have been proposed recently, using other combinations of assumptions such as

Changing bubble size with height in the bed
 Negligible bubble-cloud resistance
 Negligible cloud-emulsion resistance
 Nonspherical bubbles

In all cases the underlying rationale for these hydrodynamic models rests on the observation that beds with identical solids and gas flow rates may develop either large bubbles or small bubbles depending on bed diameter, distributor design, baffle arrangement, etc.; thus, bubble size must enter as the primary parameter in the model. A consequence of this argument is that *models which do not allow for different bubble sizes* at given imposed bed conditions *certainly cannot be adequate*.

The power of this class of model should be apparent. For example, even the simplest of these models, the one considered here, gives unexpected predictions (e.g., that most of the gas in the bed may be flowing downward) which are subsequently verified. More important still, this type of model can be tested, it can be shown to be wrong, and it can be rejected, because its one parameter, the bubble size, can be compared with observation.

20.4 THE CIRCULATING FLUIDIZED BED—CFB

At gas velocities higher than those used for BFBs we successively enter the turbulent (TB), fast fluidized (FF), and the pneumatic conveying (PC) regimes. In these contacting regimes solids are entrained out of the bed and must be replaced. Thus in continuous operations we have the CFB, shown in Fig. 20.1.

Flow models are very sketchy for these flow regimes. Let us see what is known.

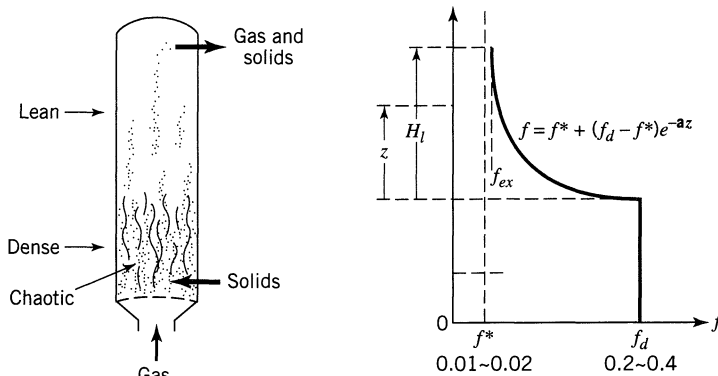


Figure 20.13 The TB and its solid distribution.

The Turbulent Bed (TB)

At higher gas velocities the BFB transforms into a TB—no distinct bubbles, much churning, and violent solid movement. The surface of the dense bed fades and solids are found increasingly in the lean region above the dense bed.

The concentration of solids in the upper lean region can be reasonably represented by an exponential decay function which starts from the value in the lower region f_d and falls to f^* the limiting value in an infinitely high vessel. This is the value for pneumatic conveying.

The flow of gas in the dense region is somewhere between the BFB and plug flow. The TB is shown in Fig. 20.13.

Unfortunately no reasonable flow model has been developed for the dense region of a TB. Research is needed here.

In beds of both coarse and fine solids one may observe a somewhat different solid distribution with height—a distinct difference between dense and lean regions and a sharp dense phase surface, as shown in Fig. 20.14. This behavior is more typical of fluidized combustors, not catalytic reaction systems.

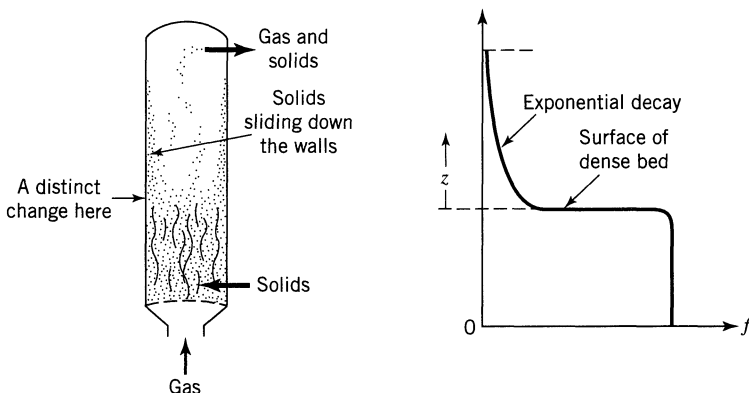


Figure 20.14 Behavior of a TB of large and small particles.

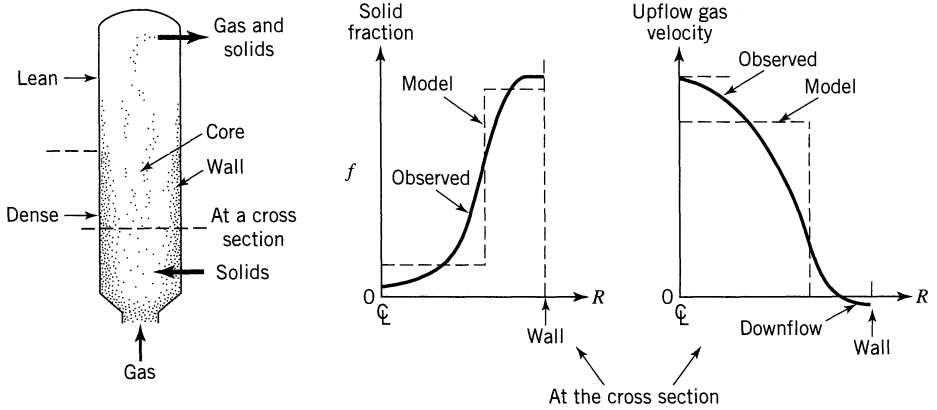


Figure 20.15 Behavior of a FF bed.

The Fast Fluidized Bed (FF)

At even higher gas velocity (see Fig. 20.5) the bed enters the FF regime. One characteristic of this transition is that the entrainment of solids rises dramatically at this point. Bi et al. (1995) found this transition to occur at

$$u_{\text{TB-FF}} = 1.53 \sqrt{\frac{(\rho_s - \rho_g)g d_p}{\rho_g}}$$

In the FF regime the solid movement in the lower region of the vessel becomes less chaotic and seems to settle to a lean core surrounded by a denser annulus or wall zone.

The upper region retains its exponential decay behavior.

Figure 20.15 shows the distribution of solids in the whole FF bed and at a cross section. The model which represents the FF bed is shown in Fig. 20.16.

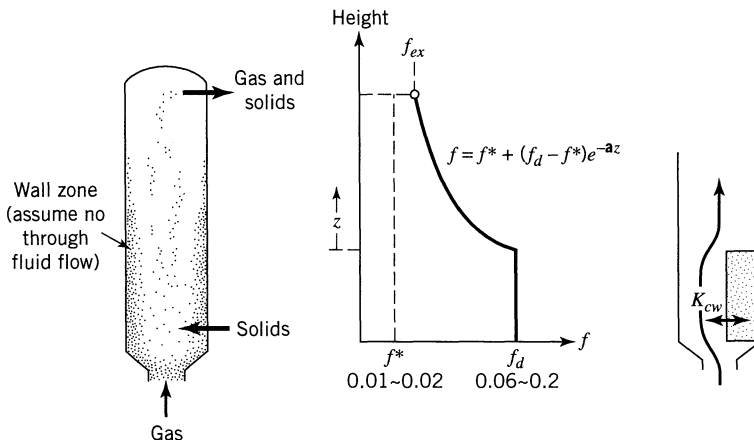


Figure 20.16 Model for a FF reactor.

The quantities that need to be known to predict the behavior of the FF reactor are “*a*,” K_{cw} , f^* , and f_d . Measurements show that

$$\begin{aligned}
 u_0 a &= 2 - 4 \text{ s}^{-1} && \text{for Geldart A solids} \\
 &= 5 \text{ s}^{-1} && \text{for Geldart AB solids} \\
 &= 7 \text{ s}^{-1} && \text{for Geldart B solids}
 \end{aligned}$$

Measured values for f^* and f_d have been summarized by Kunii and Levenspiel (1995). Values for K_{cw} have yet to be measured. The best we can do today is estimate their order of magnitude from K_{bc} and K_{ce} of the BFB. So at this time we cannot predict reactor behavior. However, to see how to make the material balance and conversion calculation see the numerical example given in Kunii and Levenspiel (1997).

Pneumatic Conveying (PC)

Finally at the highest gas velocities we exceed what is called the *choking velocity*. Above this the bed is in pneumatic transport. This transition velocity depends on the solid flow rate, and according to Bi and Fan (1991) occurs at

$$\frac{u_{\text{FF-PC}}}{\sqrt{g d_p}} = 21.6 \left(\frac{G_s}{\rho_g u_{\text{FF-PC}}} \right)^{0.542} (d_p^*)^{0.315}$$

In the PC regime particles are well distributed in the reactor, with no wall or downflow zone, but with a slight decrease in solid fraction with height. So we can assume plug flow of solids and of gas up the vessel.

The Downflow CFB

Fluidized catalytic cracking reactors, called “cat crackers” or FCC reactors, are one of society’s most important large-scale reactors. On an average, each such

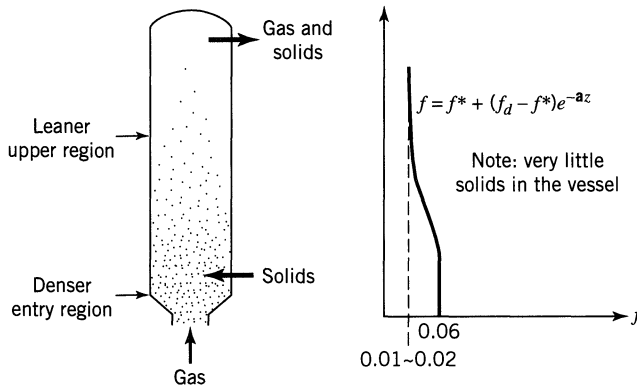
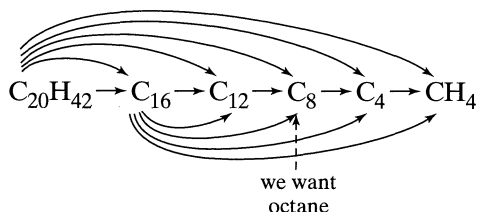


Figure 20.17 Model for a PC reactor.

unit processes about 6000 m³/day (40 000 barrels/day) of crude oil to produce gasoline, diesel fuel, and jet aircraft fuel to power the engines of today. There are about 420 FCC reactors in the world today, running day and night to satisfy the needs of our insatiable societies.

These reactors take long chain hydrocarbons and crack them to produce a whole host of shorter chain hydrocarbons. To illustrate



The original cat cracker was invented in the early 1940s and was one of chemical engineering's most important contributions to World War II. However, those early units did not use very selective catalysts and, with their large deviations from plug flow, gave very little of whatever intermediate was desired.

In the 1960s better (more selective) and more active catalysts were created, and the needed reaction time for the oil vapor was consequently reduced to seconds, so the upflow FF reactors were invented. Approaching closer to plug flow gave the designer better control of product distribution, and allowed production of a larger fraction of desired product: for example, octane for automobile fuel.

With this development, most of the BFBs in the world were cut up for scrap to be replaced by upflow FF reactors.

Today, approaching year 2000, engineers want to do better still. Why? Because increasing the production of desired product by 1% would increase the profit per reactor by \$1 million to \$2 million/year. As Fig. 20.16 shows, the upflow FF reactor has a practically stagnant or a downsliding wall zone of catalyst and gas, and this results in deviation from plug flow.

How to avoid this? The obvious answer is to use a downflow FF reactor. These can operate at very high gas velocities, and remain close to plug flow.

Today much exciting research is going on in this area, and we may some day, not too far in the future, see many of the upflow short contact time FCC units be replaced by downflow units. The payoff for this would be enormous.

Remarks About CFB

Here we have sketched the three regimes of CFB and their general behavior; however, we have not presented their performance equations. The reason is that the parameters for their reasonable models are uncertain today; hence, the predictions based on these models will likewise be uncertain. Still the general material balances and the form of the performance equations are available, see Kunii and Levenspiel (1991, 1997).

20.5 THE JET IMPACT REACTOR

The idea here is to force two streams, one of reactant, the other of a very hot heat carrier or catalyst, to collide at very high velocity and thereby mix intensely and react at high temperature.

For an all-gas product, the product stream is rapidly quenched, while for a gas-solid product, a cyclone separates the two phases, after which the gas is rapidly cooled. By using the word “rapidly” we mean that the whole operation—mixing, reacting, separating and quenching—is done in 0.1 to 0.3 seconds.

This type of reactor aims to challenge fast fluidization with its 1 to 10 second gas residence time as the prime reactor for the catalytic cracking of petroleum. The claim is that the higher cracking temperature and shorter residence time will give a very different—and better—distribution of reaction products.

Another application is to ultrapyrolyze cellulose and other biomass wastes. Commercial tests show that one can transform about 75% of wood into oil, and about 70% of sawdust into oil—useful liquids having the consistency of light engine oil. Much research is proceeding on this application (from Bergougnou, 1998).

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PROBLEMS

A suggestion for raising the conversion in Example 20.1 is to use more solids. So for the same bed diameter (2 m) and same mean bubble size (0.32 m) find X_A and the mean concentration of gas seen by the solids C_A if we use

20.1. . . . 14 tons of catalyst

20.2. . . . 21 tons of catalyst

In Example 20.1 the conversion is very low and unsatisfactory. One suggestion for improvement is to insert baffles into the bed and thereby cut down the effective bubble size. Find X_A if

20.3. . . . $d_b = 16$ cm

20.4. . . . $d_b = 8$ cm

In Example 20.1 another suggestion for improving performance is to use a shallower bed, keeping W unchanged, thereby decreasing the superficial gas velocity. Find X_A if we double the bed cross-sectional area (thus make $u_0 = 15$ cm/s) and

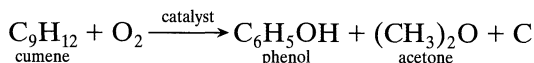
20.5. . . . keep d_b unchanged at $d_b = 32$ cm

20.6. . . . make $d_b = 8$ cm by suitable baffles

20.7. In Example 20.1 still another suggestion is to use a narrower and taller bed, keeping W unchanged. Following this suggestion find X_A if we halve the bed cross-sectional area (thus make $u_0 = 60$ cm/s) and keep $d_b = 32$ cm.

20.8. Example 20.1 showed that a 7-ton bed with 32-cm bubbles gave 32% conversion. Suppose we diluted the catalyst 1:1 with inert solids ending up with a 14-ton bed. How would this affect the conversion of reactant? Would it be higher or lower than 32%?

20.9. Mathis and Watson in *AIChE J.*, **2**, 518 (1956) reported on the catalytic conversion of cumene in both fluidized and packed beds of catalyst



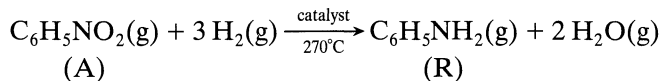
In very dilute cumene-air mixtures the kinetics are essentially first-order reversible with respect to cumene with an equilibrium conversion of 94%.

In packed bed experiments ($H_m = 76.2$ mm) using downflow of gas ($u_0 = 64$ mm/s) the conversion of cumene was found to be 60%. However, with upflow of gas at the same flow rate in the same bed, the solids fluidize ($u_{mf} = 6.1$ mm/s) and bubbles of gas were observed roughly 13.5 mm in diameter. What conversion do you expect to find under these conditions?

Estimated values:

$$\begin{aligned} \epsilon_m &= 0.4, & D_{\text{cumene-air}} &= 2 \times 10^{-5} \text{ m}^2/\text{s} \\ \epsilon_{mf} &= 0.5, & \alpha &= 0.33 \end{aligned}$$

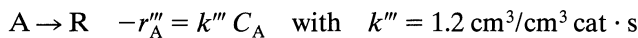
- 20.10.** Calculate the conversion in a fluidized bed reactor for the catalytic hydrogenation of nitrobenzene to aniline.



Data:

$H_m = 1.4 \text{ m}$	$\rho_c = 2.2 \text{ g/cm}^3$	$d_b = 10 \text{ cm}$
$d_t = 3.55 \text{ m}$	$\mathcal{D}_{\text{eff}} = 0.9 \text{ cm}^2/\text{s}$	$\alpha = 0.33$
$T = 270^\circ\text{C}$	$u_{mf} = 2 \text{ cm/s}$	$\epsilon_m = 0.4071$
	$u_0 = 30 \text{ cm/s}$	$\epsilon_{mf} = 0.60$

We plan to use an excess of hydrogen in which case we can ignore expansion, and can assume simple first-order kinetics:



- 20.11.** In a laboratory packed bed reactor ($H_m = 10 \text{ cm}$ and $u_0 = 2 \text{ cm/s}$) conversion is 97% for the first-order reaction $\text{A} \rightarrow \text{R}$.

- (a) Determine the rate constant k''' for this reaction.
- (b) What would be the conversion in a larger fluidized bed pilot plant ($H_m = 100 \text{ cm}$ and $u_0 = 20 \text{ cm/s}$) in which the estimated bubble size is 8 cm?
- (c) What would be the conversion in a packed bed under the conditions of part (b)?

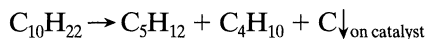
Data: From experiment, $u_{mf} = 3.2 \text{ cm/s}$, $\epsilon_{mf} \cong \epsilon_m = 0.5$

From the literature, $\mathcal{D} \cong \mathcal{D}_e = 3 \times 10^{-5} \text{ cm}^2/\text{s}$, $\alpha = 0.34$

Deactivating Catalysts

The previous chapters assumed that the effectiveness of catalysts in promoting reactions remains unchanged with time. Often this is not so, in which case the activity usually decreases as the catalyst is used. Sometimes this drop is very rapid, in the order of seconds; sometimes it is so slow that regeneration or replacement is needed only after months of use. In any case, with deactivating catalysts regeneration or replacement is necessary from time to time.

If deactivation is rapid and caused by a deposition and a physical blocking of the surface this process is often termed *fouling*. Removal of this solid is termed *regeneration*. Carbon deposition during catalytic cracking is a common example of fouling



If the catalyst surface is slowly modified by chemisorption on the active sites by materials which are not easily removed, then the process is frequently called *poisoning*. Restoration of activity, where possible, is called *reactivation*. If the adsorption is *reversible* then a change in operating conditions may be sufficient to reactivate the catalyst. If the adsorption is not reversible, then we have *permanent poisoning*. This may require a chemical retreatment of the surface or a complete replacement of the spent catalyst.

Deactivation may also be *uniform* for all sites, or it may be *selective*, in which case the more active sites, those which supply most of the catalyst activity, are preferentially attacked and deactivated.

We will use the term *deactivation* for all types of catalyst decay, both fast and slow; and we will call any material which deposits on the surface to lower its activity a *poison*.

This chapter is a brief introduction to operations with deactivating catalysts. We will consider in turn:

- The mechanisms of catalyst decay
- The form of rate equation for catalyst decay
- How to develop a suitable rate equation from experiment
- How to discover the mechanism from experiment
- Some consequences for design

Although this is basically a rather involved subject, still its very importance from the practical standpoint requires at least an introductory treatment.

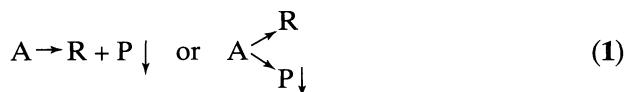
21.1 MECHANISMS OF CATALYST DEACTIVATION

The observed deactivation of a porous catalyst pellet depends on a number of factors: the actual decay reactions, the presence or absence of pore diffusion slowdown, the way poisons act on the surface, etc. We consider these in turn.

Decay Reactions. Broadly speaking, decay can occur in four ways. First, the reactant may produce a side product which deposits on and deactivates the surface. This is called *parallel deactivation*. Second, the reaction product may decompose or react further to produce a material which then deposits on and deactivates the surface. This is called *series deactivation*. Third, an impurity in the feed may deposit on and deactivate the surface. This is called *side-by-side deactivation*.

If we call P the material which deposits on and deactivates the surface, we can represent these reactions as follows:

Parallel deactivation:



Series deactivation:



Side-by-side deactivation:



The key difference in these three forms of decay reactions is that the deposition depends, respectively, on the concentration of reactant, product, and some other substance in the feed. Since the distribution of these substances will vary with position in the pellet, the location of deactivation will depend on which decay reaction is occurring.

A fourth process for catalyst decay involves the structural modification or sintering of the catalyst surface caused by exposure of the catalyst to extreme conditions. This type of decay is dependent on the time that the catalyst spends in the high temperature environment, and since it is unaffected by the materials in the gas stream we call it *independent deactivation*.

Pore Diffusion. For a pellet, pore diffusion may strongly influence the progress of catalyst decay. First consider parallel deactivation. From Chapter 18 we know that reactant may either be evenly distributed throughout the pellet ($M_T < 0.4$

and $\mathcal{E} = 1$) or may be found close to the exterior surface ($M_T > 4$ and $\mathcal{E} < 1$). Thus the poison will be deposited in a like manner—uniformly for no pore resistance, and at the exterior for strong pore resistance. In the extreme of very strong diffusional resistance a thin shell at the outside of the pellet becomes poisoned. This shell thickens with time and the deactivation front moves inward. We call this the *shell model* for poisoning.

On the other hand, consider series deactivation. In the regime of strong pore resistance the concentration of product R is higher within the pellet than at the exterior. Since R is the source of the poison, the latter deposits in higher concentration within the pellet interior. Hence we can have poisoning from the inside-out for series deactivation.

Finally, consider side-by-side deactivation. Whatever the concentration of reactants and products may be, the rate at which the poison from the feed reacts with the surface determines where it deposits. For a small poison rate constant the poison penetrates the pellet uniformly and deactivates all elements of the catalyst surface in the same way. For a large rate constant poisoning occurs at the pellet exterior, as soon as the poison reaches the surface.

The above discussion shows that the progress of deactivation may occur in different ways depending on the type of decay reaction occurring and on the value of the pore diffusion factor. For parallel and series poisoning, the Thiele modulus for the main reaction is the pertinent pore diffusion parameter. For side-by-side reactions, the Thiele modulus for the deactivation is the prime parameter.

Nonisothermal effects within pellets may also cause variations in deactivation with location, especially when deactivation is caused by surface modifications due to high temperatures.

Additional Factors Influencing Decay. Numerous other factors may influence the observed change in activity of catalyst. These include pore mouth blocking by deposited solid, equilibrium, or reversible poisoning where some activity always remains, and the action of regeneration (this often leaves catalyst with an active exterior but inactive core).

Most important of all, the observed deactivation may result from a number of processes at work simultaneously; for example, the speedy immobilization of the most active sites by poison P_1 , and then the slower attack of the remainder of the sites by P_2 .

Although the possible influence of all these factors should be examined in the real case, in this introductory treatment we will concentrate on the first two factors: the decay reaction and pore diffusion. There are enough lessons here to illustrate how to approach the more complete problem.

21.2 THE RATE AND PERFORMANCE EQUATIONS

The activity of a catalyst pellet at any time is defined as

$$\mathbf{a} = \frac{\text{rate at which the pellet converts reactant A}}{\text{rate of reaction of A with a fresh pellet}} = \frac{-r'_A}{-r'_{A0}} \quad (4)$$

and in terms of the fluid bathing the pellet the rate of reaction of A should be of the following form:

$$\left(\begin{array}{c} \text{reaction} \\ \text{rate} \end{array} \right) = f_1 \left(\begin{array}{c} \text{main stream} \\ \text{temperature} \end{array} \right) \cdot f_3 \left(\begin{array}{c} \text{main stream} \\ \text{concentration} \end{array} \right) \cdot f_5 \left(\begin{array}{c} \text{present activity of} \\ \text{the catalyst pellet} \end{array} \right) \quad (5)$$

Similarly, the rate at which the catalyst pellet deactivates may be written as

$$\left(\begin{array}{c} \text{deactivation} \\ \text{rate} \end{array} \right) = f_2 \left(\begin{array}{c} \text{main stream} \\ \text{temperature} \end{array} \right) \cdot f_4 \left(\begin{array}{c} \text{main stream} \\ \text{concentration} \end{array} \right) \cdot f_6 \left(\begin{array}{c} \text{present state of} \\ \text{the catalyst pellet} \end{array} \right) \quad (6)$$

In terms of n th-order kinetics, Arrhenius temperature dependency, and isothermal conditions, Eq. 5 becomes, for the main reaction:

$$\boxed{-r'_A = k' \cdot C_A^n \cdot \mathbf{a} = k'_0 e^{-E/RT} \cdot C_A^n \cdot \mathbf{a}} \quad (7)$$

and for deactivation which in general is dependent on the concentration of gas-phase species, Eq. 6 becomes

$$\boxed{-\frac{d\mathbf{a}}{dt} = k_d \cdot C_i^m \cdot \mathbf{a}^d = k_{d0} e^{-E_d/RT} \cdot C_i^m \cdot \mathbf{a}^d} \quad (8)$$

where d is called the *order of deactivation*, m measures the concentration dependency and E_d is the activation energy or temperature dependency of the deactivation.

For different decay reactions we may expect different forms for the above equations. Thus

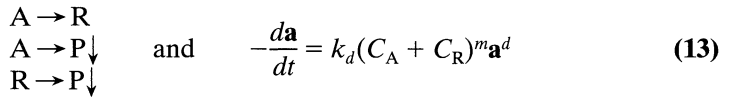
$$\left. \begin{array}{l} \text{For parallel deactivation} \\ (A \rightarrow R; A \rightarrow P \downarrow) \end{array} \right\} \begin{array}{l} -r'_A = k' C_A^n \mathbf{a} \\ -\frac{d\mathbf{a}}{dt} = k_d C_A^m \mathbf{a}^d \end{array} \quad (9)$$

$$\left. \begin{array}{l} \text{For series deactivation} \\ (A \rightarrow R \rightarrow P \downarrow) \end{array} \right\} \begin{array}{l} -r'_A = k' C_A^n \mathbf{a} \\ -\frac{d\mathbf{a}}{dt} = k_d C_R^m \mathbf{a}^d \end{array} \quad (10)$$

$$\left. \begin{array}{l} \text{For side-by-side deactivation} \\ (A \rightarrow R; P \rightarrow P \downarrow) \end{array} \right\} \begin{array}{l} -r'_A = k' C_A^n a \\ -\frac{da}{dt} = k_d C_P^m a^d \end{array} \quad (11)$$

$$\left. \begin{array}{l} \text{For independent deactivation} \\ (\text{concentration independent}) \end{array} \right\} \begin{array}{l} -r'_A = k' C_A^n a \\ -\frac{da}{dt} = k_d a^d \end{array} \quad (12)$$

In certain reactions, such as isomerizations and cracking, deactivation may be caused both by reactant and product, or



Since $C_A + C_R$ remains constant for a specific feed this type of deactivation reduces to the simple-to-treat independent deactivation of Eq. 12.

Although the above n th-order expressions are quite simple they are general enough to embrace many of the decay equations used to date [see Szepe and Levenspiel (1968)].

The Rate Equation from Experiment

Experimental devices for studying deactivating catalysts fall into two classes: those which use a batch of solids, and those which use a through flow of solids. Figure 21.1 shows some of these devices.

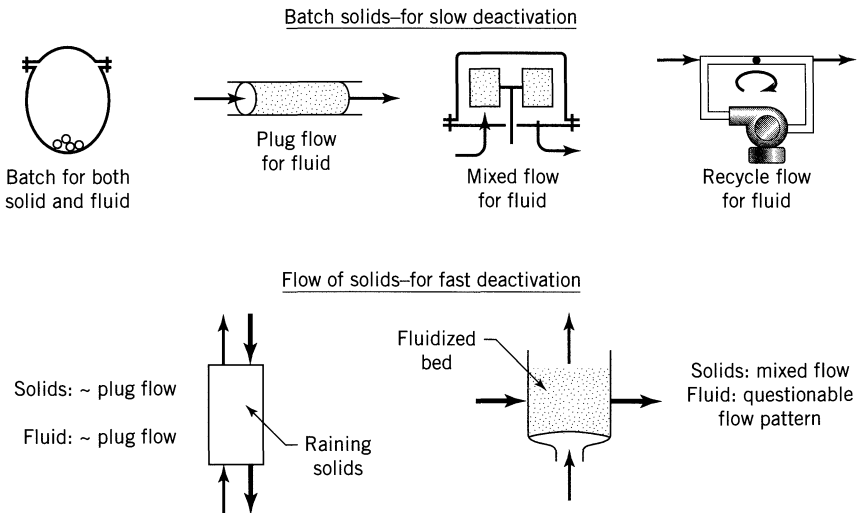


Figure 21.1 Slow deactivation may use a batch of solids in experimentation; fast deactivation requires a flow of solids.

Because of the ease of experimentation batch-solids devices are much preferred; however, they can only be used when deactivation is slow enough (in the order of minutes or longer) so that sufficient data on the changing fluid composition can be obtained before exhaustion of the catalyst. When deactivation is very rapid (in the order of seconds or less) then a flowing-solids system must be used. Cracking catalysts whose activity half-lives can be as short as 0.1 second fall into this class.

The method of searching for a rate equation is analogous to that of homogeneous reactions: start with the simplest kinetic form and see if it fits the data. If it doesn't, try another kinetic form and so on. The main complication here is that we have an extra factor, the activity, to contend with. Nevertheless, the strategy is the same; always start by trying to fit the simplest rate expression.

In the following sections we treat the batch-solids devices in some detail, and then briefly consider the flowing-solids system.

Now the type of batch-solids flowing-fluid reactor that we find convenient to use depends on whether the deactivation expression da/dt is concentration independent or not. When it is concentration independent, any type of batch-solids system may be used and can be analyzed simply, but when it is concentration dependent, then unless one particular type of reactor is used (that in which C_A is forced to stay unchanged with time) the analysis of the experimental results becomes horrendously awkward and difficult.

We treat these two classes of experimental devices in turn.

Batch-Solids: Determining the Rate for Independent Deactivation

Let us illustrate how to interpret experiments from the various batch-solids reactors of Fig. 21.1 and how to manipulate the basic performance equations for these reactors by testing the fit for the simplest of equation forms for independent deactivation.

$$\left. \begin{aligned} -r'_A &= k' C_A \mathbf{a} \quad \text{with} \quad \varepsilon_A = 0 \\ -\frac{d\mathbf{a}}{dt} &= k_d \mathbf{a} \end{aligned} \right\} \quad \begin{aligned} (14a) \\ (14b) \end{aligned}$$

This represents first-order reaction and first-order deactivation which, in addition, is concentration independent.

Batch-Solids, Batch-Fluid. Here we need to develop an expression relating the changing gas concentration with time. Using time as the one independent variable throughout the run the kinetic expressions of Eq. 14 become

$$-\frac{dC_A}{dt} = \frac{W}{V} \left(-\frac{1}{W} \frac{dN_A}{dt} \right) = \frac{W}{V} (-r'_A) = \frac{W}{V} k' C_A \mathbf{a} \quad (15)$$

$$-\frac{d\mathbf{a}}{dt} = k_d \mathbf{a} \quad (16)$$

Integrating Eq. 16 yields

$$\mathbf{a} = \mathbf{a}_0 e^{-k_d t} \quad (17)$$

and for unit initial activity, or $\mathbf{a}_0 = 1$, this becomes

$$\mathbf{a} = e^{-k_d t} \quad (18)$$

Replacing Eq. 18 in Eq. 15 we then find

$$-\frac{dC_A}{dt} = \frac{Wk'}{V} e^{-k_d t} C_A \quad (19)$$

and on separation and integration

$$\ln \frac{C_{A0}}{C_A} = \frac{Wk'}{Vk_d} (1 - e^{-k_d t}) \quad (20)$$

This expression shows that even at infinite time the concentration of reactant in an irreversible reaction does not drop to zero but is governed by the rate of reaction and of deactivation, or

$$\ln \frac{C_{A0}}{C_{A\infty}} = \frac{Wk'}{Vk_d} \quad (21)$$

Combining the above two expression and rearranging then yields

$$\boxed{\ln \ln \frac{C_A}{C_{A\infty}} = \ln \frac{Wk'}{Vk_d} - k_d t} \quad (22)$$

A plot as shown in Fig. 21.2 provides a test for this rate form.

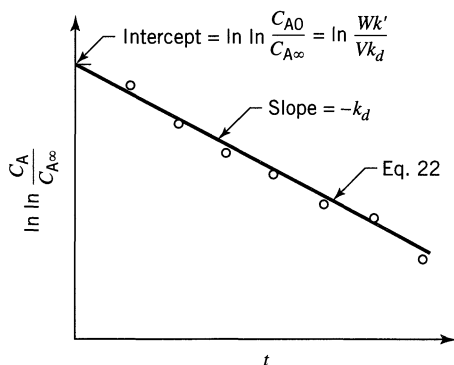


Figure 21.2 Test of the kinetic expressions of Eq. 14 using a batch-solids, batch-fluid reactor.

The batch-batch reactor becomes a practical device when the characteristic times for reaction and deactivation are of the same order of magnitude. If they are not and if deactivation is much slower, then $C_{A\infty}$ becomes very low and difficult to measure accurately. Fortunately, this ratio can be controlled by the experimenter by proper choice of W/V .

Batch-Solids, Mixed Constant Flow of Fluid. Inserting the rate of Eq. 14a into the performance expression for mixed flow gives

$$\tau' = \frac{WC_{A0}}{F_{A0}} = \frac{W}{v} = \frac{C_{A0} - C_A}{k' a C_A} \quad (23)$$

and on rearrangement

$$\frac{C_{A0}}{C_A} = 1 + k' a \tau' \quad (24)$$

In Eq. 24 the activity varies with the chronological time. To eliminate this quantity integrate Eq. 14b (see Eq. 18) and insert in Eq. 24. Thus

$$\frac{C_{A0}}{C_A} = 1 + k' e^{-k_d t} \tau' \quad (25)$$

Rearranging gives, in more useful form,

$$\ln \left(\frac{C_{A0}}{C_A} - 1 \right) = \ln(k' \tau') - k_d t \quad (26)$$

This expression shows how the reactant concentration at the outlet rises with time, while the plot of Fig. 21.3 provides the test of this kinetic equation. If the

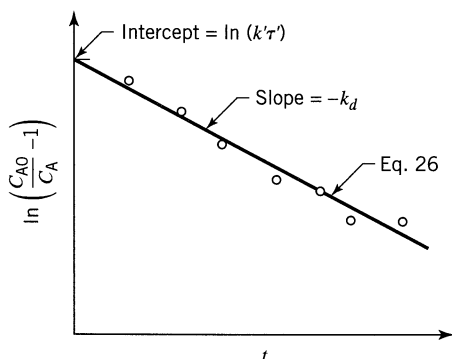


Figure 21.3 Test of the kinetic expressions of Eq. 14 using a batch of solids and steady-state mixed flow of fluids.

data fall on a straight line then the slope and intercept yield the two rate constants of Eq. 14.

We should mention that this and the succeeding batch-solids derivations are based on the pseudo steady-state assumption. This assumes that conditions change slowly enough with time for the system to be at steady state at any instant. Since a batch of solids can only be used if deactivation is not too rapid this assumption is reasonable.

Batch-Solids, Mixed Changing Flow of Fluid (to keep C_A fixed). For steady flow in a mixed reactor we have found

$$\frac{C_{A0}}{C_A} = 1 + k' e^{-k_d t} \tau' \quad (25)$$

To keep C_A constant the flow rate must be slowly changed with time. In fact, it must be lowered because the catalyst is deactivating. Hence the variables in this situation are τ' and t . So, on rearranging we have

$$\ln \tau' = k_d t + \ln \left(\frac{C_{A0} - C_A}{k' C_A} \right) \quad (27)$$

Figure 21.4 shows how to test for the kinetic expressions of Eq. 14 by this procedure.

Actually there is no particular advantage in using varying flow over constant flow when testing for the kinetics of Eq. 14 or any other independent deactivation. However, for other deactivation kinetics this reactor system is by far the most useful because it allows us to decouple the three factors C , T , and \mathbf{a} and study them a pair at a time.

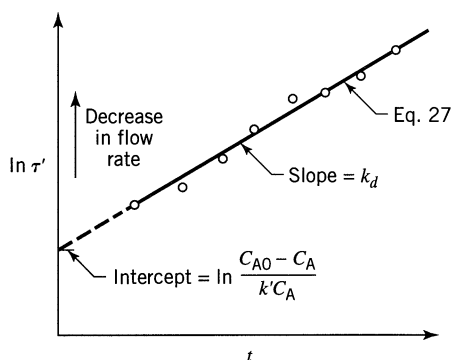


Figure 21.4 Test of the kinetic expressions of Eq. 14 using a batch of solids and changing flow of fluid in a mixed reactor so as to keep C_A constant.

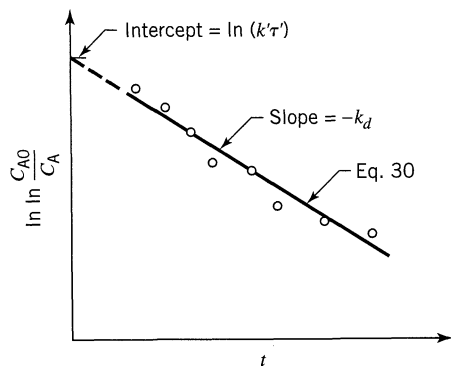


Figure 21.5 Test of the kinetic expressions of Eq. 14 using a batch of solids and steady-state plug flow of fluid.

Batch-Solids, Plug Constant Flow of Fluid. For plug flow the performance equation combined with the rate of Eq. 14a becomes

$$\frac{W}{F_{A0}} = \int \frac{dX_A}{-r'_A} = \int \frac{dX_A}{k' a C_A} = \frac{1}{k' a} \int \frac{dX_A}{C_A} \quad (28)$$

Integrating and replacing a by the expression of Eq. 18 gives

$$\frac{W C_{A0}}{F_{A0}} = \tau' = \frac{1}{k' a} \ln \frac{C_{A0}}{C_A} = \frac{1}{k' e^{-k_d t}} \ln \frac{C_{A0}}{C_A} \quad (29)$$

which becomes, on rearrangement,

$$\boxed{\ln \ln \frac{C_{A0}}{C_A} = \ln(k' \tau') - k_d t} \quad (30)$$

Figure 21.5 shows how to test for the kinetics of Eq. 14, and how to evaluate the rate constants with data from this type of reactor.

Batch-Solids, Plug Changing Flow of Fluid (to keep $C_{A, \text{out}}$ fixed). At any instant in the plug flow reactor Eq. 29 applies. Thus noting that τ' and t are the two variables we obtain, on suitable rearrangement,

$$\ln \tau' = k_d t + \ln \left(\frac{1}{k'} \ln \frac{C_{A0}}{C_A} \right) \quad (31)$$

Figure 21.4, with one modification (the intercept given by the last term of Eq. 31), shows how to test for the kinetic expressions of Eq. 14 with this device.

So far we have illustrated how to use a batch, plug flow or mixed flow of fluid to search for the rate constants of a particular rate form, Eq. 14.

As long as the deactivation is concentration independent, the activity and concentration effects can be decoupled and any of the above experimental devices will give simple easy-to-interpret results. Thus the above analyses can be extended with no difficulty to any reaction order n and any deactivation order d , as long as $m = 0$, or for

$$\left. \begin{aligned} -r'_A &= k' C_A^n a \\ -\frac{da}{dt} &= k_d a^d \end{aligned} \right\} \quad (32)$$

On the other hand, if the deactivation is concentration dependent, or $m \neq 0$, then the concentration and activity effects do not decouple and analysis becomes difficult unless the proper experimental device is used, one deliberately chosen so as to decouple these factors. Reactors which keep C_A constant by slowing the flow rate of feed, as treated above, are such devices. They can be used to find the rate constants for the reactions

$$\left. \begin{aligned} -r'_A &= k' C_A^n a \\ -\frac{da}{dt} &= k_d C_A^m a^d \end{aligned} \right\} \quad (33)$$

as well as for parallel, series, and side-by-side deactivation [see Levenspiel (1972, 1996)].

How Pore Diffusion Resistance Distorts the Kinetics of Reactions with Deactivating Catalysts

Consider the following rate scheme for reactions on spherical particles

$$\left. \begin{aligned} -r'_A &= k' C_A a \\ -\frac{da}{dt} &= k_d a^d \end{aligned} \right\} \text{where } k' \rho_s = k'' \quad (34)$$

For *no deactivation* but with or without pore diffusion resistance these rate expressions become

$$\left. \begin{aligned} -r'_A &= k' C_A \mathcal{E} \\ a &= 1 \end{aligned} \right\} \quad (35)$$

where

$$\left. \begin{aligned} \mathcal{E} &= 1 \quad \text{for no diffusional slowdown} \\ \mathcal{E} &= \frac{1}{M_T}, \quad M_T = L \sqrt{\frac{k''}{\mathcal{D}_e}} \quad \text{for strong diffusional} \\ &\quad \quad \quad \text{resistance} \end{aligned} \right\} \quad (36)$$

With deactivation, Eq. 34 above becomes

$$\left. \begin{aligned} -r'_A &= k' a C_A \mathcal{E} \\ -\frac{da}{dt} &= k_d a^d \end{aligned} \right\} \quad (37)$$

where

$$\left. \begin{aligned} \mathcal{E} &= 1 \quad \text{for no diffusional slowdown} \\ \mathcal{E} &= \frac{1}{M_{Td}}, \quad M_{Td} = L \sqrt{\frac{k'' a}{\mathcal{D}_e}} = M_T a^{1/2}, \quad \text{for strong diffusional resistance} \end{aligned} \right\} \quad (38)$$

Also as time passes, from Eq. 37,

$$\left. \begin{aligned} a &= \exp(-k_d t) \quad \text{for } d = 1 \\ a &= [1 + (d - 1)k_d t]^{1/(1-d)} \quad \text{for } d \neq 1 \end{aligned} \right\} \quad (39)$$

These expressions show that in the regime of strong pore diffusion resistance a decreases (see Eq. 39), causing M_{Td} to also decrease. This means that \mathcal{E} rises with time, as shown in Fig. 21.6. However a decreases faster than \mathcal{E} rises so the reaction rate decreases with time.

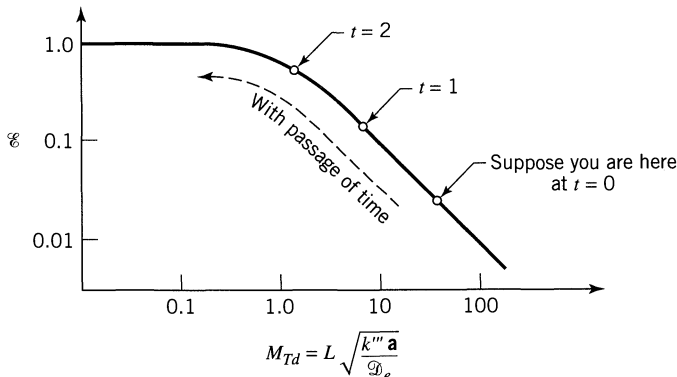


Figure 21.6 Effectiveness factor increases with time as catalyst deactivates: batch S/plug flow G.

Table 21.1 Performance equations for plug flow G/batch S, with the simple first order system of Eq. 14

	No Resistance to Pore Diffusion	Strong Resistance to Pore Diffusion
Without deactivation	$\ln \frac{C_{A0}}{C_A} = k' \tau' \quad \dots (40)$ <p style="text-align: center;">(Chapters 5, 18)</p>	$\ln \frac{C_{A0}}{C_A} = \frac{k' \tau'}{M_T} \quad \dots (41)$ <p style="text-align: center;">(Chapter 18)</p>
With deactivation	$\ln \frac{C_{A0}}{C_A} = (k' \mathbf{a}) \tau' \quad \dots (42)$ $= k' \tau' \cdot \exp(-k_d t)$	$\ln \frac{C_{A0}}{C_A} = \frac{(k' \mathbf{a}) \tau'}{M_{Td}} \quad \dots (43)$ $= \frac{k' \tau'}{M_T} \cdot \exp\left(-\frac{k_d t}{2}\right)$

Performance Equations in the Regime of Strong Diffusional Resistance

There are so many different forms of deactivation rate, it is not worthwhile trying to present their performance equations. Let us illustrate what happens with just one rate form, the simplest,

$$\left. \begin{aligned} -r'_A &= k' C_A \mathbf{a} \\ -\frac{d\mathbf{a}}{dt} &= k_d \mathbf{a} \end{aligned} \right\} \quad (14)$$

For batch S/plug flow G integration of the various diffusion deactivation regimes gives the values in Table 21.1.

For given $k' \tau'$, in other words for given treatment rate, Fig. 21.7 shows that C_A at the exit rises with time, or that conversion decreases with time.

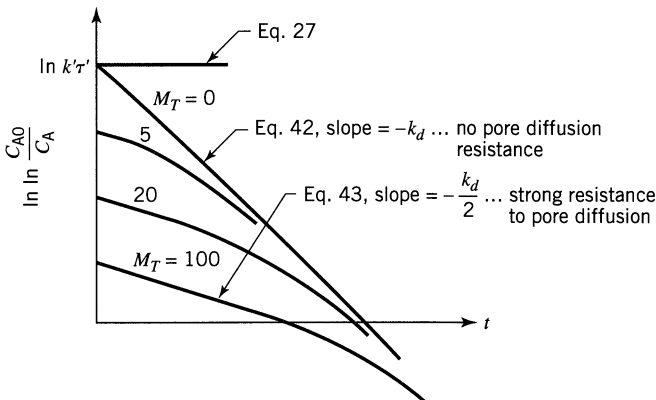


Figure 21.7 With deactivation and pore diffusional resistance reactor performance decreases with time.

Comments

- (a) For mixed flow we get equations and charts identical to the above except for the following change

$$\ln \frac{C_{A0}}{C_A} \Rightarrow \frac{C_{A0} - C_A}{C_A}$$

- (b) For other reaction orders and deactivation orders similar equations can be developed for the above four kinetic regimes. For example, for second-order reaction batch *S*/mixed flow *G* we have, with Eq. 18.28

$$\tau''' = \frac{C_{A0} - C_A}{k''' a C_A^2 \mathcal{E}} \text{ with } a = e^{-k_d t} \dots \text{ and with } M_T = L \sqrt{\frac{3 k''' C_{A0}}{2 \mathcal{D}_e}}$$

- (c) Figure 21.7 for first-order systems shows that the conversion decreases more slowly in the presence of strong pore diffusion resistance than in the diffusion-free regime. This result should apply generally to all reactor types and reaction kinetics.

EXAMPLE 21.1 INTERPRETING KINETIC DATA IN THE PRESENCE OF PORE DIFFUSION RESISTANCE AND DEACTIVATION

The catalytic decomposition of reactant ($A \rightarrow R$) is studied in a packed bed reactor filled with 2.4-mm pellets and using a very high recycle rate of product gases (assume mixed flow). The results of a long-time run and additional data are given below.

$t, \text{ hr}$	0	2	4	6	$\mathcal{D}_e = 5 \times 10^{-10} \text{ m}^3/\text{m cat} \cdot \text{s}$ $\rho_s = 1500 \text{ kg}/\text{m}^3 \text{ cat}$ $\tau' = 4000 \text{ kg} \cdot \text{s}/\text{m}^3$
X_A	0.75	0.64	0.52	0.39	

Find the kinetics of reaction and deactivation, both in the diffusion-free and in the strong pore diffusion resistance regime.

SOLUTION

First of all, note that deactivation occurs during the run, so guess or try to fit the data with the simplest rate form for such situations, or

$$\left. \begin{aligned} -r'_A &= k' C_A a \\ -\frac{da}{dt} &= k_d a \end{aligned} \right\}$$

The performance equations for this rate form and mixed flow are analogous to those for plug flow, shown in Table 21.1,

$$\text{In diffusion-free regime} \quad \dots \left(\frac{C_{A0}}{C_A} - 1 \right) = k' \tau' a = k' \tau' e^{-k_d t} \quad (\text{i})$$

$$\text{In strong diffusion regime} \quad \dots \left(\frac{C_{A0}}{C_A} - 1 \right) = k' \tau' a \mathcal{E} = \frac{k' \tau'}{M_{Td}} a = \frac{k' \tau'}{M_T} \frac{e^{-k_d t/2}}{a^{1/2}} \quad (\text{ii})$$

see Eq. 38

If this rate form is correct then for both strong or no diffusion resistance effects a plot of $\ln \left(\frac{C_{A0}}{C_A} - 1 \right)$ vs t should give a straight line. Making this tabulation and plot, as shown in Fig. E21.1 shows that the above rate form fits the data.

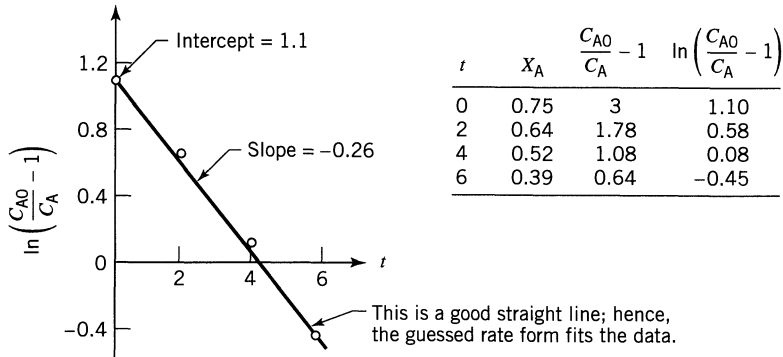


Figure E21.1

Let us next see whether the reactor is operating in the diffusion-free or strong diffusion regime.

Guess No Intrusion of Diffusional Resistances. Then from Eq. (i) we have

$$\ln \left(\frac{C_{A0}}{C_A} - 1 \right) = \ln(k' \tau') - k_d t$$

From Fig. E21.1

$$\left. \begin{array}{l} \text{the intercept} = 1.1 \\ \text{the slope} = -0.26 \end{array} \right\} \text{thus } \begin{cases} k' = 7.5 \times 10^{-4} \frac{\text{m}^3}{\text{kg} \cdot \text{s}} \\ k_d = 0.26 \text{ hr}^{-1} \end{cases}$$

Now check the Thiele modulus to verify that we really are in the diffusion resistance free regime. Thus at $t = 0$

$$M_T = L \sqrt{\frac{k'''}{\mathcal{D}_e}} = \frac{2.4 \times 10^{-3}}{6} \sqrt{\frac{(7.5 \times 10^{-4})(1500)}{5 \times 10^{-10}}} = 18.9!!!$$

Unfortunately, this value indicates strong resistance to pore diffusion. This contradicts our starting assumption, so our original guess was wrong.

Guess That the Runs Were Made in the Regime of Strong Resistance to Pore Diffusion. Then Eq. (ii) becomes

$$\ln \left(\frac{C_{A0}}{C_A} - 1 \right) = \ln \left(\frac{k' \tau'}{M_T} \right) - \frac{k_d}{2} t$$

From Fig. E21.1 we have

$$\left. \begin{array}{l} \text{the intercept} = 1.1 \\ \text{the slope} = -0.26 \end{array} \right\} \text{thus } \left\{ \begin{array}{l} \ln \left(\frac{k' \tau'}{M_T} \right) = 1.1 \\ k_d = 0.52 \text{ hr}^{-1} \end{array} \right.$$

From the value for the intercept

$$\frac{k' \tau'}{M_T} = 3.0$$

we find

$$k' = 9 \frac{L^2 \rho_s}{(\tau')^2 \mathcal{D}_e} = (9) \cdot \frac{(2.4 \times 10^{-3}/6)^2 (1500)}{(4000)^2 (5 \times 10^{-10})} = 0.27 \frac{\text{m}^3}{\text{kg} \cdot \text{s}}$$

Check the Thiele modulus at $t = 0$

$$M_T = L \sqrt{\frac{k' \rho_s}{\mathcal{D}_e}} = \frac{2.4 \times 10^{-3}}{6} \sqrt{\frac{(0.27)(1500)}{5 \times 10^{-10}}} = 360$$

This value of Thiele modulus represents strong pore diffusional resistance. This is consistent with our original guess.

Hence the final rate equations:

(a) In the diffusion-free regime (for very small d_p) with deactivation

$$-r'_A = 0.27 C_A \mathbf{a}, \quad \frac{\text{mol}}{\text{kg} \cdot \text{s}} \cdot \cdot \cdot \text{with } \cdot \cdot \cdot - \frac{d\mathbf{a}}{dt} = 0.52 \mathbf{a}, \text{ hr}^{-1}$$

(b) *In the strong pore diffusion resistance regime (for large d_p) with deactivation*

$$-r'_A = 0.27 C_A a^{\mathcal{E}} \quad \dots \text{ with } \dots \quad -\frac{da}{dt} = 0.52 a$$

$$\mathcal{E} = \frac{1}{M_{TD}} = \frac{1}{L} \sqrt{\frac{5 \times 10^{-10}}{0.27(1500)a}} = \frac{1.11 \times 10^{-6}}{La^{1/2}}$$

combining all gives

$$-r'_A = \frac{3 \times 10^{-7}}{L} C_A a^{1/2}, \quad \frac{\text{mol}}{\text{kg} \cdot \text{s}} \dots \text{ with } \dots -\frac{da}{dt} = 0.52 a, \text{ hr}^{-1}$$

Note: In the strong pore diffusion regime the rate is lower but the catalyst deactivates more slowly. Actually, for the catalyst used here if we could have been free of diffusional resistances reaction rates would have been 360 times as fast as those measured. ■

Reflection on this example leaves us with the impression that even with the simplest of rate forms the analysis is quite involved. It suggests that it is not worthwhile in this general text to try to treat more complicated rate forms.

21.3 DESIGN

When reacting fluid flows through a batch of deactivating catalyst the conversion drops progressively during the run, and steady state conditions cannot be maintained. If conditions change slowly with time, then the average conversion during a run can be found by calculating the steady-state conversion at various times and summing over time. In symbols, then,

$$\bar{X}_A = \frac{\int_0^{t_{\text{run}}} X_A(t) dt}{t_{\text{run}}} \quad (40)$$

When conversion drops too low the run is terminated, the catalyst is either discarded or regenerated, and the cycle is repeated. Example 21.2 illustrates this type of calculation.

There are two important and real problems with deactivating catalysts.

The operational problem: how to best operate a reactor during a run. Since temperature is the most important variable affecting reaction and deactivation this problem reduces to finding the best temperature progression during the run.

The regeneration problem: when to stop a run and either discard or regenerate the catalyst. This problem is easy to treat once the first problem has been solved for a range of run times and final catalyst activities. (*Note:* each pair of values for time and final activity yields the corresponding mean conversion.)

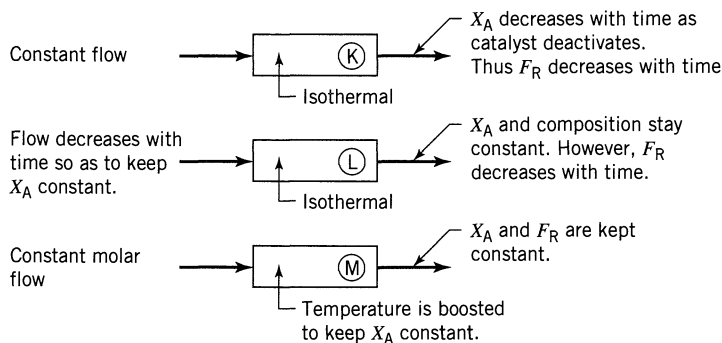


Figure 21.8 Three possible reactor policies for a batch of deactivating catalyst.

The operational problem has been solved analytically for a rather general family of kinetic equations:

$$-r'_A = k' C_A^n a = (k'_0 e^{-E/RT}) C_A^n a \quad (41)$$

$$-\frac{da}{dt} = k_d a^d = (k_{d0} e^{-E_d/RT}) a^d \quad (42)$$

Note the restriction here, that deactivation is concentration independent.

Consider the operational problem. For rather slow deactivation we can use a batch of catalyst with a choice of running the reactor in one of three ways, as shown in Fig. 21.8. Whatever policy is chosen the performance equations for the rates of Eqs. 41 and 42 are obtained by solving the following expressions:

$$\frac{W}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{k_0 e^{E/RT} C_A^n a} \quad (43)$$

with

$$\int_1^a \frac{da}{a^d} = k \int_0^t dt \quad (44)$$

The integrated performance equations take on a whole host of forms

- for plug or mixed flow
- for $n = 1, 2, \dots$
- for $d = 0, 1, 2, 3$

Some of these are given in Chapter 32 of Levenspiel (1996). We do not present them here.

In general we can evaluate \bar{X}_A by solving Eq. 40 with Eqs. 43 and 44. Referring to Fig. 21.8 we see that for case (K) a decreases with time, and so does X_A . For

case \textcircled{L} \mathbf{a} decreases with time so the feed rate must also be lowered so that at any time

$$\frac{F_{A0}}{\mathbf{a}} = f_{A0, \text{initial}} \quad (45)$$

Nearly always we find that case \textcircled{M} is optimum. Here Eq. 43 becomes

$$\frac{W}{F_{A0}} = \frac{1}{k' \mathbf{a} C_{A0}} \int_0^{X_A} \frac{dX_A}{(1 - X_A)^n} \quad (46)$$

constant
constant

so $k' \mathbf{a} C_{A0}$ should remain constant as the temperature is raised. This means that in the regime of *no pore diffusion resistance* we must change T with time such that

$$k' \mathbf{a} = \text{constant} \cdot \cdot \cdot \text{for all liquid systems} \quad (47)$$

$$\frac{k' \mathbf{a}}{T^n} = \text{constant} \cdot \cdot \cdot \text{for } \begin{cases} \text{ideal gases with} \\ \text{\textit{n}th-order reactions} \end{cases} \quad (48)$$

In the regime of *strong resistance to pore diffusion* we must change T with time such that

$$k' \mathbf{a} \mathcal{D}_e = \text{constant} \cdot \cdot \cdot \text{for liquids} \quad (49)$$

$$\frac{k' \mathbf{a} \mathcal{D}_e}{T^{n+1}} = \text{constant} \cdot \cdot \cdot \text{for } \begin{cases} \text{ideal gases and} \\ \text{\textit{n}th-order reactions} \end{cases} \quad (50)$$

Discussion

The overall problem is finding which policy \textcircled{K} \textcircled{L} \textcircled{M} is best. We have the following findings:

- (a) For the longest run time for given \bar{X}_A and for any $\mathbf{a}_{\text{final}}$ if the deactivation is very temperature sensitive compared to reaction, then the optimal policy is a rising temperature with time *so as to keep the conversion from the reactor unchanged*, thus use policy \textcircled{M} , ending the run at the maximum allowable temperature T^* , as shown in Fig. 21.9, see Szepe (1966, 1968, 1971).
- (b) If deactivation is less temperature sensitive than is the reaction use policy \textcircled{K} or \textcircled{L} whichever is more convenient, but make the run at the maximum allowable temperature T^* .
- (c) For deactivations which are concentration dependent the catalyst activity will vary with position in the reactor. The optimum requires that the temperature vary with position along the reactor as well as with time. This is a difficult situation to analyze.

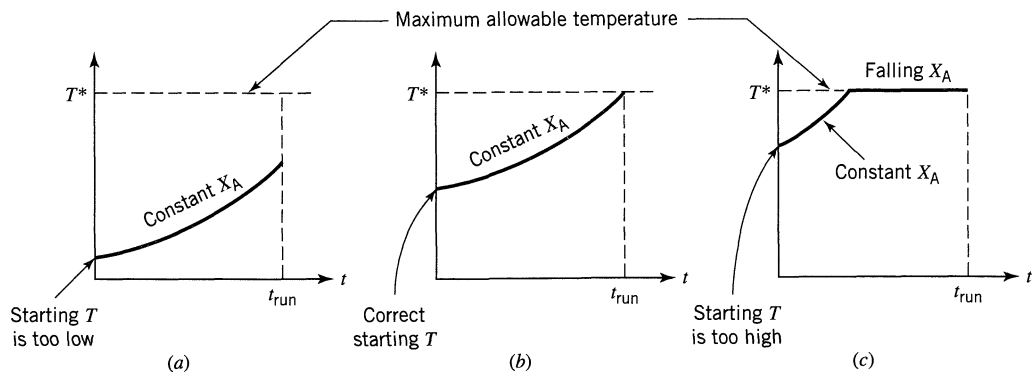


Figure 21.9 These sketches show the correct and incorrect starting temperatures for policy (M).

- (d) For catalysts which deactivate very rapidly packed bed reactors are impractical, and one has to use solid-flow systems. We do not treat these here. Such systems are treated in Chapter 33 of Levenspiel (1996).

EXAMPLE 21.2 DEACTIVATION IN A PACKED BED REACTOR

We plan to run an isomerization of A to R in a packed bed reactor (pure A feed, $F_{A0} = 5$ kmol/hr, $W = 1$ -ton catalyst, $\pi = 3$ atm, $T = 730$ K). The catalyst deactivates so we plan to make 120 day runs, then regenerate the catalyst.

- (a) Plot conversion and activity versus time for the run
 (b) find \bar{X}_A for the 120 day run

The rate of reaction with C_A in mol/m³ is described by

$$-r'_A = 0.2 C_A^2 \mathbf{a} \frac{\text{mol A}}{\text{kg cat} \cdot \text{hr}}$$

and the rate of deactivation is given by

(a) . . . $-\frac{d\mathbf{a}}{dt} = 8.3125 \times 10^{-3}, \quad \text{day}^{-1}$

This expression represents poisoning by a feed impurity.

(b) . . . $-\frac{d\mathbf{a}}{dt} = 10^{-3}(C_A + C_R)\mathbf{a}, \quad \text{day}^{-1}$

This represents poisoning by both reactant and by product, thus pore diffusion resistance does not influence the deactivation rate.

(c) . . . $-\frac{d\mathbf{a}}{dt} = 3.325 \mathbf{a}^2, \quad \text{day}^{-1}$

This represents fairly strong pore diffusion resistance.

(d) . . . $-\frac{d\mathbf{a}}{dt} = 666.5 \mathbf{a}^3, \quad \text{day}^{-1}$

This represents very strong pore diffusion resistance.

SOLUTION

In general for parts (a), (b), (c), and (d) we can write

$$\begin{aligned}
 -r'_A &= 0.2 C_A^2 \mathbf{a} \frac{\text{mol A}}{\text{kg cat} \cdot \text{hr}} \\
 C_{A0} &= \frac{p_{A0}}{RT} = \frac{3 \text{ atm}}{\left(82.06 \times 10^{-6} \frac{\text{m}^3 \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (730 \text{ K})} = 50 \frac{\text{mol}}{\text{m}^3} \\
 \tau' &= \frac{WC_{A0}}{F_{A0}} = \frac{(1000 \text{ kg}) \left(50 \frac{\text{mol}}{\text{m}^3}\right)}{\left(5000 \frac{\text{mol}}{\text{hr}}\right)} = 10 \frac{\text{kg} \cdot \text{hr}}{\text{m}^3} \\
 &= \int_{C_{A0}}^{c_A} \frac{dC_A}{0.2 C_A^2 \mathbf{a}} = \frac{1}{0.2 \mathbf{a}} \left(\frac{1}{C_A} - \frac{1}{C_{A0}} \right)
 \end{aligned}$$

or on rearranging

$$X_A = 1 - \frac{C_A}{C_{A0}} = \frac{100 \mathbf{a}}{1 + 100 \mathbf{a}} \quad (\text{i})$$

Let us now replace the activity term in Eq. (i).

Part (a)

$$-\int_1^{\mathbf{a}} d\mathbf{a} = 8.3125 \times 10^{-3} \int_0^t dt$$

or $\mathbf{a} = 1 - 8.3125 \times 10^{-3} t \quad (\text{ii})$

Replacing Eq. (ii) in Eq. (i) and evaluating X_A at various values of t gives the topmost curve shown in Fig. E21.2.

Part (b) Separating and integrating $-\frac{d\mathbf{a}}{dt} = 10^{-3}(C_A + C_R)\mathbf{a}$ gives

$$\int_{\mathbf{a}}^1 \frac{d\mathbf{a}}{\mathbf{a}} = 0.05 \int_0^t dt$$

or $\mathbf{a} = e^{-0.05 t} \quad (\text{iii})$

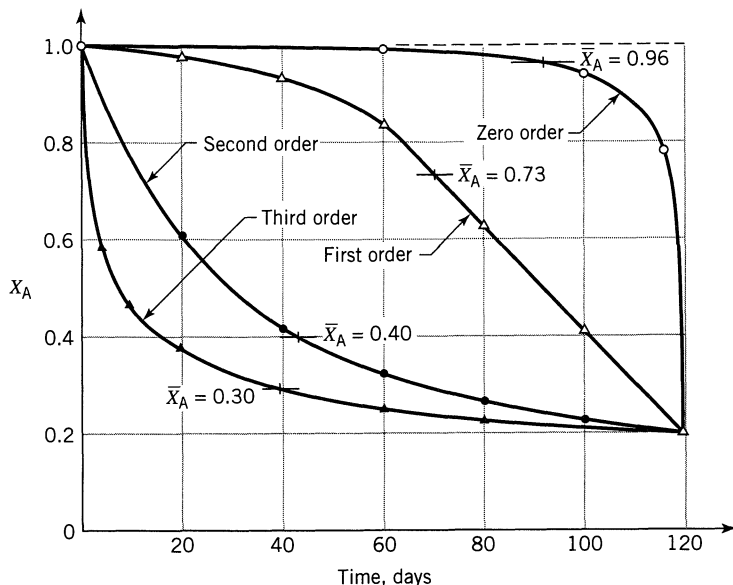


Figure E21.2 Decrease in conversion as a function of time for various deactivation orders.

Replacing Eq. (iii) in Eq. (i) and evaluating X_A at various t values gives the corresponding curve in Fig. E21.2.

Part (c) Separating and integrating $-\frac{da}{dt} = 3.325 a^2$ gives

$$\int_1^a \frac{da}{a^2} = 3.325 \int_0^t dt$$

or
$$a = \frac{1}{1 + 3.325 t} \quad (\text{iv})$$

Again, replacing Eq. (iv) in (i) gives the corresponding curve in Fig. E21.2.

Part (d) Separating and integrating $-\frac{da}{dt} = 666.5 a^3$ gives

$$a = \frac{1}{\sqrt{1 + 1333 t}} \quad (\text{v})$$

Combining Eq. (v) in (i) gives the lowest curve shown in Fig. E21.2.

From Fig. E21.2 we find by graphical integration that for the 120-day period, $X_{A, \text{start}} = 0.99$, $X_{A, \text{end}} = 0.20$ for

$d = 0$ the mean conversion	$\underline{\underline{\bar{X}_A = 0.96}}$
$d = 1$ the mean conversion	$\underline{\underline{\bar{X}_A = 0.73}}$
$d = 2$ the mean conversion	$\underline{\underline{\bar{X}_A = 0.40}}$
$d = 3$ the mean conversion	$\underline{\underline{\bar{X}_A = 0.30}}$

It also clearly shows how different is the progress of the reaction with the different orders of deactivation.

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PROBLEMS

The kinetics of a particular catalytic reaction $A \rightarrow R$ are studied at temperature T in a basket reactor (batch-solids and mixed flow of gas) in which the gas composition is kept unchanged, despite deactivation of the catalyst. What can you say about the rates of reaction and deactivation from the results of the following runs? Note, to keep the gas concentration in the reactor unchanged the flow rate of reactant had to be lowered to about 5% of the initial value.

21.1. . . . Run 1

$C_{A0} = 1$ mol/liter	t , time from start of run, hr	0	1	2	3
$X_A = 0.5$	τ' , gm cat · min/liter	1	e	e ²	e ³

Run 2

$C_{A0} = 2$ mol/liter	t , hr	0	1	2	3
$X_A = 0.667$	τ' , gm cat · min/liter	2	2e	2e ²	2e ³

21.2. . . . Run 1

$C_{A0} = 2$ mol/liter	t , hr	0	1	2	3
$X_A = 0.5$	τ' , gm · min/liter	1	e	e ²	e ³

<u>Run 2</u>							
$C_{A0} = 20$ mol/liter	t , hr		0	0.5	1	1.5	
$X_A = 0.8$	τ' , gm · min/liter		1	e	e ²	e ³	

- 21.3.** In an automobile's catalytic converter, CO and hydrocarbons present in the exhaust gases are oxidized. Unfortunately the effectiveness of these units decreases with use. The phenomenon was studied by Summers and Hegedus in *J. Catalysis*, **51**, 185 (1978) by means of an accelerated aging test on a palladium impregnated porous pellet packed bed converter. From the reported data on hydrocarbon conversion shown below, develop an expression to represent the deactivation rate of this catalyst.

t , hr		5	10	15	20	25	30	35	40
$X_{\text{hydrocarbon}}$		0.57	0.53	0.52	0.50	0.48	0.45	0.43	0.41

This problem was prepared by Dennis Timberlake.

- 21.4.** A recycle reactor with very high recycle ratio is used to study the kinetics of a particular irreversible catalytic reaction, $A \rightarrow R$. For a constant flow rate of feed ($\tau' = 2$ kg · sec/liter) the following data are obtained:

Time after start of operation, hr		1	2	4
X_A		0.889	0.865	0.804

The progressive drop in conversion suggests that the catalyst deactivates with use. Find rate equations for the reaction and for the deactivation which fit these data.

- 21.5.** The reversible catalytic reaction



proceeds with decaying catalyst in a batch reactor (batch-solids, batch-fluid). What can you say of the kinetics of reaction and deactivation from the following data:

t , hr		0	0.25	0.5	1	2	(∞)
C_A , mol/liter		1.000	0.901	0.830	0.766	0.711	0.684

- 21.6.** The following data on an irreversible reaction are obtained with decaying catalyst in a batch reactor (batch-solids, batch-fluid) What can you say about the kinetics

C_A		1.000	0.802	0.675	0.532	0.422	0.363
t , hr		0	0.25	0.5	1	2	(∞)

- 21.7.** With fresh catalyst the packed bed reactor is run at 600K. Four weeks later when the temperature reaches 800K the reactor is shut down to reactivate the catalyst. In addition, at any instant the reactor is isothermal.

Assuming optimal operations what is the activity of the catalyst at the time of reactivation.

Data: The rate of reaction with fresh catalyst is

$$-r_A = kC_A^2, \quad k = k_0 e^{-7200/T}$$

The rate of deactivation is unknown.

Our reaction $A \rightarrow R$ proceeds isothermally in a packed bed of large, slowly deactivating catalyst particles and is performing well in the strong pore diffusion regime. With fresh pellets conversion is 88%; however, after 250 days conversion drops to 64%. How long can we run the reactor before conversion drops to

21.8. . . . 50%?

It has been suggested that we replace these large particles with very small particles so as to operate wholly in the diffusion-free regime and thus use less catalyst for the same conversions. How long a run time can we expect before the conversion drops from 88% to 64% if the catalyst is used in

21.9. . . . a packed bed reactor?

21.10. . . . a fluidized solids reactor (assume mixed flow of fluid)?

21.11. Under conditions of strong pore diffusion the reaction $A \rightarrow R$ proceeds at 700°C on a slowly deactivating catalyst by a first-order rate

$$-r'_A = 0.030 C_A a, \quad [\text{mol/gm} \cdot \text{min}]$$

Deactivation is caused by strong absorption of unavoidable and irremovable trace impurities in the feed, giving third-order deactivation kinetics, or

$$-\frac{da}{dt} = 3a^3, \quad [1/\text{day}]$$

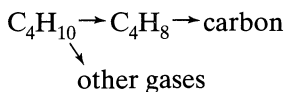
We plan to feed a packed bed reactor ($W = 10$ kg) with $v = 100$ liters/min of fresh A at 8 atm and 700°C until the catalyst activity drops to 10% of the fresh catalyst, then regenerate the catalyst and repeat the cycle,

(a) What is the run time for this operation?

(b) What is the mean conversion for the run?

21.12. In catalytic dehydrogenation of hydrocarbons the catalyst activity decays with use because of carbon deposition on the active surfaces. Let us study this process in a specific system.

A gaseous feed (10% C₄H₁₀ - 90% inerts, $\pi = 1$ atm, $T = 555^\circ\text{C}$) flows ($\tau' = 1.1$ kg·hr/m³) through a packed bed of alumina-chromia catalyst. The butane decomposes by a first-order reaction



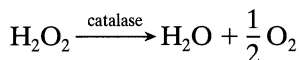
and the behavior with time is as follows:

t , hr	0	1	2	3	4	5
X_A	0.89	0.78	0.63	0.47	0.34	0.26

Examination of the 0.55-mm pellets shows the same extent of carbon deposition at the entrance and the exit of the reactor, suggesting concentration independent deactivation. Develop rate equations for reaction and deactivation.

This problem was devised from the information given by Kunugita et al., *J. Chem. Eng. (Japan)*, **2**, 75 (1969).

The enzyme catalase effectively decomposes hydrogen peroxide



and the kinetics of this reaction are to be evaluated from an experiment in which dilute H₂O₂ flows through a packed bed of kieselguhr particles impregnated with immobilized enzyme.

From the following data, reported by Krishnaswamy and Kitterell, *AIChE J.*, **28**, 273 (1982), develop rate expressions to represent this decomposition, both in the diffusion free regime and in the strong pore diffusion regime, for the catalyst at hand. Note that the conversion decreases with time in all runs showing that the catalyst deactivates with use.

21.13. . . . run E (modified)

	Elapsed Time, hr	X_A
	0	0.795
	1.25	0.635
$\tau' = 4100$ kg cat·s/m ³	2.0	0.510
$\bar{d}_p = 72 \times 10^{-6}$ m	3.0	0.397
$\rho_s = 630$ kg/m ³ cat	4.25	0.255
$\mathcal{D}_e = 5 \times 10^{-10}$ m ² /m cat·s	5.0	0.22
	6.0	0.15
	7.0	0.104

21.14. . . . run B

	Elapsed Time, hr	X_A
	0.25	0.57
	1.0	0.475
$\tau' = 4560 \text{ kg cat} \cdot \text{s}/\text{m}^3$	2.0	0.39
$\bar{d}_p = 1.45 \times 10^{-3} \text{ m}$	3.0	0.30
$\rho_s = 630 \text{ kg}/\text{m}^3 \text{ cat}$	4.0	0.23
$\mathcal{D}_e = 5 \times 10^{-10} \text{ m}^2/\text{s}$	5.0	0.186
	6.0	0.14
	7.0	0.115

21.15. At 730K the isomerization of A to R (rearrangement of atoms in the molecule) proceeds on a slowly deactivating catalyst with a second-order rate

$$-r'_A = k' C_A^2 \mathbf{a} = 200 C_A^2 \mathbf{a}, \text{ [mol A/hr} \cdot \text{gm cat]}$$

Since reactant and product molecules are similar in structure, deactivation is caused by both A and R. With diffusional effects absent, the rate of deactivation is found to be

$$-\frac{d\mathbf{a}}{dt} = k_d(C_A + C_R)\mathbf{a} = 10(C_A + C_R)\mathbf{a}, \quad [\text{day}^{-1}]$$

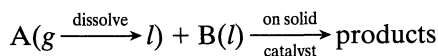
We plan to operate a packed bed reactor containing $W = 1$ metric ton of catalyst for 12 days using a steady feed of pure A, $F_{A0} = 5 \text{ kmol/hr}$ at 730 K and 3 atm ($C_{A0} = 0.05 \text{ mol/liter}$).

- First evaluate $-d\mathbf{a}/dt$, τ' , and then the general expression for $1 - X_A$.
- What is the conversion at the start of the run?
- What is the conversion at the end of the run?
- What is the average conversion over the 12-day run?

Chapter 22

G/L Reactions on Solid Catalysts: Trickle Beds, Slurry Reactors, and Three-Phase Fluidized Beds

These multiphase reactions are of the type

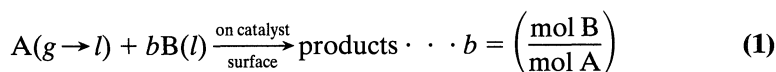


and they can be run in a number of ways, as shown in Fig. 22.1. The packed bed contactors use large solid particles, the slurry reactors very fine suspended solids, while the fluidized bed can use either depending on the flow rates.

Flow pattern: Overall, all other things equal (which they are not) countercurrent plug flow is the most desirable flow pattern while the worst of all in terms of driving forces is mixed/mixed flow.

22.1 THE GENERAL RATE EQUATION

Consider the following reaction and stoichiometry



$$\left. \begin{array}{l} -r_A''' = k_A''' C_A C_B \\ -r_B''' = k_B''' C_A C_B \end{array} \right\} \text{where} \quad \left. \begin{array}{l} -r_A''' = -r_B'''/b \cdot \cdot \cdot \text{mol A/m}^3 \text{ cat} \cdot \text{s} \\ k_A''' = k_B'''/b \cdot \cdot \cdot \text{m}^6/\text{mol B} \cdot \text{m}^3 \text{ cat} \cdot \text{s} \end{array} \right\}$$

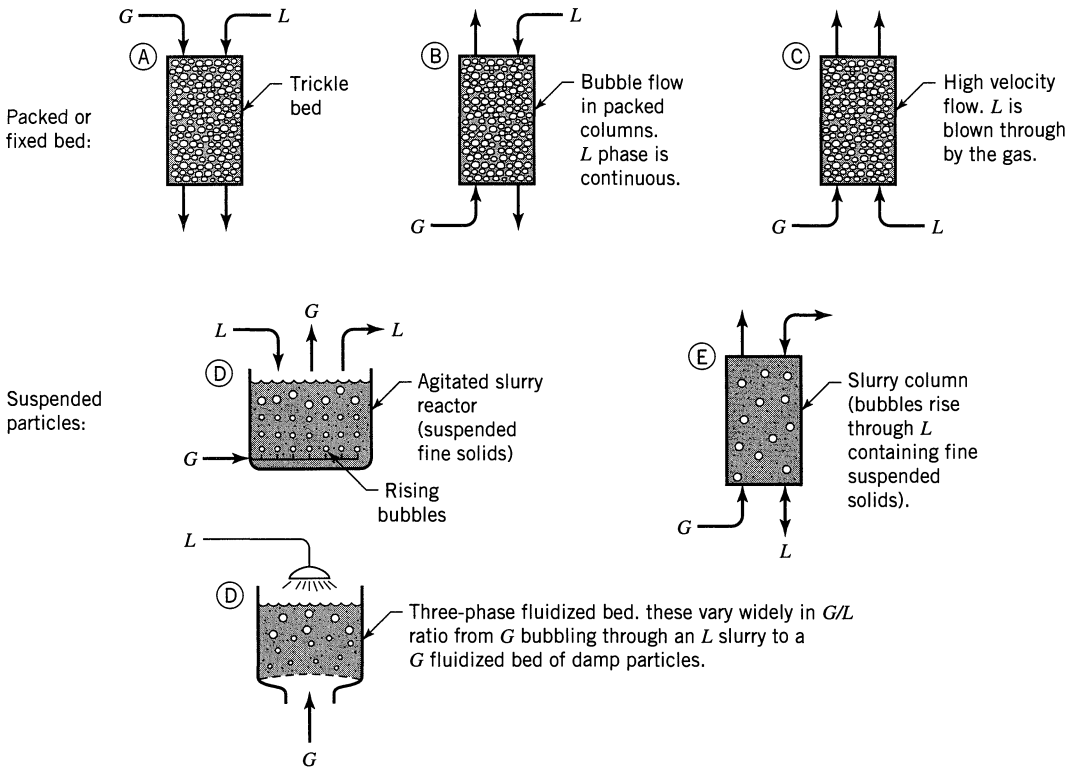
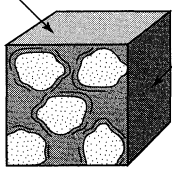


Figure 22.1 Various ways of running G/L reactions catalyzed by solids.

Gas reactant must first dissolve in the L , then both reactants must diffuse or move to the catalyst surface for reaction to occur. Thus the resistance to transfer across the G/L interface and then to the surface of solid both enter the general rate expression.

To develop the rate equation, let us draw on the two-film theory, and let us use the following nomenclature:

Typical element of volume contains G , L , and S .



$$\left. \begin{aligned}
 H_A &= \frac{P_A}{C_A}, \text{ Henry's law constant } [\text{Pa} \cdot \text{m}^3/\text{mol}] \\
 a_i &= \frac{\text{gas-liquid interfacial area}}{\text{volume of reactor}} \\
 a_c &= \frac{\text{external surface of particles}}{\text{volume of reactor}} \text{ for } \frac{6f_s}{d_p} \\
 f_s &= \frac{\text{volume of particles}}{\text{volume of reactor}}, \text{ called solid loading} \\
 f_l &= \frac{\text{volume of liquid}}{\text{volume of reactor}}, \text{ called liquid holdup}
 \end{aligned} \right\}$$

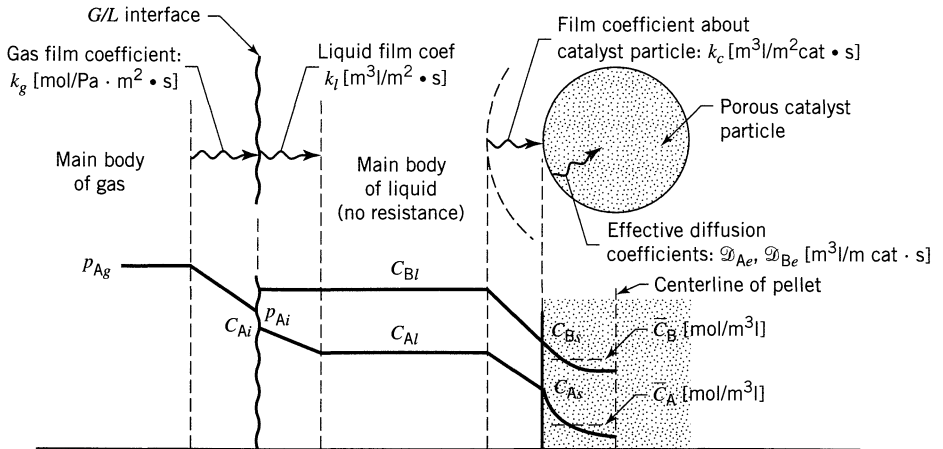


Figure 22.2 Sketch showing the resistances involved in the G/L reaction on a catalyst surface.

Graphically we show the resistances as in Fig. 22.2. We can then write the following general rate equations:

For A:

$$-r_A''' = \frac{1}{\frac{1}{k_{Ag}a_i} + \frac{H_A}{k_{Al}a_i} + \frac{H_A}{k_{Ac}a_c} + \frac{H_A}{(k_A''' \bar{C}_B) \epsilon_A f_s}} p_{Ag} \quad (2)$$

these rates are related by $-r_A''' = \frac{-r_B'''}{b}$

effectiveness factor for the first-order reaction of A with rate constant $(k_A''' \bar{C}_B)$

Henry's law constant $H_A = p_A' / C_A$

For B:

$$-r_B''' = \frac{1}{\frac{1}{k_{Bc}a_c} + \frac{1}{(k_B''' \bar{C}_A) \epsilon_B f_s}} C_{B_I} \quad (3)$$

mol B/m³ reactor-s

effectiveness factor for the first order reaction of B with rate constant $(k_B''' \bar{C}_A)$

Now either Eq. 2 or Eq. 3 should give the rate of reaction. Unhappily, even with all the system parameters known (k, a, f , etc.) we still cannot solve these expressions without trial and error because \bar{C}_B is not known in Eq. 2 and \bar{C}_A is not known in Eq. 3. However, we usually encounter either of two simplifying extremes, which are very useful.

Extreme 1: $C_{B_I} \gg C_{A_I}$. In systems with pure liquid B and slightly soluble gas A we can take

$$C_{B_s} = \bar{C}_{B, \text{within pellet}} = C_{B_I} \dots \text{same value everywhere}$$

With C_B constant the reaction becomes first order with respect to A overall and the above rate expressions with their required trial and error all reduce to one directly solvable expression

$$-r_A''' = \frac{1}{\frac{1}{k_{Ag}a_i} + \frac{H_A}{k_{Al}a_i} + \frac{H_A}{k_{Ac}a_c} + \frac{H_A}{(k_A'''C_B)\mathcal{E}_A f_s}} p_{Ag} \quad (4)$$

first-order rate constant for A

Extreme 2: $C_{Bl} \ll C_{Al}$. In systems with dilute liquid reactant B, highly soluble A, and high pressure, we can take

$$C_{Al} = \frac{p_{Ag}}{H_A} \cdot \cdot \cdot \text{throughout the reactor}$$

The rate then becomes first order with respect to B and reduces to

$$-r_B''' = \frac{1}{\frac{1}{k_{Bc}a_c} + \frac{1}{\left(\frac{k_B'''p_{Ag}}{H_A}\right)\mathcal{E}_B f_s}} C_{Bl} \quad (5)$$

first-order rate constant which is used to calculate \mathcal{E}_B

How to Test Whether these Extremes Apply, and Other Comments

- (a) By the unequal signs \gg or \ll we mean two or three times as large.
- (b) More generally compare the rates calculated from Eqs. 4 and 5 and use the smaller one. Thus,
 - if $r_{Eq.4}''' \ll r_{Eq.5}'''$, then C_{Bl} is in excess and extreme 1 applies.
 - if $r_{Eq.4}''' \gg r_{Eq.5}'''$, then Eq. 5 gives the rate of reaction.
- (c) Nearly always does one or other of the extremes apply.

22.2 PERFORMANCE EQUATIONS FOR AN EXCESS OF B

All types of contactors—trickle beds, slurry reactors, and fluidized beds—can be treated at the same time. What is important is to recognize the flow patterns of the contacting phases and which component, A or B, is in excess. First consider an excess of B. Here the flow pattern of liquid is not important. We only have to consider the flow pattern of the gas phase. So we have the following cases.

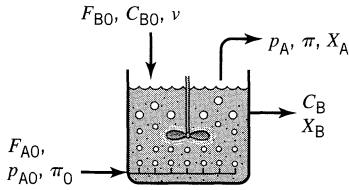


Figure 22.3 Gas bubbles swim around the bed; hence, gas is in mixed flow.

Mixed Flow G/Any Flow L (excess of B)

Here we have the situation shown in Fig. 22.3. A material balance about the whole reactor gives

$$F_{A0}X_A = \frac{1}{b}F_{B0}X_B = (-r_A^m)V_r$$

I	II	III
rate of loss of A	rate of loss of B	rate of reaction

(6)

Solution is straightforward. Just combine I and III or II and III.

Plug Flow G/Any Flow L (excess of B)

With a large excess of B, C_B stays roughly constant throughout the reactors shown in Fig. 22.4 even though the concentration of A in the gas phase changes as the gas flows through the reactors. For a thin slice of reactor as shown in Fig.

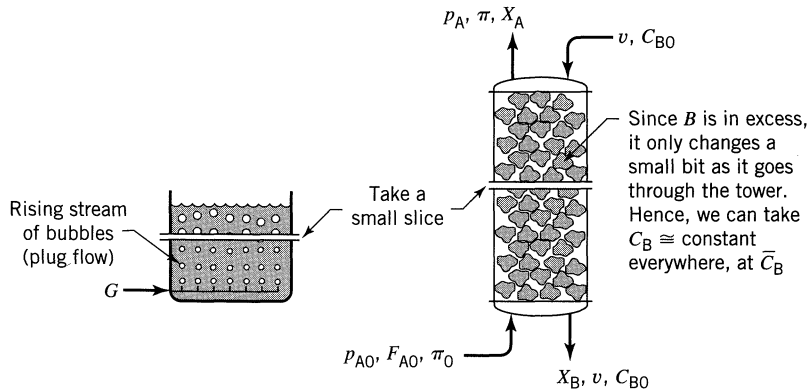


Figure 22.4 Gas rises in plug flow in these two contactors.

22.4, we can write

$$F_{A0} dX_A = (-r_A''') dV_r \quad (7)$$

where

$$1 - X_A = \frac{p_A(\pi_0 - p_{A0})}{p_{A0}(\pi - p_A)} \xrightarrow[\text{only}]{\text{dilute}} \frac{p_A \pi_0}{p_{A0} \pi} \xrightarrow[\pi = \text{const.}]{\text{dilute}} \frac{p_A}{p_{A0}} \quad (8)$$

and

$$-dX_A = \frac{\pi(\pi_0 - p_{A0}) dp_A}{p_{A0}(\pi - p_A)^2} \xrightarrow[\text{only}]{\text{dilute}} \frac{\pi_0 dp_A}{p_{A0} \pi} \xrightarrow[\pi = \text{const.}]{\text{dilute}} \frac{dp_A}{p_{A0}} \quad (9)$$

Overall, around the whole reactor

$$\frac{V_r}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{(-r_A''')} \quad \dots \text{ with } \dots \quad F_{A0} X_A = \frac{F_{B0}}{b} X_B \quad (10)$$

use \bar{C}_B here
 $\frac{v}{b} C_{B0} - C_B$

Mixed Flow G/Batch L (excess of B)

With throughflow of L its composition stays roughly constant when B is in excess. However, with a batch of L its composition slowly changes with time as B is being used up, but B is roughly constant in the reactor at any time, as shown in Fig. 22.5. Here the material balance at any time t becomes

$$F_{A0} X_{A, \text{exit}} = \frac{V_l}{b} \left(-\frac{dC_B}{dt} \right) = (-r_A''') V_r \quad (11)$$

I
II
III

\swarrow mol A/m³ reactor · s

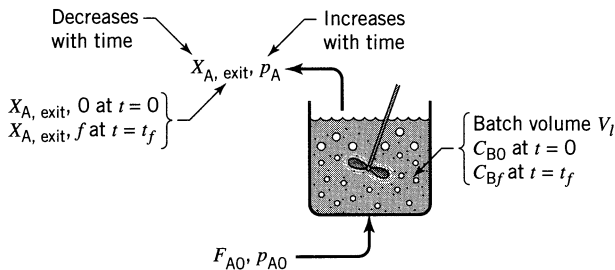


Figure 22.5 Gas bubbles through a batch of liquid, B in excess.

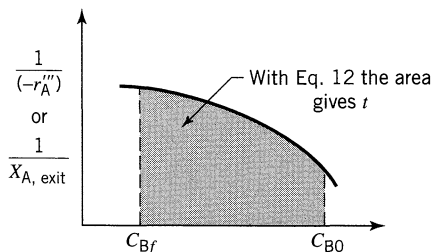


Figure 22.6 Evaluation of the reaction time for a batch of liquid.

The general procedure for finding the processing time is as follows:

Pick a number of C_B values	From III calculate	From I and II calculate
C_{B0}	$(-r_A)_0$	$X_{A, \text{exit}, 0}$
—	—	—
C_{Bf}	$(-r_A)_f$	$X_{A, \text{exit}, f}$

Then from II and III, or I and II solve for t

$$t = \frac{V_l}{bV_r} \int_{C_{Bf}}^{C_{B0}} \frac{dC_B}{(-r_A''')} = \frac{V_l}{bF_{A0}} \int_{C_{Bf}}^{C_{B0}} \frac{dC_B}{X_{A, \text{exit}}} \quad (12)$$

as shown in Fig. 22.6.

Plug Flow G/Batch L (excess of B)

As with the previous case, C_B changes slowly with time; however, any element of gas sees the same C_B as it flows through the reactor, as shown in Fig. 22.7.

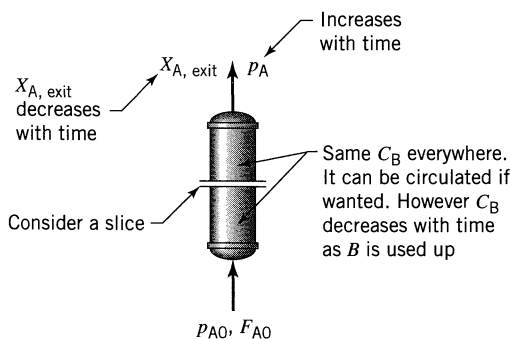


Figure 22.7 Plug flow of gas through a batch of liquid.

Consider a slice of contactor in a short time interval in which C_B is practically unchanged. Then a material balance gives

$$F_{A0} dX_A = (-r_A''''') dV_r \quad (13)$$

Integrating gives the exit conversion of A

$$\boxed{\frac{V_r}{F_{A0}} = \int_0^{X_{A, \text{exit}}} \frac{dX_A}{(-r_A''''')}} \quad (14)$$

Considering B we may now write

$$F_{A0} X_{A, \text{exit}} = \frac{V_l}{b} \left(-\frac{dC_B}{dt} \right), \quad \left[\frac{\text{mol}}{\text{s}} \right]$$

and on integrating we find the processing time to be

$$\boxed{t = \frac{V_l}{b F_{A0}} \int_{C_{Bf}}^{C_{B0}} \frac{dC_B}{X_{A, \text{exit}}}} \quad (15)$$

The procedure is as follows:

Choose C_B	Solve Eq. 14 to Give $X_{A, \text{exit}}$
C_{B0}	$X_{A, \text{exit}} (t = 0)$
—	—
—	—
C_{Bf}	$X_{A, \text{exit}} (\text{at } t)$

Then solve Eq. 15 graphically to find the time as shown in Fig. 22.8.

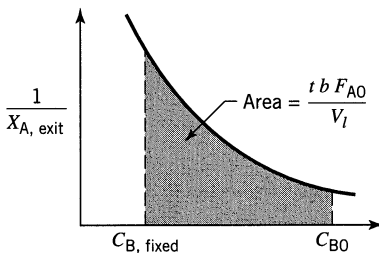


Figure 22.8 Evaluation of the reaction time in a batch L reactor.

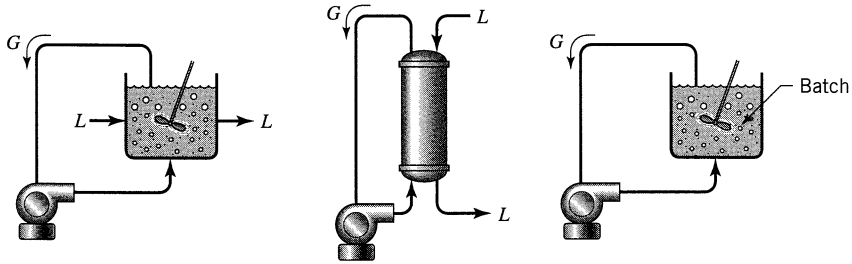
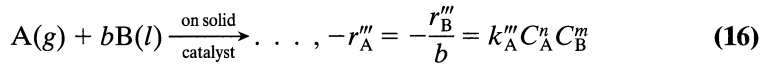


Figure 22.9 Pure gaseous A can be recompressed and recycled.

Special Case of Pure Gaseous A (excess of B)

One often encounters this situation, especially in hydrogenations. Here one usually recycles the gas, in which case p_A and C_A stay unchanged; hence, the preceding equations for both batch and flow systems simplify enormously, see Fig. 22.9. When solving problems, it is suggested that one write down the basic material balances and then carefully see what simplifications apply . . . is p_A constant? . . . and so on.

Comments The rate expressions used so far have been first order with respect to A and first order with respect to B. But how do we deal with more general rate forms, for example:



To be able to combine the chemical step with the mass transfer steps in simple fashion, we must replace the above awkward rate equation with a first-order approximation, as follows:

$$-r_A''' = k_A''' C_A^n C_B^m \Rightarrow -r_A''' = [(k_A''' \bar{C}_B^m) \bar{C}_A^{n-1}] C_A \quad (17)$$

mean values at
 locations where
 reaction occurs

This approach is not completely satisfactory, but it is the best we can do. Thus, instead of Eq. 4, the rate form to be used in all the performance expressions will be

$$-r_A''' = \frac{1}{\frac{1}{H_A k_{Ag} a_i} + \frac{1}{k_{Ai} a_i} + \frac{1}{k_{Ac} a_c} + \frac{1}{(k_A''' \bar{C}_B^m \bar{C}_A^{n-1}) \mathcal{E}_{Afs}}} \frac{p_A}{H_A} \quad (18)$$

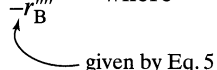
22.3 PERFORMANCE EQUATIONS FOR AN EXCESS OF A

Here the flow pattern of gas is of no concern. All we need to worry about is the flow pattern of liquid.

Plug Flow *L*/Any Flow *G* (tower and packed bed operations)

Making the material balances gives on integration

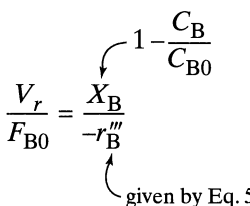
$$\frac{V_r}{F_{B0}} = \int_0^{X_B} \frac{dX_B}{-r_B^m} \quad \text{where} \quad 1 - X_B \cong \frac{C_B}{C_{B0}} \quad (19)$$



Mixed Flow *L*/Any Flow *G* (tank operations of all types)

Here the performance equation is simply

$$\frac{V_r}{F_{B0}} = \frac{X_B}{-r_B^m} \quad (20)$$



Batch *L*/Any Flow *G*

Noting that $C_A \cong \text{constant}$ throughout time (because it is in excess), the performance equation for B becomes

$$-\frac{dC_B}{dt} = -r_B = \frac{V_r}{V_l} (-r_B^m) \cdot \cdot \cdot \quad \text{or} \quad \cdot \cdot \cdot t = \int_0^t \frac{dC_B}{-r_B} \quad (21)$$

22.4 WHICH KIND OF CONTACTOR TO USE

The selection of a good contactor depends on

- where the controlling resistance lies in the rate expression,
- the advantages of one contacting pattern over another, and
- the difference in auxiliary equipment needed.

The overall economics which accounts for these three factors will determine which set up and reactor type is best. Let us briefly look at these factors in turn.

The Rate: We should favor the contactor which favors the weakest step in the rate. For example,

- if the main resistance lies in the G/L film, use a contactor with large interfacial surface area.
- if the resistance lies at the L/S boundary, use a large exterior surface of solid, thus large f_s or small particles.
- if the resistance to pore diffusion intrudes, use tiny particles.

From prediction we can find the weakest step by inserting all transfer coefficients (k_g, k_l, \dots) and system parameters (a_i, a_s, \dots) into the rate equation and then see which resistance term dominates. Unfortunately, the values for these quantities usually are not well known.

From experiment, we can change one or another factor in the rate expression; for example,

- solid loading (this changes f_s alone, hence, only changes the last resistance term in the rate expression)
- size of catalyst particle (affects both \mathcal{E} and a_s)
- intensity of agitation of the liquid (affects the mass transfer terms in the rate)
- π, C_B, p_A .

This should tell which factor strongly affects the rate and which does not.

Boosting the weakest step in the rate by a proper choice of particle size, solid loading and reactor type can strongly affect the overall economics of the process.

Contacting: Plug flow of the limiting component, the one which is not in excess, is certainly better than mixed flow. However, except for very high conversions this factor is of minor importance.

Supporting equipment: Slurry reactors can use very fine catalyst particles, and this can lead to problems of separating catalyst from liquid. Trickle beds don't have this problem, and this is the big advantage of trickle beds. Unfortunately, these large particles in trickle beds mean much lower reaction rates. With regard to rate, the trickle bed can only hold its own

- for very slow reactions on porous solids where pore diffusion limitations do not appear, even for large particles and
- for very fast reactions on nonporous catalyst-coated particles.

Overall, the trickle bed is simpler, the slurry reactor usually has a higher rate, and the fluidized bed is somewhere in between.

22.5 APPLICATIONS

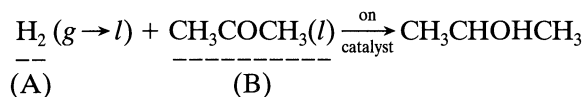
Here is a short list of applications of these reactors.

- The catalytic hydrogenation of petroleum fractions to remove sulfur impurities. Hydrogen is very soluble in the liquid; high pressure is used while the impurity is present in the liquid in low concentration. All these factors tend to lead to extreme 2 (excess of A).

- The catalytic oxidation of liquid hydrocarbons with air or oxygen. Since oxygen is not very soluble in the liquid, while the hydrocarbon could well be present in high concentration we could end up in extreme 1 (excess of B).
- The removal of dissolved organics from industrial waste water by catalytic oxidation as an alternative to biooxidation. Here oxygen is not very soluble in water, but the organic waste is also present in low concentration. It is therefore not clear in what regime the kinetics lie. The catalytic oxidation of phenol is an example of such an operation.
- The removal of airborne pollutants by adsorption and/or reaction. These operations usually lead to extreme 1 (excess of B).
- The illustrative examples and many of the problems which follow are adapted from or are extensions of problems prepared by Ramachandran and Choudhary (1980).

EXAMPLE 22.1 HYDROGENATION OF ACETONE IN A PACKED BUBBLE COLUMN

Aqueous acetone ($C_{B0} = 1000 \text{ mol/m}^3 \text{ l}$, $v_l = 10^{-4} \text{ m}^3 \text{ l/s}$) and hydrogen (1 atm, $v_g = 0.04 \text{ m}^3 \text{ g/s}$, $H_A = 36845 \text{ Pa} \cdot \text{m}^3 \text{ l/mol}$) are fed to the bottom of a long, slender column (5-m high, 0.1-m^2 cross section) packed with porous Raney nickel catalyst ($d_p = 5 \times 10^{-3} \text{ m cat}$, $\rho_s = 4500 \text{ kg/m}^3 \text{ cat}$, $f_s = 0.6$, $\mathcal{D}_e = 8 \times 10^{-10} \text{ m}^2 \text{ l/m cat} \cdot \text{s}$) and kept at 14°C , as shown in Fig. E22.1. At these conditions acetone is hydrogenated to propanol according to the reaction



with rate given by


$$-r'_A = -r'_B = k' C_A^{1/2} C_B^0 \quad \text{and} \quad \dots k' = 2.35 \times 10^{-3} \frac{\text{m}^3 \text{l}}{\text{kg} \cdot \text{s}} \left(\frac{\text{mol}}{\text{m}^3 \text{l}} \right)^{1/2}$$

What will be the conversion of acetone in this unit?

Additional Data

The mass transfer rate constants are estimated to be

$$(k_{A_i} a_i)_{\text{g+l}} = 0.02 \frac{\text{m}^3 \text{l}}{\text{m}^3 \text{r} \cdot \text{s}} \quad k_{Ac} a_c = 0.05 \frac{\text{m}^3 \text{l}}{\text{m}^3 \text{r} \cdot \text{s}}$$


 the sum of the gas + liquid film conductances

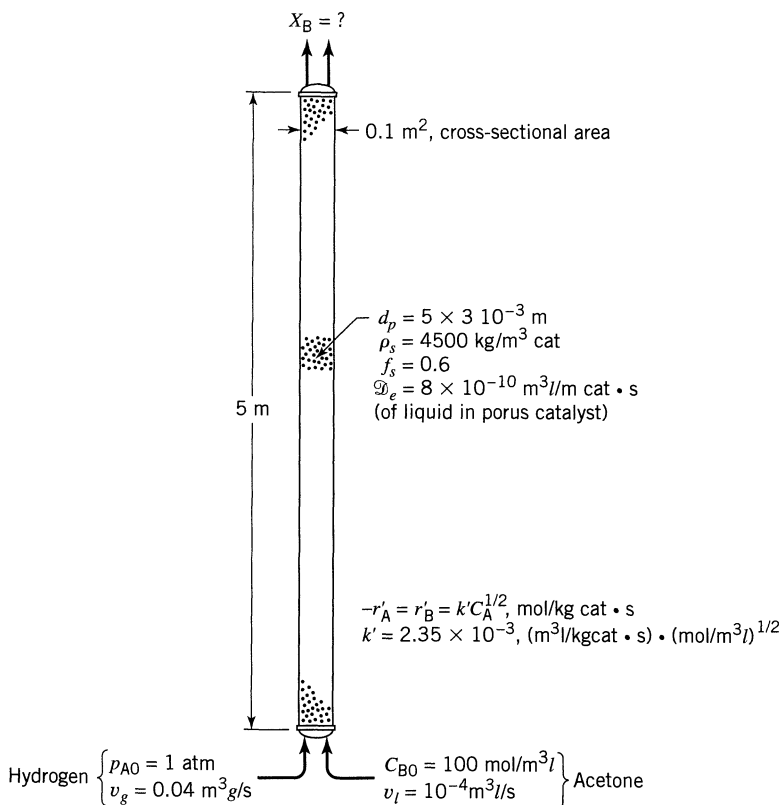


Figure E22.1

SOLUTION

Before rushing to our equations to do the appropriate integrations needed for plug flow, let us consider the situation

- $C_{B0} = 1000$ while C_A is given by Henry's law as

$$C_A = \frac{p_A}{H_A} = \frac{101\,325}{36\,845} = 2.75 \text{ mol/m}^3 \text{ l}$$

Comparing values shows that $C_B \gg C_A$; hence, we are in extreme 1 (excess of B).

- Next, we are dealing with pure hydrogen; thus, p_A is constant throughout the packed column. And since the rate is only dependent on C_A and not on C_B , this means that the rate of reaction is constant throughout the column.

Let us next look at the rate. From Eq. 18.28 we have for a half order reaction

$$M_T = L \sqrt{\frac{n+1}{2} \cdot \frac{k' C_A^{n-1} \rho_s}{\mathcal{D}_e}}$$

$$= \frac{5 \times 10^{-3}}{6} \sqrt{\frac{1.5 \cdot (2.35 \times 10^{-3})(2.75)^{-1/2}(4500)}{8 \times 10^{-10}}} = 64.4$$

$$\therefore \mathcal{E} = \frac{1}{64.4} = 0.0155$$

Replacing all known values into Eq. 18 gives

$$-r_A''' = \frac{1}{\frac{1}{0.02} + \frac{1}{0.05} + \frac{1}{(2.35 \times 10^{-3})(1)(2.75)^{-1/2}(0.0155)(0.6)(4500)}} \frac{101\,325}{36\,845}$$

↙ 58%
↙ 23%
↙ 19%

$$= 0.0317 \text{ mol/m}^3 \text{ r} \cdot \text{s}$$

Next, to the material balance of Eq. 11. With constant rate this becomes

$$\frac{F_{A0} X_A}{b} = \frac{F_{B0} X_B}{b} = (-r_A''') V_r$$

↙ not particularly useful
↙ use this term in which $F_{B0} = v_r C_{B0} = 10^{-4}(1000) = 0.1 \text{ mol/s}$

Thus on rearranging

$$X_B = \frac{b(-r_A''') V_r}{F_{B0}} = \frac{(1)(0.0317)(5 \times 0.1)}{0.1}$$

$$= 0.158, \text{ or } \underline{\underline{16\% \text{ conversion}}}$$

EXAMPLE 22.2 HYDROGENATION OF A BATCH OF BUTYNYEDIOL IN A SLURRY REACTOR

Hydrogen gas is bubbled into an agitated tank ($V_r = 2 \text{ m}^3 \text{ r}$) containing liquid butynediol ($C_{B0} = 2500 \text{ mol/m}^3 \text{ l}$) plus a dilute suspension of palladium-impregnated porous catalyst pellets ($d_p = 5 \times 10^{-5} \text{ m cat}$, $\rho_s = 1450 \text{ kg/m}^3 \text{ cat}$, $\mathcal{D}_e = 5 \times 10^{-10} \text{ m}^2 \text{ l/m cat} \cdot \text{s}$, $f_s = 0.0055$). Hydrogen dissolves in the liquid ($H_A =$

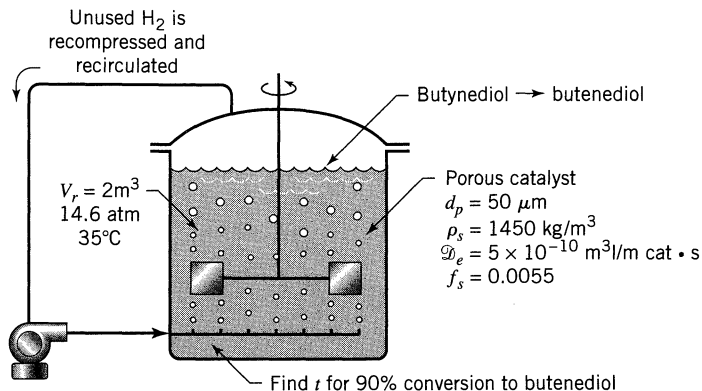
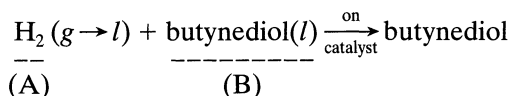


Figure E22.2a

148 000 Pa · m³ l/mol) and reacts with the butynediol on the catalyst surface as follows (see Fig. E22.2a):



and at 35°C

$$-r'_A = k' C_A C_B \quad \text{and} \quad k' = 5 \times 10^{-5} \text{ m}^6/\text{kg} \cdot \text{mol cat} \cdot \text{s}$$

Unused hydrogen is recompressed and recirculated, and the whole operation takes place at 1.46 atm and 35°C.

Find out how long it will take for 90% conversion of reactant.

Additional Data

The mass transfer rates are given as

$$(k_{Al} a_i)_{g+l} = 0.277 \frac{\text{m}^3 \text{l}}{\text{m}^3 \text{r} \cdot \text{s}} \quad k_{Ac} = 4.4 \times 10^{-4} \frac{\text{m}^3 \text{l}}{\text{m}^3 \text{r} \cdot \text{s}}$$

↑
the sum of the gas and liquid films

SOLUTION

First compare C_A and C_B :

$$C_A = \frac{p_A}{H_A} = \frac{1.46(101\,325)}{148\,000} = 10 \text{ mol/m}^3 \text{ l}$$

$$C_{B0} = 2500 \text{ and } C_{Bf} = 250 \text{ mol/m}^3 \text{ l}$$

} Both at the beginning and at the end of the batch run
 $C_B \gg C_A$; therefore, the system is in extreme 1.

Although C_A stays constant throughout the batch run, C_B does not, so we will have a changing rate with time and with C_B . Therefore, let us evaluate the rate at any particular value of C_B .

$$a_c = \frac{6f_s}{d_p} = \frac{6(0.0055)}{5 \times 10^{-5}} = 660 \text{ m}^2 \text{ cat/m}^3 \text{ l}$$

therefore,

$$k_{Ac}a_c = 4.4 \times 10^{-4}(660) = 0.29 \frac{\text{m}^3 \text{ l}}{\text{m}^3 \text{ r} \cdot \text{s}}$$

and

$$M_T = L \sqrt{\frac{k' C_B \rho_s}{\mathcal{D}_e}} = \frac{5 \times 10^{-5}}{6} \sqrt{\frac{(5 \times 10^{-5}) C_B (1450)}{5 \times 10^{-10}}} = 0.1 C_B^{1/2} \quad (\text{i})$$

Replacing in the rate expression of Eq. 18 gives

$$\begin{aligned} -r_A''' &= \frac{1}{\frac{1}{0.277} + \frac{1}{0.29} + \frac{1}{(5 \times 10^{-5}) C_B (1450) (\mathcal{E}_A) (0.0055)}} \frac{14.6(101\ 325)}{148\ 000} \\ &= \frac{1}{0.705\ 84 + \frac{250.8}{C_B (\mathcal{E}_A \text{ at } M_T = 0.1 C_B^{1/2})}} \end{aligned} \quad (\text{ii})$$

Choose a Number of C_B Values	M_T from Eq. (i)	\mathcal{E}_A from Eq. 18.6	$-r_A'''$ from Eq. (ii)	$1/(-r_A''')$
2500	5	0.19	0.8105	1.23
1000	3.16	0.29	0.6367	1.57
250	1.58	0.5	0.3687	2.71

Now from Eq. 12 the reaction time is given by

$$t = \frac{V_l}{bV_r} \int_{C_{Bf}}^{C_{B0}} \frac{dC_B}{(-r_A''')} \quad (\text{12})$$

With $b = 1$ and $V_l \cong V_r$, making the plot of Fig. E22.2b, and taking the area under the curve gives

$$t = \underline{\underline{3460 \text{ s}}}, \text{ or } \underline{\underline{58 \text{ min}}}$$

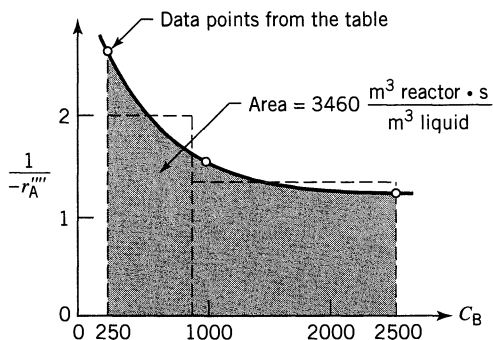


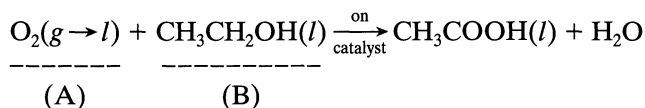
Figure E22.2b

REFERENCE

Ramachandran, P. A., and Choudry, V. R., *Chem. Eng.*, p. 74 (December 1, 1980).

PROBLEMS

22.1. Trickle bed oxidation. Dilute aqueous ethanol (about 2–3%) is oxidized to acetic acid by the action of pure oxygen at 10 atm in a trickle bed reactor packed with palladium-alumina catalyst pellets and kept at 30°C. According to Sato et al., Proc. First Pacific Chem. Eng. Congress, Kyoto, p. 197, 1972, the reaction proceeds as follows:



with rate

$$-r'_A = k' C_A, \quad k' = 1.77 \times 10^{-5} \text{ m}^3/\text{kg} \cdot \text{s}$$

Find the fractional conversion of ethanol to acetic acid if gas and liquid are fed to the top of a reactor in the following system:

Gas stream: $v_g = 0.01 \text{ m}^3/\text{s}$, $H_A = 86\,000 \text{ Pa} \cdot \text{m}^3/\text{mol}$

Liquid stream: $v_l = 2 \times 10^{-4} \text{ m}^3/\text{s}$, $C_{B0} = 400 \text{ mol/m}^3$

Reactor: 5 m high, 0.1 m² cross section, $f_s = 0.58$

Catalyst: $d_p = 5 \text{ mm}$, $\rho_s = 1800 \text{ kg/m}^3$
 $\mathcal{D}_e = 4.16 \times 10^{-10} \text{ m}^2/\text{s}$

Kinetics: $k_{Ag}a_i = 3 \times 10^{-4} \text{ mol/m}^3 \cdot \text{Pa} \cdot \text{s}$, $k_{Al}a_i = 0.02 \text{ s}^{-1}$
 $k_{Ac} = 3.86 \times 10^{-4} \text{ m/s}$

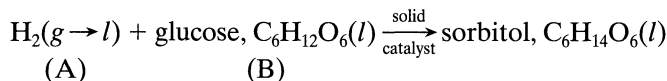
22.2. Slurry column oxidation. Instead of using a trickle bed reactor for ethanol oxidation (see previous problem), let us consider using a slurry reactor. For this type of unit

$$(k_{Ag}a_i)_{g+l} = 0.052 \text{ s}^{-1}, \quad k_{Ac} = 4 \times 10^{-4} \text{ m/s}$$

$$d_p = 10^{-4} \text{ m}, \quad f_g = 0.05, \quad f_l = 0.75, \quad f_s = 0.2$$

Take all flows and other values from the previous problem, and then find the expected fractional conversion of ethanol in this reactor.

22.3. Slurry tank hydrogenation. Predict the conversion of glucose to sorbitol in a stirred slurry reactor using pure hydrogen gas at 200 atm and 150°C. The catalyst used is porous Raney nickel, and under these conditions Brahme and Doraiswamy, *IEC/PDD*, **15**, 130 (1976) report that the reaction proceeds as follows:



with

$$-r'_A = -r'_B = k' C_A^{0.6} C_B, \quad k' = 5.96 \times 10^{-6} \frac{\text{mol}}{\text{kg} \cdot \text{s}} \left(\frac{\text{m}^3}{\text{mol}} \right)^{1.6}$$

Data:

Gas stream: $v_g = 0.2 \text{ m}^3/\text{s}$, $H_A = 277\,600 \text{ Pa} \cdot \text{m}^3/\text{mol}$

Liquid stream: $v_l = 0.01 \text{ m}^3/\text{s}$, $C_{B0} = 2000 \text{ mol/m}^3$

Reactor: $V_r = 2 \text{ m}^3$, $f_s = 0.056$

Catalyst: $d_p = 10 \text{ }\mu\text{m}$, $\rho_s = 8900 \text{ kg/m}^3$, $\mathcal{D}_e = 2 \times 10^{-9} \text{ m}^2/\text{m cat} \cdot \text{s}$

Kinetics: $(k_{Ag}a_i)_{g+l} = 0.05 \text{ s}^{-1}$, $k_{Ac} = 10^{-4} \text{ m/s}$

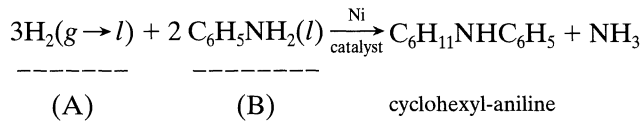
22.4. Multistage bubble column hydrogenation. In the previous problem, conversion to sorbitol is not as high as desired so let us consider an alternative design, one which uses an upflow of gas and liquid through a long, narrow multistage column 0.25 m² in cross section and 8 m high containing suspended solids ($d_p = 10^{-3} \text{ m}$ and $f_s = 0.4$). What will be the conversion with this arrangement?

Data: $(k_{Ag}a_i)_{g+l} = 0.025 \text{ s}^{-1}$, $k_{Ac} = 10^{-5} \text{ m/s}$

All other values are unchanged from the previous problem.

22.5. Three-phase fluidized bed hydrogenation. Aniline is to be hydrogenated in a three-phase fluidized bed of porous clay particles impregnated with nickel catalyst. The well-agitated batch of liquid is kept at 130°C by heat exchanger tubes passing through the fluidized bed, and by bubbling hydro-

gen vigorously and at a high rate through the bed at 1 atm. According to Govindarao and Murthy, *J. Appl. Chem. Biotechnol.* **25**, 196 (1975), at these conditions reaction proceeds as follows:



with rate

$$-r'_A = k' C_A, \quad k' = 0.05 \text{ m}^3/\text{kg cat} \cdot \text{s}$$

Find the time needed for 90% conversion of this batch of aniline.

Data:

Gas stream: pure H_2 at 1 atm, $H_A = 28\,500 \text{ Pa} \cdot \text{m}^3/\text{mol}$

Batch of liquid: $C_{B0} = 1097 \text{ mol}/\text{m}^3$

Reactor: $f_g = 0.10$, $f_l = 0.65$, $f_s = 0.25$

Catalyst: $d_p = 300 \mu\text{m}$, $\rho_s = 750 \text{ kg}/\text{m}^3$
 $\mathcal{D}_e = 8.35 \times 10^{-10} \text{ m}^2/\text{cat} \cdot \text{s}$

Kinetics: $(k_{Ag}a_i)_{g+l} = 0.04 \text{ s}^{-1}$, $k_{Ac} = 10^{-5} \text{ m}/\text{s}$

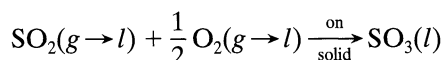
Assume that the fraction of NH_3 in the gas stream is very small at any time.

22.6. Bubble column hydrogenation. Consider a different design to effect the hydrogenation of the previous problem, one which uses a long, narrow bubble column of semisuspended 3-mm catalyst particles ($f_s = 0.4$, $f_l = 0.5$, $f_g = 0.1$). The batch of liquid aniline is circulated through an external heat exchanger (volume of liquid in the loop outside the reactor equals the total volume of the reactor), and hydrogen is bubbled through the column. Find the time needed for 90% conversion of aniline in this unit.

Data: $(k_{Ag}a_i)_{g+l} = 0.02 \text{ s}^{-1}$, $k_{Ac} = 7 \times 10^{-5} \text{ m}/\text{s}$

All other values not mentioned here remain unchanged from the previous problem.

22.7. Trickle bed gas absorber-reactor. Sulfur dioxide is to be removed from a gas by passing the gas and water through a bed of highly porous activated carbon kept at 25°C . In this system sulfur dioxide and oxygen dissolve in water and react on the solid to give sulfur trioxide, as follows:



where

$$-r_{\text{SO}_2} = k' C_{\text{oxygen}}, \quad k' = 0.01553 \text{ m}^3/\text{kg} \cdot \text{s}$$

Find the fraction of sulfur dioxide removed from a gas stream under the following conditions:

Gas stream: $v_g = 0.01 \text{ m}^3/\text{s}$, $\pi = 101325 \text{ Pa}$
 entering $\text{SO}_2 = 0.2\%$, $H = 380000 \text{ Pa} \cdot \text{m}^3/\text{mol}$
 entering $\text{O}_2 = 21\%$, $H = 87000 \text{ Pa} \cdot \text{m}^3/\text{mol}$

Liquid stream: $v_l = 2 \times 10^{-4} \text{ m}^3/\text{s}$

Reactor: 2 m high, 0.1 m^2 cross section, $f_s = 0.6$

Catalyst: $d_p = 5 \text{ mm}$, $\rho_s = 850 \text{ kg/m}^3$
 $\mathcal{D}_e = 5.35 \times 10^{-10} \text{ m}^2/\text{s}$

Kinetics: $(k_i a_i)_{g+l} = 0.01 \text{ s}^{-1}$, $k_c = 10^{-5} \text{ m/s}$

22.8. Hydrogenation in a slurry reactor. The batch hydrogenation of Example 22.2 takes just about an hour to run. Let us suppose that in practical operations we can run eight batches of fluid per day in this unit. Thus, in the long run a batch of fluid is processed every three hours.

Another way of running this reaction is to feed the agitated reactor continuously at such a rate that we get 90% conversion of butynediol. How do these two processing rates compare in the long term? Give your answer as $F_{\text{B0, continuous}}/F_{\text{B0, batch}}$. Assume that the liquid feed composition, gas composition and pressure, mass transfer and chemical rates are the same in both batch and continuous operations.

Part IV

Non-Catalytic Systems

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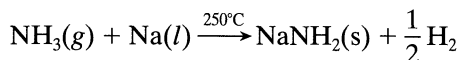
Chapter 25 Fluid–Particle Reactions: Kinetics /566

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Chapter 23

Fluid–Fluid Reactions: Kinetics

Heterogeneous fluid-fluid reactions are made to take place for one of three reasons. First, the product of reaction may be a desired material. Such reactions are numerous and can be found in practically all areas of the chemical industry where organic syntheses are employed. An example of liquid-liquid reactions is the nitration of organics with a mixture of nitric and sulfuric acids to form materials such as nitroglycerin. The chlorination of liquid benzene and other hydrocarbons with gaseous chlorine is an example of gas-liquid reactions. In the inorganic field we have the manufacture of sodium amide, a solid, from gaseous ammonia and liquid sodium:



Fluid-fluid reactions may also be made to take place to facilitate the removal of an unwanted component from a fluid. Thus, the absorption of a solute gas by water may be accelerated by adding a suitable material to the water which will react with the solute being absorbed. Table 23.1 shows the reagents used for various solute gases.

The third reason for using fluid-fluid systems is to obtain a vastly improved product distribution for homogeneous multiple reactions than is possible by using the single phase alone. Let us turn to the first two reasons, both of which concern the reaction of materials originally present in different phases.

The following factors will determine how we approach this process.

The Overall Rate Expression. Since materials in the two separate phases must contact each other before reaction can occur, both the mass transfer and the chemical rates will enter the overall rate expression.

Equilibrium Solubility. The solubility of the reacting components will limit their movement from phase to phase. This factor will certainly influence the form of the rate equation since it will determine whether the reaction takes place in one or both phases.

The Contacting Scheme. In gas-liquid systems semibatch and countercurrent contacting schemes predominate. In liquid-liquid systems mixed flow (mixer-

Table 23.1 Absorption Systems with Chemical Reaction^a

Solute Gas	Reagent
CO ₂	Carbonates
CO ₂	Hydroxides
CO ₂	Ethanolamines
CO	Cuprous amine complexes
CO	Cuprous ammonium chloride
SO ₂	Ca(OH) ₂
SO ₂	Ozone-H ₂ O
SO ₂	HCrO ₄
SO ₂	KOH
Cl ₂	H ₂ O
Cl ₂	FeCl ₂
H ₂ S	Ethanolamines
H ₂ S	Fe(OH) ₃
SO ₃	H ₂ SO ₄
C ₂ H ₄	KOH
C ₂ H ₄	Trialkyl phosphates
Olefins	Cuprous ammonium complexes
NO	FeSO ₄
NO	Ca(OH) ₂
NO	H ₂ SO ₄
NO ₂	H ₂ O

^a Adapted from Teller (1960).

settlers) and batch contacting are used in addition to counter and concurrent contacting.

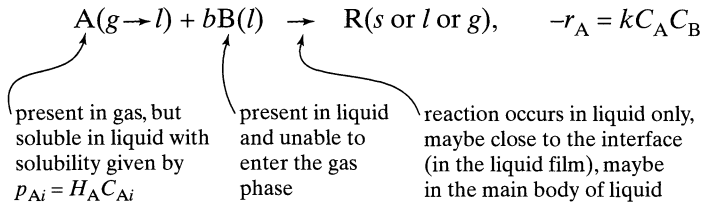
Many possible permutations of rate, equilibrium, and contacting pattern can be imagined; however, only some of these are important in the sense that they are widely used on the technical scale.

23.1 THE RATE EQUATION

For convenience in notation let us talk of G/L reactions, even though what we say holds equally for L/L reactions. Further, let us assume that gaseous A is soluble in the liquid but that B does not enter the gas. Thus A must enter and move into the liquid phase before it can react, and reaction occurs in this phase alone.

Now the overall rate expression for the reaction will have to account for the mass transfer resistance (to bring reactants together) and the resistance of the chemical reactions step. Since the relative magnitude of these resistances can vary greatly we have a whole spectrum of possibilities to consider.

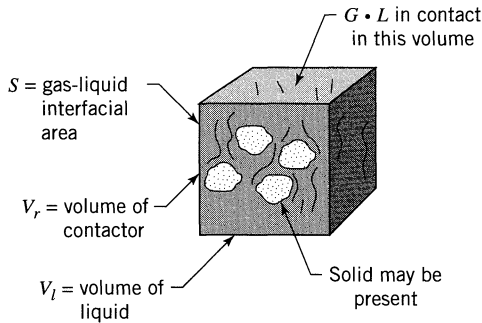
Our analysis considers the following second-order reaction



For notation consider a unit volume of contactor V_r with its gas, liquid, and solid

$$f_l = \frac{V_l}{V_r}, \quad f_g = \frac{V_g}{V_r}, \quad \epsilon = f_l + f_g,$$

$$a_l = \frac{S}{V_l}, \quad a = \frac{S}{V_r}$$



The rate of reaction is usefully written in a number of ways, as follows:

$$\left. \begin{aligned} -r_A''' &= -\frac{1}{V_r} \frac{dN_A}{dt} \\ -r_{Al} &= -\frac{1}{V_l} \frac{dN_A}{dt} \\ -r_A'' &= -\frac{1}{S} \frac{dN_A}{dt} \end{aligned} \right\} \quad (1)$$

These rates are related by

$$r_A''' V_r = r_{Al} V_l = r_A'' S$$

or

$$r_A''' = f_l r_{Al} = a r_A''$$

Since reactant A must move from gas to liquid for reaction to occur, diffusional resistances enter the rate. Here we will develop everything in terms of the two-film theory. Other theories can and have been used; however, they give essentially the same result, but with more impressive mathematics.

The Rate Equation for Straight Mass Transfer (Absorption) of A

Here we have two resistances in series, of the gas film and of the liquid film. Thus, as shown in Fig. 23.1, the rate of transfer of A from gas to liquid is given by the rate expressions, for the gas film

$$r_A'' = \overbrace{k_{Ag}}^{\frac{\text{mol}}{\text{m}^2 \cdot \text{Pa} \cdot \text{s}}} (p_A - p_{Ai}) \quad \dots \text{or} \quad -r_A''' = \overbrace{k_{Ag} a}_{\frac{\text{mol}}{\text{m}^3 \text{ contactor} \cdot \text{Pa} \cdot \text{s}}} (p_A - p_{Ai}) \quad (2)$$

and for the liquid film

$$r_A'' = \overbrace{k_{Al}}^{\frac{\text{m}^3 \text{ liquid}}{\text{m}^2 \text{ surface} \cdot \text{s}}} (C_{Ai} - C_A) \quad \dots \text{or} \quad -r_A''' = \overbrace{k_{Al} a}_{\frac{\text{m}^3 \text{ liquid}}{\text{m}^3 \text{ contactor} \cdot \text{s}}} (C_{Ai} - C_A) \quad (3)$$

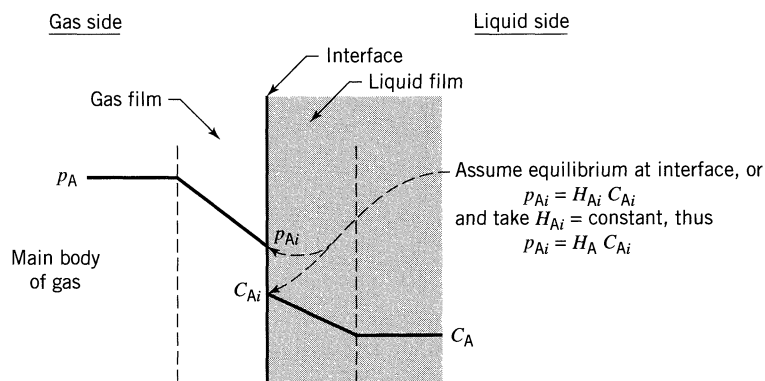


Figure 23.1 Setting up the rate equation for straight mass transfer based on the two film theory.

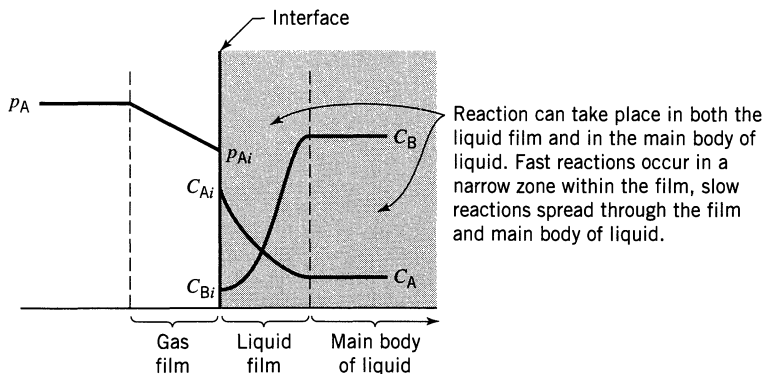


Figure 23.2 Setting up the rate equation for absorption of A in the liquid, and reaction in the liquid, based on the two-film theory.

Combining Eqs. 2 and 3 with Henry's law $p_{Ai} = H_A C_{Ai}$ to eliminate the unknown interface conditions p_{Ai} and C_{Ai} we obtain the final rate expression for straight mass transfer at any point in the absorber.

$$-r_A''' = \frac{1}{\frac{1}{k_{Ag}a} + \frac{H_A}{k_{Al}a}} (p_A - H_A C_A) \quad (4)$$

$\frac{\text{Pa} \cdot \text{m}^3 \text{ liquid}}{\text{mol}}$

The Rate Equation for Mass Transfer and Reaction

Here we have three factors to consider: what happens in the gas film; in the liquid film; and in the main body of the liquid, as shown in Fig. 23.2.

All sorts of special forms of the rate equation can result depending on the relative values of the rate constants k , k_g , and k_l , the concentration ratio of reactants p_A/C_B , and Henry's law constant H_A . It turns out that there are eight cases to consider, going from the extreme of infinitely fast reaction rate (mass transfer control) to the other extreme of very slow reaction rate (no mass transfer resistance need be considered).

The eight special cases, each with its particular rate equation, are, from infinitely fast to very slow reaction, as follows:

- Case A: Instantaneous reaction with low C_B
- Case B: Instantaneous reaction with high C_B
- Case C: Fast reaction in liquid film, with low C_B
- Case D: Fast reaction in liquid film, with high C_B

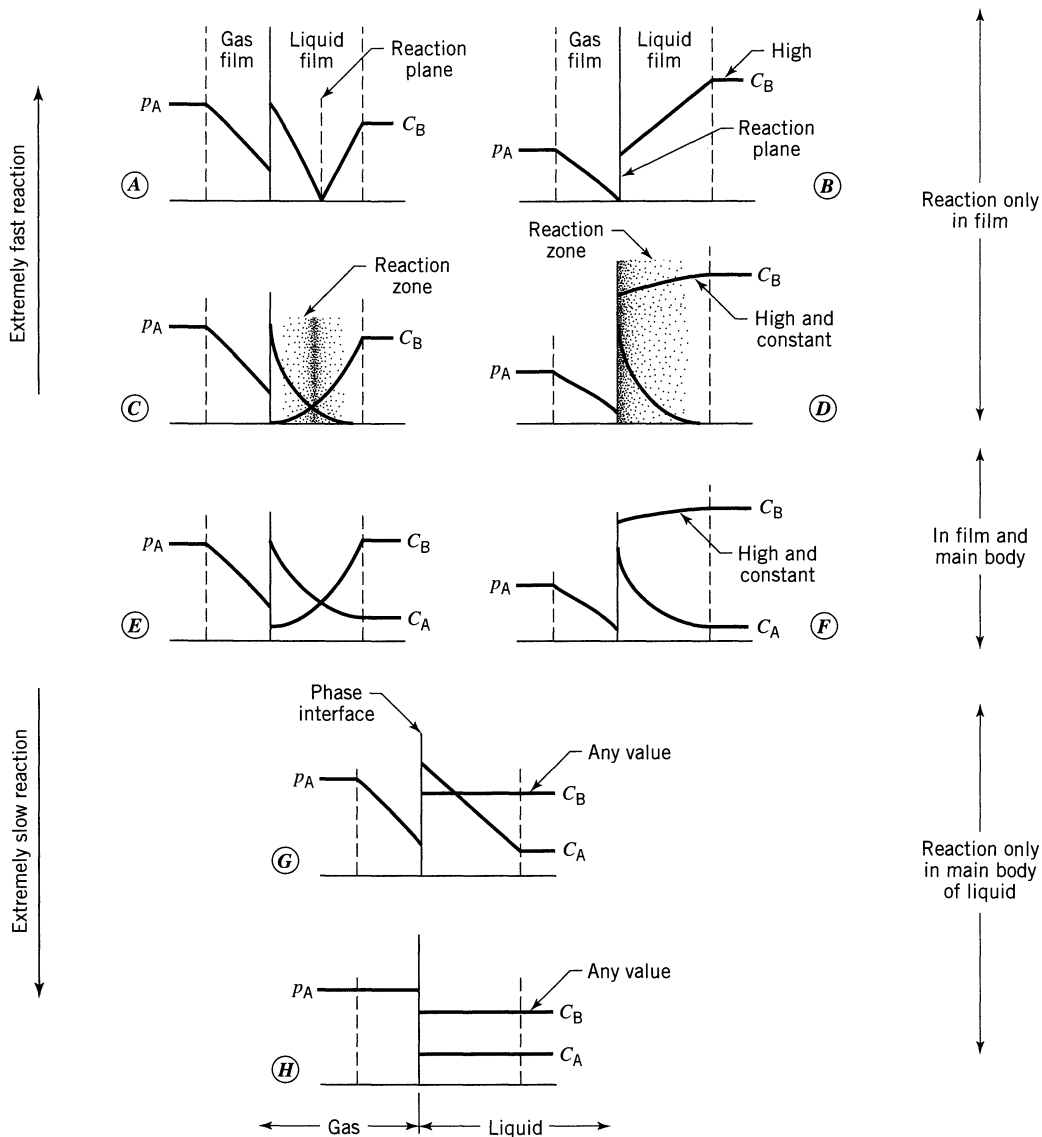
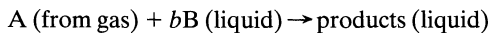


Figure 23.3 Interface behavior for the liquid-phase reaction



for the complete range of rates of the reaction and of the mass transfer.

Case E and F: Intermediate rate with reaction in the film and in the main body of the liquid

Case G: Slow reaction in main body but with film resistance

Case H: Slow reaction, no mass transfer resistance

We show these eight cases in Fig. 23.3.

We discuss these special cases and present their particular rate equations later, after we present the general rate equation.

$$-r_A''' = \frac{1}{\underbrace{\frac{1}{k_{Ag}a}}_{\text{gas film resistance}} + \underbrace{\frac{H_A}{k_{Al}aE}}_{\text{liquid film resistance}} + \underbrace{\frac{H_A}{kC_Bf_l}}_{\text{liquid bulk resistance}}} p_A \quad (5)$$

The absorption of A from gas is larger when reaction occurs within the liquid film than for straight mass transfer. Thus for the same concentrations at the two boundaries of the liquid film we have

$$\left(\begin{array}{c} \text{Liquid film} \\ \text{enhancement} \\ \text{factor} \end{array} \right), E = \left(\frac{\text{rate of take up of A} \\ \text{when reaction occurs}}{\text{rate of take up of A for} \\ \text{straight mass transfer}} \right)_{\text{same } C_{Ai}, C_A, C_{Bi}, C_B \\ \text{in the two cases}} \quad (6)$$

The value of E is always greater or equal to one. The only problem now is to evaluate E , the enhancement factor. Figure 23.4 shows that E is dependent on two quantities:

$$E_i = \left(\begin{array}{c} \text{the enhancement factor for} \\ \text{an infinitely fast reaction} \end{array} \right) \quad (7)$$

$$M_H^2 = \left(\begin{array}{c} \text{maximum possible conversion in the} \\ \text{film compared with maximum transport} \\ \text{through the film} \end{array} \right) \quad (8)$$

M_H stands for the Hatta modulus, in recognition of the scientist who first dealt with this problem, Hatta (1932).

Let us now examine the eight special cases.

Case A: Instantaneous Reaction with Respect to Mass Transfer. Since an element of liquid can contain either A or B, but not both, reaction will occur at a plane between A-containing and B-containing liquid. Also, since reactants must diffuse to this reaction plane the rate of diffusion of A and B will determine the rate, so that a change in p_A or C_B will move the plane one way or the other (see Fig. 23.5). At steady state the flow rate of B toward the reaction zone will be b

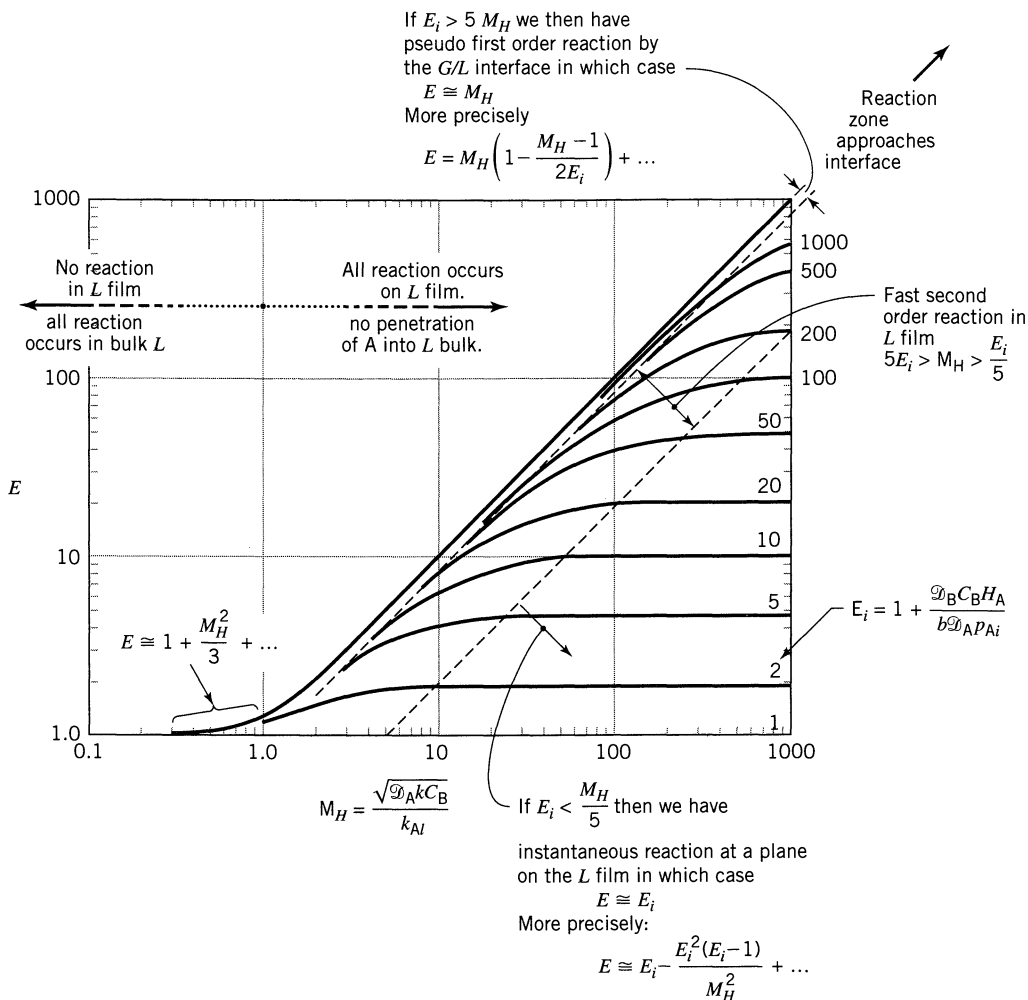


Figure 23.4 The enhancement factor for fluid-fluid reactions as a function of M_H and E_i , modified from the numerical solution of van Krevelens and Hoftijzer (1954).

times the flow rate of A toward the reaction zone. Thus,

$$\underbrace{-r_A'' = -\frac{r_B''}{b}}_{\text{A in gas film}} = \underbrace{k_{Ag}(p_A - p_{Ai})}_{\text{A in liquid film}} = \underbrace{k_{Ai}(C_{Ai} - 0)}_{\text{B in liquid film}} \frac{x_0}{x} = \frac{k_{Bl}}{b} (C_B - 0) \frac{x_0}{x_0 - x} \quad (9)$$

where k_{Ag} and k_{Ai} , k_{Bl} are the mass transfer coefficients in gas and liquid phases. The liquid side coefficients are for straight mass transfer without chemical reaction and are therefore based on flow through the whole film of thickness x_0 .

At the interface the relationship between p_A and C_A is given by the distribution coefficient, called Henry's law constant for gas-liquid systems. Thus,

$$p_{Ai} = H_A C_{Ai} \quad (10)$$

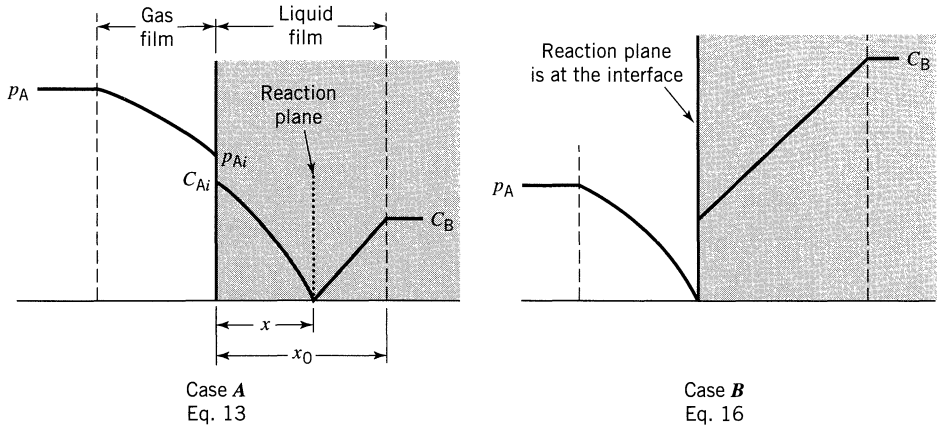


Figure 23.5 Concentration of reactants as visualized by the two-film theory for an infinitely fast irreversible reactions of any order, $A + bB \rightarrow \text{products}$. Case A—low C_B , Case B—high C_B (see Eq. 17).

In addition, since the movement of material within the film is visualized to occur by diffusion alone, the transfer coefficients for A and B are related by¹

$$\frac{k_{Al}}{k_{Bl}} = \frac{\mathcal{D}_{Al}/x_0}{\mathcal{D}_{Bl}/x_0} = \frac{\mathcal{D}_{Al}}{\mathcal{D}_{Bl}} \quad (12)$$

Eliminating the unmeasured intermediates x , x_0 , p_{Ai} , C_{Ai} by Eqs. 9, 10, and 12, we obtain

for Case A: $\left(k_{Ag}p_A > \frac{k_{Bl}C_B}{b} \right)$

$$-r_A'' = -\frac{1}{S} \frac{dN_A}{dt} = \frac{\frac{\mathcal{D}_{Bl} C_B}{b} + \frac{p_A}{H_A}}{\frac{1}{H_A k_{Ag}} + \frac{1}{k_{Al}}} \quad (13)$$

For the special case of negligible gas-phase resistance, for example, if you used pure reactant A in the gas phase, then $p_A = p_{Ai}$ or $k_g \Rightarrow \infty$, in which case Eq.

¹ Alternatives to the film theory are also in use. These models [Higbie (1935); Danckwerts (1950, 1955)] view that the liquid at the interface is continually washed away and replaced by fresh fluid from the main body of the liquid, and that this is the means of mass transport. These unsteady-state surface renewal theories all predict

$$\frac{k_{Al}}{k_{Bl}} = \sqrt{\frac{\mathcal{D}_{Al}}{\mathcal{D}_{Bl}}} \quad (11)$$

as opposed to Eq. 12, for the film theory.

With the exception of this one difference, these models, so completely different from a physical standpoint, give essentially identical predictions of steady-state behavior. Because of this, and because the film theory is so much easier to develop and use than the other theories, we deal with it exclusively.

13 reduces to

$$-r_A'' = k_{Ai} C_{Ai} \left(1 + \frac{\mathcal{D}_{Bl} C_B}{b \mathcal{D}_{Al} C_{Ai}} \right) \quad (14)$$

Case B: Instantaneous Reaction; High C_B . Returning to the general situation shown in Fig. 23.5, if the concentration of B is raised, or more precisely, if

$$k_{Ag} p_A \leq \frac{k_{Bl}}{b} C_B \quad (15)$$

then this condition, combined with Eq. 5, requires that the reaction zone move to and stay at the interface rather than remain in the liquid film. This is shown in Fig. 23.5. When this happens, the resistance of the gas-phase controls, and the rate is not affected by any further increase in concentration of B. In addition, Eq. 9 simplifies to

for Case B: $\left(k_{Ag} p_A \leq \frac{k_{Bl} C_B}{b} \right)$ $-r_A'' = -\frac{1}{S} \frac{dN_A}{dt} = k_{Ag} p_A$ (16)

Equation 17 tells whether Case A or Case B applies in any situation. Thus,

if $k_{Ag} p_A \geq \frac{k_{Bl}}{b} C_B$, then use Eq. 13: Case A

if $k_{Ag} p_A \leq \frac{k_{Bl}}{b} C_B$, then use Eq. 16: Case B

(17)

Let us now look at the other cases.

Case C: Fast Reaction; Low C_B . The plane of reaction for case A now spreads into a zone of reaction in which A and B are both present. However, reaction is fast enough so that this reaction zone remains totally within the liquid film. Thus, no A enters the main body of liquid to react there.

Since the last resistance term in the general rate equation, Eq. 5, is negligible (large k), the rate form for this case is

$$-r_A''' = \frac{1}{\frac{1}{k_{Ag} a} + \frac{H_A}{k_{Al} a E}} p_A \quad (18)$$

Case D: Fast Reaction; High C_B , Hence Pseudo First-Order Rate with Respect to A. For the special case where C_B does not drop appreciably within the film, it can be taken to be constant throughout, and the second-order reaction rate (Case C) simplifies to the more easily solved first-order rate expression. Thus,

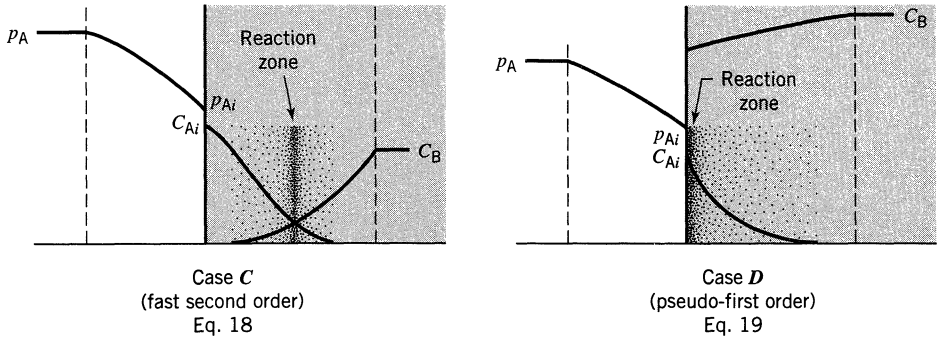


Figure 23.6 Location of reaction in the liquid film for a fast (but not infinitely fast) second-order reaction. Case *C*—low C_B , Case *D*—high C_B .

the general rate expression, Eq. 5, reduces to

$$-r_A''' = \frac{1}{\frac{1}{k_{Ag}a} + \frac{H_A}{a\sqrt{\mathcal{D}_A k C_B}}} p_A \quad (19)$$

Figure 23.6 sketches Cases *C* and *D*.

Cases E and F: Intermediate Rate with Respect to Mass Transfer. Here reaction is slow enough for some A to diffuse through the film into the main body of the fluid. Consequently, A reacts both within the film and in the main body of the fluid. Here we have to use the general rate expression with its three resistances, Eq. 5.

Case G: Slow Reaction with Respect to Mass Transfer. This represents the somewhat curious case where all reaction occurs in the main body of the liquid; however, the film still provides a resistance to the transfer of A into the main body of liquid. Thus, three resistances enter into the rate expression, and Eq. 5 reduces to

$$-r_A''' = \frac{1}{\frac{1}{k_{Ag}a} + \frac{H_A}{k_A a} + \frac{H_A}{k C_B f_l}} p_A \quad (20)$$

Case H: Infinitely Slow Reaction. Here the mass transfer resistance is negligible, the compositions of A and B are uniform in the liquid, and the rate is determined by chemical kinetics alone.

$$-r_A''' = \frac{k f_l}{H_A} p_A C_B = k f_l C_A C_B \quad (21)$$

Figure 23.7 shows cases *G* and *H*.

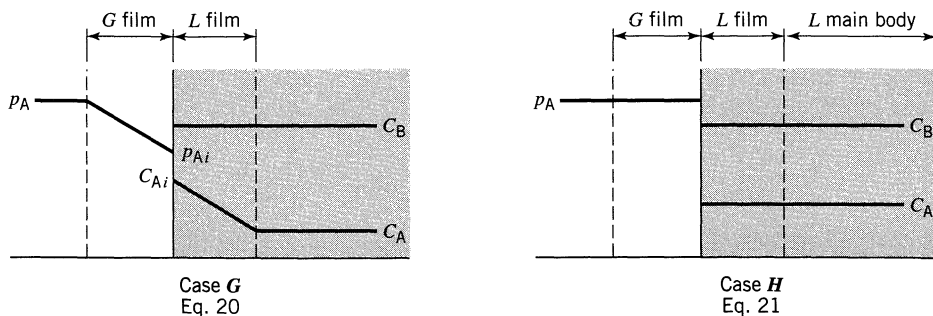


Figure 23.7 Slow reactions Case **G** still shows film resistance. Case **H** shows no film resistance.

Review of the Role of the Hatta Number, M_H

To tell whether reaction is fast or slow, we focus on unit surface of gas-liquid interface, we assume that gas-phase resistance is negligible, and we define a film conversion parameter

$$\begin{aligned}
 M_H^2 &= \frac{\text{maximum possible conversion in the film}}{\text{maximum diffusional transport through the film}} \\
 &= \frac{k C_{Ai} C_B x_0}{\frac{\mathcal{D}_{Al}}{x_0} \cdot C_{Ai}} = \frac{k C_B \mathcal{D}_{Al}}{k_{Ai}^2}
 \end{aligned} \tag{22}$$

If $M_H \gg 1$, all reaction occurs in the film, and surface area is the controlling rate factor. On the other hand, if $M_H \ll 1$ no reaction occurs in the film, and bulk volume becomes the controlling rate factor. More precisely, it has been found that:

1. If $M_H > 2$, reaction occurs in the film and we have Cases **A**, **B**, **C**, **D**.
2. If $0.02 < M_H < 2$, we then have the intermediate Cases **E**, **F**, **G**.
3. If $M_H < 0.02$, we have the infinitely slow reaction of Case **H**.

When M_H is large, we should pick a contacting device which develops or creates large interfacial areas; energy for agitation is usually an important consideration in these contacting schemes. On the other hand, if M_H is very small, all we need is a large volume of liquid. Agitation to create large interfacial areas is of no benefit here.

Table 24.1 of the next chapter presents typical data for various contacting devices, and from this we see that spray or plate columns should be efficient devices for systems with fast reaction (or large M_H), while bubble contactors should be more efficient for slow reactions (or small M_H).

Clues to the Kinetic Regime from Solubility Data

For reactions which occur in the film, the phase distribution coefficient H can suggest whether the gas-phase resistance is likely to be important or not. To

show this we write the expression for straight mass transfer of A across the gas and liquid films

$$-\frac{1}{S} \frac{dN_A}{dt} = \frac{1}{\frac{1}{k_{Ag}} + \frac{H_A}{k_{Al}}} \Delta p_A \quad (23)$$

Now for slightly soluble gases H_A is large; hence, with all other factors unchanged the above rate equation shows that the liquid film resistance term is large. The reverse holds for highly soluble gases. Thus, we see that:

Gas film resistance controls for highly soluble gases.

Liquid film resistance controls for slightly soluble gases.

Table 23.2 Typical Values of $H_A = p_{Ai}/C_{Ai}$, Pa · m³/mol, for Common Gases in Water

	N ₂	H ₂	O ₂	CO	CO ₂	NH ₃
20°C	1.45 × 10 ⁵	1.23 × 10 ⁵	0.74 × 10 ⁵	0.96 × 10 ⁵	2600	0.020
60°C	2.16 × 10 ⁵	1.34 × 10 ⁵	1.13 × 10 ⁵	1.48 × 10 ⁵	6300	0.096

slightly soluble gas ←————→ highly soluble gas

Note that gases are more soluble at lower temperatures. Additional values for many different gases can be extracted, with difficulty, from Perry and Green (1984) and from references given by Danckwerts (1970).

Since a highly soluble gas is easy to absorb and has its main resistance in the gas phase, we would not need to add a liquid-phase reactant B to promote the absorption. On the other hand, a sparingly soluble gas is both difficult to absorb and has its main resistance in the liquid phase; hence it is this system which would benefit greatly by a reaction in the liquid phase.

Final Comments

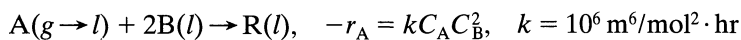
To find the size of process unit needed for a given job (this is discussed in the next chapter), we need to know the overall rate of reaction. This chapter explains how to evaluate the overall rate of reaction.

Many sources report on the physical and chemical constants used in this chapter. I recommend the following ones:

- Doraiswamy and Sharma (1984): an extensive treatment of this whole subject
- Shah (1979): evaluation of the mass transfer coefficients in various types of equipment. Also experimental devices for finding these coefficients.
- Danckwerts (1970): easy to follow discussion, sources for Henry's law constants, equations to use for finding mass transfer coefficients.

EXAMPLE 23.1 FINDING THE RATE OF A G/L REACTION

Air with gaseous A bubbles through a tank containing aqueous B. Reaction occurs as follows:



For this system

$$\begin{aligned} k_{A_g} a &= 0.01 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{Pa} & f_i &= 0.98 \\ k_{A_l} a &= 20 \text{ hr}^{-1} & H_A &= 10^5 \text{ Pa} \cdot \text{m}^3/\text{mol}, \text{ very low solubility} \\ \mathcal{D}_{A_l} &= \mathcal{D}_{B_l} = 10^{-6} \text{ m}^2/\text{hr} & a &= 20 \text{ m}^2/\text{m}^3 \end{aligned}$$

For a point in the absorber-reactor where

$$p_A = 5 \times 10^3 \text{ Pa} \quad \text{and} \quad C_B = 100 \text{ mol/m}^3$$

- locate the resistance to reaction (what % is in the gas film, in the liquid film, in the main body of liquid)
- locate the reaction zone
- determine the behavior in the liquid film (whether pseudo first-order reaction, instantaneous, physical transport, etc.)
- calculate the rate of reaction ($\text{mol/m}^3 \cdot \text{hr}$)

SOLUTION

This chapter has only analyzed second-order reactions, however, this problem deals with a third-order reaction. Since no analysis is available for other than second-order reactions, let us replace our third-order reaction with a second-order approximation. Thus,

$$kC_A C_B^2 \Rightarrow (kC_B)C_A C_B$$

To find the rate from the general expression (Eq. 5), we need to first evaluate E_i and M_H . Let us do this:

$$\left. \begin{aligned} M_H &= \frac{\sqrt{\mathcal{D}_A k C_B^2}}{k_{A_l}} = \frac{\sqrt{10^{-6} 10^6 100^2}}{1} = 100 \\ (E_i)_{\text{first guess}} &= 1 + \frac{\mathcal{D}_B C_B H_A}{b \mathcal{D}_A p_{A_i}} = 1 + \frac{100 \times 10^5}{2(5 \times 10^5)} = 10^3 \end{aligned} \right\}$$

guess $p_{A_i} = p_A$ \nearrow

Since $(E_i)_{\text{first guess}} > 5 M_H$, then for any other smaller guess for p_{A_i} we will still have $E_i > 5 M_H$. Therefore, from Fig. 23.4 we have pseudo first-order reaction

in the film with

$$E = M_H = 100$$

Now to the rate expression, Eq. 5,

$$\begin{aligned} -r_A''' &= \frac{p_A}{\frac{1}{k_{Ag}a} + \frac{H_A}{k_{Al}aE} + \frac{H_A}{kC_{B,l}^2f_l}} \\ &= \frac{5 \times 10^3}{\frac{1}{0.01} + \frac{10^5}{20(100)} + \frac{10^5}{(10^6)(100^2)(.098)}} = 33 \text{ mol/hr} \cdot \text{m}^3 \text{ reactor} \end{aligned}$$

$\leftarrow \frac{2}{3}$ $\leftarrow \frac{1}{3}$ $\leftarrow \sim 0$

Thus,

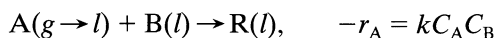
- (a) 2/3 of the resistance is in the gas film, 1/3 is in the liquid film ←
- (b) the reaction zone is in the liquid film ←
- (c) reaction proceeds by a pseudo first-order reaction of A, at the interface ←
- (d) the rate is $-r_A''' = 33 \text{ mol/hr} \cdot \text{m}^3 \leftarrow$

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PROBLEMS

Gaseous A absorbs and reacts with B in liquid according to



in a packed bed under conditions where

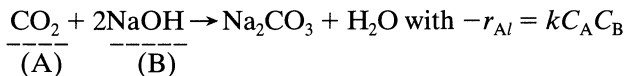
$$\begin{aligned}
 k_{Ag}a &= 0.1 \text{ mol/hr} \cdot \text{m}^2 \text{ of reactor} \cdot \text{Pa} & f_l &= 0.01 \text{ m}^3 \text{ liquid/m}^3 \text{ reactor} \\
 k_{Al}a &= 100 \text{ m}^3 \text{ liquid/m}^3 \text{ reactor} \cdot \text{hr} & \mathcal{D}_{Al} = \mathcal{D}_{Bl} &= 10^{-6} \text{ m}^2/\text{hr} \\
 a &= 100 \text{ m}^2/\text{m}^3 \text{ reactor}
 \end{aligned}$$

At a point in the reactor where $p_A = 100 \text{ Pa}$ and $C_B = 100 \text{ mol/m}^3 \text{ liquid}$

- (a) calculate the rate of reaction in $\text{mol/hr} \cdot \text{m}^3$ of reactor.
 (b) describe the following characteristics of the kinetics:
- location of the major resistance (gas film, liquid film, main body of liquid)
 - behavior in the liquid film (pseudo first-order reaction, instantaneous, second-order reaction, physical transport)
- for the following values of reaction rate and Henry's law constant.

	$k, \text{ m}^3 \text{ liquid/mol} \cdot \text{hr}$	$H_A, \text{ Pa} \cdot \text{m}^3 \text{ liquid/mol}$
23.1.	10	10^5
23.2.	10^6	10^4
23.3.	10	10^3
23.4.	10^{-4}	1
23.5.	10^{-2}	1
23.6.	10^8	1

- 23.7. Redo Example 23.1 with just one change. Let us suppose that C_B is very low, or $C_B = 1$.
- 23.8. At high pressure CO_2 is absorbed into a solution of NaOH in a packed column. The reaction is as follows:

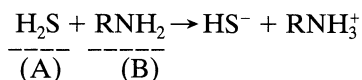


Find the rate of absorption, the controlling resistance, and what is happening in the liquid film, at a point in the column where $p_A = 10^5 \text{ Pa}$ and $C_B = 500 \text{ mol/m}^3$.

$$\begin{aligned}
 \text{Data: } k_{Ag}a &= 10^{-4} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa} & H_A &= 25\,000 \text{ Pa} \cdot \text{m}^3/\text{mol} \\
 k_{Al} &= 1 \times 10^{-4} \text{ m/s} & \mathcal{D}_A &= 1.8 \times 10^{-9} \text{ m}^2/\text{s} \\
 a &= 100 \text{ m}^{-1} & \mathcal{D}_B &= 3.06 \times 10^{-9} \text{ m}^2/\text{s} \\
 k &= 10 \text{ m}^3/\text{mol} \cdot \text{s} & f_l &= 0.1
 \end{aligned}$$

This problem was adapted from Danckwerts (1970).

- 23.9.** Hydrogen sulfide is absorbed by a solution of methanolamine (MEA) in a packed column. At the top of the column, gas is at 20 atm and it contains 0.1% of H_2S , while the absorbent contains 250 mol/m^3 of free MEA. The diffusivity of MEA in solution is 0.64 times that of H_2S . The reaction is normally regarded as irreversible and instantaneous.



For the flow rates and packing used

$$k_{A1}a = 0.03 \text{ s}^{-1}$$

$$k_{Ag}a = 60 \text{ mol/m}^3 \cdot \text{s} \cdot \text{atm}$$

$$H_A = 1 \times 10^{-4} \text{ m}^3 \cdot \text{atm/mol}, \text{ Henry's law constant for } \text{H}_2\text{S} \text{ in water.}$$

- (a) Find the rate of absorption of H_2S in MEA solution.
 (b) To find out whether it is worthwhile using MEA absorbent, determine how much faster is absorption with MEA compared to absorption in pure water.

This problem was adapted from Danckwerts (1970).

Chapter 24

Fluid–Fluid Reactors: Design

We must first choose the right kind of contactor, then find the size needed. There are two kinds of contactor—towers and tanks, and Fig. 24.1 shows some examples. As may be expected, these contactors have widely different G/L volume ratios, interfacial areas, k_g and k_l , and concentration driving forces. The particular properties of the system you are dealing with, the solubility of gaseous reactant, the concentration of reactants, etc.—in effect the location of the main resistance in the rate equation—will suggest that you use one class of contactor and not the other.

Table 24.1 shows some of the characteristics of these contactors.

Factors to Consider in Selecting a Contactor

(a) Contacting pattern. We idealize these as shown in Fig. 24.2.

- Towers approximate plug G /plug L .
- Bubble tanks approximate plug G /mixed L .
- Agitated tanks approximate mixed G /mixed L .

As we shall see, towers have the largest mass transfer driving force and in this respect have an advantage over tanks. Agitated tanks have the smallest driving force.

(b) k_g and k_l . For liquid droplets in gas k_g is high, k_l is low. For gas bubbles rising in liquid k_g is low, k_l is high.

(c) Flow rates. Packed beds work best with relative flow rates of about $F_l/F_g \cong 10$ at 1 bar. Other contactors are more flexible in that they work well in a wider range of F_l/F_g values.

(d) If the resistance is in the gas and/or liquid films you want a large interfacial area “a,” thus most agitated contactors and most columns. If the L film dominates, stay away from spray contactors. If the G film dominates stay away from bubble contactors.

(e) If the resistance is in the main body of the L you want large $f_l = V_l/V_r$. Stay away from towers. Use tank contactors.

(f) Solubility. For very soluble gases, those with a small value of Henry’s law constant H (ammonia, for example), gas film controls, thus you should

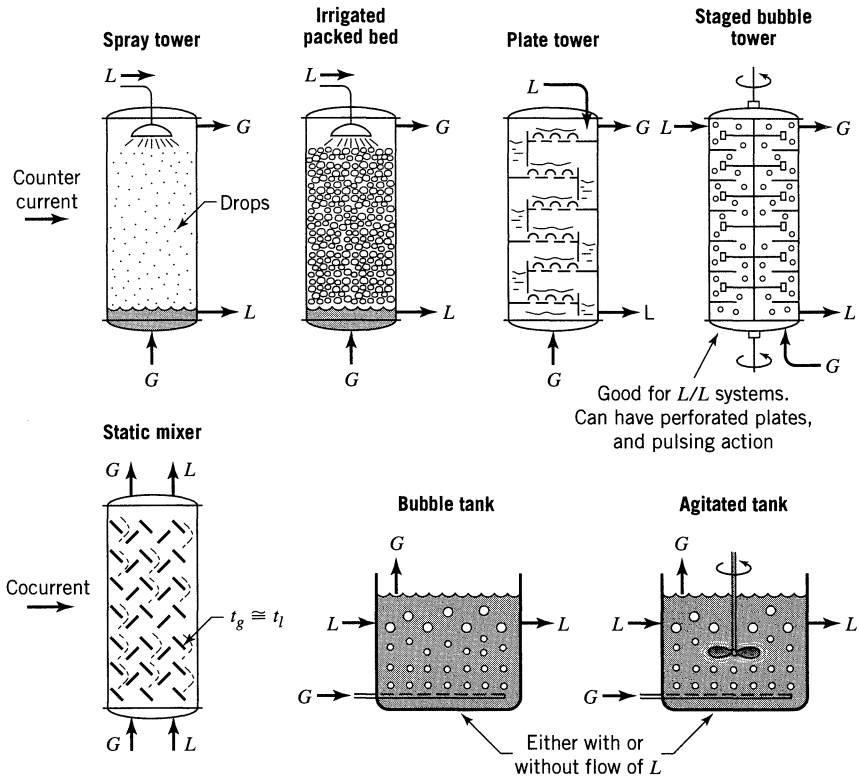


Figure 24.1 Tower and tank contactors for G/L reactions.

avoid bubble contactors. For gases of low solubility in the liquid, thus high H value (O_2 , N_2 , as examples) liquid film controls, so avoid spray towers.

(g) Reaction lowers the resistance of the liquid film, so

- For absorption of highly soluble gases, chemical reaction is not helpful.
- For absorption of slightly soluble gases, chemical reaction is helpful and does speed up the rate.

Nomenclature. We use the following symbols in our development.

A_{cs} = cross-sectional area of column.

a = interfacial contact area per unit volume of reactor (m^2/m^3).

f_l = volume fraction of liquid (-).

i = any participant, reactant or product, in the reaction.

A, B, R, S = participants in the reaction.

U = carrier or inert component in a phase, hence neither reactant nor product.

T = total moles in the reacting (or liquid) phase.

$Y_A = p_A/p_U$, moles A/mole inert in the gas (-).

$X_A = C_A/C_U$, moles A/mole inert in the liquid (-).

F'_g, F'_l = molar flow rate of all the gas and the liquid (mol/s).

$F_g = F'_g p_U / \pi$, upward molar flow rate of inerts in the gas (mol/s).

Table 24.1 Characteristics of G/L Contactors (from Kramers and Westerterp, 1961).

Flow Pattern	Contactor	a (m^2/m^3)	$f_t = \frac{V_l}{V}$ (-)	Capacity	Comments
Counter Current Flow	Spray tower	60	0.05	Low	Good for very soluble gases high k_g/k_l
	Packed bed	100	0.08	High	Good all rounder, but must have $F_l/F_g \cong 10$
	Plate tower	150	0.15	Medium-high	
Cocurrent flow	Staged bubble column	200	0.9	Low	Needs mechanical mixer or pulsing device. Good for slightly soluble gases and L_1/L_2 . Has low k_g/k_l .
	Static mixer	200	0.2-0.8	Very high	Very flexible, little reported data $t_g \cong t_l$.
	Bubble tank	20	0.98	Medium	Cheap to build
Mixed flow of L	Agitated tank	200	0.9	Medium	Cheap to build but needs a mechanical agitator

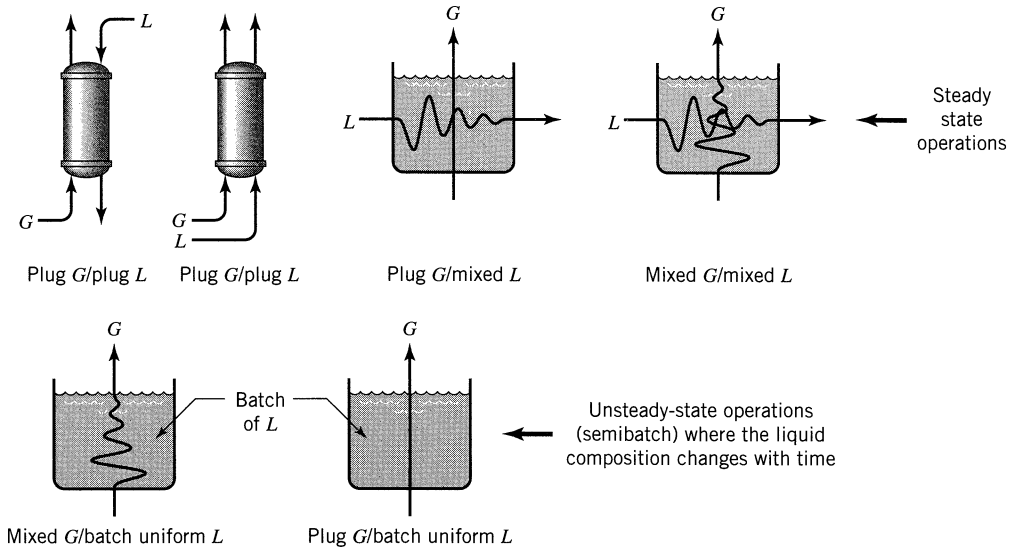


Figure 24.2 Contacting patterns for G/L contactors.

$$F_l = F'_l C_U / C_T, \text{ downward molar flow rate of inerts in the liquid phase (mol/s).}$$

With this nomenclature, we have the following relationships among the various concentration measures.

$$\pi = p_A + p_B + \cdots + p_U$$

$$C_T = C_A + C_B + \cdots + C_U$$

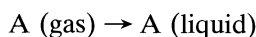
$$dY_A = d\left(\frac{p_A}{p_U}\right) = \frac{p_U dp_A - p_A dp_U}{p_U^2} \stackrel{\text{dilute}}{\approx} \frac{dp_A}{p_U}$$

$$dX_A = d\left(\frac{C_A}{C_U}\right) = \frac{C_U dC_A - C_A dC_U}{C_U^2} \stackrel{\text{dilute}}{\approx} \frac{dC_A}{C_U}$$

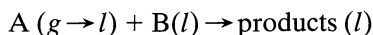
The performance equations which are written in terms of F_g and F_l are useful when the flowing streams have inert carrier material. The equation written in terms of F'_g and F'_l are useful when the flowing streams only contain reactive materials and no inerts.

24.1 STRAIGHT MASS TRANSFER

Since the approach for reacting systems is a straightforward extension of straight mass transfer, let us first develop equations for absorption alone of A by liquid



then go to reacting systems.



Note the similarity in the performance equations.

Plug Flow *G*/Plug Flow *L*—Countercurrent Flow in a Tower

To develop the performance equation, we combine the rate equation with the material balance. Thus for steady-state countercurrent operations we have for a differential element of volume

$$(\text{A lost by gas}) = (\text{A gained by liquid}) = (-r_A''')dV_r$$

or

$$F_g dY_A = F_l dX_A = (-r_A''')dV_r \quad (1)$$

$$\frac{F_g \pi dp_A}{(\pi - p_A)^2} = d \left(\frac{F'_g p_A}{\pi} \right) = \frac{F_g dp_A}{\pi - p_A} \quad \frac{F_l C_T dC_A}{(C_T - C_A)^2} \quad (-r_A''')a = k_{A_g} a(p_A - p_{A_i}) = k_{A_l} a(C_{A_i} - p_A)$$

Integrating for the whole tower gives

$$V_r = \frac{F_g}{a} \int_{Y_{A1}}^{Y_{A2}} \frac{dY_A}{Y_{A1} - r_A''} = \frac{F_l}{a} \int_{X_{A1}}^{X_{A2}} \frac{dX_A}{X_{A1} - r_A''}$$

$$= F_g \pi \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{k_{A_g} a (\pi - p_A)^2 (p_A - p_{A_i})} = \int_{p_{A1}}^{p_{A2}} \frac{F'_g dp_A}{k_{A_g} a (\pi - p_A) (p_A - p_{A_i})} \quad (2)$$

$$= F_l C_T \int_{C_{A1}}^{C_{A2}} \frac{dC_A}{k_{A_l} a (C_T - C_A)^2 (C_{A_i} - C_A)} = \int_{C_{A1}}^{C_{A2}} \frac{F'_g dC_A}{k_{A_l} a (C_T - C_A) (C_{A_i} - C_A)}$$

In brief, the design procedure is summarized in Fig. 24.3. For dilute systems $C_A \ll C_T$ and $p_A \ll \pi$, so $F'_g \cong F_g$ and $F'_l \cong F_l$. In this situation the differential material balance becomes

$$\frac{F_g}{\pi} dp_A = \frac{F_l}{C_T} dC_A = -r_A'' dV_r \quad (3)$$

and for any two points in the absorber

$$p_{A2} - p_{A1} = \frac{F_l \pi}{F_g C_T} (C_{A2} - C_{A1}) \quad (4)$$

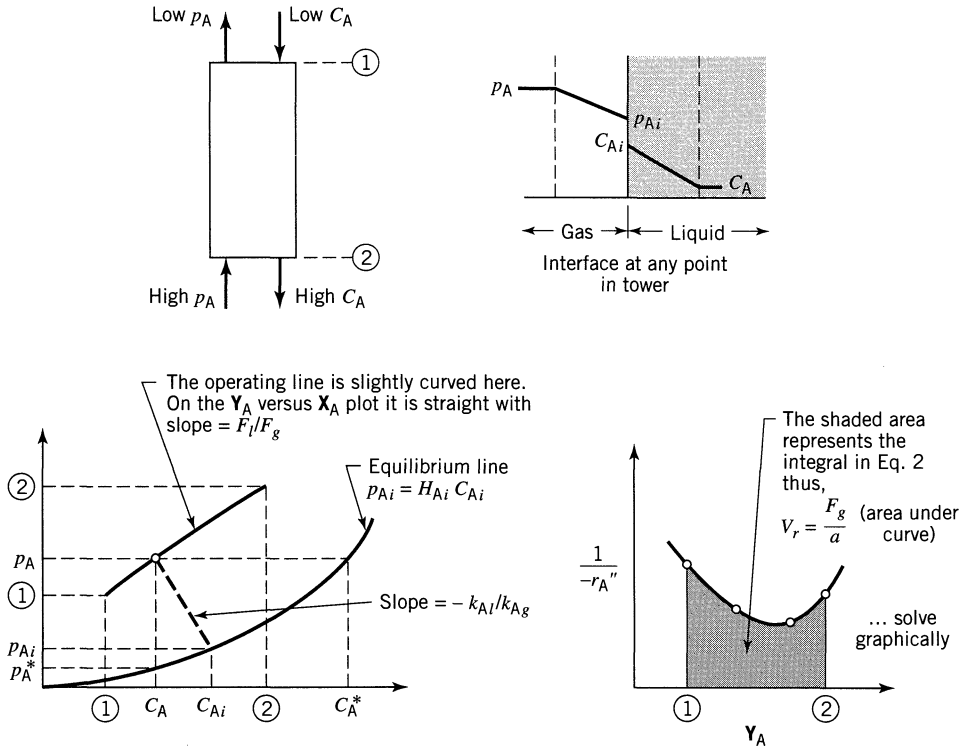


Figure 24.3 Illustration of the design procedure for straight mass transfer in countercurrent towers.

The rate expression reduces to

$$\begin{aligned}
 -r_A''' &= (-r_A'')a = \left(\frac{1}{\frac{1}{k_{Ag}a} + \frac{H_A}{k_{Al}a}} \right) (p_A - p_A^*) \\
 &= K_{Ag}a(p_A - p_A^*) = K_{Al}a(C_A^* - C_A)
 \end{aligned} \tag{5}$$

Thus the general integrated rate expression of Eq. 2 becomes, with Eq. 3,

$$\begin{aligned}
 V_r = hA_{cs} &= \frac{F_g}{\pi} \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{-r_A'''} = \frac{F_l}{C_T} \int_{C_{A1}}^{C_{A2}} \frac{dC_A}{-r_A'''} \\
 &= \frac{F_g}{\pi K_{Ag}a} \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{p_A - p_A^*} = \frac{F_l}{C_T K_{Al}a} \int_{C_{A1}}^{C_{A2}} \frac{dC_A}{C_A^* - C_A}
 \end{aligned} \tag{6}$$

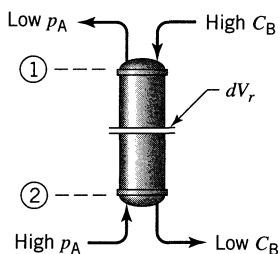
coefficient on gas basis $\frac{1}{K_{Ag}} = \frac{1}{k_{Ag}} + \frac{H_A}{k_{Al}}$ gas in equilibrium with liquid C_A , or $p_A^* = H_A C_A$ coefficient on liquid basis $\frac{1}{K_{Al}} = \frac{1}{H_A k_{Ag}} + \frac{1}{k_{Al}}$ liquid in equilibrium with gas p_A , or $C_A^* = p_A/H_A$

For the other contacting patterns of Fig. 24.2 plug G /plug L cocurrent, mixed G /mixed L , plug G /mixed L , mixed G /plug L , mixed G /batch L see Levenspiel (1996) Chapter 42, or recall the equations and methods from your lessons in mass transfer and unit operations.

24.2 MASS TRANSFER PLUS NOT VERY SLOW REACTION

Here we only treat the reaction $A(g \rightarrow l) + bB(l) \rightarrow \text{products}(l)$. We assume that the rate is fast enough so that no unreacted A enters the main body of the liquid. This assumes that the Hatta modulus is not very much smaller than unity.

Plug Flow G /Plug Flow L —Mass Transfer + Reaction in a Countercurrent Tower



For a differential slice of absorber-reactor we write

$$\underbrace{\left(\text{A lost} \right)}_{\text{I}} = \frac{1}{b} \underbrace{\left(\text{B lost} \right)}_{\text{II}} = \underbrace{\left(\text{disappearance} \right)}_{\text{III}} \underbrace{\left(\text{of A by reaction} \right)}$$

or

$$F_g dY_A = -\frac{F_l dX_B}{b} = (-r_A''') dV_r \quad (7)$$

For Dilute Systems. $p_U \cong \pi$ and $C_U \cong C_T$ in which case the above expressions simplify to

$$\frac{F_g}{\pi} dp_A = -\frac{F_l}{bC_T} dC_B = (-r_A'') a dV_r \quad (8)$$

Rearranging and integrating I and II, II and III, I and III gives the following:

In general

$$V_r = F_g \int_{Y_{A1}}^{Y_{A2}} \frac{dY_A}{(-r_A'')a}$$

$$= \frac{F_l}{b} \int_{X_{B2}}^{X_{B1}} \frac{dX_B}{(-r_B'')a} \quad \dots \text{with} \quad F_g(Y_{A2} - Y_{A1}) = \frac{F_l}{b}(X_{B1} - X_{B2}) \quad (9)$$

For dilute systems

$$V_r = \frac{F_g}{\pi} \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{(-r_A'')a}$$

$$= \frac{F_l}{bC_T} \int_{C_{B2}}^{C_{B1}} \frac{dC_B}{(-r_A'')a} \quad \dots \text{with} \quad \frac{F_g}{\pi}(p_{A2} - p_{A1}) = \frac{F_l}{bC_T}(C_{B1} - C_{B2}) \quad (10)$$

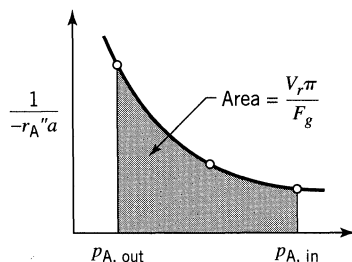
also good from point 1 to and point i in the tower

To Solve for V_r ,

- pick a few p_A values, usually p_{A1} , p_{A2} and one intermediate value are enough, and for each p_A find the corresponding C_B .
- evaluate the rate for each point from

$$(-r_A'')a = \left[\frac{1}{\frac{1}{k_{Ag}a} + \frac{H_A}{k_{Al}aE} + \frac{H_A}{k_{Cb}f_i}} \right] p_A$$

- integrate the performance equation graphically



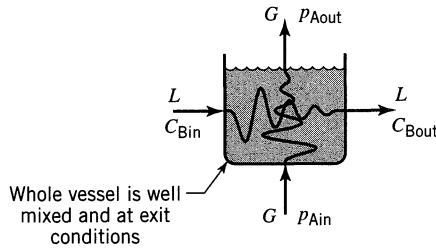
Plug Flow G /Plug Flow L —Mass Transfer + Reaction in a Cocurrent Tower

Here simply change F_l to $-F_l$ (for upflow of both streams) or F_g to $-F_g$ (for downflow of both streams) in the equations for countercurrent flow. Be sure to find the proper C_B value for each p_A . The rest of the procedure remains the same.

Mixed Flow *G*/Mixed Flow *L*—Mass Transfer + Reaction in an Agitated Tank Contactor

Since the composition is the same everywhere in the vessel make an accounting about the vessel as a whole. Thus,

$$\left(\begin{array}{c} \text{A lost} \\ \text{by gas} \end{array} \right) = \frac{1}{b} \left(\begin{array}{c} \text{B lost} \\ \text{by liquid} \end{array} \right) = \left(\begin{array}{c} \text{disappearance of} \\ \text{A by reaction} \end{array} \right)$$



In symbols these equalities become

$$F_g(\mathbf{Y}_{Ain} - \mathbf{Y}_{Aout}) = \frac{F_l}{b} (\mathbf{X}_{Bin} - \mathbf{X}_{Bout}) = (-r_A''')|_{\text{at exit conditions}} V_r \quad (11)$$

for both *G* and *L*

and for dilute systems

$$\frac{F_g}{\pi} (p_{Ain} - p_{Aout}) = \frac{F_l}{b C_T} (C_{Bin} - C_{Bout}) = (-r_A''')|_{\text{at exit}} V_r \quad (12)$$

To find V_r , the solution is direct; evaluate $-r_A'''$ from known stream compositions and solve Eq. 11 or 12.

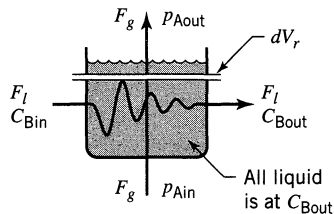
To find C_{Bout} and p_{Aout} given V_r guess p_{Aout} , evaluate C_{Bout} , then $-r_A'''$, then V_r . Compare the calculated V_r value with the true value. If different, guess another p_{Aout} .

Plug Flow *G*/Mixed Flow *L*—Mass Transfer + Reaction in Bubble Tank Contactors

Here we must make two accountings, a differential balance for the loss of *A* from the gas because *G* is in plug flow, and an overall balance for *B* because *L* is in mixed flow.

Focusing on a bit of rising gas, we have

$$\left(\begin{array}{c} \text{A lost} \\ \text{by gas} \end{array} \right) = \left(\begin{array}{c} \text{disappearance of} \\ \text{A by reaction} \end{array} \right) \dots \text{or} \dots F_g d\mathbf{Y}_A = (-r_A''')|_{L \text{ at exit conditions}} dV_r \quad (13)$$



For the liquid as a whole and for the gas as a whole, a balance about the whole reactor gives

$$\left(\begin{array}{l} \text{all A lost} \\ \text{by gas} \end{array} \right) = \frac{1}{b} \left(\begin{array}{l} \text{all B lost} \\ \text{by liquid} \end{array} \right) \quad \dots \text{ or } \dots \quad F_g \Delta Y_A = \frac{F_l}{b} \Delta X_B \quad (14)$$

Integrating Eq. 13 along the path of the bubble and also using Eq. 14 gives

In general

$$V_r = F_g \int_{Y_{Aout}}^{Y_{Ain}} \frac{dY_A}{(-r_A'')a} \quad \dots \text{with} \dots \quad F_g(Y_{Ain} - Y_{Aout}') = \frac{F_l}{b}(X_{Bin} - X_{Bout}) \quad (15)$$

for liquid at C_{Bout}

For dilute systems

$$V_r = \frac{F_g}{\pi} \int_{p_{Aout}}^{p_{Ain}} \frac{dp_A}{(-r_A'')a} \quad \dots \text{with} \dots \quad \frac{F_g}{\pi}(p_{Ain} - p_{Aout}) = \frac{F_l}{bC_T}(C_{Bin} - C_{Bout}) \quad (16)$$

If V_r is to be found and the exit conditions are known, then the procedure is direct. Pick a number of p_A values and integrate graphically.

If p_{Aout} and C_{Bout} are to be found in a reactor of known volume V_r , then we require a trial and error solution. Simply guess C_{Bout} and then see if $V_{calculated} = V_{given}$.

Mixed Flow G /Batch Uniform L —Absorption + Reaction in a Batch Agitated Tank Contactor

Since this is not a steady-state operation, composition and rates all change with time, as shown in Fig. 24.4. At any instant the material balance equates the three

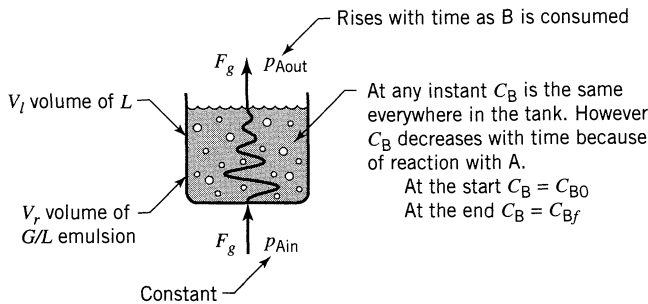


Figure 24.4 History of a batch of reacting liquid.

quantities shown below and thus in general

$$\underbrace{F_g(Y_{Ain} - Y_{Aout})}_{\text{I}} = - \underbrace{\frac{V_l}{b} \frac{dC_B}{dt}}_{\text{II}} = \underbrace{(-r_A^m)V_r}_{\text{III}} \quad (17)$$

loss of A from gas decrease of B with time in L disappearance of A or B by reaction. In the rate expression use p_{Aout} since G is in mixed flow.

For dilute systems

$$\frac{F_g}{\pi}(p_{Ain} - p_{Aout}) = - \frac{V_l}{b} \frac{dC_B}{dt} = (-r_A^m)V_r \quad (18)$$

To Find the Time Needed for a Given Operation

- Choose a number of C_B values, say C_{B0} , C_{Bf} and an intermediate C_B value. For each C_B value guess p_{Aout} .
- Next calculate M_H , E_i , and then E and $-r_A^m$. This may require trial and error, but not often.
- See if terms I and III are equal to each other

$$(-r_A^m)V_r \stackrel{?}{=} F_g \left(\frac{p_{Ain}}{\pi - p_{Ain}} - \frac{p_{Aout}}{\pi - p_{Aout}} \right)$$

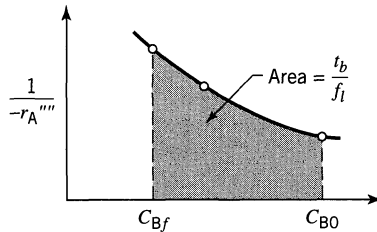
and keep adjusting p_{Aout} until they do.

As a shortcut: if $p_A \ll \pi$ and if $E = M_H$ then E is independent of p_A in which case I and III combine to give

$$-r_A^m = p_{Ain} / \left(\frac{\pi V_r}{F_g} + \frac{1}{k_{Ag}a} + \frac{H_A}{k_{Al}aE} + \frac{H_A}{kC_{Bf}l} \right)$$

- Next combine terms II and III to find the processing time

$$t = \frac{f_I}{b} \int_{C_{Bf}}^{C_{B0}} \frac{dC_B}{-r_A''' } \quad \dots \text{ solve graphically} \quad (19)$$



- This time can be compared with the minimum needed if all A reacts and none escapes the vessel. This situation is represented by $p_{Aout} = 0$ at all times. Thus

$$t_{\min} = \frac{\frac{1}{b} V_l (C_{B0} - C_{Bf})}{F_g \left(\frac{p_{Ain}}{\pi - p_{Ain}} \right)} = \frac{\frac{1}{b} \left(\text{amount of B reacted} \right)}{\left(\text{amount of A entering} \right)} \quad (20)$$

- Combining t and t_{\min} gives the efficiency of utilization of A. Thus

$$\left(\begin{array}{l} \text{percent of entering A} \\ \text{which reacts with B} \end{array} \right) = \frac{t_{\min}}{t} \quad (21)$$

Example 24.6 illustrates this procedure for batch absorber-reactors.

EXAMPLE 24.1 TOWERS FOR STRAIGHT ABSORPTION

The concentration of undesirable impurity in air (at 1 bar = 10^5 Pa) is to be reduced from 0.1% (or 100 Pa) to 0.02% (or 20 Pa) by absorption in pure water. Find the height of tower required for countercurrent operations.

Data

For consistency let us use SI units throughout.

For the packing

$$k_{Ag}a = 0.32 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{Pa}$$

$$k_{Al}a = 0.1/\text{hr}$$

The solubility of A in water is given by Henry's law constant

$$H_A = p_{A_i}/C_{A_i} = 12.5 \text{ Pa} \cdot \text{m}^3/\text{mol}$$

The flow rates per meter squared cross section of tower are

$$F_g/A_{cs} = 1 \times 10^5 \text{ mol/hr} \cdot \text{m}^2$$

$$F_l/A_{cs} = 7 \times 10^5 \text{ mol/hr} \cdot \text{m}^2$$

The molar density of liquid under all conditions is

$$C_T = 56\,000 \text{ mol/m}^3$$

Figure E24.1 shows the quantities known at this point.

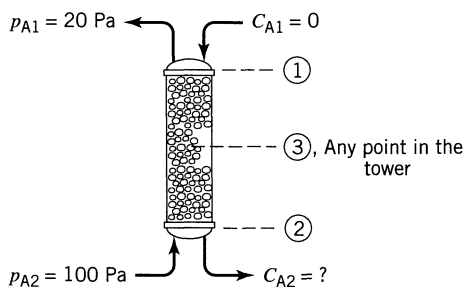


Figure E24.1

SOLUTION

Our strategy is to first solve the material balance, then determine the tower height. Since we are dealing with dilute solutions we may use the simplified form of the material balance. So for any point in the tower p_A and C_A are related by Eq. 4.

$$p_{A3} - p_{A1} = \frac{(F_l/A_{cs})}{(F_g/A_{cs})} \frac{\pi}{C_T} (C_{A3} - C_{A1})$$

or

$$p_{A3} - 20 = \frac{(7 \times 10^5)(1 \times 10^5)}{(1 \times 10^5)(56\,000)} (C_{A3} - 0)$$

or

$$C_{A3} = 0.08p_{A3} - 1.6$$

(i)

from which the concentration of A in the liquid leaving the tower is

$$C_{A2} = 0.08(100) - 1.6 = 6.4 \text{ mol/m}^3 \quad \text{(ii)}$$

The expression for tower height is, from Eq. 6,

$$h = \frac{V_r}{A_{cs}} = \frac{(F_g/A_{cs})}{\pi(K_{Ag}a)} \int_{20}^{100} \frac{dp_A}{p_A - p_A^*} \quad \text{(iii)}$$

Now evaluate terms

$$\frac{1}{(K_{Ag}a)} = \frac{1}{(k_{Ag}a)} + \frac{H_A}{(k_{Al}a)} = \frac{1}{0.32} + \frac{12.5}{0.1} = 3.125 + 125 = 128.125$$

This expression shows that

$$G \text{ film resistance} = 3.125/128.125 = 0.024, \text{ or } 2.4\%$$

$$L \text{ film resistance} = 125/128.125 = 0.976, \text{ or } 97.6\%$$

and

$$(K_{Ag}a) = 1/128.125 = 0.0078 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{Pa} \quad \text{(iv)}$$

Next evaluate $p_A - p_A^*$. Thus with Eq. (i) we get

$$\begin{aligned} p_A - p_A^* &= p_A - H_A C_A = p_A - 1.25(0.08p_A - 1.6) \\ p_A &= 20 \text{ Pa} \end{aligned} \quad \text{(v)}$$

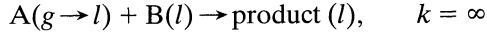
Inserting Eqs. (iv) and (v) in (iii) gives

$$\begin{aligned} h &= \frac{(1 \times 10^5 \text{ mol/hr} \cdot \text{m}^2)}{(10^5 \text{ Pa})(0.0078 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{Pa})} \int_{20}^{100} \frac{dp_A}{20} \\ &= (128.125) \left(\frac{100 - 20}{20} \right) = \underline{\underline{512.5 \text{ m}}} \end{aligned}$$

Comment. Here the tower is very high, unacceptably high. Also note that most of the resistance (over 97%) lies in the liquid film, making this a liquid-film-controlling process. However, if we added component B to the liquid which reacts with A, we should be able to speed things up. Let's see if this is so.

EXAMPLE 24.2 TOWERS FOR HIGH CONCENTRATION OF LIQUID REACTANT

To the water of Example 24.1 add a high concentration of reactant B, $C_{B1} = 800 \text{ mol/m}^3$ or approximately 0.8 N. Material B reacts with A extremely rapidly



Assume that the diffusivities of A and B in water are the same, thus

$$k_{Al} = k_{Bl} = k_l$$

Figure E24.2 shows what is known at this point.

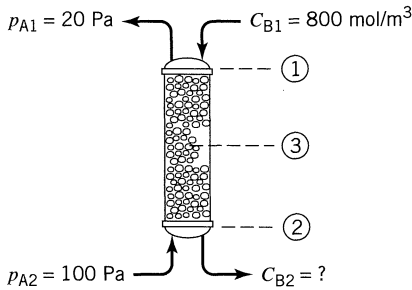


Figure E24.2

SOLUTION

The strategy in solving the problem is as follows

- Step 1.** Express the material balance and find C_{B2} in the exit stream.
- Step 2.** Find which of the many forms of rate equation should be used.
- Step 3.** Determine the tower height.

Step 1. Material balance. For dilute solutions with rapid reaction Eq. 6 gives for any point in the tower, p_{A3} , C_{B3}

$$(p_{A3} - p_{A1}) = \frac{(F_l/A_{cs})\pi}{(F_g/A_{cs})bC_T} (C_{B1} - C_{B3})$$

or

$$(p_{A3} - 20) = \frac{(7 \times 10^5)(1 \times 10^5)}{(1 \times 10^5)(1)(56\,000)} (800 - C_{A3})$$

or

$$p_{A3} = 10\,020 - 12.5C_{B3}$$

At the bottom of the tower $p_{A3} = p_{A2}$, so

$$C_{B2} = \frac{1}{12.5} (10\,020 - 100) = 793.6 \text{ mol/m}^3$$

Step 2. Form of rate equation to use. Check both ends of the tower:

$$\text{at top} \begin{cases} k_{A_g} a p_A = (0.32)(20) = 6.4 \text{ mol/hr} \cdot \text{m}^3 \\ k_l a C_B = (0.1)(800) = 80 \text{ mol/hr} \cdot \text{m}^3 \end{cases}$$

$$\text{at bottom} \begin{cases} k_{A_g} a p_A = (0.32)(100) = 32 \\ k_l a C_B = (0.1)(793.6) = 79.36 \end{cases}$$

At both ends of the tower $k_{A_g} p_A < k_l C_B$; therefore, gas-phase resistance controls and we have a pseudo first-order reaction as given by Eq. 16 of Chapter 23

$$-r_A''' = k_{A_g} a p_A = 0.32 p_A$$

Step 3. Height of tower. From Eq. 10

$$\begin{aligned} h &= \frac{(F_g/A_{cs})}{\pi} \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{(-r_A''')} = \frac{10^5}{10^5} \int_{20}^{100} \frac{dp_A}{0.32 p_A} \\ &= \frac{1}{0.32} \ln \frac{100}{20} = \underline{\underline{5.03 \text{ m}}} \end{aligned}$$

Comment. Even though the liquid phase controls in physical absorption (see Example 24.1), it does not necessarily follow that it should still control when reaction occurs. In fact, we see here in Example 24.2 that it is the gas phase alone which influences the rate of the overall process. Reaction serves merely to eliminate the resistance of the liquid film. Also note the remarkable improvement in performance; 5 versus 500 m.

EXAMPLE 24.3

TOWERS FOR LOW CONCENTRATION OF LIQUID REACTANT; CASE A

Repeat Example 24.2 using a feed with $C_{B1} = 32 \text{ mol/m}^3$, instead of 800 mol/m^3 , see Fig. E24.3.

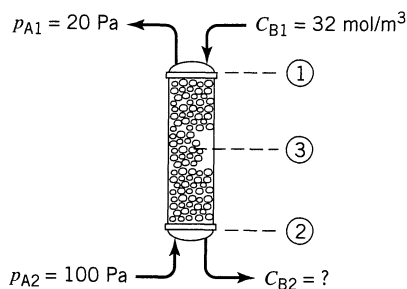


Figure E24.3

SOLUTION

As in the previous examples, solve by making a material balance, check the form of rate equation to use, then apply the performance equation to find the tower height.

Step 1. Material Balance. As in Example 24.2, for any point in the tower,

$$p_{A3} = 420 - 12.5C_{B3} \quad \text{or} \quad C_{B3} = \frac{420 - p_{A3}}{12.5}$$

and for the bottom of the tower where $p_A = 100$ Pa,

$$C_{B2} = \frac{320}{12.5} = 25.6 \text{ mol/m}^3$$

Step 2. Which Rate Form to Use. Again check both ends of the tower to see which rate form applies

$$\text{at top} \begin{cases} k_{A_g} a p_A = 0.32(20) = 6.4 \\ k_l a C_B = 0.1(32) = 3.2 \end{cases}$$

$$\text{at bottom} \begin{cases} k_{A_g} a p_A = 0.32(100) = 32 \\ k_l a C_B = 0.1(35.6) = 2.56 \end{cases}$$

At both ends of the tower $k_{A_g} a p_A > k_l a C_B$, therefore, the reaction takes place within the liquid film and Eq. 13 in Chapter 23 should be used,

$$-r_A''' = \frac{H_A C_B + p_A}{\frac{1}{k_{A_g} a} + \frac{H_A}{k_l a}} = \frac{12.5 \left[\frac{420 - p_{A3}}{12.5} \right] + p_A}{\frac{1}{0.32} + \frac{12.5}{0.1}} = 3.278 \text{ mol/m}^3 \text{ reactor} \cdot \text{hr}$$

Step 3. Height of Tower. From Eq. 6,

$$h = \frac{V_r}{A_{cs}} = \frac{10^5}{10^5} \int_{20}^{100} \frac{dp_A}{3.278} = \frac{100 - 20}{3.278} = \underline{\underline{24.4 \text{ m}}}$$

EXAMPLE 24.4 TOWERS FOR INTERMEDIATE CONCENTRATIONS OF LIQUID REACTANT

Repeat Example 24.2 using a feed in which $C_B = 128 \text{ mol/m}^3$.

SOLUTION

Refer to Fig. E24.4, and solve as with the previous examples.

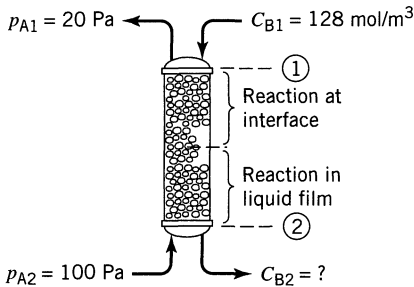


Figure E24.4

Step 1. Material balance. As with Examples 24.2 and 24.3 we have at any point in the tower,

$$p_{A3} = 1620 - 12.5C_{B3}$$

and at the bottom of the tower,

$$C_{B2} = \frac{1520}{12.5} = 121.6 \text{ mol/m}^3$$

Step 2. Form of rate equation to use. Check both ends of the tower:

$$\text{at top} \begin{cases} k_{A_g} a p_A = 6.4 \text{ mol/hr} \cdot \text{m}^3 \\ k_l a C_B = 12.8 \text{ mol} \cdot \text{hr} \cdot \text{m}^3 \end{cases}$$

$$\text{at bottom} \begin{cases} k_{A_g} a p_A = 32 \\ k_l a C_B = 12.16 \end{cases}$$

At the top $k_{Ag}p_A < k_l C_B$; hence, Eq. 16 in Chapter 23 must be used. At the bottom $k_{Ag}p_A > k_l C_B$; hence, Eq. 13 in Chapter 23 must be used.

Let us now find the condition at which the reaction zone just reaches the interface and where the form of rate equation changes. This occurs where

$$k_{Ag}p_A = k_l C_B \quad \text{or} \quad 0.32p_A = 0.1C_B$$

Solving with the material balance we find that the change occurs at $p_A = 39.5$ Pa.

Step 3. Height of Tower. Writing the performance equation we have, from Eq. 6,

$$h = \frac{(F_g/A_{cs})}{\pi} \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{-r_A'''} \quad \text{(iii)}$$

Noting that two different rate forms must be used, we have

$$\begin{aligned} h &= \frac{(F_g/A_{cs})}{\pi} \int_{20}^{39.5} \frac{dp_A}{(k_{Ag}a)p_A} + \frac{F_g/A_{cs}}{\pi} \int_{39.5}^{100} \frac{(1/k_{Ag}a + H_A/k_l a)}{C_B H_A + p_A} dp_A \\ &= \frac{10^5}{10^5(0.32)} \ln \frac{39.5}{20} + \frac{10^5}{10^5} \int_{39.5}^{100} \frac{(1/0.32 + 12.5/0.1)}{(1620 - p_A + p_A)} dp_A \\ &= 2.1268 + \frac{128.125}{1620} (100 - 39.5) = \underline{\underline{6.91 \text{ m}}} \end{aligned}$$

Comment. In this example we see that two distinct zones are present. Situations may be encountered where even another zone may be present. For example, if the entering liquid contains insufficient reactant, a point is reached in the tower where all this reactant is consumed. Below this point physical absorption alone takes place in reactant-free liquid. The methods of these examples, when used together, deal in a straightforward manner with this three-zone situation and van Krevelens and Hoftijzer (1948) discuss actual situations where these three distinct zones are present.

Comparing solutions for the four examples shows how reaction increases the effectiveness of the absorption process. ■

EXAMPLE 24.5 REDO EXAMPLE 24.2 BY THE GENERAL METHOD

In Example 24.2 we found which of the eight special cases (see Fig. 23.3) applied and then used its corresponding rate equation (it was Eq. 23.16). Alternatively we could have used the general rate expression (Eq. 23.5). This is what we will show here.

SOLUTION

From Example 24.2 a material balance gives the tower end conditions, as shown in Fig. E24.5. Now the rate of reaction at any point in the tower is, from Eq. 23.5,

$$-r_A''' = \left(\frac{1}{\frac{1}{0.32} + \frac{12.5}{0.1E} + \frac{12.5}{\infty(C_B)}} \right) p_A = \left(\frac{1}{3.125 + \frac{125}{E}} \right) p_A \quad (\text{i})$$

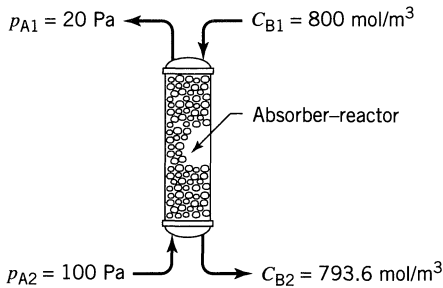


Figure E24.5

Evaluate E at various points in the tower. For this we need to first evaluate M_H and E_i .

At the Top of the Tower. From Fig. 23.4

$$M_H = \frac{\sqrt{\mathcal{D}_B C_B k}}{k_{A1}} = \infty, \quad \text{because } k = \infty$$

$$E_i = 1 + \frac{\mathcal{D}_B C_B H_A}{\mathcal{D}_A p_{Ai}} = 1 + \frac{800(12.5)}{p_{Ai}} = \frac{10^4}{p_{Ai}} \quad (\text{ii})$$

We have to guess the value of p_{Ai} . It can be anywhere between 0 Pa (gas film controls) up to 20 Pa (liquid film controls). Let us guess no gas-phase resistance. Then $p_{Ai} = p_A$, in which case

$$E_i = \frac{10^4}{20} = 500$$

and from Fig. 23.4, for $M_H = \infty$, $E_i = 500$, we see that

$$E = 500$$

Replacing in Eq. (i) we find

$$-r_A''' = \frac{1}{3.125 + \frac{125}{500}} p_A = \frac{1}{3.125 + 0.25} p_A = 0.296 p_A$$

↙ 93%
↘ 7%...resistance

Our guess was wrong, so let's try again. Let us guess the other extreme, $p_{Ai} = 0$, meaning that the total resistance is in the gas film. Then from Eq. (ii) we see that $E_i = \infty$, $E = \infty$ and the rate equation becomes

$$-r_A''' = \frac{1}{\underbrace{3.125 + 0}_{\text{gas film control}}} p_A = 0.32 p_A \quad \text{(iii)}$$

Thus our guess was correct.

At the Bottom of the Tower. We follow the same procedure and find the same result. Thus the rate at all points in the tower is given by Eq. (iii). The height of the tower, from Eq. 10, is then (see step 3 of Example 24.2)

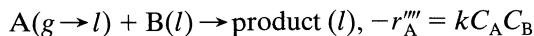
$$\underline{h = 5.03 \text{ m}}$$

Suggestion. Whenever $M_H > E_i$ we end up having to guess p_{Ai} , and that is tedious. In those cases try to use the special case expressions.

In other cases (and this is what we usually find) the general rate equation is easier to use. ■

EXAMPLE 24.6 REACTION OF A BATCH OF LIQUID

We wish to lower the concentration of B in the liquid ($V_l = 1.62 \text{ m}^3$, $C_U = 5555.6 \text{ mol/m}^3$) of an agitated tank reactor by bubbling gas ($F_g = 9000 \text{ mol/hr}$, $\pi = 10^5 \text{ Pa}$) containing A ($p_{Ain} = 1000 \text{ Pa}$) through it. A and B react as follows:



- How long must we bubble gas through the vessel to lower the concentration from $C_{B0} = 555.6$ to $C_{Bf} = 55.6 \text{ mol/m}^3$?
- What percent of entering A passes through the vessel unreacted?

Additional Data

$$k_{Ag}a = 0.72 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{Pa}$$

$$f_l = 0.9 \text{ m}^3 \text{ liquid/m}^3 \text{ total}$$

$$k_{Al}a = 144 \text{ hr}^{-1}$$

$$\mathcal{D}_A = \mathcal{D}_B = 3.6 \times 10^{-6} \text{ m}^2/\text{hr},$$

$$a = 100 \text{ m}^2/\text{m}^3$$

$$H_A = 10^3 \text{ Pa} \cdot \text{m}^3/\text{mol}$$

$$k = 2.6 \times 10^5 \text{ m}^3/\text{mol} \cdot \text{hr}$$

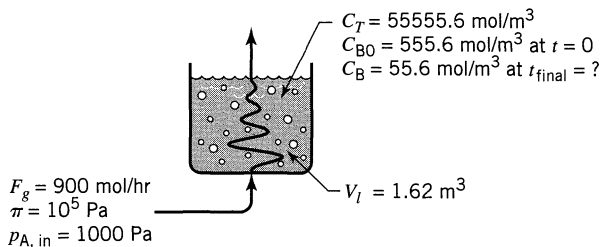


Figure E24.6

SOLUTION

Let us sketch what is known in Fig. E24.6.

At the start

$$M_H = \frac{\sqrt{\mathcal{D}_B k C_B}}{k_{Al}} = \frac{\sqrt{3.6 \times 10^{-6} (2.6 \times 10^5) (555.6)}}{144/100} = 15.84$$

$$E_i = 1 + \frac{C_B H_A}{p_{Ai}} = \frac{555.6(10^3)}{1000} = 555.6, \text{ or higher}$$

↑
or lower

$$\therefore E = M_H = 15.84$$

Since $p_A \ll \pi$ and $E = M_H$ the text says we can use the shortcut outlined above Eq. 19. Let us do it.

$$\begin{aligned}
 -r_A''' &= p_{A \text{in}} \left/ \left(\frac{\pi V_r}{F_g} + \frac{1}{k_{Ag} a} + \frac{H_A}{k_{Al} a E} + \frac{H_A}{k C_B f_l} \right) \right. \\
 &= 1000 \left/ \left(\frac{10^5 (1.62)}{9000} + \frac{1}{0.72} + \frac{10^3}{144(15.84)} + \frac{10^3}{2.6 \times 10^5 (555.6) 0.9} \right) \right. \\
 &= 50.44 \text{ mol/m}^3 \cdot \text{hr}
 \end{aligned}$$

At the end, following a similar treatment, we find

$$\left. \begin{aligned}
 M_H &= 5 \\
 E_i &= 55.6, \text{ or higher}
 \end{aligned} \right\} E = M_H = 5.0$$

$$-r_A''' = 1000 \left/ \left(\frac{10^5 (1.62)}{9000} + \frac{1}{0.72} + \frac{10^3}{144(5)} + \sim 0 \right) \right. = 48.13 \text{ mol/m}^3 \cdot \text{hr}$$

The rate of reaction at the beginning and at the end of the run is just about the same, so

$$-r_{A,ave}''' = \frac{50.44 + 48.13}{2} = 49.28$$

Thus the run time needed is

$$t = \frac{f_I}{b} \int_{C_{Bf}}^{C_{B0}} \frac{dC_B}{-r_A'''} = \frac{0.9(555.6 - 55.6)}{49.28} = \underline{\underline{9.13 \text{ hr}}}$$

The minimum time required is

$$t_{\min} = \frac{V_I(C_{B0} - C_{Bf})}{F_g(p_{Ain}/(\pi - p_{Ain}))} = \frac{1.62(555.6 - 55.6)}{9000(1000/(10^5 - 100))} = \underline{\underline{8.91 \text{ hr}}}$$

Thus the fraction of reactant which passes through the tank untreated is

$$\text{Fraction} = \frac{9.13 - 8.91}{8.91} = 0.025 = \underline{\underline{2.5\%}}$$

REFERENCES

- van Krevelens, D. W., and Hoftijzer, P., *Rec. Trav. Chim.*, **67**, 563 (1948).
 Kramers, H., and Westerterp, K. R., *Elements of Chemical Reactor Design and Operation*,

PROBLEMS

- 24.1.** The four p_A versus C_A sketches of Fig. 24.2 represent various possible ideal contacting schemes of gas with liquid. Sketch the contacting scheme for straight physical absorption corresponding to the p_A versus C_A operating lines XY shown in Fig. P24.1.

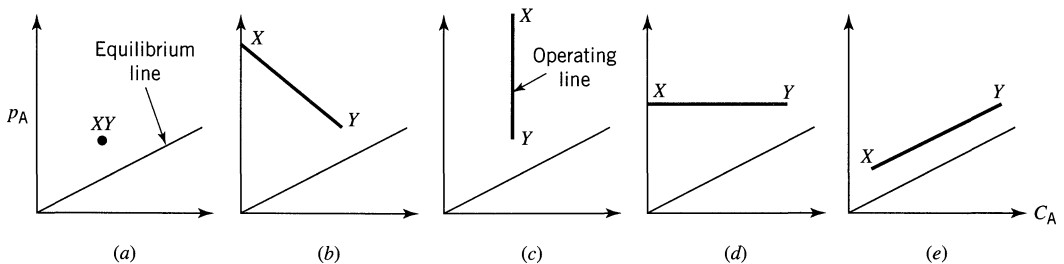
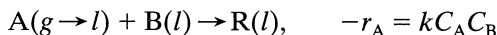


Figure P24.1

We plan to remove about 90% of the A present in a gas stream by absorption in water which contains reactant B. Chemicals A and B react in the liquid as follows:



B has a negligible vapor pressure, hence does not go into the gas phase. We plan to do this absorption in either a packed bed column, or an agitated tank contactor.

- (a) What volume of contactor is needed?
 (b) Where does the resistance of absorption reaction lie?

Data

For the gas stream:

$$\begin{aligned} F_g &= 90\,000 \text{ mol/hr at } \pi = 10^5 \text{ Pa} \\ p_{Ain} &= 1000 \text{ Pa} \\ p_{Aout} &= 100 \text{ Pa} \end{aligned}$$

Physical data

$$\begin{aligned} \mathcal{D} &= 3.6 \times 10^{-6} \text{ m}^2/\text{hr} \\ C_U &= 55\,556 \text{ mol H}_2\text{O}/\text{m}^3 \text{ liquid, at all } C_B \end{aligned}$$

For the packed bed

$$\begin{aligned} F_l &= 900\,000 \text{ mol/hr} & k_{Al}a &= 72 \text{ hr}^{-1} \\ C_{Bin} &= 55.56 \text{ mol/m}^3 & a &= 100 \text{ m}^2/\text{m}^3 \\ k_{Ag}a &= 0.36 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{Pa} & f_l &= V_l/V = 0.08 \end{aligned}$$

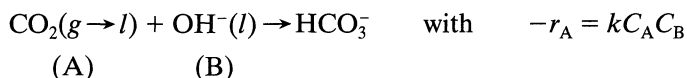
For the agitated tank

$$\begin{aligned} F_l &= 9000 \text{ mol/hr} & k_{Al}a &= 144 \text{ hr}^{-1} \\ C_{Bin} &= 5556 \text{ mol/m}^3 \text{ (about 10\% B)} & a &= 200 \text{ m}^2/\text{m}^3 \\ k_{Ag}a &= 0.72 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{Pa} & f_l &= V_l/V = 0.9 \end{aligned}$$

Note that F_l and C_{Bin} are very different in packed beds and tank contactors, and here is the reason why. Packed columns need $F_l/F_g \cong 10$ for satisfactory operations. This means large F_l , and so as not to waste reactant B, it is introduced in low concentration. On the other hand, tank contactors do not have this flow restriction. Thus we can use low F_l and high C_{Bin} , as long as we introduce sufficient B to react with A.

	Henry's Law Constant: H_A , $\text{Pa} \cdot \text{m}^3/\text{mol}$	For Reaction: k , $\text{m}^3/\text{mol} \cdot \text{hr}$	Type of Contactor T = Tower, Countercurrent A = Agitated Tank	
24.2.	0.0	0	In these problems of straight mass transfer assume that no B is present in the system.	A
24.3.	18	0		T
24.4.	1.8	0		T
24.5.	10^5	∞		T
24.6.	10^5	2.6×10^7	A	
24.7.	10^5	2.6×10^5	A	
24.8.	10^3	2.6×10^3	T	
24.9.	10^5	2.6×10^7	T	
24.10.	10^3	2.6×10^5	T	

24.11. Danckwerts and Gillham, in *Trans. I. Chem. E.*, **44**, 42, March 1966, studied the rate of CO_2 absorption into an alkaline buffered solution of K_2CO_3 and KHCO_3 . The resulting reaction can be represented as



In the experiment pure CO_2 at 1 atm was bubbled into a packed column irrigated by rapidly recirculating solution kept at 20°C and close to constant C_B . Find the fraction of entering CO_2 absorbed.

Data

Column: $V_r = 0.6041 \text{ m}^3$ $f_l = 0.08$ $a = 120 \text{ m}^2/\text{m}^3$
 Gas: $\pi = 101\,325 \text{ Pa}$ $H_A = 3500 \text{ Pa} \cdot \text{m}^3/\text{mol}$ $v_0 = 0.0363 \text{ m}^3/\text{s}$
 Liquid: $\bar{C}_B = 300 \text{ mol}/\text{m}^3$ $\mathcal{D}_{Al} = \mathcal{D}_{Bl} = 1.4 \times 10^{-9} \text{ m}^2/\text{s}$
 Rates: $k = 0.433 \text{ m}^3/\text{mol} \cdot \text{s}$ $k_{Al}a = 0.025 \text{ s}^{-1}$

This problem is by Barry Kelly.

24.12. A column packed with 5-cm polypropylene saddles ($a = 55 \text{ m}^2/\text{m}^3$) is being designed for the removal of chlorine from a gas stream ($G = 100 \text{ mol}/\text{s} \cdot \text{m}^2$, 2.36% Cl_2) by countercurrent contact with an NaOH solution

($L = 250 \text{ mol/s} \cdot \text{m}^2$, 10% NaOH, $C_B = 2736 \text{ mol/m}^3$) at about 40–45°C and 1 atm.

How high should the tower be for 99% removal of chlorine? Double the calculated height to take care of deviations from plug flow.

Data

The reaction $\text{Cl}_2 + 2\text{NaOH} \rightarrow \text{product}$ is very very fast and irreversible. For these very high flow rates (close to the limits allowed) an extrapolation of the correlations in Perry 6th ed., section 14, gives

$$k_g a = 133 \text{ mol/hr} \cdot \text{m}^3 \cdot \text{atm} \quad H_A = 125 \times 10^6 \text{ atm} \cdot \text{m}^3/\text{mol}$$

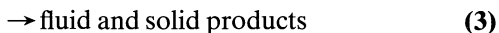
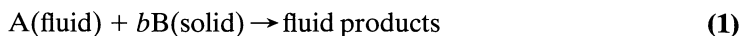
$$k_{fA} = 45 \text{ hr}^{-1} \quad \mathcal{D} = 1.5 \times 10^{-9} \text{ m}^2/\text{s}$$

Repeat Example 24.6 with the following two changes

	Henry's Law Constant $H_A, \text{ Pa} \cdot \text{m}^3/\text{mol}$	Second-Order Reaction Rate, Constant $k, \text{ m}^3/\text{mol} \cdot \text{hr}$
24.13.	10^5	2.6×10^5
24.14.	10^5	2.6×10^9
24.15.	10^5	2.6×10^3
24.16.	10^3	2.6×10^{11}

Fluid–Particle Reactions: Kinetics

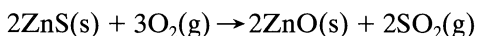
This chapter treats the class of heterogeneous reactions in which a gas or liquid contacts a solid, reacts with it, and transforms it into product. Such reactions may be represented by



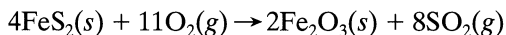
As shown in Fig. 25.1, solid particles remain unchanged in size during reaction when they contain large amounts of impurities which remain as a nonflaking ash or if they form a firm product material by the reactions of Eq. 2 or Eq. 3. Particles shrink in size during reaction when a flaking ash or product material is formed or when pure B is used in the reaction of Eq. 1.

Fluid–solid reactions are numerous and of great industrial importance. Those in which the solid does not appreciably change in size during reaction are as follows.

1. The roasting (or oxidation) of sulfide ores to yield the metal oxides. For example, in the preparation of zinc oxide the sulfide ore is mined, crushed, separated from the gangue by flotation, and then roasted in a reactor to form hard white zinc oxide particles according to the reaction



Similarly, iron pyrites react as follows:



2. The preparation of metals from their oxides by reaction in reducing atmospheres. For example, iron is prepared from crushed and sized magnetite

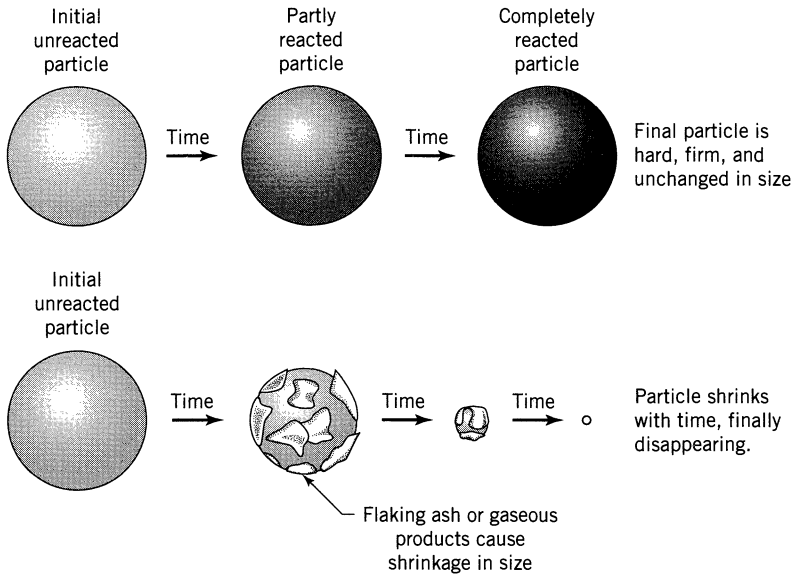
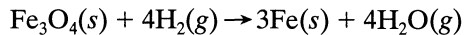


Figure 25.1 Different sorts of behavior of reacting solid particles.

ore in continuous-countercurrent, three-stage, fluidized-bed reactors according to the reaction

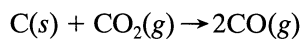
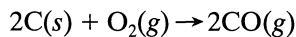
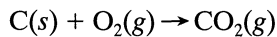


3. The nitrogenation of calcium carbide to produce cyanamide

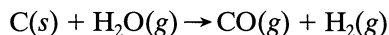


4. The protective surface treatment of solids such as the plating of metals.

The most common examples of fluid–solid reactions in which the size of solid changes are the reactions of carbonaceous materials such as coal briquettes, wood, etc. with low ash content to produce heat or heating fuels. For example, with an insufficient amount of air, producer gas is formed by the reactions

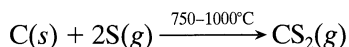


With steam, water gas is obtained by the reactions

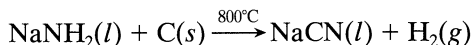


Other examples of reactions in which solids change in size are as follows.

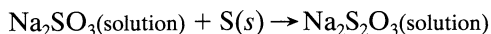
1. The manufacture of carbon disulfide from the elements



2. The manufacture of sodium cyanide from sodium amide



3. The manufacture of sodium thiosulfate from sulfur and sodium sulfite



Still other examples are the dissolution reactions, the attack of metal chips by acids, and the rusting of iron.

In Chapter 17 we pointed out that the treatment of heterogeneous reaction required the consideration of two factors in addition to those normally encountered in homogeneous reactions: the modification of the kinetic expressions resulting from the mass transfer between phases and the contacting patterns of the reacting phases.

In this chapter we develop the rate expressions for fluid-solid reactions. The next chapter will then use this information in design.

25.1 SELECTION OF A MODEL

We should clearly understand that every conceptual picture or model for the progress of reaction comes with its mathematical representation, its rate equation. Consequently, if we choose a model we must accept its rate equation, and vice versa. If a model corresponds closely to what really takes place, then its rate expression will closely predict and describe the actual kinetics; if a model differs widely from reality, then its kinetic expressions will be useless. We must remember that the most elegant and high-powered mathematical analysis based on a model which does not match reality is worthless for the engineer who must make design predictions. What we say here about a model holds not only in deriving kinetic expressions but in all areas of engineering.

The requirement for a good engineering model is that it be the closest representation of reality which can be treated without too many mathematical complexities. It is of little use to select a model which very closely mirrors reality but which is so complicated that we cannot do anything with it. Unfortunately, in today's age of computers, this all too often happens.

For the noncatalytic reaction of particles with surrounding fluid, we consider two simple idealized models, the *progressive-conversion* model and the *shrinking unreacted-core* model.

Progressive-Conversion Model (PCM). Here we visualize that reactant gas enters and reacts throughout the particle at all times, most likely at different rates at different locations within the particle. Thus, solid reactant is converted continuously and progressively throughout the particle as shown in Fig. 25.2.

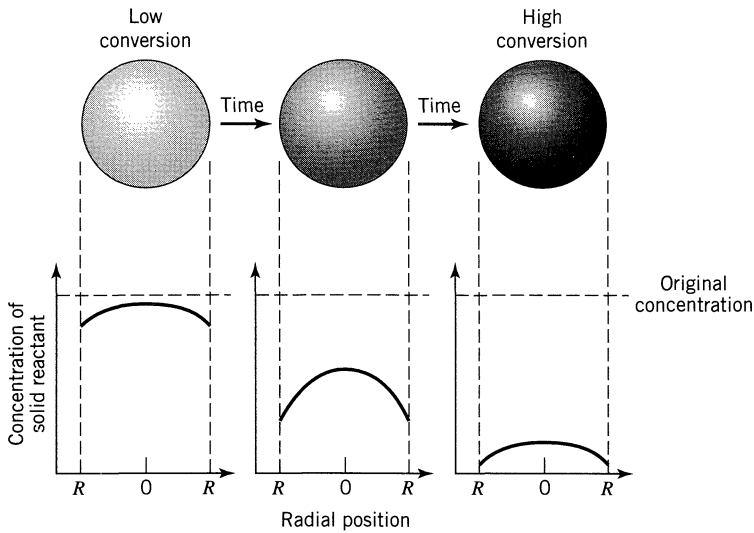


Figure 25.2 According to the progressive-conversion model, reaction proceeds continuously throughout the solid particle.

Shrinking-Core Model (SCM). Here we visualize that reaction occurs first at the outer skin of the particle. The zone of reaction then moves into the solid, leaving behind completely converted material and inert solid. We refer to these as “ash.” Thus, at any time there exists an unreacted core of material which shrinks in size during reaction, as shown in Fig. 25.3.

Comparison of Models with Real Situations. In slicing and examining the cross section of partly reacted solid particles, we usually find unreacted solid material surrounded by a layer of ash. The boundary of this unreacted core may not

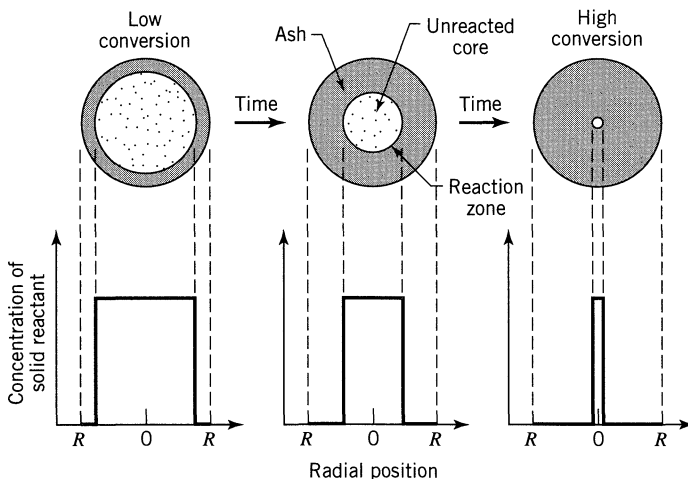


Figure 25.3 According to the shrinking-core model, reaction proceeds at a narrow front which moves into the solid particle. Reactant is completely converted as the front passes by.

always be as sharply defined as the model pictures it; nevertheless, evidence from a wide variety of situations indicates that in most cases the shrinking-core model (SCM) approximates real particles more closely than does the progressive-conversion model (PCM). Observations with burning coal, wood, briquettes, and tightly wrapped newspapers also favor the shrinking-core model. For further discussion on the many other models used (at least ten), see Chapter 55 in Levenspiel (1996).

Since the SCM seems to reasonably represent reality in a wide variety of situations, we develop its kinetic equations in the following section. In doing this we consider the surrounding fluid to be a gas. However, this is done only for convenience since the analysis applies equally well to liquids.

25.2 SHRINKING-CORE MODEL FOR SPHERICAL PARTICLES OF UNCHANGING SIZE

This model was first developed by Yagi and Kunii (1955, 1961), who visualized five steps occurring in succession during reaction (see Fig. 25.4).

- Step 1.* Diffusion of gaseous reactant A through the film surrounding the particle to the surface of the solid.
- Step 2.* Penetration and diffusion of A through the blanket of ash to the surface of the unreacted core.
- Step 3.* Reaction of gaseous A with solid at this reaction surface.

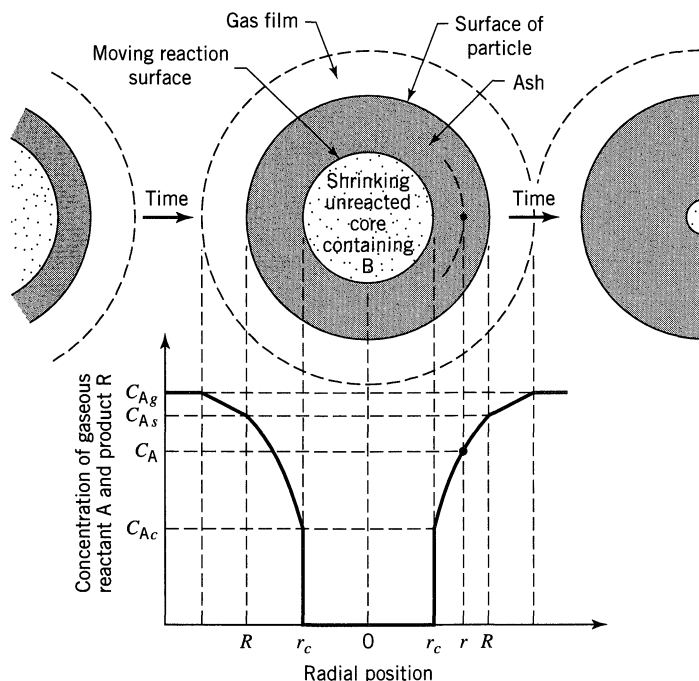


Figure 25.4 Representation of concentrations of reactants and products for the reaction $A(g) + bB(s) \rightarrow \text{solid product}$ for a particle of unchanging size.

- Step 4. Diffusion of gaseous products through the ash back to the exterior surface of the solid.
- Step 5. Diffusion of gaseous products through the gas film back into the main body of fluid.

In some situations some of these steps do not exist. For example, if no gaseous products are formed, steps 4 and 5 do not contribute directly to the resistance to reaction. Also, the resistances of the different steps usually vary greatly one from the other. In such cases we may consider that step with the highest resistance to be rate-controlling.

In this treatment we develop the conversion equations for spherical particles in which steps 1, 2, and 3, in turn, are rate-controlling. We then extend the analysis to nonspherical particles and to situations where the combined effect of these three resistances must be considered.

Diffusion Through Gas Film Controls

Whenever the resistance of the gas film controls, the concentration profile for gaseous reactant A will be shown as in Fig. 25.5. From this figure we see that no gaseous reactant is present at the particle surface; hence, the concentration driving force, $C_{Ag} - C_{As}$ becomes C_{Ag} and is constant at all times during reaction of the particle. Now since it is convenient to derive the kinetic equations based on available surface, we focus attention on the unchanging exterior surface of a particle S_{ex} . Noting from the stoichiometry of Eqs. 1, 2, and 3 that $dN_B = b dN_A$, we write

$$-\frac{1}{S_{ex}} \frac{dN_B}{dt} = -\frac{1}{4\pi R^2} \frac{dN_B}{dt} = -\frac{b}{4\pi R^2} \frac{dN_A}{dt} = b k_g (C_{Ag} - C_{As}) = b k_g C_{Ag} = \text{constant} \quad (4)$$

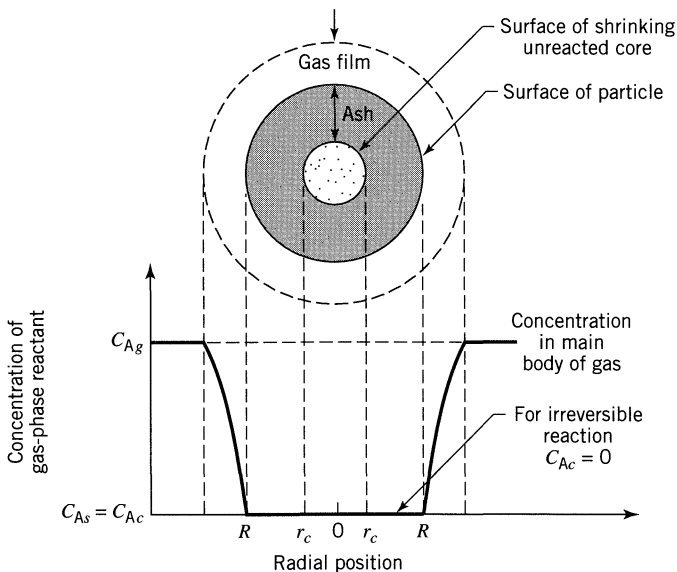


Figure 25.5 Representation of a reacting particle when diffusion through the gas film is the controlling resistance.

If we let ρ_B be the molar density of B in the solid and V be the volume of a particle, the amount of B present in a particle is

$$N_B = \rho_B V = \left(\frac{\text{moles B}}{\text{m}^3 \text{ solid}} \right) (\text{m}^3 \text{ solid}) \quad (5)$$

The decrease in volume or radius of unreacted core accompanying the disappearance of dN_B moles of solid reactant is then given by

$$-dN_B = -b dN_A = -\rho_B dV = -\rho_B d\left(\frac{4}{3}\pi r_c^3\right) = -4\pi\rho_B r_c^2 dr_c \quad (6)$$

Replacing Eq. 6 in 4 gives the rate of reaction in terms of the shrinking radius of unreacted core, or

$$-\frac{1}{S_{ex}} \frac{dN_B}{dt} = -\frac{\rho_B r_c^2 dr_c}{R^2 dt} = bk_g C_{Ag} \quad (7)$$

where k_g is the mass transfer coefficient between fluid and particle; see the discussion leading up to Eq. 24. Rearranging and integrating, we find how the unreacted core shrinks with time. Thus,

$$-\frac{\rho_B}{R^2} \int_R^{r_c} r_c^2 dr_c = bk_g C_{Ag} \int_0^t dt \quad (8)$$

$$t = \frac{\rho_B R}{3bk_g C_{Ag}} \left[1 - \left(\frac{r_c}{R} \right)^3 \right]$$

Let the time for complete conversion of a particle be τ . Then by taking $r_c = 0$ in Eq. 8, we find

$$\tau = \frac{\rho_B R}{3bk_g C_{Ag}} \quad (9)$$

The radius of unreacted core in terms of fractional time for complete conversion is obtained by combining Eqs. 8 and 9, or

$$\frac{t}{\tau} = 1 - \left(\frac{r_c}{R} \right)^3$$

This can be written in terms of fractional conversion by noting that

$$1 - X_B = \left(\frac{\text{volume of unreacted core}}{\text{total volume of particle}} \right) = \frac{\frac{4}{3}\pi r_c^3}{\frac{4}{3}\pi R^3} = \left(\frac{r_c}{R} \right)^3 \quad (10)$$

Therefore

$$\boxed{\frac{t}{\tau} = 1 - \left(\frac{r_c}{R}\right)^3 = X_B} \quad (11)$$

Thus we obtain the relationship of time with radius and with conversion, which is shown graphically in Figs. 25.9 and 25.10, pp. 582 and 583.

Diffusion through Ash Layer Controls

Figure 25.6 illustrates the situation in which the resistance to diffusion through the ash controls the rate of reaction. To develop an expression between time and radius, such as Eq. 8 for film resistance, requires a two-step analysis. First examine a typical partially reacted particle, writing the flux relationships for this condition. Then apply this relationship for all values of r_c ; in other words, integrate r_c between R and 0.

Consider a partially reacted particle as shown in Fig. 25.6. Both reactant A and the boundary of the unreacted core move inward toward the center of the particle. But for G/S systems the shrinkage of the unreacted core is slower than the flow rate of A toward the unreacted core by a factor of about 1000, which is roughly the ratio of densities of solid to gas. Because of this it is reasonable for us to assume, in considering the concentration gradient of A in the ash layer at any time, that the unreacted core is stationary.

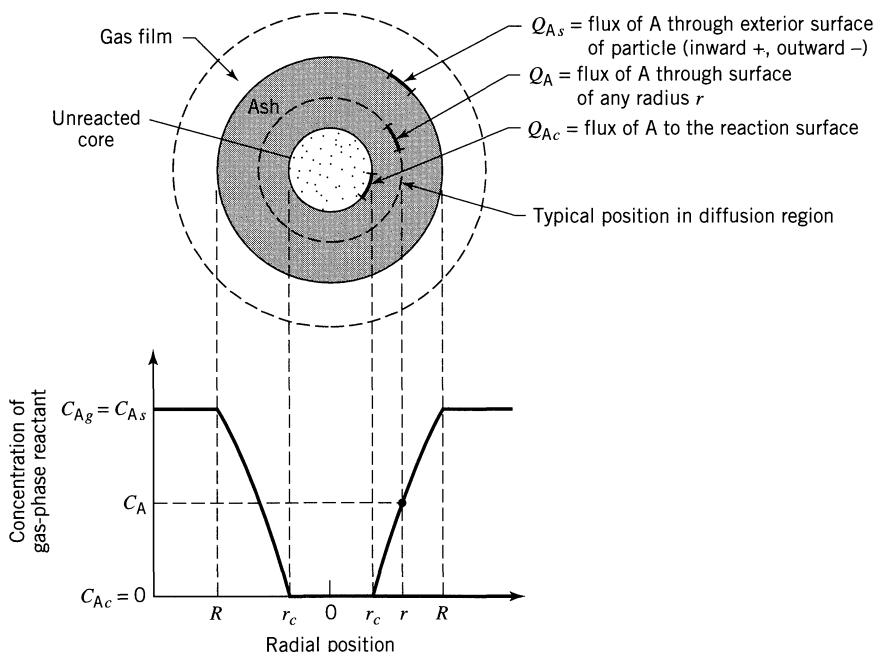


Figure 25.6 Representation of a reacting particle when diffusion through the ash layer is the controlling resistance.

With L/S systems we have a problem because the velocity ratio is closer to unity than to 1000. Yoshida et al. (1975) consider a relaxation of the above assumption.

For G/S systems the use of the steady-state assumption allows great simplification in the mathematics which follows. Thus the rate of reaction of A at any instant is given by its rate of diffusion to the reaction surface, or

$$-\frac{dN_A}{dt} = 4\pi r^2 Q_A = 4\pi R^2 Q_{As} = 4\pi r_c^2 Q_{Ac} = \text{constant} \quad (12)$$

For convenience, let the flux of A within the ash layer be expressed by Fick's law for equimolar counterdiffusion, though other forms of this diffusion equation will give the same result. Then, noting that both Q_A and dC_A/dr are positive, we have

$$Q_A = \mathcal{D}_e \frac{dC_A}{dr} \quad (13)$$

where \mathcal{D}_e is the effective diffusion coefficient of gaseous reactant in the ash layer. Often it is difficult to assign a value beforehand to this quantity because the property of the ash (its sintering qualities, for example) can be very sensitive to small amounts of impurities in the solid and to small variations in the particle's environment. Combining Eqs. 12 and 13, we obtain for any r

$$-\frac{dN_A}{dt} = 4\pi r^2 \mathcal{D}_e \frac{dC_A}{dr} = \text{constant} \quad (14)$$

Integrating across the ash layer from R to r_c , we obtain

$$-\frac{dN_A}{dt} \int_R^{r_c} \frac{dr}{r^2} = 4\pi \mathcal{D}_e \int_{C_{Ag}=C_{As}}^{C_{Ac}=0} dC_A$$

or

$$-\frac{dN_A}{dt} \left(\frac{1}{r_c} - \frac{1}{R} \right) = 4\pi \mathcal{D}_e C_{Ag} \quad (15)$$

This expression represents the conditions of a reacting particle at any time.

In the second part of the analysis we let the size of unreacted core change with time. For a given size of unreacted core, dN_A/dt is constant; however, as the core shrinks the ash layer becomes thicker, lowering the rate of diffusion of A. Consequently, integration of Eq. 15 with respect to time and other variables should yield the required relationship. But we note that this equation contains three variables, t , N_A , and r_c , one of which must be eliminated or written in terms of the other variables before integration can be performed. As with film diffusion, let us eliminate N_A by writing it in terms of r_c . This relationship is given by Eq. 6; hence, replacing in Eq. 15, separating variables, and integrating,

we obtain

$$-\rho_B \int_{r_c=R}^{r_c} \left(\frac{1}{r_c} - \frac{1}{R} \right) r_c^2 dr_c = b \mathcal{D}_e C_{A_g} \int_0^t dt$$

or

$$t = \frac{\rho_B R^2}{6b \mathcal{D}_e C_{A_g}} \left[1 - 3 \left(\frac{r_c}{R} \right)^2 + 2 \left(\frac{r_c}{R} \right)^3 \right] \quad (16)$$

For the complete conversion of a particle, $r_c = 0$, and the time required is

$$\tau = \frac{\rho_B R^2}{6b \mathcal{D}_e C_{A_g}} \quad (17)$$

The progression of reaction in terms of the time required for complete conversion is found by dividing Eq. 16 by Eq. 17, or

$$\frac{t}{\tau} = 1 - 3 \left(\frac{r_c}{R} \right)^2 + 2 \left(\frac{r_c}{R} \right)^3 \quad (18a)$$

which in terms of fractional conversion, as given in Eq. 10, becomes

$$\frac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B) \quad (18b)$$

These results are presented graphically in Figs. 25.9 and 25.10, pp. 582 and 583.

Chemical Reaction Controls

Figure 25.7 illustrates concentration gradients within a particle when chemical reaction controls. Since the progress of the reaction is unaffected by the presence of any ash layer, the rate is proportional to the available surface of unreacted core. Thus, based on unit surface of unreacted core, r_c , the rate of reaction for the stoichiometry of Eqs. 1, 2, and 3 is

$$-\frac{1}{4\pi r_c^2} \frac{dN_A}{dt} = -\frac{b}{4\pi r_c^2} \frac{dN_A}{dt} = bk'' C_{A_g} \quad (19)$$

where k'' is the first-order rate constant for the surface reaction. Writing N_B in terms of the shrinking radius, as given in Eq. 6, we obtain

$$-\frac{1}{4\pi r_c^2} \rho_B 4\pi r_c^2 \frac{dr_c}{dt} = -\rho_B \frac{dr_c}{dt} = bk'' C_{A_g} \quad (20)$$

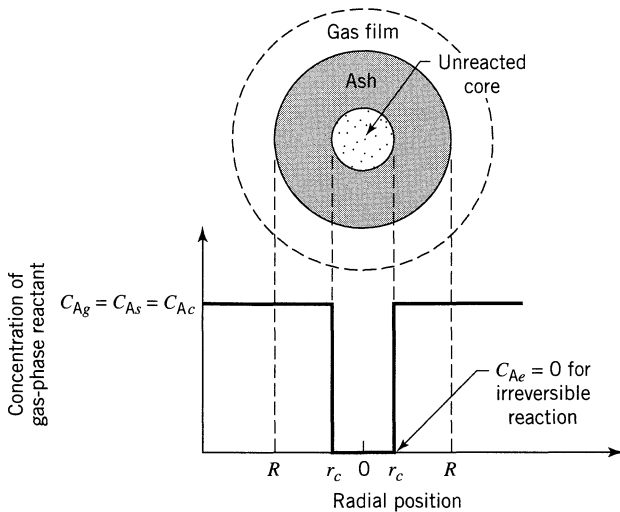


Figure 25.7 Representation of a reacting particle when chemical reaction is the controlling resistance, the reaction being $A(g) + bB(s) \rightarrow$ products.

which on integration becomes

$$-\rho_B \int_R^{r_c} dr_c = bk''C_{Ag} \int_0^t dt$$

or

$$t = \frac{\rho_B}{bk''C_{Ag}} (R - r_c) \quad (21)$$

The time τ required for complete conversion is given when $r_c = 0$, or

$$\tau = \frac{\rho_B R}{bk''C_{Ag}} \quad (22)$$

The decrease in radius or increase in fractional conversion of the particle in terms of τ is found by combining Eqs. 21 and 22. Thus,

$$\frac{t}{\tau} = 1 - \frac{r_c}{R} = 1 - (1 - X_B)^{1/3} \quad (23)$$

This result is plotted in Figs. 25.9 and 25.10, pp. 582 and 583.

25.3 RATE OF REACTION FOR SHRINKING SPHERICAL PARTICLES

When no ash forms, as in the burning of pure carbon in air, the reacting particle shrinks during reaction, finally disappearing. This process is illustrated in Fig. 25.8. For a reaction of this kind we visualize the following three steps occurring in succession.

- Step 1.* Diffusion of reactant A from the main body of gas through the gas film to the surface of the solid.
- Step 2.* Reaction on the surface between reactant A and solid.
- Step 3.* Diffusion of reaction products from the surface of the solid through the gas film back into the main body of gas. Note that the ash layer is absent and does not contribute any resistance.

As with particles of constant size, let us see what rate expressions result when one or the other of the resistances controls.

Chemical Reaction Controls

When chemical reaction controls, the behavior is identical to that of particles of unchanging size; therefore, Fig. 25.7 and Eq. 21 or 23 will represent the conversion-time behavior of single particles, both shrinking and of constant size.

Gas Film Diffusion Controls

Film resistance at the surface of a particle is dependent on numerous factors, such as the relative velocity between particle and fluid, size of particle, and fluid properties. These have been correlated for various ways of contacting fluid with

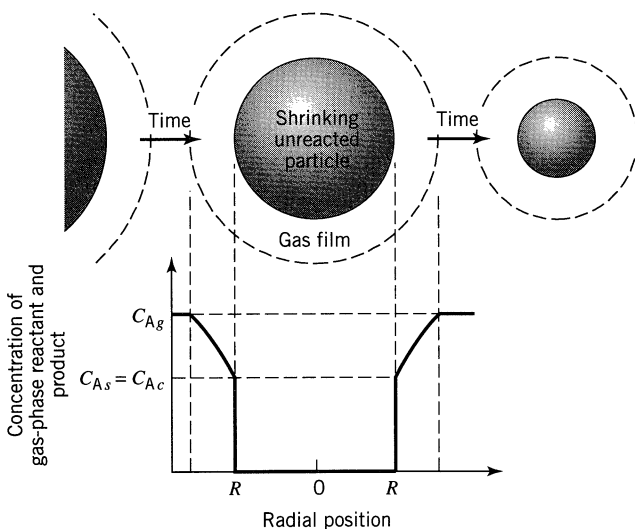


Figure 25.8 Representation of concentration of reactants and products for the reaction $A(g) + bB(s) \rightarrow rR(g)$ between a shrinking solid particle and gas.

solid, such as packed beds, fluidized beds, and solids in free fall. As an example, for mass transfer of a component of mole fraction y in a fluid to free-falling solids Froessling (1938) gives

$$\frac{k_g d_p y}{\mathcal{D}} = 2 + 0.6(\text{Sc})^{1/3}(\text{Re})^{1/2} = 2 + 0.6 \left(\frac{\mu}{\rho \mathcal{D}} \right)^{1/3} \left(\frac{d_p u \rho}{\mu} \right)^{1/2} \quad (24)$$

During reaction a particle changes in size; hence k_g also varies. In general k_g rises for an increase in gas velocity and for smaller particles. As an example, Fig. 12 and Eq. 24 show that

$$k_g \sim \frac{1}{d_p} \quad \text{for small } d_p \text{ and } u \quad (25)$$

$$k_g \sim \frac{u^{1/2}}{d_p^{1/2}} \quad \text{for large } d_p \text{ and } u \quad (26)$$

Equation 25 represents particles in the Stokes law regime. Let us develop conversion-time expressions for such particles.

Stokes Regime (Small Particles). At the time when a particle, originally of size R_0 , has shrunk to size R , we may write

$$dN_B = \rho_B dV = 4\pi\rho_B R^2 dR$$

Thus, analogous to Eq. 7, we have

$$-\frac{1}{S_{ex}} \frac{dN_B}{dt} = \frac{\rho_B 4\pi R^2}{4\pi R^2} \frac{dR}{dt} = -\rho_B \frac{dR}{dt} = bk_g C_{A_g} \quad (27)$$

Since in the Stokes regime Eq. 24 reduces to

$$k_g = \frac{2\mathcal{D}}{d_p} = \frac{\mathcal{D}}{R} \quad (28)$$

we have on combining and integrating

$$\int_{R_0}^R R dR = \frac{bC_{A_g}\mathcal{D}}{\rho_B} \int_0^t dt$$

or

$$t = \frac{\rho_B R_0^2}{2bC_{A_g}\mathcal{D}} \left[1 - \left(\frac{R}{R_0} \right)^2 \right]$$

The time for complete disappearance of a particle is thus

$$\tau = \frac{\rho_B R_0^2}{2bC_{Ag}\mathcal{D}} \quad (29)$$

and on combining we obtain

$$\frac{t}{\tau} = 1 - \left(\frac{R}{R_0}\right)^2 = 1 - (1 - X_B)^{2/3} \quad (30)$$

This relationship of size versus time for shrinking particles in the Stokes regime is shown in Figs. 25.9 and 25.10, pp. 582 and 583, and it well represents small burning solid particles and small burning liquid droplets.

25.4 EXTENSIONS

Particles of Different Shape. Conversion-time equations similar to those developed above can be obtained for various-shaped particles, and Table 25.1 summarizes these expressions.

Combination of Resistances. The above conversion-time expressions assume that a single resistance controls throughout reaction of the particle. However, the relative importance of the gas film, ash layer, and reaction steps will vary as particle conversion progresses. For example, for a constant size particle the gas film resistance remains unchanged, the resistance to reaction increases as the surface of unreacted core decreases, while the ash layer resistance is nonexistent at the start because no ash is present, but becomes progressively more and more important as the ash layer builds up. In general, then, it may not be reasonable to consider that just one step controls throughout reaction.

To account for the simultaneous action of these resistances is straightforward since they act in series and are all linear in concentration. Thus on combining Eqs. 7, 15, and 20 with their individual driving forces and eliminating intermediate concentrations we can show that the time to reach any stage of conversion is the sum of the times needed if each resistance acted alone, or

$$t_{\text{total}} = t_{\text{film alone}} + t_{\text{ash alone}} + t_{\text{reaction alone}} \quad (32a)$$

Similarly, for complete conversion

$$\tau_{\text{total}} = \tau_{\text{film alone}} + \tau_{\text{ash alone}} + \tau_{\text{reaction alone}} \quad (32b)$$

In an alternative approach, the individual resistances can be combined directly to give, at any particular stage of conversion,

$$-\frac{1}{S_{ex}} \frac{dN_B}{dt} = \frac{bC_A}{\frac{1}{k_g} + \frac{R(R-r_c)}{r_c\mathcal{D}_e} + \frac{R^2}{r_c^2 k''}} \quad (33a)$$

Table 25.1 Conversion-Time Expressions for Various Shapes of Particles, Shrinking-Core Model

	Film Diffusion Controls	Ash Diffusion Controls	Reaction Controls
Flat plate $X_B = 1 - \frac{1}{L}$ $L = \text{half thickness}$	$\frac{t}{\tau} = X_B$ $\tau = \frac{\rho_B L}{bk_g C_{A_g}}$	$\frac{t}{\tau} = X_B^2$ $\tau = \frac{\rho_B L^2}{2b\mathcal{D}_e C_{A_g}}$	$\frac{t}{\tau} = X_B$ $\tau = \frac{\rho_B L}{bk'' C_{A_g}}$
Cylinder $X_B = 1 - \left(\frac{r_c}{R}\right)^2$	$\frac{t}{\tau} = X_B$ $\tau = \frac{\rho_B R}{2bk_g C_{A_g}}$	$\frac{t}{\tau} = X_B + (1 - X_B) \ln(1 - X_B)$ $\tau = \frac{\rho_B R^2}{4b\mathcal{D}_e C_{A_g}}$	$\frac{t}{\tau} = 1 - (1 - X_B)^{1/2}$ $\tau = \frac{\rho_B R}{bk'' C_{A_g}}$
Sphere $X_B = 1 - \left(\frac{r_c}{R}\right)^3$	$\frac{t}{\tau} = X_B$ $\tau = \frac{\rho_B R}{3bk_g C_{A_g}}$	$\frac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)$ $\tau = \frac{\rho_B R^2}{6b\mathcal{D}_e C_{A_g}}$	$\frac{t}{\tau} = 1 - (1 - X_B)^{1/3}$ $\tau = \frac{\rho_B R}{bk'' C_{A_g}}$
Small particle Stokes regime	$\frac{t}{\tau} = 1 - (1 - X_B)^{2/3}$ $\tau = \frac{\rho_B R_0^2}{2b\mathcal{D}_e C_{A_g}}$	Not applicable	$\frac{t}{\tau} = 1 - (1 - X_B)^{1/3}$ $\tau = \frac{\rho_B R_0}{bk'' C_{A_g}}$
Large particle ($u = \text{constant}$)	$\frac{t}{\tau} = 1 - (1 - X_B)^{1/2}$ $\tau = (\text{const}) \frac{R_0^{3/2}}{C_{A_g}}$	Not applicable	$\frac{t}{\tau} = 1 - (1 - X_B)^{1/3}$ $\tau = \frac{\rho_B R}{bk'' C_{A_g}}$

Constant Size Particles

Shrinking Sphere

or

$$-\frac{dr_c}{dt} = \frac{bC_A/\rho_B}{\underbrace{\frac{r_c^2}{R^2k_g}}_{\text{film}} + \underbrace{\frac{(R-r_c)r_c}{R\mathcal{D}_e}}_{\text{ash}} + \underbrace{\frac{1}{k''}}_{\text{reaction}}} \quad (33b)$$

As may be seen, the relative importance of the three individual resistances varies as conversion progresses, or as r_c decreases.

On considering the whole progression from fresh to completely converted constant size particle, we find on the average that the relative roles of these three resistances is given by

$$-\frac{1}{S_{ex}} \frac{dN_A}{dt} = \bar{k}'' C_A = \frac{C_A}{\frac{1}{k_g} + \frac{R}{2\mathcal{D}_e} + \frac{3}{k''}} \quad (34)$$

For ash-free particles which shrink with reaction, only two resistances, gas film and surface reaction, need to be considered. Because these are both based on the changing exterior surface of particles, we may combine them to give at any instant

$$-\frac{1}{S_{ex}} \frac{dN_A}{dt} = \frac{1}{\frac{1}{k_g} + \frac{1}{k''}} C_A \quad (35)$$

Various forms of these expressions have been derived by Yagi and Kunii (1955), Shen and Smith (1965), and White and Carberry (1965).

Limitations of the Shrinking Core Model. The assumptions of this model may not match reality precisely. For example, reaction may occur along a diffuse front rather than along a sharp interface between ash and fresh solid, thus giving behavior intermediate between the shrinking core and the continuous reaction models. This problem is considered by Wen (1968), and Ishida and Wen (1971).

Also, for fast reaction the rate of heat release may be high enough to cause significant temperature gradients within the particles or between particle and the bulk fluid. This problem is treated in detail by Wen and Wang (1970).

Despite these complications Wen (1968) and Ishida et al. (1971), on the basis of studies of numerous systems, conclude that the shrinking core model is the best simple representation for the majority of reacting gas-solid systems.

There are, however, two broad classes of exceptions to this conclusion. The first comes with the slow reaction of a gas with a very porous solid. Here reaction can occur throughout the solid, in which situation the continuous reaction model may be expected to better fit reality. An example of this is the slow poisoning of a catalyst pellet, a situation treated in Chapter 21.

The second exception occurs when solid is converted by the action of heat, and without needing contact with gas. Baking bread, boiling missionaries, and

roasting puppies are mouthwatering examples of such reactions. Here again the continuous reaction model is a better representation of reality. Wen (1968) and Kunii and Levenspiel (1991) treat these kinetics.

25.5 DETERMINATION OF THE RATE-CONTROLLING STEP

The kinetics and rate-controlling steps of a fluid-solid reaction are deduced by noting how the progressive conversion of particles is influenced by particle size and operating temperature. This information can be obtained in various ways, depending on the facilities available and the materials at hand. The following observations are a guide to experimentation and to the interpretation of experimental data.

Temperature. The chemical step is usually much more temperature-sensitive than the physical steps; hence, experiments at different temperatures should easily distinguish between ash or film diffusion on the one hand and chemical reaction on the other hand as the controlling step.

Time. Figures 25.9 and 25.10 show the progressive conversion of spherical solids when chemical reaction, film diffusion, and ash diffusion in turn control. Results of kinetic runs compared with these predicted curves should indicate the rate-controlling step. Unfortunately, the difference between ash diffusion and chemical reaction as controlling steps is not great and may be masked by the scatter in experimental data.

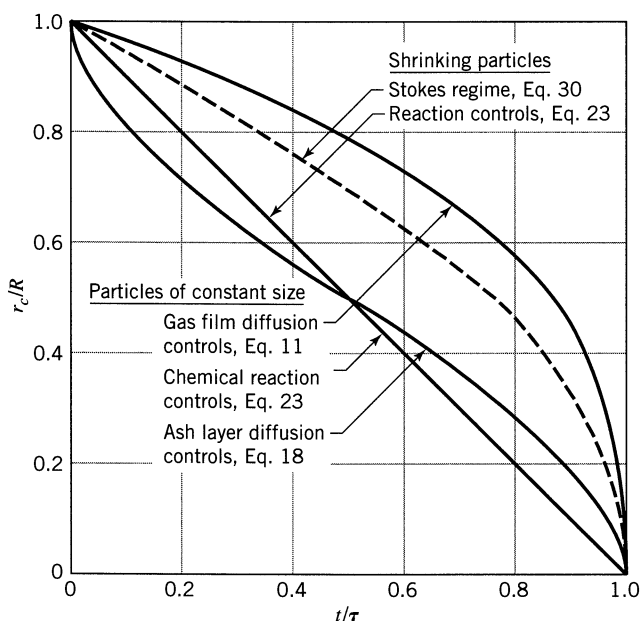


Figure 25.9 Progress of reaction of a single spherical particle with surrounding fluid measured in terms of time for complete reaction.

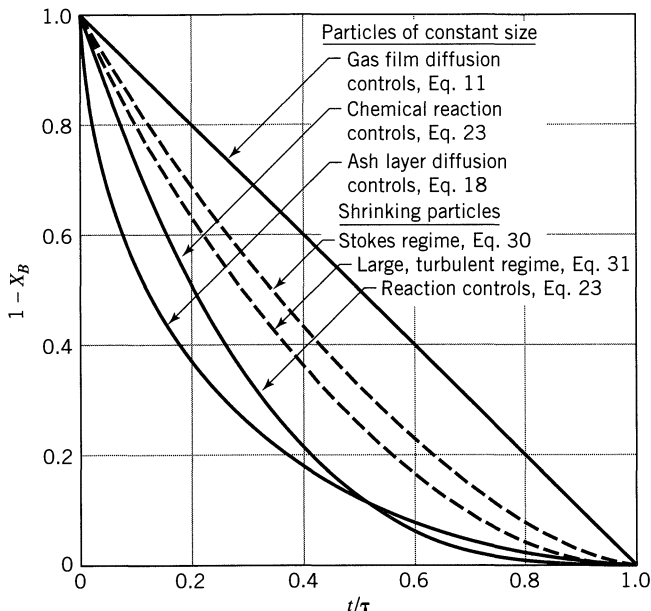


Figure 25.10 Progress of reaction of a single spherical particle with surrounding fluid measured in terms of time for complete conversion.

Conversion-time curves analogous to those in Figs. 25.9 and 25.10 can be prepared for other solid shapes by using the equations of Table 25.1.

Particle Size. Equations 16, 21, and 8 with Eq. 24 or 25 show that the time needed to achieve the same fractional conversion for particles of different but unchanging sizes is given by

$$t \propto R^{1.5 \text{ to } 2.0} \quad \text{for film diffusion controlling (the exponent drops as Reynolds number rises)} \quad (36)$$

$$t \propto R^2 \quad \text{for ash diffusion controlling} \quad (37)$$

$$t \propto R \quad \text{for chemical reaction controlling} \quad (38)$$

Thus kinetic runs with different sizes of particles can distinguish between reactions in which the chemical and physical steps control.

Ash Versus Film Resistance. When a hard solid ash forms during reaction, the resistance of gas-phase reactant through this ash is usually much greater than through the gas film surrounding the particle. Hence in the presence of a nonflaking ash layer, film resistance can safely be ignored. In addition, ash resistance is unaffected by changes in gas velocity.

Predictability of Film Resistance. The magnitude of film resistance can be estimated from dimensionless correlations such as Eq. 24. Thus an observed rate approximately equal to the calculated rate suggests that film resistance controls.

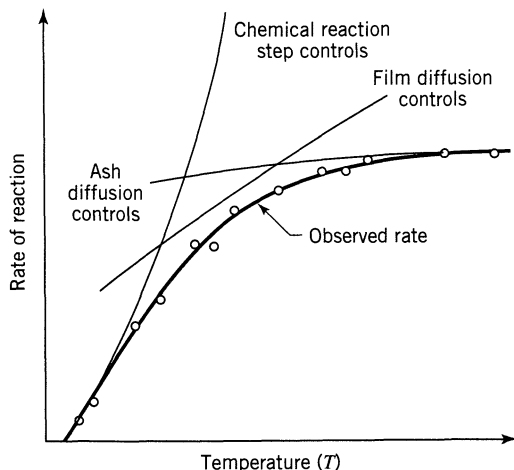
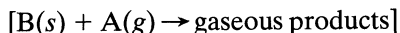
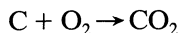


Figure 25.11 Because of the series relationship among the resistances to reaction, the net or observed rate is never higher than for any of the individual steps acting alone.

Overall Versus Individual Resistance. If a plot of individual rate coefficients is made as a function of temperature, as shown in Fig. 25.11, the overall coefficient given by Eq. 34 or 35 cannot be higher than any of the individual coefficients.

With these observations we can usually discover with a small, carefully planned experimental program which is the controlling mechanism.

Let us illustrate the interplay of resistances with the well-studied gas-solid reaction of pure carbon particles with oxygen:



with rate equation

$$-\frac{1}{S_{ex}} \frac{dN_B}{dt} = -\frac{1}{4\pi R^2} 4\pi R^2 \rho_B \frac{dR}{dt} = -\rho_B \frac{dR}{dt} = \bar{k}'' C_A \quad (27)$$

Since no ash is formed at any time during reaction, we have here a case of kinetics of shrinking particles for which two resistances at most, surface reaction and gas film, may play a role. In terms of these, the overall rate constant at any instant from Eq. 35 is

$$\frac{1}{\bar{k}''} = \frac{1}{k''} + \frac{1}{k_g}$$

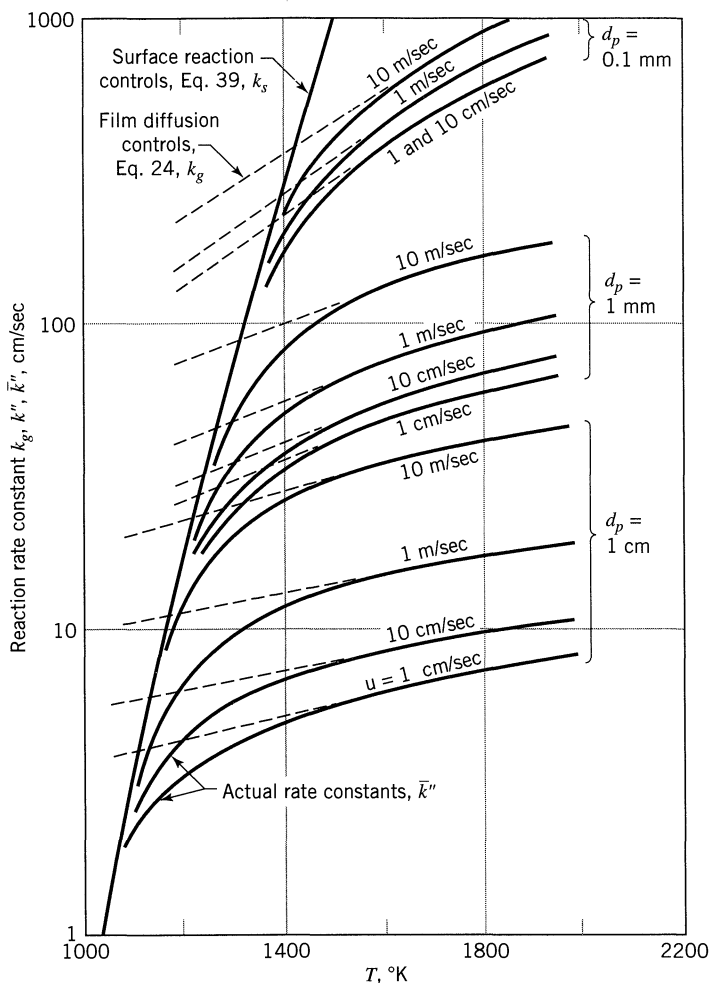


Figure 25.12 Rate of combustion of pure carbon particles; this figure is adapted from Yagi and Kunii (1955).

k_g is given by Eq. 24, while k'' is given by the following expression of Parker and Hottel (1936):

$$-\frac{1}{S_{ex}} \frac{dN_B}{dt} = 4.32 \times 10^{11} C_{Ag} \sqrt{T} e^{-(184\,000)/RT} = k_s C_{Ag} \quad (39)$$

where R is in $J/mol \cdot K$, T is in kelvin, and C_{Ag} is in gram moles per liter. Figure 25.12 shows all this information in convenient graphical form and allows determination of \bar{k}'' for different values of the system variables. Note that when film resistance controls, the reaction is rather temperature insensitive but is dependent on particle size and relative velocity between solid and gas. This is shown by the family of lines, close to parallel and practically horizontal.

In extrapolating to new untried operating conditions, we must know when to be prepared for a change in controlling step and when we may reasonably expect the rate-controlling step not to change. For example, for particles with nonflaking ash a rise in temperature and to a lesser extent an increase in particle size may cause the rate to switch from reaction to ash diffusion controlling. For reactions in which ash is not present, a rise in temperature will cause a shift from reaction to film resistance controlling.

On the other hand, if ash diffusion already controls, then a rise in temperature should not cause it to shift to reaction control or film diffusion control.

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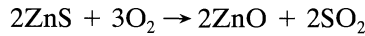
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PROBLEMS

- 25.1.** A batch of solids of uniform size is treated by gas in a uniform environment. Solid is converted to give a nonflaking product according to the shrinking-core model. Conversion is about $\frac{7}{8}$ for a reaction time of 1 h, conversion is complete in two hours. What mechanism is rate controlling?
- 25.2.** In a shady spot at the end of Brown Street in Lewisburg, Pennsylvania, stands a Civil War memorial—a brass general, a brass cannon which persistent undergraduate legend insists may still fire some day, and a stack of iron cannonballs. At the time this memorial was set up, 1868, the cannonballs were 30 inches in circumference. Today due to weathering, rusting, and the once-a-decade steel wire scrubbing by the DCW, the cannonballs are only 29.75 in. in circumference. Approximately, when will they disappear completely?
- 25.3.** Calculate the time needed to burn to completion particles of graphite ($R_0 = 5$ mm, $\rho_B = 2.2$ gm/cm³, $k'' = 20$ cm/sec) in an 8% oxygen stream.

For the high gas velocity used assume that film diffusion does not offer any resistance to transfer and reaction. Reaction temperature = 900°C.

- 25.4.** Spherical particles of zinc blende of size $R = 1$ mm are roasted in an 8% oxygen stream at 900°C and 1 atm. The stoichiometry of the reaction is



Assuming that reaction proceeds by the shrinking-core model calculate the time needed for complete conversion of a particle and the relative resistance of ash layer diffusion during this operation.

Data

Density of solid, $\rho_B = 4.13$ gm/cm³ = 0.0425 mol/cm³

Reaction rate constant, $k'' = 2$ cm/sec

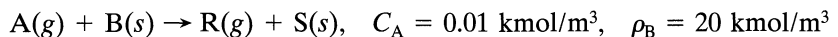
For gases in the ZnO layer, $\mathcal{D}_e = 0.08$ cm²/sec

Note that film resistance can safely be neglected as long as a growing ash layer is present.

On doubling the particle size from R to $2R$ the time for complete conversion triples. What is the contribution of ash diffusion to the overall resistance for particles of size

- 25.5.** $R?$ **25.6.** $2R?$

Spherical solid particles containing B are roasted isothermally in an oven with gas of constant composition. Solids are converted to a firm nonflaking product according to the SCM as follows:



From the following conversion data (by chemical analysis) or core size data (by slicing and measuring) determine the rate controlling mechanism for the transformation of solid.

25.7.	d_p , mm	X_B	t , min	25.8.	d_p	X_B	t , sec
	1	1	4		1	0.3	2
	1.5	1	6		1	0.75	5
25.9.	d_p , mm	X_B	t , sec	25.10.	d_p	X_B	t , sec
	1	1	200		2	0.875	1
	1.5	1	450		1	1	1

- 25.11.** Uniform-sized spherical particles UO_3 are reduced to UO_2 in a uniform environment with the following results:

t, hr	0.180	0.347	0.453	0.567	0.733
X_B	0.45	0.68	0.80	0.95	0.98

If reaction follows the SCM, find the controlling mechanism and a rate equation to represent this reduction.

- 25.12.** A large stockpile of coal is burning. Every part of its surface is in flames. In a 24-hr period the linear size of the pile, as measured by its silhouette against the horizon, seems to decrease by about 5%.
- How should the burning mass decrease in size?
 - When should the fire burn itself out?
 - State the assumptions on which your estimation is based.

Fluid–Particle Reactors: Design

Three factors control the design of a fluid–solid reactor; the reaction kinetics for single particles, the size distribution of solids being treated, and the flow patterns of solids and fluid in the reactor. Where the kinetics are complex and not well known, where the products of reaction form a blanketing fluid phase, where temperature within the system varies greatly from position to position, analysis of the situation becomes difficult and present design is based largely on the experiences gained by many years of operations, innovation, and small changes made on existing reactors. The blast furnace for producing iron is probably the most important industrial example of such a system.

Though some real industrial reactions may never yield to simple analysis, this should not deter us from studying idealized systems. These satisfactorily represent many real systems and in addition may be taken as the starting point for more involved analyses. Here we consider only the greatly simplified idealized systems in which the reaction kinetics, flow characteristics, and size distribution of solids are known.

Referring to Fig. 26.1, let us discuss briefly the various types of contacting in gas–solid operations.

Solids and Gas Both in Plug Flow. When solids and gas pass through the reactor in plug flow, their compositions change during passage. In addition, such operations are usually nonisothermal.

The plug flow contacting of phases may be accomplished in many ways: by countercurrent flow as in blast furnaces and cement kilns [Fig. 26.1(a)], by cross-flow as in moving belt feeders for furnaces [Fig. 26.1(b)], or by cocurrent flow as in polymer driers [Fig. 26.1(c)].

Solids in Mixed Flow. The fluidized bed [Fig. 26.1(d)] is the best example of a reactor with mixed flow of solids. The gas flow in such reactors is difficult to characterize and often is worse than mixed flow. Because of the high heat capacity of the solids, isothermal conditions can frequently be assumed in such operations.

Semibatch Operations. The ion exchange column of Fig. 26.1(e) is an example of the batch treatment of solids in which the flow of fluid closely approximates

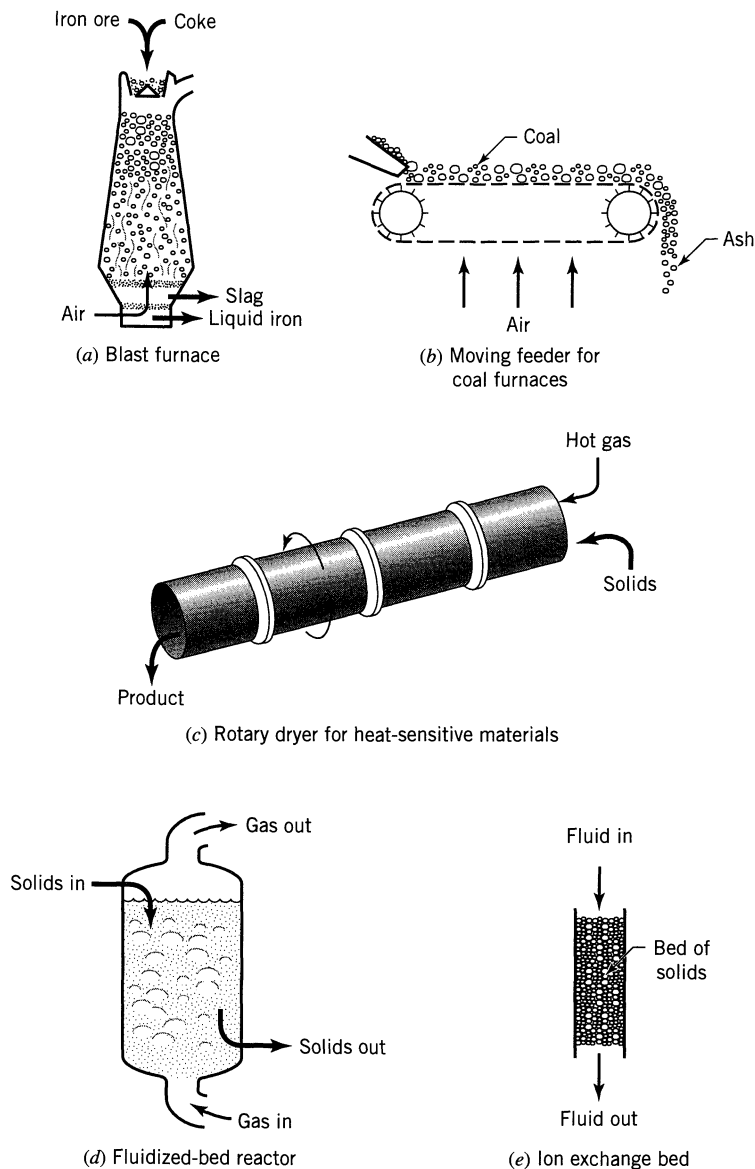


Figure 26.1 Various contacting patterns in fluid-solid reactors: (a-d) countercurrent, crosscurrent, and cocurrent plug flow; (d) intermediate gas flow, mixed solid flow; (e) semibatch operations.

the ideal of plug flow. On the contrary, an ordinary home fireplace, another semibatch operation, has a flow which is difficult to characterize.

Batch Operations. The reaction and dissolution of a batch of solid in a batch of fluid, such as the acid attack of a solid, is a common example of batch operations. Analysis and design of fluid-solid systems are greatly simplified if the composi-

tion of the fluid can be considered to be uniform throughout the reactor. Since this is a reasonable approximation where fractional conversion of fluid-phase reactants is not too great, where fluid backmixing is considerable, or where solids wander about the reactor, sampling all the fluid as in fluidized beds, this assumption frequently can be used without deviating too greatly from reality. We use this assumption in the analyses that follow.

We then conclude this chapter with a brief treatment of extremely fast reactions which are representative of some combustions. Here the analysis simplifies considerably, since the kinetics do not enter the picture.

Let us now turn to a number of frequently met contacting patterns, and let us develop their performance equations, employing in every case the assumptions of uniform gas composition within the reactor.

Particles of a Single Size, Plug Flow of Solids, Uniform Gas Composition

The contact time or reaction time needed for any specific conversion of solid is found directly from the equations of Table 25.1.

Mixture of Particles of Different but Unchanging Sizes, Plug Flow of Solids, Uniform Gas Composition

Consider a solid feed consisting of a mixture of different-size particles. The size distribution of this feed can be represented either as a continuous distribution or as a discrete distribution. We use the latter representation because screen analysis, our way of measuring size distributions, gives discrete measurements.

Let F be the quantity of solid being treated in unit time. Since the density of solid may change during reaction, F is defined as the volumetric feed rate of solid in the general case. Where density change of the solid is negligible, F can represent the mass feed rate of solid as well. In addition, let $F(R_i)$ be the quantity of material of size about R_i fed to the reactor. If R_m is the largest particle size in the feed, we have for particles of unchanging size

$$F = \sum_{R_i=0}^{R_m} F(R_i), \quad \text{cm}^3/\text{sec or gm/sec}$$

Figure 26.2 shows the general characteristics of a discrete size distribution.

When in plug flow all solids stay in the reactor for the same length of time t_p . From this and the kinetics for whatever resistance controls, the conversion $X_B(R_i)$ for any size of particle R_i can be found. Then the mean conversion \bar{X}_B of the solids leaving the reactor can be obtained by properly summing to find the overall contribution to conversion of all sizes of particles. Thus,

$$\left(\begin{array}{l} \text{mean value for} \\ \text{the fraction of} \\ \text{B unconverted} \end{array} \right) = \sum_{\text{all sizes}} \left(\begin{array}{l} \text{fraction of reactant} \\ \text{B unconverted in} \\ \text{particles of size } R_i \end{array} \right) \left(\begin{array}{l} \text{fraction of} \\ \text{feed which is} \\ \text{of size } R_i \end{array} \right) \quad (1)$$

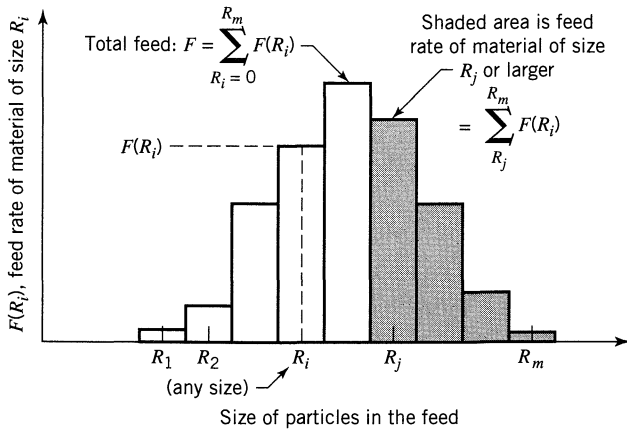


Figure 26.2 Representation of the feed rate of a mixture of particles.

or in symbols

$$1 - \bar{X}_B = \sum_{R(t_p = \tau)}^{R_m} [1 - X_B(R_i)] \frac{F(R_i)}{F} \quad (2)$$

where $R(t_p = \tau)$ is the radius of the largest particle completely converted in the reactor.

Equation 2 requires some discussion. First of all, we know that a smaller particle requires a shorter time for complete conversion. Hence some of our feed particles, those smaller than $R(t_p = \tau)$, will be completely reacted. But if we automatically apply our conversion-time equations to these particles we can come up with \bar{X}_B values greater than unity, which makes no sense physically. Thus the lower limit of the summation indicates that particles smaller than $R(t_p = \tau)$ are completely converted and do not contribute to the fraction unconverted, $1 - \bar{X}_B$.

EXAMPLE 26.1 CONVERSION OF A SIZE MIXTURE IN PLUG FLOW

A feed consisting

- 30% of 50- μm -radius particles
- 40% of 100- μm -radius particles
- 30% of 200- μm -radius particles

is to be fed continuously in a thin layer onto a moving grate crosscurrent to a flow of reactant gas. For the planned operating conditions the time required for complete conversion is 5, 10, and 20 min for the three sizes of particles. Find

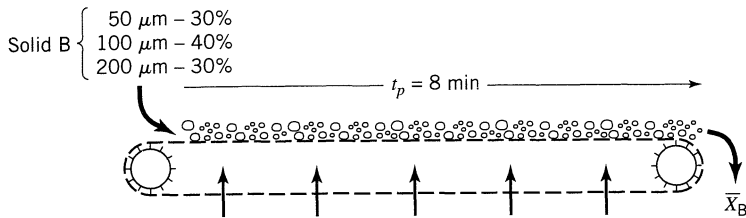


Figure E26.1

the conversion of solids on the grate for a residence time of 8 min in the reactor (see Fig. E26.1).

SOLUTION

From the statement of the problem we may consider the solids to be in plug flow with $t_p = 8$ min and the gas to be uniform in composition. Hence for a mixed feed Eq. 2 is applicable, or

$$1 - \bar{X}_B = [1 - X_B(50 \mu\text{m})] \frac{F(50 \mu\text{m})}{F} + [1 - X_B(100 \mu\text{m})] \frac{F(100 \mu\text{m})}{F} + \dots \quad (\text{i})$$

where

$$\frac{F(50 \mu\text{m})}{F} = 0.30 \quad \text{and} \quad \tau(50 \mu\text{m}) = 5 \text{ min}$$

$$\frac{F(100 \mu\text{m})}{F} = 0.40 \quad \text{and} \quad \tau(100 \mu\text{m}) = 10 \text{ min}$$

$$\frac{F(200 \mu\text{m})}{F} = 0.30 \quad \text{and} \quad \tau(200 \mu\text{m}) = 20 \text{ min}$$

Because for the three sizes of particles

$$R_1 : R_2 : R_3 = \tau_1 : \tau_2 : \tau_3,$$

we see from Eq. 25.38 that chemical reaction controls and the conversion-time characteristics for each size is given by Eq. 25.23 or

$$[1 - X_B(R_i)] = \left(1 - \frac{t_p}{\tau(R_i)}\right)^3$$

Replacing in Eq. (i) we obtain for unconverted reactant

$$1 - \bar{X}_B = 0 + \underbrace{\left(1 - \frac{8 \text{ min}}{10 \text{ min}}\right)^3 (0.4)}_{\text{for } R = 100 \mu\text{m}} + \underbrace{\left(1 - \frac{8}{20}\right)^3 (0.3)}_{\text{for } R = 200 \mu\text{m}}$$

$$= 0.0032 + 0.0648 = 0.068$$

Hence the fraction of solid converted equals 93.2%.

Note that the smallest size of particles is completely converted and does not contribute to the summation of Eq. (i).

Mixed Flow of Particles of a Single Unchanging Size, Uniform Gas Composition

Consider the reactor of Fig. 26.1(d) with constant flow rates of both solids and gas into and out of the reactor. With the assumption of uniform gas concentration and mixed flow of solids, this model represents a fluidized-bed reactor in which there is no elutriation of fine particles.

The conversion of reactant in a single particle depends on its length of stay in the bed, and its appropriate controlling resistance is given by Eq. 25.11, 25.18, or 25.23. However, the length of stay is not the same for all the particles in the reactor; hence we must calculate a mean conversion \bar{X}_B of material. Recognizing that the solid behaves as a macrofluid, this can be done by the methods leading to Eq. 11.13. Thus, for the solids leaving the reactor

$$\left(\begin{array}{l} \text{mean value for} \\ \text{the fraction of} \\ \text{B unconverted} \end{array}\right) = \sum_{\substack{\text{particles} \\ \text{of all} \\ \text{ages}}} \left(\begin{array}{l} \text{fraction of reactant} \\ \text{unconverted for} \\ \text{particles staying in} \\ \text{the reactor for time} \\ \text{between } t \text{ and } t + dt \end{array}\right) \left(\begin{array}{l} \text{fraction of exit} \\ \text{stream which has} \\ \text{stayed in the reactor} \\ \text{for a time between} \\ t \text{ and } t + dt \end{array}\right) \quad (3)$$

or in symbols

$$1 - \bar{X}_B = \int_0^{\infty} (1 - X_B) \mathbf{E} dt, \quad X_B \leq 1$$

or

$$1 - \bar{X}_B = \int_0^{\tau} (1 - X_B) \mathbf{E} dt \quad (4)$$

where \mathbf{E} is the exit age distribution of the solids in the reactor (see Chapter 11).

For mixed flow of solids with mean residence time \bar{t} in the reactor, see Fig. 26.3, we find from Fig. 11.14 or Eq. 14.1 that

$$\mathbf{E} = \frac{e^{-t/\bar{t}}}{\bar{t}} \quad (5)$$

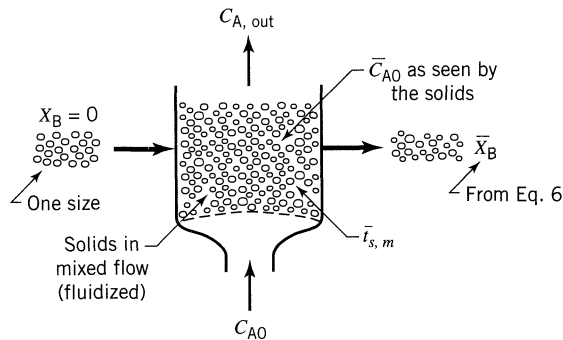


Figure 26.3 Conversion of one size of solids in mixed flow.

Thus, for mixed flow of the single size of solid which is completely converted in time τ , we obtain

$$1 - \bar{X}_B = \int_0^\tau (1 - X_B)_{\text{individual particle}} \frac{e^{-t/\bar{t}}}{\bar{t}} dt \quad (6)$$

This expression may be integrated for the various controlling resistances. For *film resistance controlling*, Eq. 25.11 with Eq. 6 yields

$$1 - \bar{X}_B = \int_0^\tau \left(1 - \frac{t}{\tau}\right) \frac{e^{-t/\bar{t}}}{\bar{t}} dt \quad (7)$$

which on integration by parts gives

$$\bar{X}_B = \frac{\bar{t}}{\tau} (1 - e^{-\tau/\bar{t}}) \quad (8a)$$

or in equivalent expanded form, useful for large \bar{t}/τ , thus for very high conversion

$$1 - \bar{X}_B = \frac{1}{2} \frac{\tau}{\bar{t}} - \frac{1}{3!} \left(\frac{\tau}{\bar{t}}\right)^2 + \frac{1}{4!} \left(\frac{\tau}{\bar{t}}\right)^3 - \dots \quad (8b)$$

For *chemical reaction controlling*, Eq. 25.23 replaced in Eq. 6 gives

$$1 - \bar{X}_B = \int_0^\tau \left(1 - \frac{t}{\tau}\right)^3 \frac{e^{-t/\bar{t}}}{\bar{t}} dt \quad (9)$$

Integrating by parts using the recursion formula, found in any table of integrals, we obtain

$$\bar{X}_B = 3 \frac{\bar{t}}{\tau} - 6 \left(\frac{\bar{t}}{\tau} \right)^2 + 6 \left(\frac{\bar{t}}{\tau} \right)^3 (1 - e^{-\tau/\bar{t}}) \quad (10a)$$

or in equivalent form, useful for large \bar{t}/τ , or for very high conversion

$$1 - \bar{X}_B = \frac{1}{4} \frac{\tau}{\bar{t}} - \frac{1}{20} \left(\frac{\tau}{\bar{t}} \right)^2 + \frac{1}{120} \left(\frac{\tau}{\bar{t}} \right)^3 - \dots \quad (10b)$$

For *ash resistance controlling* replacement of Eq. 25.18 in Eq. 6 followed by integration leads to a cumbersome expression which on expansion yields [see Yagi and Kunii (1961)]

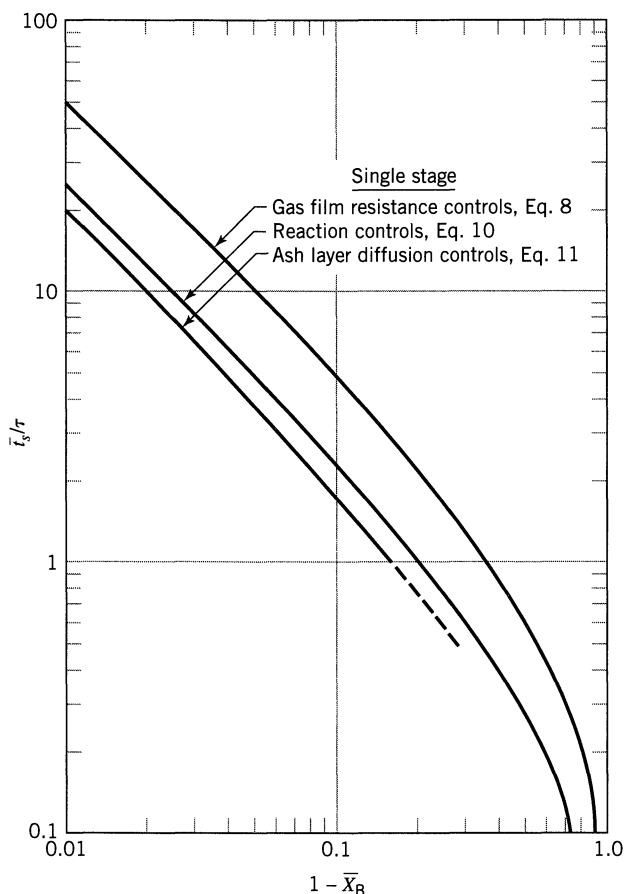


Figure 26.4 Mean conversion versus mean residence time in mixed flow reactors, single size of solid.

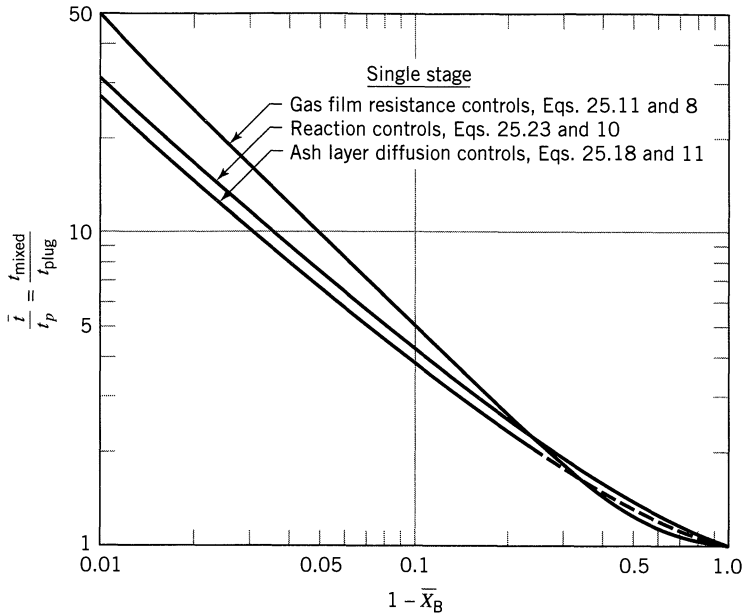


Figure 26.5 Comparison of holding times needed to effect a given conversion for mixed flow and plug flow of a single size of solid.

$$1 - \bar{X}_B = \frac{1}{5} \left(\frac{\tau}{t} \right) - \frac{19}{420} \left(\frac{\tau}{t} \right)^2 + \frac{41}{4620} \left(\frac{\tau}{t} \right)^3 - 0.00149 \left(\frac{\tau}{t} \right)^4 + \dots \quad (11)$$

Figures 26.4 and 26.5 present these results for solids in mixed flow in convenient graphical form. Figure 26.5 shows clearly that at high conversion the mixed flow reactor requires a much larger holding time for solids than does a plug flow reactor.

Extension to multistage operations is not difficult; see Levenspiel (1996, p. 52.14) or Kunii and Levenspiel (1991).

EXAMPLE 26.2 CONVERSION OF A SINGLE-SIZED FEED IN A MIXED FLOW REACTOR

Yagi et al. (1951) roasted pyrrhotite (iron sulfide) particles dispersed in asbestos fibers and found that the time for complete conversion was related to particle size as follows:

$$\tau \propto R^{1.5}$$

Particles remained as hard solids of unchanging size during reaction.

A fluidized-bed reactor is planned to convert pyrrhotite ore to the corresponding oxide. The feed is to be uniform in size, $\tau = 20$ min, with mean residence

time $\bar{t} = 60$ min in the reactor. What fraction of original sulfide ore remains unconverted?

SOLUTION

Since a hard product material is formed during reaction, film diffusion can be ruled out as the controlling resistance. For chemical reaction controlling Eq. 25.38 shows that

$$\tau \propto R$$

whereas for ash layer diffusion controlling Eq. 25.37 shows that

$$\tau \propto R^2$$

As the experimentally found diameter dependency lies between these two values, it is reasonable to expect that both these mechanisms offer resistance to conversion. Using in turn ash diffusion and chemical reaction as the controlling resistance should then give the upper and lower bound to the conversion expected.

The solids in a fluidized bed approximate mixed flow; hence, for chemical reaction controlling, Eq. 10, with $\tau/\bar{t} = 20 \text{ min}/60 \text{ min} = \frac{1}{3}$, gives

$$1 - \bar{X}_B = \frac{1}{4} \left(\frac{1}{3}\right) - \frac{1}{20} \left(\frac{1}{3}\right)^2 + \frac{1}{120} \left(\frac{1}{3}\right)^3 - \dots = 0.078$$

For ash layer diffusion controlling Eq. 11 gives

$$1 - \bar{X}_B = \frac{1}{5} \left(\frac{1}{3}\right) - \frac{19}{420} \left(\frac{1}{3}\right)^2 + \frac{41}{4620} \left(\frac{1}{3}\right)^3 - \dots = 0.062$$

Hence the fraction of sulfide remaining is between 6.2% and 7.8%, or on averaging

$$\underline{\underline{1 - \bar{X}_B \cong 0.07}}, \quad \text{or} \quad \underline{\underline{7.0\%}}$$

Mixed Flow of a Size Mixture of Particles of Unchanging Size, Uniform Gas Composition

Often a range of particle sizes is used as feed to a mixed flow reactor. For such a feed and a single-exit stream (no elutriation of the fines) the methods leading to Eqs. 2 and 6, when combined, should yield the required conversion.

Consider the reactor shown in Fig. 26.6. Since the exit stream is representative of the bed conditions, the size distributions of the bed as well as the feed and exit streams are all alike, or

$$\frac{F(R_i)}{F} = \frac{W(R_i)}{W} \quad (12)$$

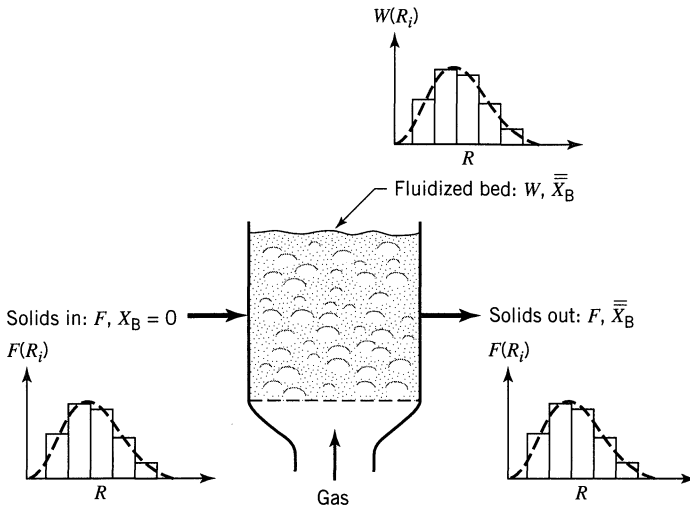


Figure 26.6 Fluidized bed with single exit stream treating a size mixture of solids. Note that the size distribution of the flow streams and the bed are all the same.

where W is the quantity of material in the reactor and where $W(R_i)$ is the quantity of material of size R_i in the reactor. In addition, for this flow the mean residence time $\bar{t}(R_i)$ of material of any size R_i is equal to the mean residence time of solid in the bed, or

$$\bar{t} = \bar{t}(R_i) = \frac{W}{F} = \frac{\text{(weight of all solids in the reactor)}}{\text{(feed rate of all solids to the reactor)}} \quad (13)$$

Letting $\bar{X}_B(R_i)$ be the mean conversion of particles of size R_i in the bed, we have from Eq. 6

$$1 - \bar{X}_B(R_i) = \int_0^{\tau(R_i)} [1 - X_B(R_i)] \frac{e^{-t/\bar{t}}}{\bar{t}} dt \quad (14)$$

However, the feed consists of particles of different sizes; hence the overall mean of B unconverted in all these sizes is

$$\left(\begin{array}{c} \text{mean value for} \\ \text{fraction of B} \\ \text{unconverted} \end{array} \right) = \sum_{\text{all sizes}} \left(\begin{array}{c} \text{fraction unconverted} \\ \text{in particles of size } R_i \end{array} \right) \left(\begin{array}{c} \text{fraction of exit or} \\ \text{entering stream consisting} \\ \text{of particles of size } R_i \end{array} \right) \quad (15)$$

or in symbols

$$1 - \bar{\bar{X}}_B = \sum_{R=0}^{R_m} [1 - X_B(R_i)] \frac{F(R_i)}{F}$$

Combining Eqs. 14 and 15 and replacing the first term expression with Eqs. 8, 10, or 11 for each size of particle, we obtain in turn, for *film diffusion controlling*,

$$1 - \bar{X}_B = \sum^{R_m} \left\{ \frac{1}{2!} \frac{\tau(R_i)}{\bar{t}} - \frac{1}{3!} \left[\frac{\tau(R_i)}{\bar{t}} \right]^2 + \dots \right\} \frac{F(R_i)}{F} \quad (16)$$

for *chemical reaction controlling*,

$$1 - \bar{X}_B = \sum^{R_m} \left\{ \frac{1}{4} \frac{\tau(R_i)}{\bar{t}} - \frac{1}{20} \left[\frac{\tau(R_i)}{\bar{t}} \right]^2 + \dots \right\} \frac{F(R_i)}{F} \quad (17)$$

for *ash diffusion controlling*,

$$1 - \bar{X}_B = \sum^{R_m} \left\{ \frac{1}{5} \frac{\tau(R_i)}{\bar{t}} - \frac{19}{420} \left[\frac{\tau(R_i)}{\bar{t}} \right]^2 + \dots \right\} \frac{F(R_i)}{F} \quad (18)$$

where $\tau(R_i)$ is the time for complete reaction of particles of size R_i . The following example illustrates the use of these expressions.

EXAMPLE 26.3 CONVERSION OF A FEED MIXTURE IN A MIXED FLOW REACTOR

A feed consisting

- 30% of 50- μm -radius particles
- 40% of 100- μm -radius particles
- 30% of 200- μm -radius particles

is to be reacted in a fluidized-bed steady-state flow reactor constructed from a vertical 2-m long 20-cm ID pipe. The fluidizing gas is the gas-phase reactant, and at the planned operating conditions the time required for complete conversion is 5, 10, and 20 min for the three sizes of feed. Find the conversion of solids in the reactor for a feed rate of 1 kg solids/min if the bed contains 10 kg solids.

Additional Information:

- The solids are hard and unchanged in size and weight during reaction.
- A cyclone separator is used to separate and return to the bed any solids that may be entrained by the gas.
- The change in gas-phase composition in the bed is small.

SOLUTION

From the statement of the problem we may consider the solids to be in mixed flow. For a feed mixture Eq. 15 is applicable, and since chemical reaction controls (see Example 26.1), this equation reduces to Eq. 17, where from the problem

statement

$$\begin{aligned} F &= 1000 \text{ gm/min} & \bar{t} &= \frac{W}{F} = \frac{10\,000 \text{ gm}}{1000 \text{ gm/min}} = 10 \text{ min} \\ W &= 10\,000 \text{ gm} \end{aligned}$$

$$\begin{aligned} F(50 \mu\text{m}) &= 300 \text{ gm/min} & \text{and} & & \tau(50 \mu\text{m}) &= 5 \text{ min} \\ F(100 \mu\text{m}) &= 400 \text{ gm/min} & \text{and} & & \tau(100 \mu\text{m}) &= 10 \text{ min} \\ F(200 \mu\text{m}) &= 300 \text{ gm/min} & \text{and} & & \tau(200 \mu\text{m}) &= 20 \text{ min} \end{aligned}$$

Replacing in Eq. 17 we obtain

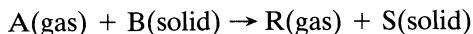
$$\begin{aligned} 1 - \bar{X}_B &= \left[\frac{1}{4} \frac{5 \text{ min}}{10 \text{ min}} - \frac{1}{20} \left(\frac{5}{10} \right)^2 + \dots \right] \frac{300 \text{ gm/min}}{1000 \text{ gm/min}} \\ &\quad \text{for } R = 50 \mu\text{m} \\ &+ \left[\frac{1}{4} \left(\frac{10 \text{ min}}{10 \text{ min}} \right) - \frac{1}{20} \left(\frac{10}{10} \right)^2 + \dots \right] \frac{400}{1000} \\ &\quad \text{for } R = 100 \mu\text{m} \\ &+ \left[\frac{1}{4} \left(\frac{20 \text{ min}}{10 \text{ min}} \right) - \frac{1}{20} \left(\frac{20}{10} \right)^2 + \dots \right] \frac{300}{1000} \\ &\quad \text{for } R = 200 \mu\text{m} \\ &= \left(\frac{1}{8} - \frac{1}{80} + \dots \right) \frac{3}{10} + \left(\frac{1}{4} - \frac{1}{20} + \frac{1}{120} - \dots \right) \frac{4}{10} \\ &\quad + \left(\frac{1}{2} - \frac{1}{5} + \frac{1}{15} - \frac{2}{10} + \dots \right) \frac{3}{10} \\ &= 0.034 + 0.083 + 0.105 = 0.222 \end{aligned}$$

The mean conversion of solids is then

$$\bar{X}_B = 77.8\%$$

EXAMPLE 26.4 FINDING THE SIZE OF A FLUIDIZED BED

In a gas-phase environment, particles of B are converted to solid product as follows:



Reaction proceeds according to the shrinking core model with reaction control and with time for complete conversion of particles of 1 hr.

A fluidized bed is to be designed to treat 1 ton/hr of solids to 90% conversion using a stoichiometric feed rate of A, fed at C_{A0} . Find the weight of solids in

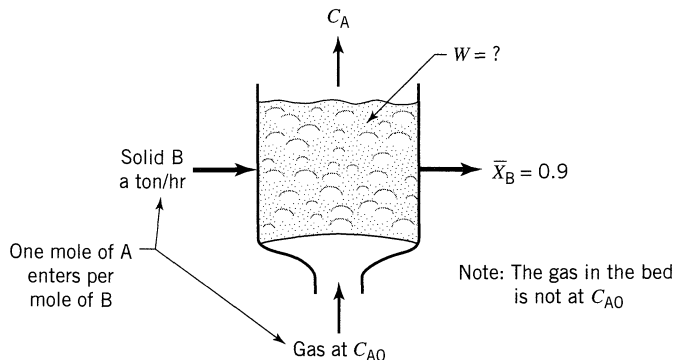


Figure E26.4

the reactor if gas is assumed to be in mixed flow. Note that the gas in the reactor is not at C_{A0} . Figure E26.4 sketches this problem.

SOLUTION

In a C_{A0} environment with reaction controlling

$$\tau = \frac{\rho_B R}{k_s C_{A0}} = 1 \text{ hr}$$

and in any other environment $\tau \propto \frac{1}{C_{A0}}$

Now for equal stoichiometric feed $X_A = \bar{X}_B$. Thus, the leaving gas is at $0.1 C_{A0}$. Since the gas is in mixed flow, the solids see this exit gas, or $\tau = 10$ hr.

From Eq. 10 let us find τ/\bar{t} which gives $\bar{X}_B = 0.9$. Thus, solve

$$1 - \bar{X}_B = 0.1 = \frac{1}{4} \left(\frac{\tau}{\bar{t}} \right) - \frac{1}{20} \left(\frac{\tau}{\bar{t}} \right)^2 + \dots$$

Solving by trial and error we find

$$\tau/\bar{t} = 0.435, \quad \text{or} \quad \bar{t} = \frac{W}{F_{B0}} = 23 \text{ hr}$$

Thus, the needed weight of bed is

$$W = \bar{t} F_{B0} = 23(1) = \underline{\underline{23 \text{ tons}}}$$

Instantaneous Reaction

When reaction between gas and solid is fast enough so that any volume element of reactor contains only one or other of the two reactants, but not both, then we may consider reaction to be instantaneous. This extreme is approached in the high temperature combustion of finely divided solids.

In this situation prediction of the performance of the reactor is straightforward and is dependent only on the stoichiometry of the reaction. The kinetics do not enter the picture. Let us illustrate this behavior with the following ideal contacting patterns.

Batch Solids. Figure 26.7 shows two situations, one which represents a packed bed, the other a fluidized bed with no bypassing of gas in the form of large gas bubbles. In both cases the leaving gas is completely converted and remains that way so long as solid reactant is still present in the bed. As soon as the solids are all consumed, and this occurs the instant the stoichiometric quantity of gas has been added, then the conversion of gas drops to zero.

Countercurrent Plug Flow of Gas and Solids. Since only one or other reactant can be present at any level in the bed, there will be a sharp reaction plane where the reactants meet. This will occur either at one end or the other of the reactor depending on which feed stream is in excess of stoichiometric. Assuming that each 100 moles of solid combine with 100 moles of gas, Figs. 26.8*a* and *b* show what happens when we feed a little less gas than stoichiometric and a little more than stoichiometric.

We may wish reaction to occur in the center of the bed so that both ends can be used as heat exchange regions to heat up reactants. This can be done by matching the gas and solids flow rates; however, this is inherently an unstable system and requires proper control. A second alternative, shown in Fig. 26.8*c*,

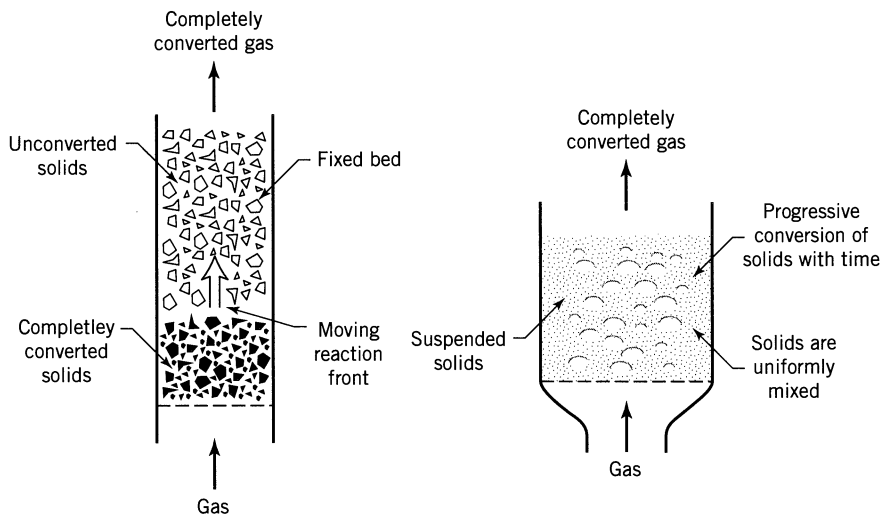


Figure 26.7 A batch of solids contacted with gas; instantaneous reaction.

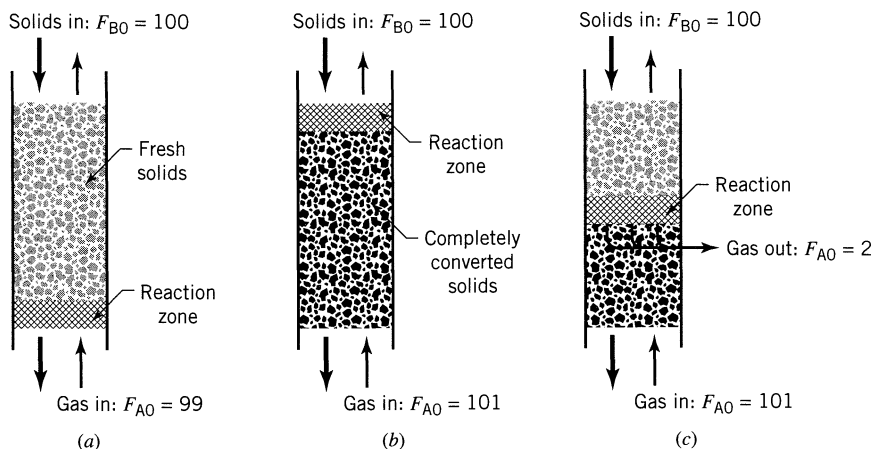


Figure 26.8 In countercurrent flow the location of the reaction zone depends on which component is in excess of stoichiometric.

introduces a slight excess of gas at the bottom of the bed, and then removes a bit more than this excess at the point where reaction is to occur.

Moving bed reactors for oil recovery from shale is one example of this kind of operation. Another somewhat analogous operation is the multistage counterflow reactor, and the four- or five-stage fluidized calciner is a good example of this. In all these operations the efficiency of heat utilization is the main concern.

Cocurrent and Crosscurrent Plug Flow of Gas and Solids. In cocurrent flow, shown in Fig. 26.9a, all reaction occurs at the feed end, and this represents a poor method of contacting with regard to efficiency of heat utilization and preheating of entering materials.

For crosscurrent flow, shown in Fig. 26.9b, there will be a definite reaction plane in the solids whose angle depends solely on the stoichiometry and the relative feed rate of reactants. In practice, heat transfer characteristics may somewhat modify the angle of this plane.

Mixed Flow of Solids and Gas. Again in the ideal situation either gas or solid will be completely converted in the reactor depending on which stream is in excess.

Extensions

Modifications and extensions of the methods presented here, for example,

- to more complicated particle kinetics
- to growing and shrinking particles in single reactors and in solid circulation systems
- to changing gas composition in a single reactor and from stage to stage in multistage operations
- to deviations from ideal plug and mixed flow
- to elutriation of fines from a reactor

are treated elsewhere: see Kunii and Levenspiel (1991), and Levenspiel (1996).

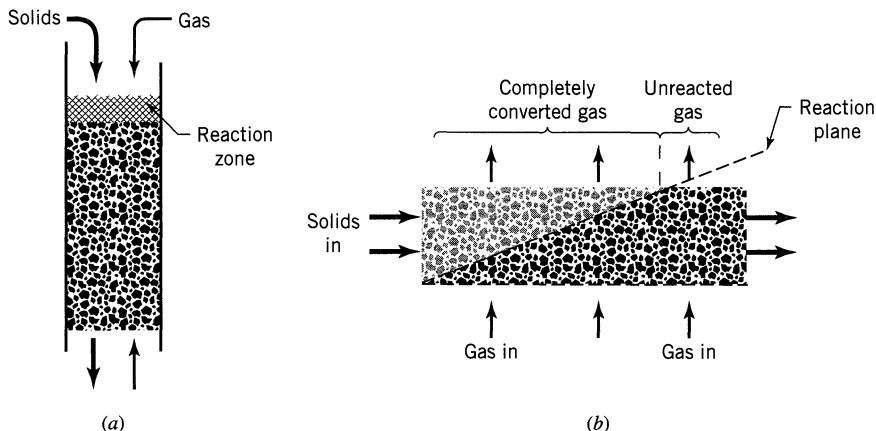


Figure 26.9 Cocurrent and crosscurrent contacting of gas-solids; instantaneous reaction.

Arbitrary Flow of Solids. Since particles flow as macrofluids, their mean conversion is given by Eq. 11.13. Thus with any RTD and with known gas composition we have

$$1 - \bar{X}_B = \int_0^{\tau} (1 - X_B)_{\text{single particle}} \mathbf{E}_{\text{solid stream}} dt \quad (19)$$

where $1 - X_B$ is given by Eq. 25.23 for SCM/reaction control, and by Eq. 25.18 for SCM/ash diffusion control.

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- Levenspiel, O., *Chemical Reactor Omnibook*, OSU Bookstores, Corvallis, OR 97339, 1996.
- Yagi, S., and Kunii, D., *Chem. Eng. Sci.*, **16**, 364, 372, 380 (1961).
- _____, Takagi, K., and Shimoyama, S., *J. Chem. Soc. (Japan), Ind. Chem. Sec.*, **54**, 1 (1951).

PROBLEMS

A stream of particles of one size are 80% converted (SCM/ash diffusion control, uniform gas environment) on passing through a reactor. If the reactor is made twice the size but with the same gas environment, same feed rate, and same flow pattern of solids, what would be the conversion of solids? The solids are in

26.1. plug flow.

26.2. mixed flow.

A solid feed consisting of
 20 wt% of 1-mm particles and smaller
 30 wt% of 2-mm particles
 50 wt% of 4-mm particles

passes through a rotating tubular reactor somewhat like a cement kiln where it reacts with gas to give a hard nonfriable solid product (SCM/ reaction control, $\tau = 4$ h for 4-mm particles).

26.3. Find the residence time needed for 100% conversion of solids.

26.4. Find the mean conversion of the solids for a residence time of 15 min.

26.5. Particles of uniform size are 60% converted on the average (shrinking core model with reaction controlling) when flowing through a single fluidized bed. If the reactor is made twice as large but contains the same amount of solids and with the same gas environment what would be the conversion of solids?

26.6. Solids of unchanging size, $R = 0.3$ mm, are reacted with gas in a steady flow bench scale fluidized reactor with the following result.

$$F_0 = 10 \text{ gm/sec}, \quad W = 1000 \text{ gm}, \quad \bar{X}_B = 0.75$$

Also, the conversion is strongly temperature-sensitive suggesting that the reaction step is rate-controlling. Design a commercial sized fluidized bed reactor (find W) to treat 4 metric tons/hr of solid feed of size $R = 0.3$ mm to 98% conversion.

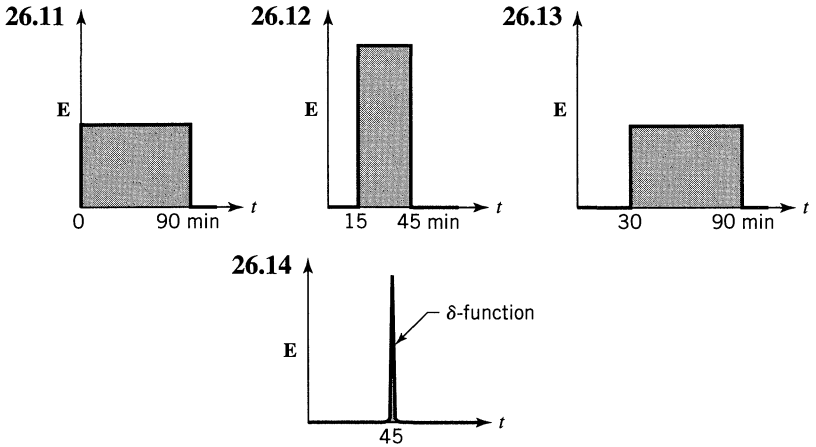
26.7. Solve Example 26.3 with the following modification: the kinetics of the reaction is ash diffusion controlled with $\tau(R = 100 \mu\text{m}) = 10$ min.

26.8. Repeat Example 26.4 if twice the stoichiometric ratio of gas to solid, still at C_{A0} , is fed to the reactor.

26.9. Repeat Example 26.4 if the gas is assumed to pass in plug flow through the reactor.

26.10. Consider the following process for converting waste shredded fibers into a useful product. Fibers and fluid are fed continuously into a mixed flow reactor where they react according to the shrinking core model with the reaction step as rate controlling. Develop the performance expression for this operation as a function of the pertinent parameters and ignore elutriation.

Hydrogen sulfide is removed from coal gas by passing the gas through a moving bed or iron oxide particles. In the coal gas environment (consider uniform) the solids are converted from Fe_2O_3 to FeS by the SCM/reaction control, $\tau = 1$ hr. Find the fractional conversion of oxide to iron sulfide if the RTD of solids in the reactor is approximated by the E curves of Figs. P26.11–P26.14.



Figures P26.11–P26.14

Part V

Biochemical Reaction Systems

Chapter 27 Enzyme Fermentation /611

Chapter 28 Microbial Fermentation—Introduction and Overall Picture /623

Chapter 29 Substrate Limiting Microbial Fermentation /630

Chapter 30 Product Limiting Microbial Fermentation /645

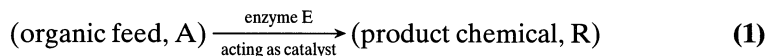
Enzyme Fermentation

The term “fermentation” can be used in its original strict meaning (to produce alcohol from sugar—nothing else) or it can be used more or less broadly. We will use the modern broad definition:

From the simplest to the most complex, biological processes may be classed as fermentations, elementary physiological processes, and the action of living entities. Further, fermentations can be divided into two broad groups: those promoted and catalyzed by microorganisms or microbes (yeasts, bacteria, algae, molds, protozoa) and those promoted by enzymes (chemicals produced by microorganisms). In general, fermentations are reactions wherein a raw organic feed is converted into product by the action of microbes or by the action of enzymes.

This whole classification is shown in Fig. 27.1.

Enzyme fermentations can be represented by



Microbial fermentations can be represented by



The key distinction between these two types of fermentation is that in enzyme fermentation the catalytic agent, the enzyme, does not reproduce itself, but acts as an ordinary chemical, while in microbial fermentation the catalytic agent, the

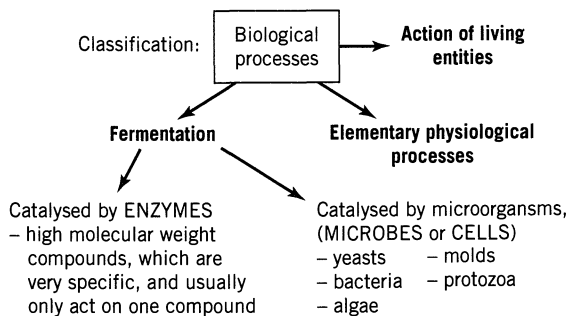


Figure 27.1 Classification of biological processes.

cell or microbe, reproduces itself. Within the cells it is the enzyme which catalyses the reaction, just as in enzyme fermentation; however, in reproducing itself the cell manufactures its own enzyme.

In this chapter we introduce enzyme fermentations, in the following chapters we take up microbial fermentations.

27.1 MICHAELIS-MENTEN KINETICS (M-M KINETICS)

In a sympathetic environment, with just the right enzyme for catalyst, organic A will react to produce R. Observations show the behavior of Fig. 27.2.

A simple expression which accounts for this behavior is

$$-r_A = r_R = k \frac{C_{E0} C_A}{C_M + C_A} \tag{3}$$

↙ total enzyme
↘ a constant, called the Michaelis constant

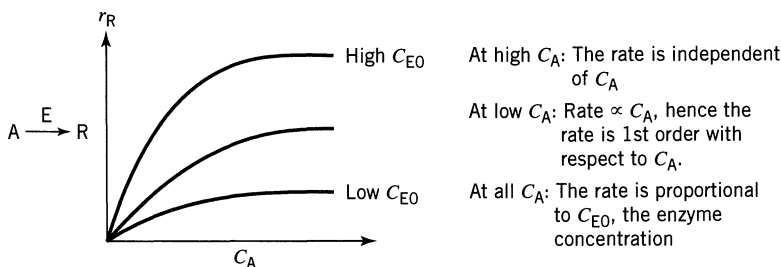


Figure 27.2 Typical rate-concentration curves for enzyme catalyzed reactions.

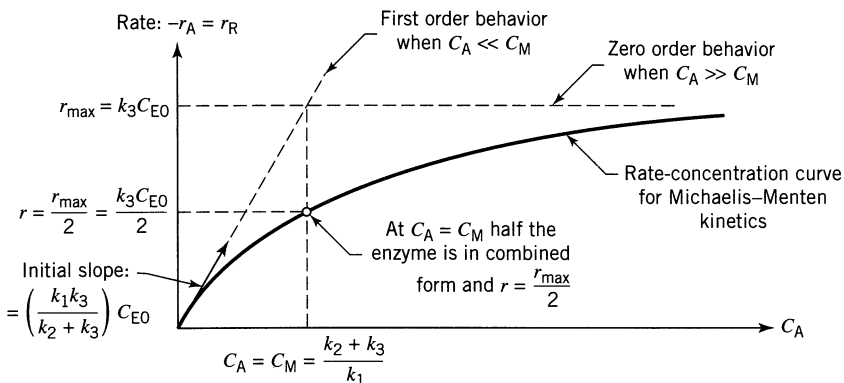
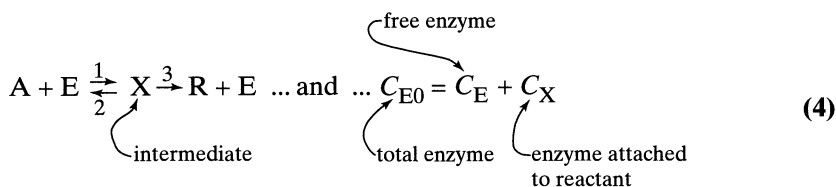


Figure 27.3 Special features of the M–M equation, Eq. 3.

In searching for the simplest mechanism to explain these observations and this rate form, Michaelis and Menten (1913) came up with the two-step elementary reaction mechanism



Example 2.2 develops and explains the relationship between the above mechanism and rate equation. Let us look at some of the special features of the Michaelis–Menten equation.

- when $C_A = C_M$ half the enzyme is in free form, the other half combined.
- when $C_A \gg C_M$ most of the enzyme is tied up as complex X .
- when $C_A \ll C_M$ most of the enzyme is in free form.

Graphically we show this equation in Fig. 27.3.

Next let us see how to evaluate the two rate constants of this important enzyme fermentation equation.

Batch or Plug Flow Fermentor

For this system, integration of the M–M equation gives [see Eq. 3.57 or see Michaelis and Menten (1913)]

$$\underbrace{C_M \ln \frac{C_{A0}}{C_A}}_{\text{first-order term}} + \underbrace{(C_{A0} - C_A)}_{\text{zero-order term}} = k_3 C_{E0} t \quad (5)$$

This concentration-time behavior is shown in Fig. 27.4.

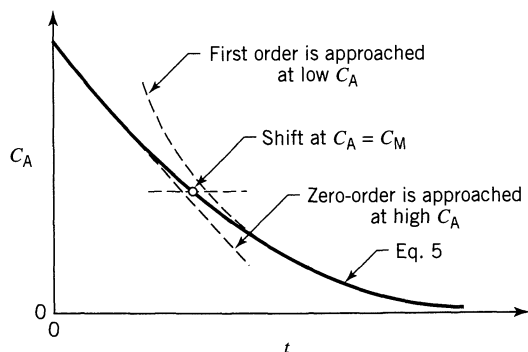


Figure 27.4 Concentration-time behavior of the M-M equation.

Unfortunately this equation cannot be plotted directly to find the values of the constants k_3 and C_M . However, by manipulation we find the following form which can be plotted, as shown in Fig. 27.5, to give the rate constants

$$\frac{C_{A0} - C_A}{\ln \frac{C_{A0}}{C_A}} = -C_M + k_3 C_{E0} \cdot \frac{t}{\ln \frac{C_{A0}}{C_A}} \quad (6)$$

Mixed Flow Fermentor

Inserting the M-M equation into the mixed flow performance expression gives

$$\tau = \frac{C_{A0} - C_A}{-r_A} = \frac{(C_{A0} - C_A)(C_M + C_A)}{k_3 C_{E0} C_A} \quad \dots \text{or} \quad (7)$$

$$k_3 C_{E0} \tau = \frac{(C_{A0} - C_A)(C_M + C_A)}{C_A}$$

Unfortunately we cannot devise a plot of this equation to give k_3 and C_M . However, on rearrangement we find an equation form which does allow a direct evaluation of k_3 and C_M , or

$$C_A = -C_M + k_3 \left(\frac{C_{E0} C_A \tau}{C_{A0} - C_A} \right) \quad (8)$$

In graphical form this gives (see Fig. 27.6).

Alternative Methods for Evaluating k and C_M

Biologists and life scientists have developed a tradition of fitting and extracting the rate constants of the M-M equation with a multistep procedure, as follows

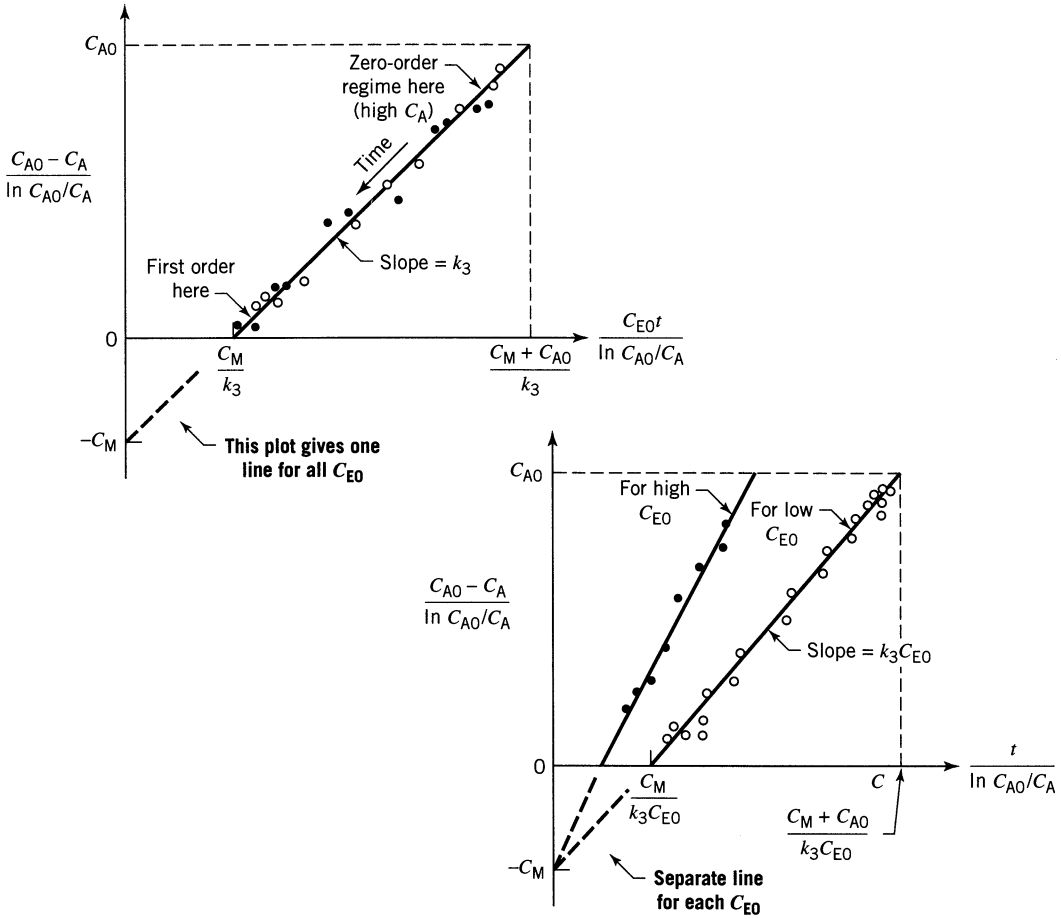


Figure 27.5 Either plot can be used to test and fit the M—M equation (Eq. 6) from batch reactor data.

- first measure C_{Aout} versus τ for data taken in any one of the three ideal reactors—batch, mixed, or plug flow.
- then evaluate $-r_A$ at various C_A , either directly from mixed flow data ($-r_A = (C_{A0} - C_{Aout})/\tau$) or by taking slopes for the plug flow or batch data, as shown in Chapter 3.
- plot C_A versus $(-r_A)$ in one of two ways

$$\begin{array}{ll} (-r_A) \text{ versus } (-r_A)/C_A & \dots \text{ the Eadie plot} \\ 1/(-r_A) \text{ versus } 1/C_A & \dots \text{ the Lineweaver plot} \end{array}$$

- and from these plots extract C_M and k .

The CRE method which leads to Eq. 6 or Eq. 8 fits the measured C_A versus τ data from any of the three ideal reactor types, is direct, is less prone to fiddling, and is more reliable.

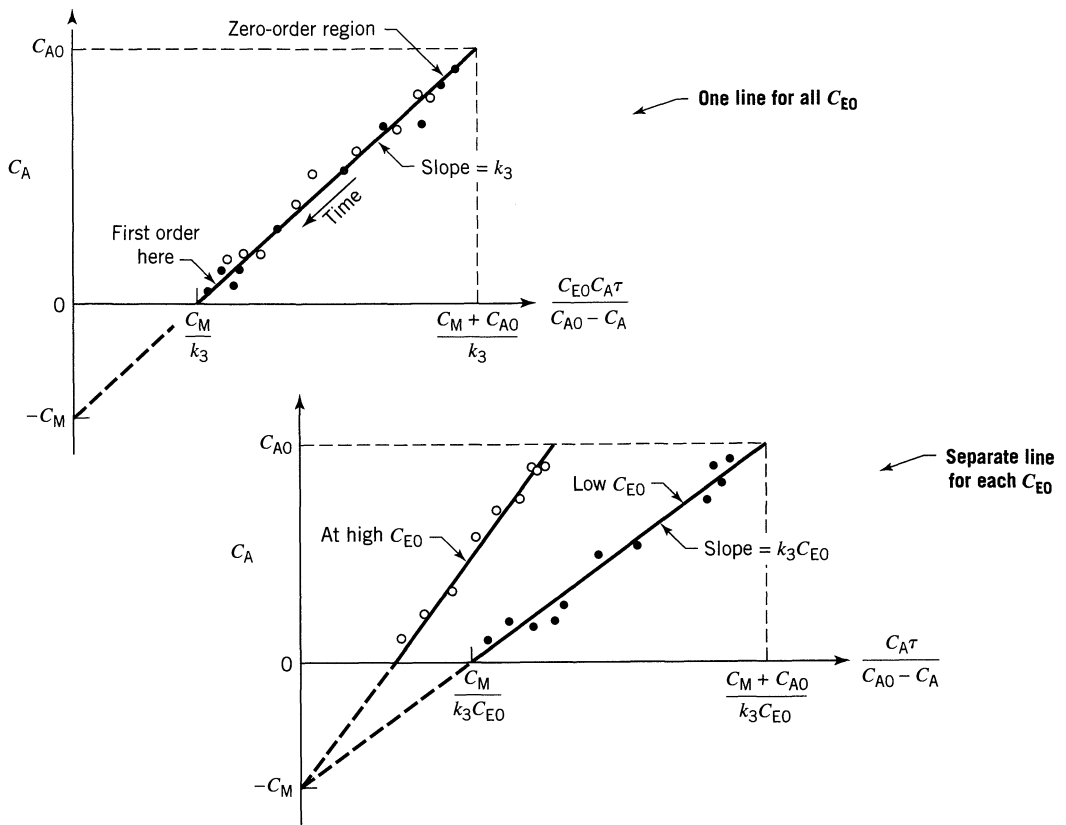


Figure 27.6 Either plot can be used to test and fit the M–M equation (Eq. 8) using data taken in a mixed-flow reactor.

27.2 INHIBITION BY A FOREIGN SUBSTANCE—COMPETITIVE AND NONCOMPETITIVE INHIBITION

When the presence of substance B causes the slowdown of the enzyme-substrate reaction of A to R, then B is called an *inhibitor*. We have various kinds of inhibitor action, the simplest models being called *competitive* and *noncompetitive*. We have competitive inhibition when A and B attack the same site on the enzyme. We have noncompetitive inhibition when B attacks a different site on the enzyme, but in doing so stops the action of A. In simple pictures this action is shown in Fig. 27.7.

Pharmacological significance: the study of enzymes and inhibition is one of the major methods in determining the action of existing drugs and in developing new drugs. This approach has changed the whole direction of pharmacological research in recent years. The main thrust today is

- to study the disease biochemically, then
- synthesize a chemical to block the action of a crucial enzyme.

Let us develop kinetic expressions for these two types of inhibition.

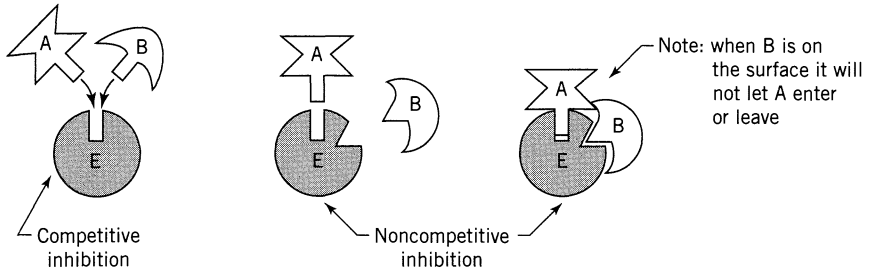
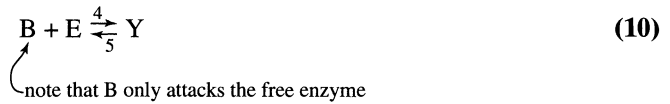


Figure 27.7 A simple representation of the action of two types of inhibitors.

Kinetics of Competitive Inhibition

With A and B competing for the same site on the enzyme we have the following mechanism:



With a procedure as shown in Chapter 2 (see Example 2.2) we end up with the following rate equation:

$$r_R = \frac{k_3 C_{E0} C_A}{C_M + C_A + N C_{B0} C_M} = \frac{k_3 C_{E0} C_A}{C_M (1 + N C_{B0}) + C_A}$$

where

$$\begin{cases} C_M = \frac{k_2 + k_3}{k_1}, \text{ mol} \\ N = \frac{k_4}{k_5}, \text{ mol} \end{cases} \quad (11)$$

Compared to systems without inhibition (Eq. 3) we see that all we need do here is replace C_M by $C_M(1 + N C_{B0})$.

Kinetics of Noncompetitive Inhibition

Here A attacks one site on the enzyme, B attacks a different site, but in doing so it stops the action of A. The mechanism of this action is represented by



Note that B attacks the enzyme irrespective of whether A is attached to it or not. The overall rate is then

$$\begin{aligned}
 r_R &= \frac{k_3 C_{E0} C_A}{C_M + C_A + N C_{B0} C_M + L C_A C_{B0}} \\
 &= \frac{\frac{k_3}{(1 + L C_{B0})} \cdot C_{E0} C_A}{C_M \left(\frac{1 + N C_{B0}}{1 + L C_{B0}} \right) + C_A} \quad \dots \text{ where } \begin{cases} C_M = \frac{k_2 + k_3}{k_1} \\ N = \frac{k_4}{k_5} \\ L = \frac{k_6}{k_7} \end{cases} \quad (15)
 \end{aligned}$$

Compared to enzyme reactions without inhibition we see that both k_3 and C_M are modified here. Thus, for noncompetitive inhibition,

- replace k_3 by $\frac{k_3}{1 + L C_{B0}}$
- replace C_M by $C_M \left(\frac{1 + N C_{B0}}{1 + L C_{B0}} \right)$

How to Tell between Competitive and Noncompetitive Inhibition from Experiment

With C versus t data obtained from either batch, mixed flow or plug flow runs make one of the recommended plots for inhibition-free systems (see Fig. 27.5 or Fig. 27.6). With inhibition these plots are modified as shown in Figs. 27.8 and 27.9.

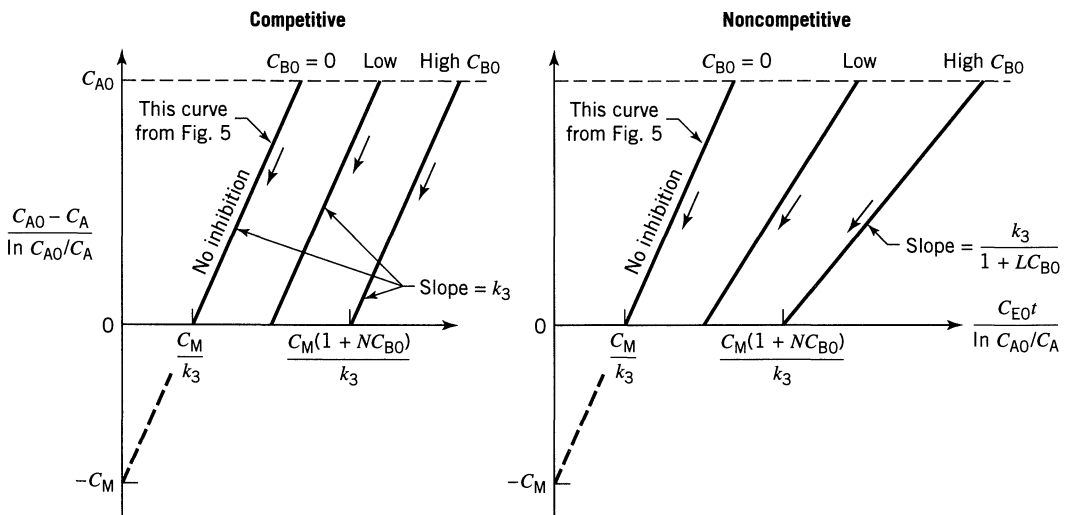


Figure 27.8 Effect of inhibition on batch or plug flow data.

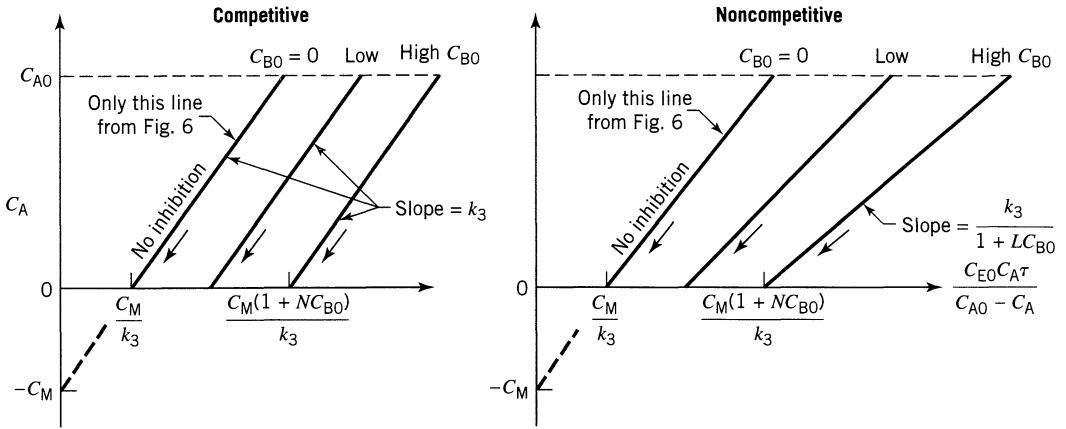


Figure 27.9 Effect of inhibition on mixed flow reactor data.

Comments

The M-M equation is the simplest expression to represent enzyme catalyzed reactions. It has been modified and extended in many ways. The two modes of inhibition introduced here are the simplest imaginable. Others are more complex to represent mathematically, so always try these first.

REFERENCE

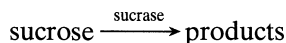
Michaelis, L., and Menten, M. L., *Biochem. Z.*, **49**, 333 (1913).

PROBLEMS

27.1. Substrate A and enzyme E flow through a mixed flow reactor ($V = 6$ liter). From the entering and leaving concentrations and flow rate find a rate equation to represent the action of enzyme on substrate.

C_{E0} , mol/liter	C_{A0} , mol/liter	C_A , mol/liter	v , liter/hr
0.02	0.2	0.04	3.0
0.01	0.3	0.15	4.0
0.001	0.69	0.60	1.2

27.2. At room temperature sucrose is hydrolyzed by the enzyme sucrase as follows:



Starting with sucrose ($C_{A0} = 1 \text{ mol/m}^3$) and sucrose ($C_{E0} = 0.01 \text{ mol/m}^3$) the following data are obtained in a batch reactor (concentrations are calculated from optical rotation measurements)

$C_A, \text{ mol/m}^3$	0.68	0.16	0.006
$t, \text{ hr}$	2	6	10

Find a rate equation to represent the kinetics of this reaction.

- 27.3.** In a number of separate runs different concentrations of substrate and enzyme are introduced into a batch reactor and allowed to react. After a certain time the reaction is quenched and the vessel contents analyzed. From the results found below find a rate equation to represent the action of enzyme on substrate.

Run	$C_{E0}, \text{ mol/m}^3$	$C_{A0}, \text{ mol/m}^3$	$C_A, \text{ mol/m}^3$	$t, \text{ hr}$
1	3	400	10	1
2	2	200	5	1
3	1	20	1	1

- 27.4.** Carbohydrate A decomposes in the presence of enzyme E. We also suspect that carbohydrate B in some way influences this decomposition. To study this phenomenon various concentrations of A, B, and E flow into and out of a mixed flow reactor ($V = 240 \text{ cm}^3$).

- (a) From the following data find a rate equation for the decomposition.
 (b) What can you say about the role of B in the decomposition?
 (c) Can you suggest a mechanism for this reaction?

$C_{A0}, \text{ mol/m}^3$	$C_A, \text{ mol/m}^3$	$C_{B0}, \text{ mol/m}^3$	$C_{E0}, \text{ mol/m}^3$	$v, \text{ cm}^3/\text{min}$
200	50	0	12.5	80
900	300	0	5	24
1200	800	0	5	48
700	33.3	33.3	33.3	24
200	80	33.3	10	80
900	500	33.3	20	120

- 27.5.** Enzyme E catalyzes the decomposition of substrate A. To see whether substance B acts as inhibitor we make two kinetic runs in a batch reactor, one with B present, the other without B. From the data recorded below
- (a) Find a rate equation to represent the decomposition of A.
 (b) What is the role of B in this decomposition?
 (c) Suggest a mechanism for the reaction.

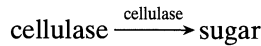
Run 1. $C_{A0} = 600 \text{ mol/m}^3$, $C_{E0} = 8 \text{ gm/m}^3$, no B present

C_A	350	160	40	10
$t, \text{ hr}$	1	2	3	4

Run 2. $C_{A0} = 800 \text{ mol/m}^3$, $C_{E0} = 8 \text{ gm/m}^3$, $C_B = C_{B0} = 100 \text{ mol/m}^3$

C_A	560	340	180	80	30
$t, \text{ hr}$	1	2	3	4	5

Cellulose can be converted to sugar by the following enzymatic attack



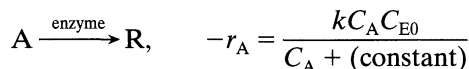
and both cellulose and glucose act to inhibit the breakdown. To study the kinetics of this reaction a number of runs are made in a mixed flow reactor kept at 50°C and using a feed of finely shredded cellulose ($C_{A0} = 25 \text{ kg/m}^3$), enzyme ($C_{E0} = 0.01 \text{ kg/m}^3$, same for all runs), and various inhibitors. The results are as follows:

Run	Exit Stream $C_A, \text{ kg/m}^3$	<i>Series 1</i> <i>no Inhibitor</i> $\tau, \text{ min}$	<i>Series 2</i> <i>with Cellobiose</i> $C_{B0} = 5 \text{ kg/m}^3$ $\tau, \text{ min}$	<i>Series 3</i> <i>with Glucose</i> $C_{G0} = 10 \text{ kg/m}^3$ $\tau, \text{ min}$
1	1.5	587	940	1020
2	4.5	279	387	433
3	9.0	171	213	250
4	21.0	36	40	50

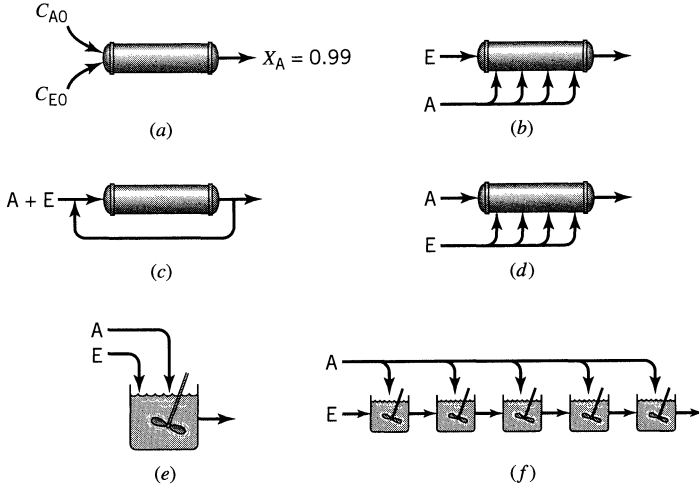
- 27.6.** Find a rate equation to represent the breakdown of cellulose by cellulase in the absence of inhibitor.
- 27.7.** What is the role of cellulose in the breakdown of cellulose (find the type of inhibition, and rate equation).
- 27.8.** What is the role of glucose in the breakdown of cellulose (find the type of inhibition, and the rate equation).

The rate data for these problems are modified from Ghose and Das, *Advances in Biochemical Engineering*, **1**, 66 (1971).

- 27.9.** Given the Michaelis–Menten rate form to represent enzyme-substrate reactions (or catalyst-reactant reaction)



which of the following contacting patterns when operated properly gives good reactor behavior (close to minimum reactor size) and which will not, if the reactor is to be fed two feed streams, one containing C_{A0} , the other C_{E0} ?



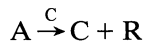
Chapter 28

Microbial Fermentation— Introduction and Overall Picture

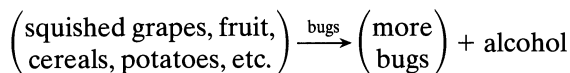
Natural fermentation is a complex situation with a hodge-podge of foods and cells all busily reacting. In this introduction let us only consider the very simplest of situations:

- one type of microbe C acting. We sometimes call this the cell or bug.
- one type of needed food A. This is called the substrate by life science workers.

If the food is right the bugs eat it, multiply, and in the process produce waste material R. In symbols

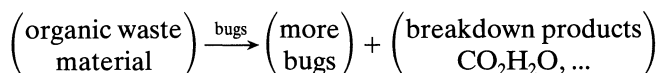


In some cases the presence of product R inhibits the action of the cells, no matter how much food is available and we have what is called poisoning by product, or product poisoning. Wine making is an example of this



As the concentration of alcohol rises the cells multiply more slowly, and at about 12% alcohol the bugs quit. Alcohol is the poison here.

Activated sludge treatment of waste water is an example of a fermentation which is free of product poisoning



Sometimes we are interested in the breakdown of A, as in waste water treatment. In other situations we are interested in producing cells C, as in the growing of yeast or single-cell protein for food. In still others we want the cell's waste material R, as in the production of penicillin and other antibiotics.

Let us see what typically happens with a single type of bug and a single food.

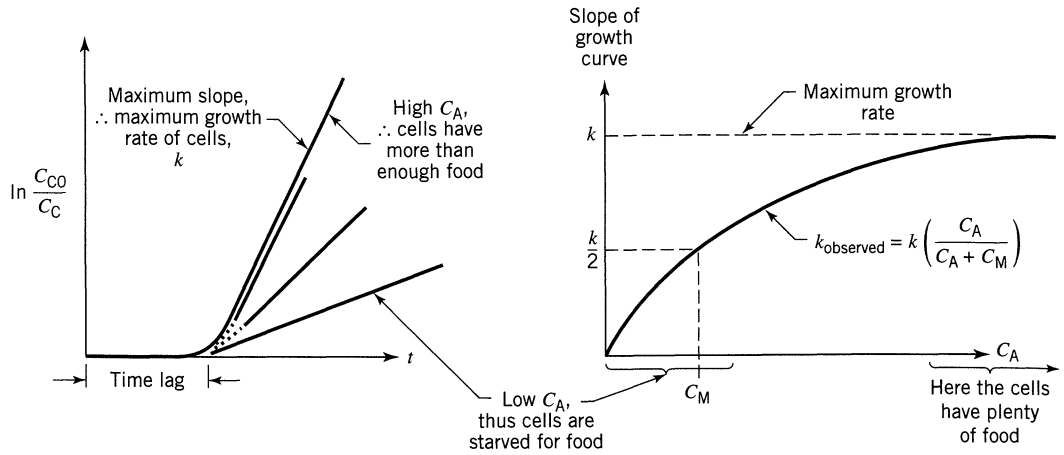


Figure 28.1 Cell growth in a uniform friendly environment.

Constant Environment Fermentation, Qualitative

What happens when we introduce a batch of microbes into a friendly constant composition medium having food of concentration C_A ? First the microbes take some time to adapt to their new environment, then they grow exponentially. Thus we have the behavior shown in Fig. 28.1. Roughly—the time lag is a result of the “shock” to the cells in finding themselves in these new surroundings.

- the growth rate of cells (after the time lag) is given by Monod as

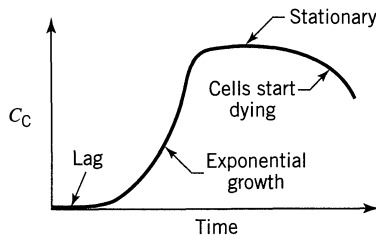
$$r_C = \frac{kC_A C_C}{C_A + C_M}$$

the concentration of A where the cells reproduce at 1/2 their maximum rate

Batch Fermentor, Qualitative

Here cells reproduce, the composition of the substrate changes, and product which can be toxic to the cells forms. Typically we see

- an induction period (time lag)
- a growth period
- a stationary period and
- a dying of cells



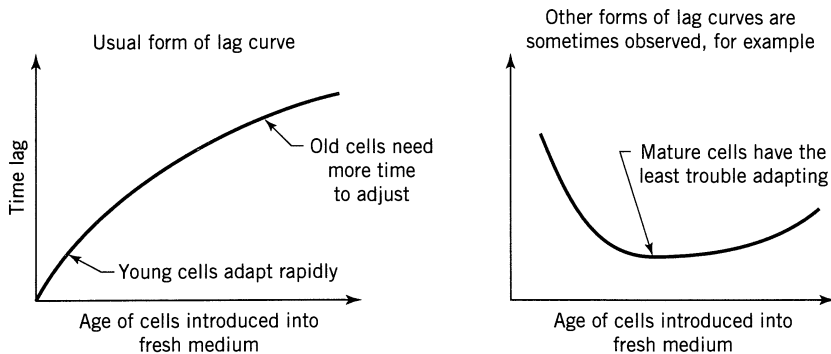


Figure 28.2 The time lag depends on the age of cells.

A few words follow about these regimes.

- (a) **Lag.** As the cells in a container use up their food supply they stop multiplying, their enzyme activity decreases, low molecular weight chemicals diffuse out, and the cells change character. They age. So when they are introduced into a new environment a time lag is observed as the cells remanufacture the chemicals needed for growth and reproduction. In general any change in environment results in an induction period as the cells adjust. We find, as shown in Fig. 28.2.
- (b) **Growth and stationary phase.** Cells grow exponentially in a uniform environment, but in a batch system the medium changes so the growth rate changes. The eventual drop in cell growth is governed either by
- depletion of food or
 - accumulation of toxic materials (toxic to the cell).

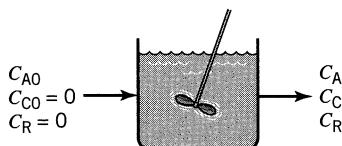
Graphically we summarize this in Fig. 28.3.

Mixed Flow Fermentor

Here the cells are in a uniform environment. No adaptation is needed and cell multiplication proceeds at a constant rate determined by the composition of the fluid in the vessel. This is frequently represented by a Monod-type equation

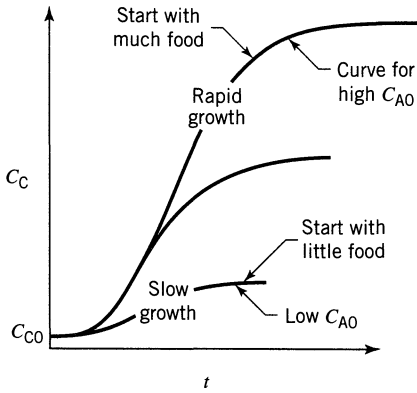
$$-r_C = \frac{kC_A C_C}{C_A + C_M}$$

The k value depends on all sorts of things: temperature, presence of trace elements, vitamins, toxic substances, light intensity, etc.



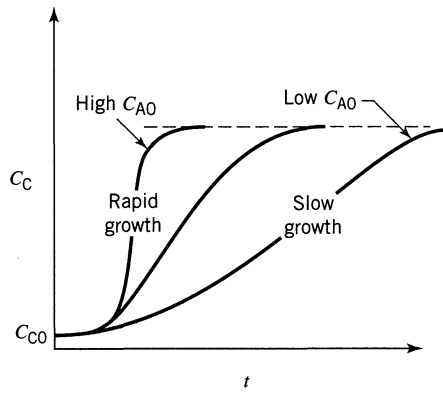
Substrate limiting

(final C_C depends on the initial amount of food. Product does not affect the rate)



Poison limiting

(C_C never exceeds a certain value. Product slows and then stops the reaction)



In general

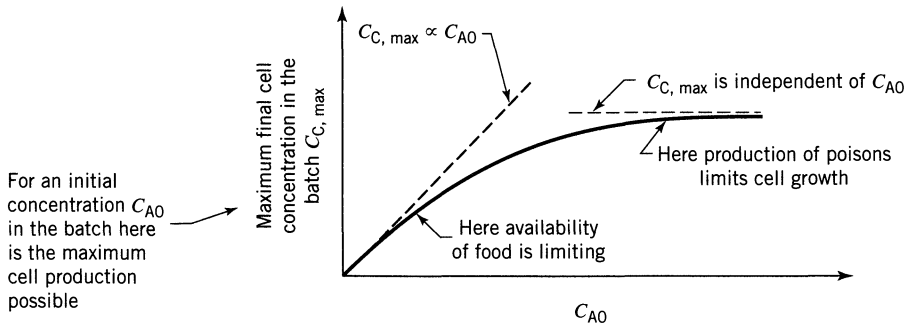
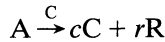


Figure 28.3 In a batch reactor the maximum cell production depends on the limiting mechanism.

Product Distribution and Fractional Yields

For the stoichiometric equation



let us use the following shorthand notation for the instantaneous fractional yields

$$\left. \begin{aligned} \textcircled{C/A} &= \varphi(C/A) = \frac{d(\text{C formed})}{d(\text{A used})} \\ \textcircled{R/A} &= \varphi(R/A) = \frac{d(\text{R formed})}{d(\text{A used})} \\ \textcircled{R/C} &= \varphi(R/C) = \frac{d(\text{R formed})}{d(\text{C used})} \end{aligned} \right\} \quad (1)$$

Then we have the following relationships

$$\left. \begin{aligned} \textcircled{R/A} &= \textcircled{R/C} \cdot \textcircled{C/A} \\ \textcircled{A/C} &= 1/\textcircled{C/A} \end{aligned} \right\} \quad (2)$$

and

$$\left. \begin{aligned} r_C &= (-r_A) \textcircled{C/A} \\ r_R &= (-r_A) \textcircled{R/A} \\ r_R &= (r_C) \textcircled{R/C} \end{aligned} \right\} \quad (3)$$

In general the stoichiometry can be messy with fractional yields changing with composition. Treatment of that case can be difficult. We'd like therefore to make the simplification that all φ values remain constant at all compositions. This assumption may be reasonable for mixed flow, or for the exponential growth period of batch reactors, otherwise it is questionable.

Let us make this assumption anyway—all φ values stay constant. In this case for any change we can write

$$\left. \begin{aligned} C_C - C_{C0} &= \textcircled{C/A} (C_{A0} - C_A) \quad \dots \text{or} \dots \quad C_C = C_{C0} + \textcircled{C/A} (C_{A0} - C_A) \\ C_R - C_{R0} &= \textcircled{R/A} (C_{A0} - C_A) \quad \dots \text{or} \dots \quad C_R = C_{R0} + \textcircled{R/A} (C_{A0} - C_A) \\ C_R - C_{R0} &= \textcircled{R/C} (C_C - C_{C0}) \quad \dots \text{or} \dots \quad C_R = C_{R0} + \textcircled{R/C} (C_C - C_{C0}) \end{aligned} \right\} \quad (4)$$

Kinetic Expressions

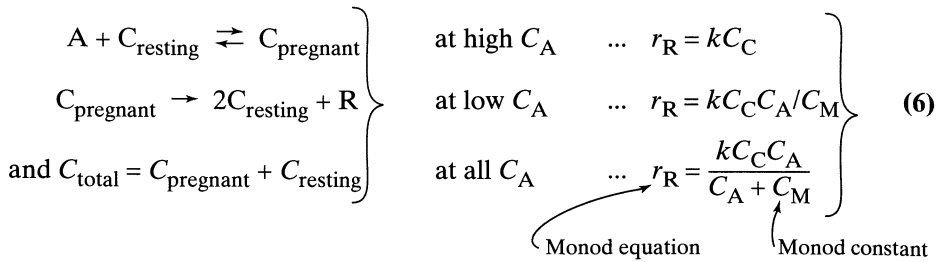
The rate of cell multiplication depends in general on the availability of food and on the build up of wastes which interfere with cell multiplication. The simplest reasonable rate forms are shown below. We use these in the following chapters.

Availability of Food. For a reasonable quantitative expression make the analogy with enzyme kinetics.

For enzymes:

$$\left. \begin{aligned} A + E &\rightleftharpoons X \\ X &\rightarrow R + E \\ \text{and } C_{E0} &= C_E + C_X \end{aligned} \right\} \begin{aligned} &\text{at high } C_A \quad \dots \quad r_R = kC_{E0} \\ &\text{at low } C_A \quad \dots \quad r_R = kC_{E0} C_A/C_M \\ &\text{at all } C_A \quad \dots \quad r_R = \frac{kC_{E0} C_A}{C_A + C_M} \end{aligned} \quad (5)$$

For microbes:



Many other kinetic forms have been proposed and have been used in the past; however, they have all been forgotten since Monod came out with his expression. Its simplicity won the day. So we will use this type of expression throughout to relate the rate of cell growth to substrate concentration.

Effect of Harmful Wastes. As harmful wastes R build up, they interfere with cell multiplication. Thus, the observed Monod rate constant k_{obs} decreases with rise in C_R . A simple form of this relationship is

$$k_{\text{obs}} = k \left(1 - \frac{C_R}{C_R^*} \right)^n \quad (7)$$

↖ order of product poisoning
 ↙ rate constant in the absence of harmful waste material

where C_R^* is that concentration of R where all cell activity stops, in which case k_{obs} becomes zero. This expression is shown in Fig. 28.4.

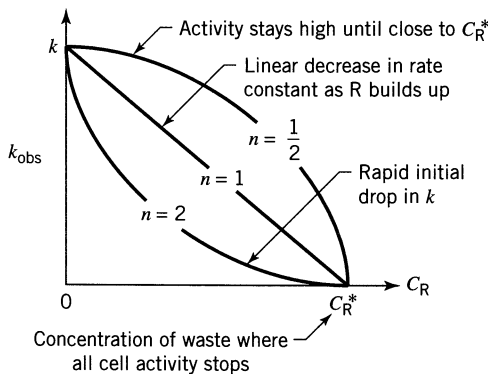


Figure 28.4 The observed k decreases as poisonous product R builds up (see Eq. 7).

General Kinetic Expression. The simplest expression of the Monod type which can account for both factors in microbial fermentation is

$$r_C = -r_A \left(\frac{C/A}{C/R} \right) = r_R \left(\frac{C/R}{C/A} \right) = k_{\text{obs}} \frac{C_A C_C}{C_A + C_M} \quad (8)$$

↙ generalized Monod equation ↘ k_{obs} decreases as C_R rises

...where... $k_{\text{obs}} = k \left(1 - \frac{C_R}{C_R^*} \right)^n$

↘ concentration where all reaction stops

In general, then, reaction and cell multiplication will slow down either by depletion of A (famine) or by build up of R (environmental pollution).

Planned Treatment of the Subject

The next two chapters treat in turn the performance expressions and design consequences for

- poison-free Monod kinetics. Here food limitation alone affects the growth rate of cells.
- product poisoning kinetics. Here some product formed during fermentation slows the rate.

We also assume in these chapters a constant fractional yield throughout, and since everything is liquid we take $\varepsilon_A = 0$, and we will use concentrations throughout.

More generally, an excess of either substrate or cells in the broth can also slow the rate of fermentation. In these situations the Monod equation should be suitably modified [see Han and Levenspiel, *Biotech. and Bioeng.*, **32**, 430 (1988), for a discussion and general treatment for all these forms of inhibition].

Chapter 29

Substrate-Limiting Microbial Fermentation

If we assume a constant fractional yield and no slowing of the rate as a result of product poisoning or increase in cell crowding in the broth, then the general rate equation of the previous chapter, Eq. 28.8, reduces to the well-known Monod equation

$$r_C = \textcircled{C/A} (-r_A) = \frac{kC_A C_C}{C_A + C_M} \quad \dots \text{where} \quad C_C - C_{C0} = \textcircled{C/A} (C_{A0} - C_A) \quad (1)$$

↑
Monod constant

and where C_{A0} and C_{C0} are the feed or starting compositions.

Let us examine ideal reactors processing feed which is reacting away according to these kinetics.

29.1 BATCH (OR PLUG FLOW) FERMENTORS

Consider the progress of this reaction. At the start C_{A0} is high, C_{C0} is low; at the end, $C_A \rightarrow 0$ while C_C is high. Thus, the rate at the beginning and at the end of a run is low, but it will be high at some intermediate composition. By putting $dr_C/dt = 0$, we find that the maximum rate occurs at

$$C_{A, \text{max rate}} = \sqrt{C_M^2 + C_M(C_{A0} + \textcircled{A/C} C_{C0})} - C_M \quad (2)$$

What this means is that with a feed C_{A0} , C_{C0} to any system, the key to proper design is to use mixed flow to reach $C_{A, \text{max rate}}$ all in one step, then use plug flow beyond this point. Thus, it is always important to know $C_{A, \text{max rate}}$.

Now let us return to our batch (or plug flow) reactor. Applying its performance equation we find

$$\begin{aligned}
 t_b = \tau_p &= \int_{C_{C0}}^{C_C} \frac{dC_C}{r_C} = \frac{1}{k} \int_{C_{C0}}^{C_C} \frac{C_A + C_M}{C_C C_A} dC_C \\
 &\quad \downarrow \text{ } C_{A0} - (A/C)(C_C - C_{C0}) \\
 &= \int_{C_A}^{C_{A0}} \frac{dC_A}{(A/C) r_C} = \frac{1}{k} \int_{C_A}^{C_{A0}} \frac{C_A + C_M}{(A/C) C_C C_A} dC_A \\
 &\quad \downarrow \text{ } C_{C0} + (C/A)(C_{A0} - C_A)
 \end{aligned}$$

Integration then gives

$$\boxed{
 \begin{aligned}
 kt_b = k\tau_p &= \left(\frac{C_M}{C_{A0} + (A/C) C_{C0}} + 1 \right) \ln \frac{C_C}{C_{C0}} - \left(\frac{C_M}{C_{A0} + (A/C) C_{C0}} \right) \ln \frac{C_A}{C_{A0}} \quad (3) \\
 \dots \text{ with } C_C - C_{C0} &= (C/A)(C_{A0} - C_A)
 \end{aligned}
 }$$

If a time lag is involved just add t_{lag} to the above times to find t_{total} . If we wish we can write the performance equation in terms of C_R instead of C_A and C_C . Just remember that

$$\boxed{C_R = C_{R0} + (R/C)(C_C - C_{C0}) = C_{R0} + (R/A)(C_{A0} - C_A)} \quad (28.4)$$

The sketches of Fig. 29.1 show the main properties of this performance equation.

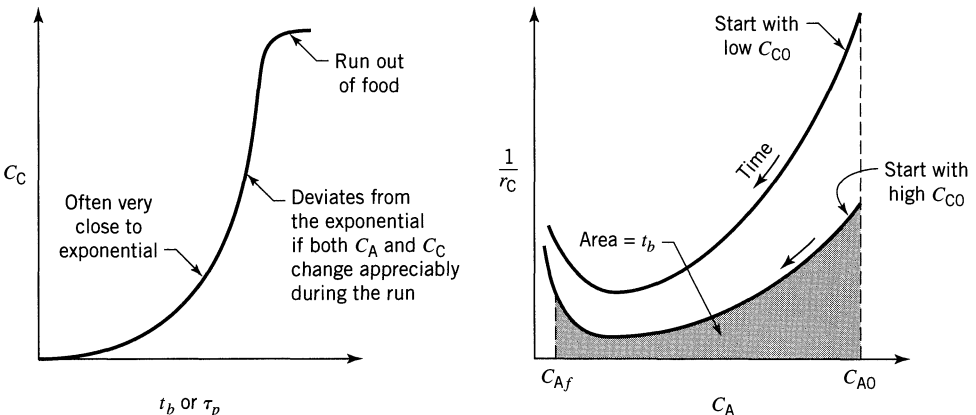


Figure 29.1 Behavior of batch or plug flow reactors for Monod type microbial fermentation.

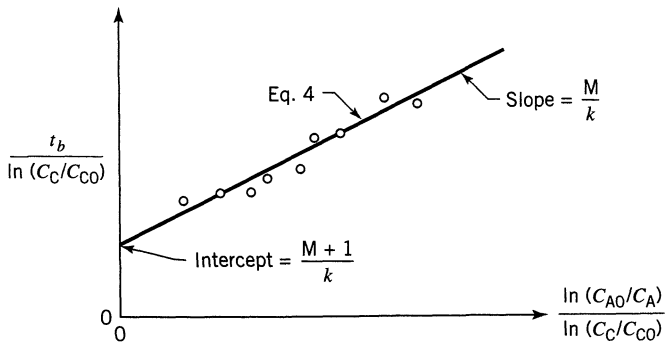


Figure 29.2 Evaluation of the Monod equation constants from batch data, method (a).

How to Find the Monod Constants from the Batch Experiment

Method (a). Rearrange Eq. 3 to give

$$\frac{t_b}{\ln(C_C/C_{C0})} = \frac{M+1}{k} + \frac{M}{k} \frac{\ln(C_{A0}/C_A)}{\ln(C_C/C_{C0})} \quad \text{with } M = \frac{C_M}{C_{A0} + \frac{A}{C} C_{C0}} \quad (4)$$

Then plot the data as shown in Fig. 29.2

Method (b). First find r_C by taking dC_C/dt data, then rearrange the Monod equation to give

$$\frac{C_C}{r_C} = \frac{1}{k} + \frac{C_M}{k} \frac{1}{C_A} \quad (5)$$

Then plot as shown in Fig. 29.3 to find C_M and k .

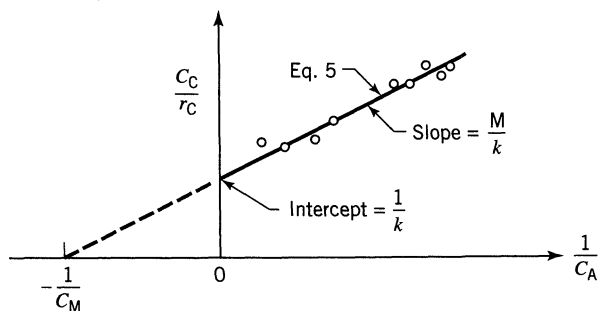


Figure 29.3 Evaluation of the constants of the Monod equation from batch reactor data, method (b).

Comments on Batch Operations

- Method (a) uses all the data directly and presents it as a linear plot. This method is probably better, all round.
- Method (b) requires taking derivatives or slopes from experimental data, is more tedious, and is probably less reliable.
- For high C_A , thus $C_A \gg C_M$, put $C_M = 0$ in the Monod equation. This gives $r_C = kC_C$, in which case the performance expression, Eq. 3, simplifies to

$$k\tau_p = \ln \frac{C_C}{C_{C0}} \quad \dots \text{an exponential growth curve}$$

- For low C_A , thus $C_A \ll C_M$, the Monod equation becomes simple autocatalytic, and the performance expression, Eq. 3, reduces to

$$k\tau_p = \frac{C_M}{C_{A0} + \frac{A}{C} C_{C0}} \ln \frac{C_{A0}C_C}{C_A C_{C0}} \quad \dots \text{S-shaped growth curve. See the autocatalytic equation in Chapter 3}$$

- For very high C_C the poison-free Monod equation just can't apply, for even if there is plenty enough food the cells will crowd out each other, and growth will slow down and will eventually stop. So, for very high cell concentration, we must go to product poison kinetics.
- It is awkward to try to evaluate the rate constants of the Monod equation from batch or plug flow data. Mixed flow data are so much simpler to interpret, as we shall see.

29.2 MIXED FLOW FERMENTORS

No Cells in Feed Stream, $C_{C0} = 0$

Assume Monod kinetics (no product poisoning), constant fractional yields φ , and no cells entering in the feed stream. Then the mixed flow performance equation becomes

$$\tau_m = \frac{\Delta C_i}{r_i} \quad \text{where} \quad i = A, C, \text{ or } R \quad (6)$$

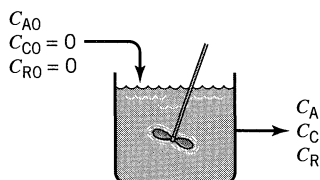


Figure 29a

Replacing r_i from Eq. 1 into Eq. 6 then gives

In terms of C_A

$$k\tau_m = \frac{C_M + C_A}{C_A} \quad \dots \text{ or } C_A = \frac{C_M}{k\tau_m - 1} \quad \dots \text{ for } k\tau_m > 1 + \frac{C_M}{C_{A0}}$$

In terms of C_C

$$k\tau_m = \frac{\textcircled{C/A} (C_{A0} + C_M) - C_C}{\textcircled{C/A} C_{A0} - C_C}$$

$$\dots \text{ or } C_C = \textcircled{C/A} \left(C_{A0} - \frac{C_M}{k\tau_m - 1} \right) \quad \dots \text{ for } k\tau_m > 1 + \frac{C_M}{C_{A0}}$$

In terms of C_R

$$k\tau_m = \frac{\textcircled{R/A} (C_{A0} + C_M) - C_R}{\textcircled{R/A} C_{A0} - C_R}$$

$$\dots \text{ or } C_R = \textcircled{R/A} \left(C_{A0} - \frac{C_M}{k\tau_m - 1} \right) \quad \dots \text{ for } k\tau_m > 1 + \frac{C_M}{C_{A0}}$$

no solution possible
if $k\tau_m < 1 + \frac{C_M}{C_{A0}}$

(7)

This intriguing expression was developed by Monod (1949), and independently, at about the same time, by Novick and Szilard (1950).

To evaluate the kinetic constants from a set of mixed flow runs, rearrange Eq. 7 to give

$$\frac{1}{C_A} = \frac{k}{C_M} \tau_m - \frac{1}{C_M} \quad (8)$$

and the plot as shown in Fig. 29.4

From the performance equation we can show that everything—washout, optimum processing time, maximum production rate—all depend on C_M and C_{A0} , combined as follows:

$$N = \sqrt{1 + \frac{C_{A0}}{C_M}} \quad (9)$$

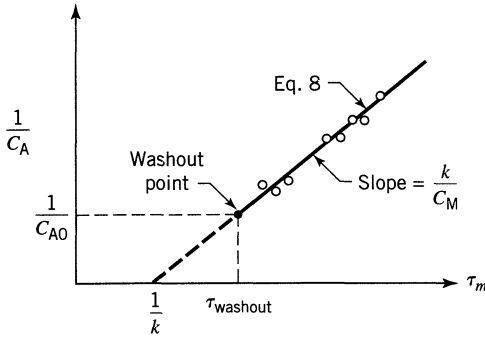


Figure 29.4 Evaluating the Monod constants from mixed flow reactor data.

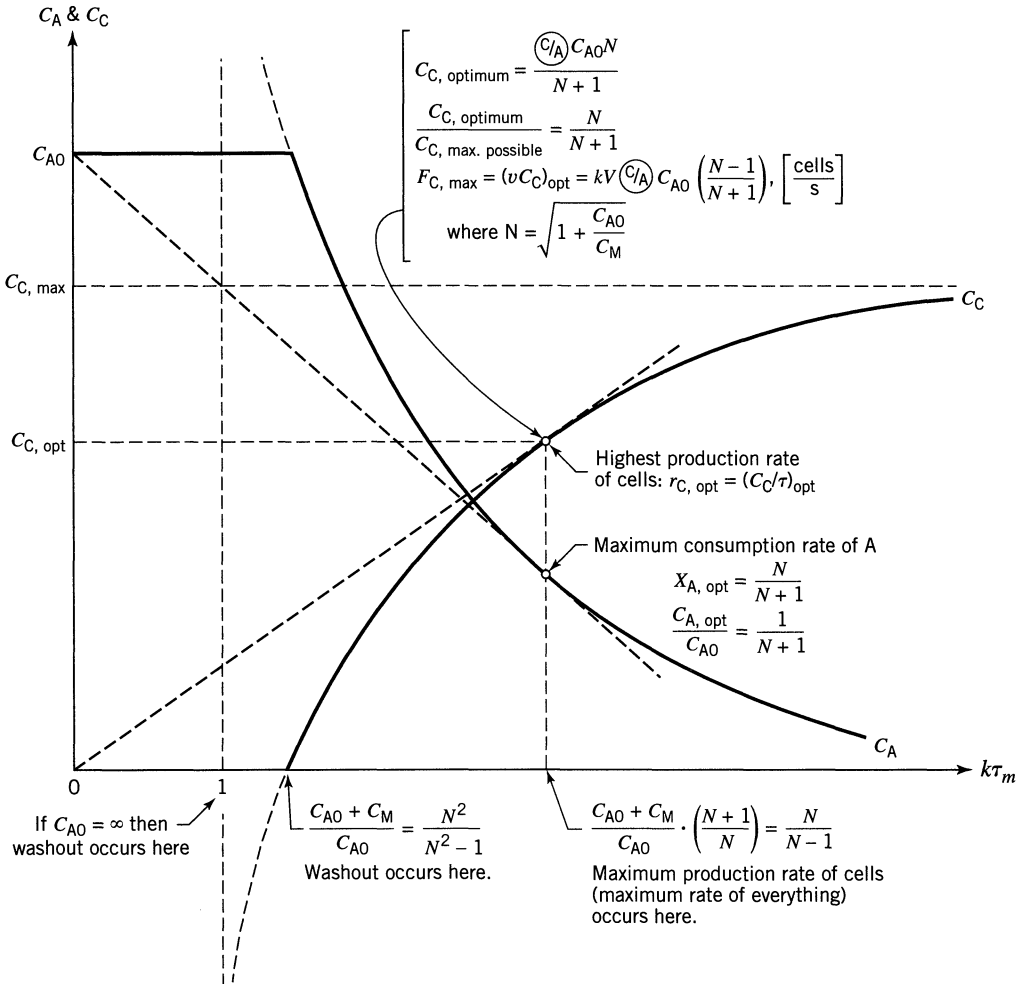


Figure 29.5 Summary of the mixed flow behavior of reactions which follow Monod kinetics.

Thus, optimum operations of a single mixed flow fermentor occurs when

$$\frac{C_A}{C_{A0}} = \frac{1}{N+1}, \quad \frac{C_C}{C_{C, \text{max possible}}} = \frac{N}{N+1}, \quad k\tau_{\text{opt}} = \frac{N}{N-1} \quad (10)$$

and washout occurs at

$$k\tau_{\text{washout}} = \frac{N^2}{N^2 - 1} \quad (11)$$

All this is shown in Fig. 29.5.

Feed Stream Contains Cells, $C_{C0} \neq 0$

With both feed and cells entering the fermentor, the Monod expression (Eq. 1) in the performance expression for the MFR (Eq. 6) gives

$$k\tau_m = \frac{(C_{A0} - C_A)(C_A + C_M)}{\left(\frac{A}{C}\right) \cdot C_{C0}C_A + C_A(C_{A0} - C_A)} \quad (12)$$

Examples 29.1d, 29.1e and 29.1f use this expression.

29.3 OPTIMUM OPERATION OF FERMENTORS

With poison-free Monod kinetics and a given feed, we have a U-shaped $1/r$ versus C curve, as shown in Fig. 29.6.

From Chapter 5 we have learned that with this form of rate-concentration curve we should operate as follows:

- To reach any point between A and B run part of the feed at A in mixed flow and mix with the rest of the feed.
- To reach any point between A and 0 go directly to point A in mixed flow, then use plug flow beyond A .

These two rules represent the key to optimum reactor behavior.

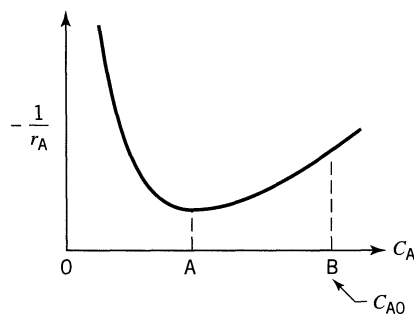


Figure 29.6 Rate-concentration behavior of Monod kinetics.

EXAMPLE 29.1 MIXED REACTORS FOR MONOD KINETICS

Let us illustrate the above important optimization principle by suggesting how to best operate various combinations of mixed flow reactors for a fermentation which follows Monod kinetics, and where

$$k = 2, \quad C_{A0} = 3, \quad C_M = 1, \quad \left(\frac{C}{A}\right) = 1 \quad \text{and} \quad V_m = 1 \quad \text{for each reactor}$$

and all quantities are expressed in consistent units. Consider in turn the following setups

- (a) A single MFR, with a feed rate $v = 3$
- (b) A single MFR, with $v = 1$
- (c) A single MFR, with $v = 1/3$
- (d) Two MFR, $v = 3$
- (e) Two MFR, $v = 1.5$
- (f) Two MFR, $v = 0.5$

Do not calculate the outlet concentration of A or C.

SOLUTION

Preliminary. From the optimization rules for mixed flow reactions (see Eqs. 9 and 10), we have

$$N = \sqrt{1 + \frac{3}{1}} = 2$$

$$\tau_{m,\text{opt}} = \frac{N}{(N-1)k} = \frac{2}{(2-1)2} = 1$$

$$\begin{aligned} \tau_{m,\text{washout}} &= \frac{N^2}{(N^2-1)k} \\ &= \frac{4}{(4-1)2} = \frac{2}{3} \end{aligned}$$

(a) High Feed Rate, Single Reactor, $v = 3$. If all the feed goes through the MFR the mean residence time $\tau = V/v = 1/3$ is too short and the cells don't stay in the reactor long enough and will wash out. So bypass some of the feed and let the reactor operate at its optimum, as shown in Fig. E29.1a.

(b) Intermediate Feed Rate, Single MFR, $v = 1$. Here if all the feed passes through the reactor $\tau = V/v = 1$, which is optimum, so operate that way, see Fig. E29.1b.

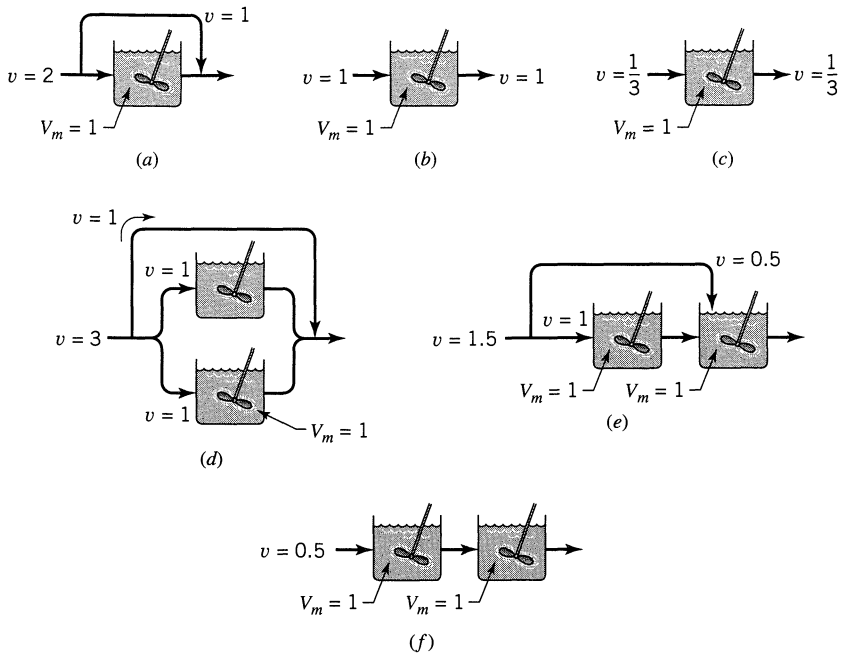


Figure E29.1

(c) **Low Feed Rate, Single Reactor, $v = 1/3$.** Here $\tau = V/v = 1/(1/3) = 3$, which is longer than the optimum, so pass everything through the reactor, as shown in Fig. E29.1c.

(d) **High Feed Rate, 2 MFR, $v = 3$.** Noting that for each MFR we want $\tau = 1$, which is optimum, we end up with the scheme shown in Fig. E29.1d.

(e) **Intermediate Feed Rate, 2 MFR, $v = 1.5$.** Here the best we can do is keep the first reactor at the best conditions, as shown in Fig. E29.1e.

(f) **Low Feed Rate, 2 MFR, $v = 0.5$.** Here the feed rate is too low to keep either reactor at the optimum so we end up with the scheme shown in Fig. E29.1f.

EXAMPLE 29.2 PLUG FLOW REACTOR FOR MONOD KINETICS

Let us extend Example 29.1 to the situation where we use a plug flow reactor (PFR) with or without recycle in place of mixed flow reactors (MFR). Find the optimum in the following situations.

- The volume of PFR $V_p = 3$, $v = 2$
- $V_p = 2$, $v = 3$

SOLUTION

First find the optimum conditions

$$N = 2, \quad \tau_{\text{opt}} = 1 \quad \text{and} \quad \tau_{\text{washout}} = \frac{2}{3}$$

- (a) **Low feed rate, $\tau = V_p/v = 3/2 = 1.5$.** Here two optimal arrangements are shown in Fig. E29.2a.
- (b) **High feed rate, $\tau = V_p/v = 2/3$.** If all the feed flows through the reactor we will have washout. So the optimum is as shown in Fig. E29.2b.

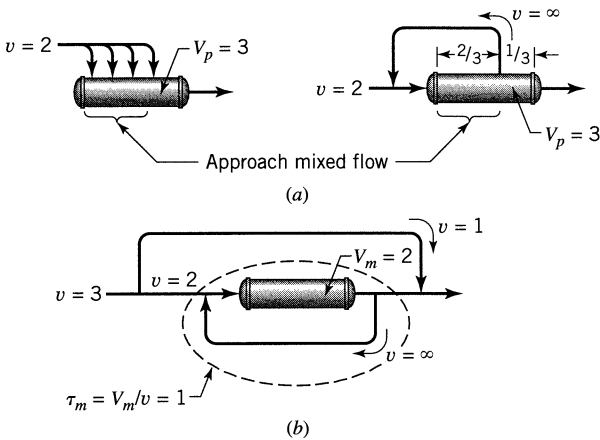


Figure E29.2

EXAMPLE 29.3 GLUCOSE FOR *E. COLI* BACTERIA

The *E. coli* microbe grows contentedly on glucose according to Monod kinetics as follows:

$$r_C = \frac{40 C_A C_C}{C_A + 0.4} \frac{\text{kg cells}}{\text{m}^3 \cdot \text{hr}} \quad \text{with} \quad \begin{cases} \textcircled{C/A} = 0.1 \\ C_A = \frac{\text{kg glucose}}{\text{m}^3} \end{cases}$$

What feed rate of glucose solution ($C_{A0} = 6 \text{ kg/m}^3$) to a mixed flow reactor ($V = 1 \text{ m}^3$) would give the maximum consumption rate of glucose, and maximum production rate of *E. coli* cells?

SOLUTION

To find the maximum consumption rate of glucose, first find N and then use the information given in Fig. 29.5.

$$N = \sqrt{1 + \frac{C_{A0}}{C_M}} = \sqrt{1 + \frac{6}{0.4}} = 4$$

$$k\tau_{\text{opt}} = \frac{N}{N-1} = \frac{4}{3} = 1.33$$

$$\therefore \tau_{\text{opt}} = \frac{1.33}{k} = \frac{1.33}{4} = 0.333 \text{ hr}$$

$$v_{\text{opt}} = \frac{V_m}{\tau_{\text{opt}}} = \frac{1}{0.333} = 3$$

The feed rate of glucose is

$$F_{A0} = (vC_{A0})_{\text{opt}} = (3)(6) = 18 \frac{\text{kg}}{\text{hr}}$$

The maximum consumption rate of glucose is

$$F_{A0}X_{A,\text{opt}} = 18 \left(\frac{N}{N+1} \right) = 18 \left(\frac{4}{5} \right) = \underline{\underline{14.4 \frac{\text{kg}}{\text{hr}}}}$$

The maximum production rate of *E. coli* is

$$\begin{aligned} F_{C\text{max}} &= v_{\text{opt}} C_{C\text{opt}} = (3) \left[\left(\frac{C}{A} \right) C_{A0} \left(\frac{N}{N+1} \right) \right] \\ &= (3)(0.1)(6) \left(\frac{4}{5} \right) = \underline{\underline{1.44 \frac{\text{kg}}{\text{hr}}}} \end{aligned}$$

Comments

- The extension of the performance equations developed in this chapter to
 - plug flow with recycle of exit fluid
 - mixed flow with a feed which contains $C_{C0} \neq 0$
 - cell separation, concentration, and recycle

and additional discussion are found in Levenspiel (1996) Chapter 83.

- The problems which follow quantitatively verify the findings of the first two examples.

- In the literature on continuous fermentation much effort is spent calculating what happens in this or that set up. Most of the schemes are nowhere near optimum so we do not consider them.
- When the φ values are constant throughout, at high and low conversions, then we have just one independent variable to deal with as composition changes with time or position. Thus, we can use any one concentration, C_A , C_R , or C_C in the performance expression. We can compare performance of various reactor types, plug flow, mixed flow, etc. with no difficulty. This is what we have done here.

In general, however, $\varphi = f(C_A, C_R, C_C)$. And when φ varies with composition, then things get more difficult and we cannot directly compare reactor types.

- In 1939, as part of his thesis, Jacques Monod proposed the equation which we use here. The thesis was published as a book in 1948 and was later condensed and translated into English in 1949 (see end-of-chapter reference).
- In microbiology they use the terms
 - *substrate* for the feed.
 - *dilution rate* for $1/\tau$. In chemical engineering, we call this the space velocity. Here we use neither term. We use space time τ .
 - *chemostat*, *turbidostat* for mixed flow reactor.

We should be aware of the difference in language.

REFERENCES

- Levenspiel, O., *Chemical Reactor Omnibook*, OSU Bookstores, Corvallis, OR (1996).
 Monod J., *Ann. Rev. Microbiology*, **3**, 371 (1949)
 ———, *Annales de l'Institut Pasteur*, **79**, 390 (1950). *Recherches sur la Croissance des Cultures Bacteriennes*, Second ed., Herman, Paris, 1958.
 Novick, A., and Szilard, L., *Proc. N.A.S.*, Washington, **36**, 708 (1950).

PROBLEMS

- 29.1.** A culture of *E. coli* was grown on lactose in a mixed flow reactor ($V = 1$ liter) using various flow rates of a $C_{A0} = 160$ mg lactose/liter feed. The following results were obtained:

v , liter/hr	C_A , mg/liter	Cell Concentration, Arbitrary
0.2	4	15.6
0.4	10	15
0.8	40	12
1.0	100	6

Find a rate equation to represent this growth.

E. coli lives and grows on mannitol with the following kinetics

$$r_C = \frac{1.2 C_A C_C}{C_A + 2}, \quad C_A = \text{gm mannitol/m}^3, \quad \textcircled{C/A} = 0.1 \text{ gm cells/gm mannitol}$$

Find the outlet concentration of cells from the reactor when 1 m³/hr of mannitol solution ($C_{A0} = 6 \text{ gm/m}^3$) is fed directly to a mixed flow reactor of volume

29.2. $V_m = 5 \text{ m}^3$ **29.3.** $V_m = 1 \text{ m}^3$.

Can you do better and produce more cells (if so, find C_C) by proper bypass or recycle of fluid from the reactor for the system of

29.4. problem 2? **29.5.** problem 3?

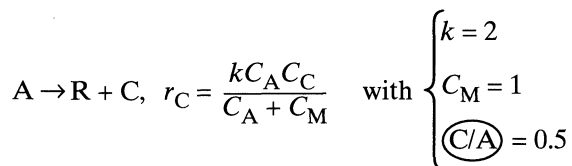
29.6. How curious—two different flow rates of $C_{A0} = 500 \text{ mol/m}^3$ feed to our 1 m³ mixed flow reactor produces the same 100 gm/hr of yeast cells in the exit stream, namely

- at 0.5 m³/hr of feed for which we find $C_A = 100 \text{ mol/m}^3$
- at 1 m³/hr of feed for which we find $C_A = 300 \text{ mol/m}^3$

Substrate limiting Monod kinetics should well represent yeast formation. From this information, find

- (a) the fractional yield of yeast,
- (b) the kinetic equation for yeast formation,
- (c) the flow rate for maximum yeast production,
- (d) the maximum production rate of yeast.

A stream of reactant A ($C_{A0} = 3, C_{R0} = 0, C_{C0} = 0$) is to be decomposed by the following microbial fermentation



In the following problems sketch your recommended reactor setup with recycle, bypass, etc., and on each sketch indicate pertinent quantities.

What is the lowest C_A which can be obtained in a single mixed flow reactor of size $V_m = 1$ for a feed rate of

29.7. $v = 1/3$ **29.8.** $v = 3$

What is the lowest C_A which can be obtained with two properly connected mixed flow reactors, each of volume $V = 1$, for a feed rate

- 29.9. $v = 2$ 29.10. $v = 1$

What is the lowest C_A which can be obtained with three wisely connected mixed flow reactors, each of volume $V_m = 1$, for a feed rate

- 29.11. $v = 6$ 29.12. $v = 2$

For a feed rate $v = 3$ what is the smallest size of plug flow reactor with appropriate piping (bypass or recycle or slide taps on the reactor) which will give

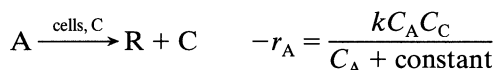
- 29.13. $C_C = 0.5$, side tap allowed

- 29.14. $C_C = 1.25$, side tap not allowed

- 29.15. $C_C = 1.44$, side tap allowed

- 29.16. Find the lowest C_A obtainable from a plug flow reactor of volume $V_p = 4$ (bypass, recycle and/or side taps are all allowed) for a feed rate $v = 6$

- 29.17. Given the Monod equation to represent a microbial fermentation



Which of the contacting patterns of Fig. P29.17 could be optimum, and which can never be? By optimum we mean minimizing reactor volume for a feed consisting only of C_{A0} .

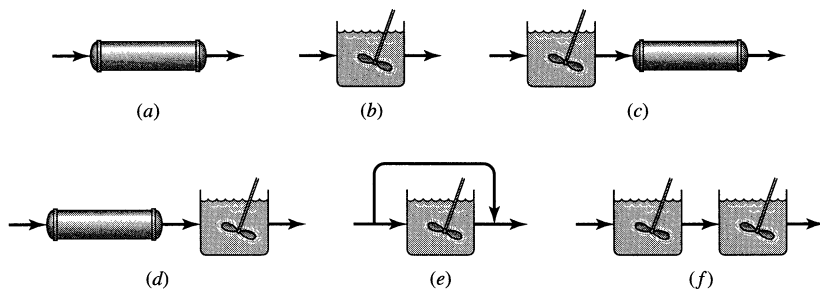


Figure P29.17

- 29.18. In his thesis, which was published as a book in 1948, Monod first proposed the celebrated equation that bears his name. As experimental support for this equation he presented results from four batch reactor runs on the

growth of a pure bacterial culture in a lactose solution (see Monod, 1958, p. 74). Here are the reported data for one of his runs.

Time Interval Number	Δt , hr	\bar{C}_A	C_C
1	0.54	137	15.5 to 23.0
2	0.36	114	23.0 to 30.0
3	0.33	90	30.0 to 38.8
4	0.35	43	38.8 to 48.5
5	0.37	29	48.5 to 58.3
6	0.38	9	58.3 to 61.3
7	0.37	2	61.3 to 62.5

Fit the Monod equation to this data.

29.19. In Example 29.1*e* we could have used any one of the three contacting schemes shown in Fig. P29.19. We stated without proof that the bypass scheme was best. Show that this is so by calculating C_{Aout} for the three contacting schemes of Fig. P29.19.

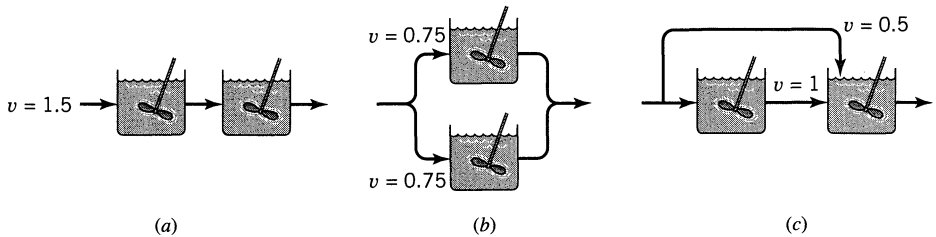


Figure P29.19

Chapter 30

Product-Limiting Microbial Fermentation

With sufficient food and harmonious environment, cells multiply freely. However, no matter how much food is available, eventually either cells crowd each other out or their waste products inhibit their growth. We call this *product poisoning*. Hence, Monod kinetics always is a special case of a more general rate form which includes product poisoning. A simple equation of the general rate form for this situation is

$$r_C = \textcircled{C/R} r_R = k \left(1 - \frac{C_R}{C_R^*} \right)^n \frac{C_A C_C}{C_A + C_M} \quad (1)$$

rate constant in a poison-free environment
 k_{obs} decreases as product builds up
order of product poisoning

In the special case of sufficient food, or $C_A \gg C_M$, and $n = 1$, the above equation reduces to the simplest expression for product poison control

$$r_C = \textcircled{R/C} r_R = k \left(1 - \frac{C_R}{C_R^*} \right) C_C \quad (2)$$

reaction stops when C_R reaches C_R^*

We start with the rate form of Eq. 2, then we extend the treatment to systems where $n \neq 1$, or Eq. 1. Let us also develop everything in terms of C_R , in which case Eq. 2 becomes

$$r_R = \textcircled{R/C} r_C = \textcircled{R/C} k \left(1 - \frac{C_R}{C_R^*} \right) C_C = k \left(1 - \frac{C_R}{C_R^*} \right) (C_R - C_{R0} + \textcircled{R/C} C_{C0}) \quad (3)$$

The maximum rate then occurs where $\frac{dr_R}{dC_R} = 0$. Solving gives

$$C_{R, \text{ max rate}} = \frac{1}{2} \left(C_{R0} + C_R^* - \frac{R}{C} C_{C0} \right) \tag{4}$$

Thus, there always is a composition where the rate is optimum.

30.1 BATCH OR PLUG FLOW FERMENTORS FOR $n = 1$

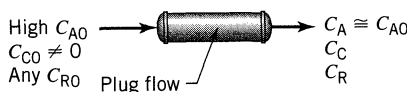


Figure 30a

To relate time to concentration, we integrate the performance expression of Eq. 3

$$t_p = \tau_b = \int_{C_{R0}}^{C_R} \frac{dC_R}{r_R} = \int_{C_{R0}}^{C_R} \frac{dC_R}{k \left(1 - \frac{C_R}{C_R^*} \right) (C_R - C_{R0} + \frac{R}{C} C_{C0})}$$

or in terms of product R,

$$k\tau_p = k\tau_b = \frac{C_R^*}{C_R - C_{R0} + \frac{R}{C} C_{C0}} \ln \frac{C_C(C_R^* - C_{R0})}{C_{C0}(C_R^* - C_R)} \tag{5}$$

Graphically this performance equation is shown in Fig. 30.1.

Since the $1/r_A$ versus C_R curve is U-shaped, the optimum way of running the plug flow reactor is shown in Fig. 30.2.

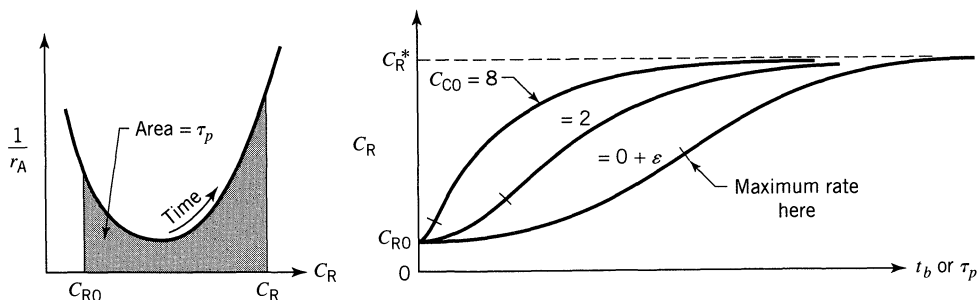


Figure 30.1 Graphical representation of Eq. 5.

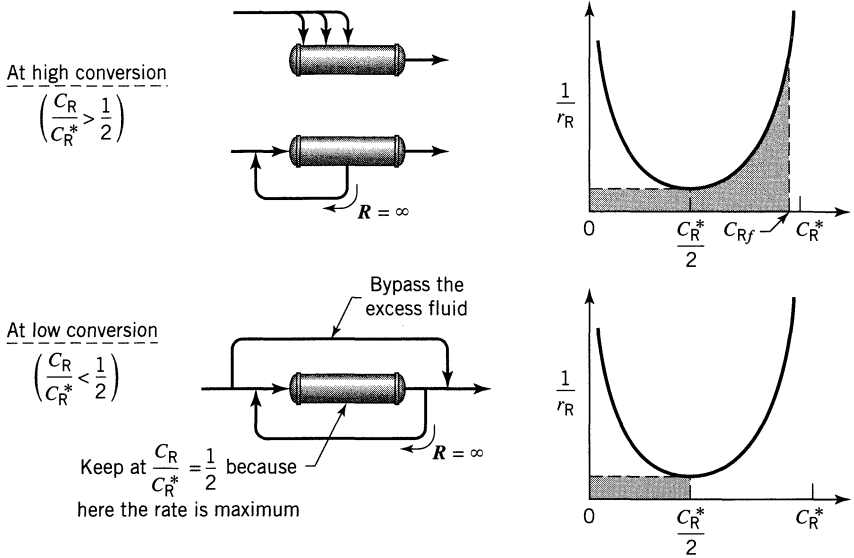


Figure 30.2 Optimum operation of a plug flow fermentor for poison limiting kinetics.

30.2 MIXED FLOW FERMENTORS FOR $n = 1$

For the case of negligible time lag for the feed cells which enter their new environment, and for high C_{A0} we have

$$\tau_m = \frac{C_R - C_{R0}}{r_R} = \frac{C_R - C_{R0}}{k \left(1 - \frac{C_R}{C_R^*}\right) (C_R - C_{R0} + \frac{R}{C} C_{C0})} \quad (9)$$

For the special case where $C_{C0} = 0$ and $C_{R0} = 0$ the above general expression simplifies to

$$k\tau_m = \frac{C_R^*}{C_R^* - C_R} = \frac{1}{1 - \frac{C_R}{C_R^*}} \quad \text{for } k\tau_m > 1 \quad (10)$$

To evaluate the kinetic constants from mixed flow experiments rearrange Eq. 10 as in Eq. 11 and plot as shown in Fig. 30.3.

$$C_R = C_R^* - \frac{C_R}{k} \cdot \frac{1}{\tau_m} \quad (11)$$

The properties of Eq. 10 are displayed in Fig. 30.4.

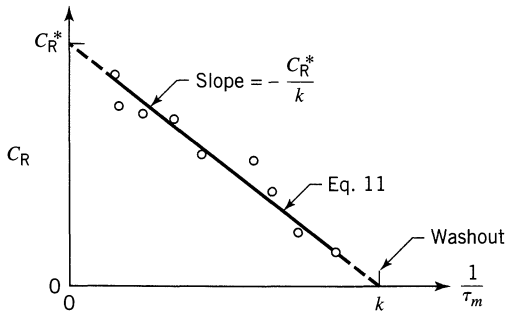


Figure 30.3 Evaluation of the rate constants of Eq. 2 from data taken in a mixed flow reactor.

Comments

For mixed flow with $C_{C0} = 0$, $C_{R0} = 0$, and any high C_{A0} .

- washout occurs at $k\tau_m = 1$ for any feed
- maximum production rate of cells and product R is obtained at

$$k\tau_m = 2 \dots \text{and} \dots C_R = C_R^*/2$$

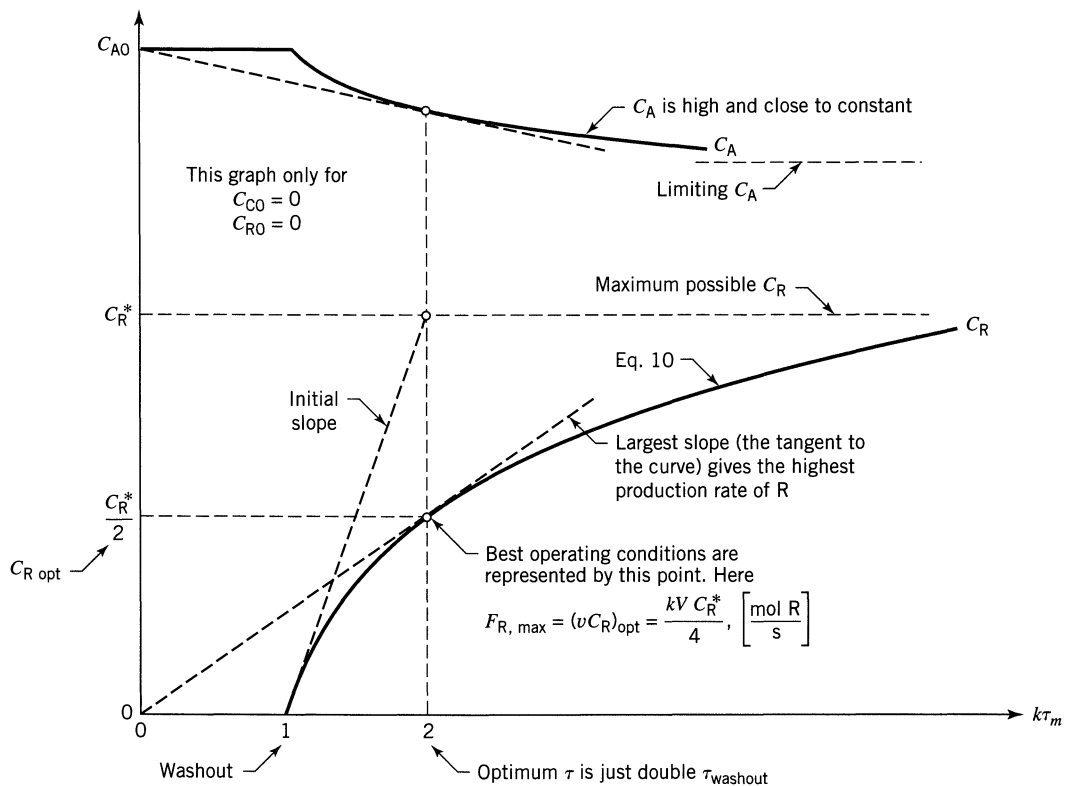


Figure 30.4 Properties of the mixed flow equation for the kinetics of Eq. 2.

- the maximum production rate of cells and product is found to be

$$F_{R, \max} = \left(\frac{R}{C}\right) F_{C, \max} = kVC_R^* / 4$$

- the C_C curve is similar in shape to the C_R curve and is proportional to it. Thus, it rises from 0 to $\left(\frac{C}{R}\right) C_R^*$.
- Optimum operations for multistage systems follow the same pattern as for poison-free systems. The general rule is to use mixed flow to reach the maximum rate in one step. Proceed beyond this with plug flow. Note that the maximum rate occurs at $C_R^*/2$ when $C_{C0} = 0$ and $C_{R0} = 0$.

Fermentation with $n \neq 1$ Poison Limiting Kinetics

For n -th order product poisoning kinetics the rate equation is

$$-r_R = k \left(1 - \frac{C_R}{C_R^*}\right)^n C_C \quad (12)$$

These kinetics are displayed in Fig. 30.5. The performance equation for plug flow is quite messy; however, for mixed flow the performance equation can be obtained directly. Thus in general, for $C_{C0} \neq 0$ and $C_{R0} \neq 0$ we have

$$k\tau_m = \frac{C_R - C_{R0}}{\left(C_R - C_{R0} + \left(\frac{R}{C}\right) C_{C0}\right) \left(1 - \frac{C_R}{C_R^*}\right)^n} \quad (13)$$

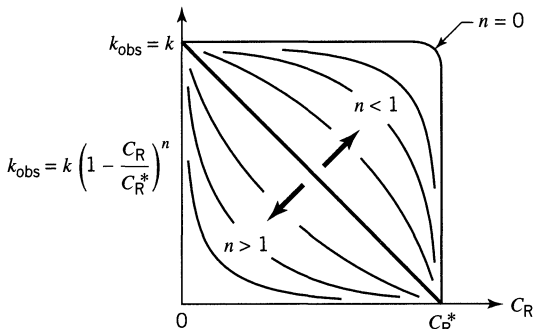


Figure 30.5 Reaction slowdown is strongly dependent on the order of poisoning, n .

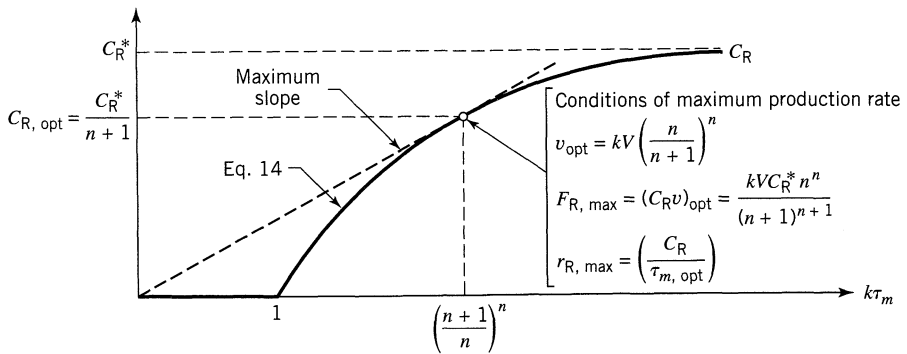


Figure 30.6 Behavior of a mixed flow reactor for the poison influenced kinetics of Eq. 12.

and for the special case where $C_{C0} = 0$ and $C_{R0} = 0$

$$k\tau_m = \frac{1}{\left(1 - \frac{C_R}{C_R^*}\right)^n} \quad \text{when} \quad k\tau_m > 1 \quad (14)$$

The properties of this equation, washout, maximum production, etc. are displayed in Fig. 30.6. To find the kinetic constants C_R^* , k and n from experiment first evaluate C_R^* in a batch run using an excess of reactant A and letting $t \rightarrow \infty$. Then rearrange the mixed flow performance equation to give

$$\log \tau_m = -\log k + n \log \left(\frac{C_R^*}{C_R^* - C_R} \right) \quad (15)$$

and plot as shown in Fig. 30.7. This will give the kinetic constants k and n .

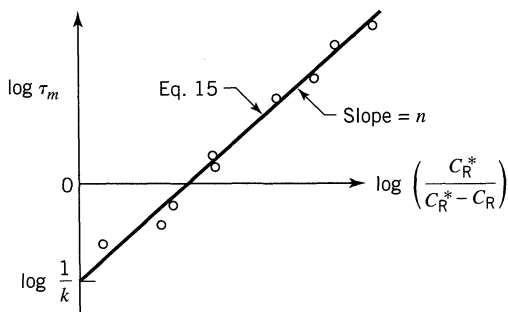


Figure 30.7 Finding the order of product poisoning and the rate constant of Eq. 12 from mixed flow reactor data.

Discussion

The similarity in shape of the mixed flow graphs for product-limiting and substrate-limiting (Monod) kinetics (Fig. 29.5 and Fig. 30.4), has led many investigators to fit product poisoning systems with the simple Monod equation. The fit will be good, but don't try to use the fitted equation for different feed conditions. Your predictions are likely to be way off because the logic of the extension is wrong.

You must first find which of these two factors is rate limiting. This is easy to do, so there is no excuse for using the wrong expression. In one case the final extent of reaction is dependent on C_{A0} and not on C_{R0} ; in the other case just the opposite holds. The discussion and sketches of Chapter 28 show this.

Expressions for related situations such as plug flow with recycle, and where both substrate and product both affect the rate are developed by Levenspiel (1996) Chapter 84.

EXAMPLE 30.1 FRUIT FLY COCKTAIL

Crushed fruit flies (A) ferment to produce an aromatic alcoholic drink (R) with product-limiting kinetics estimated as follows:

$$\left. \begin{array}{l} A \xrightarrow{C} R + C \\ r_R = k \left(1 - \frac{C_R}{C_R^*}\right)^n C_C \end{array} \right\} \text{with } \begin{cases} k = \sqrt{3}, \text{ hr}^{-1} \\ n = 1 \text{ in a springtime operation} \\ C_R^* = 0.12 \text{ kg alc/kg solution} \\ \rho = 1000 \text{ kg/m}^3 \end{cases}$$

What is the most alcohol you can produce (kg/hr) in a commercial-sized mixed flow reactor ($V_m = 30 \text{ m}^3$)? Also calculate the concentration of alcohol in the cocktail, and the feed rate needed of fragrant fresh frappéed fruit fries.

SOLUTION

From the given data and from Fig. 30.4, we find the conditions which yield the optimum. Thus

$$C_R^* = \left(\frac{0.12 \text{ kg alc}}{\text{kg sol}}\right) \left(\frac{10^3 \text{ kg sol}}{\text{m}^3 \text{ sol}}\right) = 120 \text{ kg/m}^3$$

$$\therefore C_{R, \text{opt}} = \frac{C_R^*}{2} = \left(\frac{120 \text{ kg alc}}{\text{m}^3}\right) \frac{1}{2} = 60 \frac{\text{kg alc}}{\text{m}^3} = \underline{\underline{6\% \text{ alcohol}}}$$

Again, from Fig. 30.4 we find

$$k\tau_{\text{washout}} = 1 \quad \therefore \tau_{\text{washout}} = \frac{1}{\sqrt{3}} \text{ hr}$$

and

$$\tau_{\text{opt}} = 2\tau_{\text{washout}} = \frac{2}{\sqrt{3}} \text{ hr}$$

But $\tau_{\text{opt}} = \frac{V}{v_{\text{opt}}}$ so the optimum feed rate is

$$v_{\text{opt}} = \frac{V}{\tau_{\text{opt}}} = \frac{30\sqrt{3}}{2} = \underline{\underline{25.98 \text{ m}^3/\text{hr}}}$$

The production rate of alcohol, again from Fig. 30.4, is

$$F_R = v_{\text{opt}} \cdot C_{R,\text{opt}} = (25.98) (60) = \underline{\underline{1558 \text{ kg alc/hr}}}$$

REFERENCES

Levenspiel, O., *Chemical Reactor Omnibook*, Chapter 84, OSU Bookstores, Corvallis, OR, 1996.

PROBLEMS

Material R is to be produced from the following microbial fermentation, using a feed stream $C_{A0} = 10^6$, $C_{R0} = 0$, $C_{C0} = 0$. All quantities are given in consistent SI units.

$$A \xrightarrow{C} R + C \quad \text{with} \quad \begin{cases} k = 2 \\ C_M = 50 \\ C_R^* = 12 \\ \textcircled{R/A} = 0.1 \\ \textcircled{C/A} = 0.01 \end{cases} \quad (9)$$

$$r_C = k \left(1 - \frac{C_R}{C_R^*} \right) \frac{C_A C_C}{C_A + C_M}$$

In each of the following problems sketch your recommended reactor setup and on the sketch indicate pertinent quantities.

What C_R is obtainable in a single mixed flow reactor of size $V_m = 1$ for a feed rate

30.1. . . . $v = 1$

30.2. . . . $v = 4$

What C_R is obtainable using two mixed flow reactors, each of volume $V_m = 1$, for a feed rate

30.3. . . . $v = 1$

30.4. . . . $v = 3$

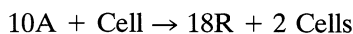
For a feed rate $v = 3$ what size of plug flow reactor with appropriate piping, recycle, bypass or anything you want to use is needed to give

30.5. . . . $C_R = 6$

30.6. . . . $C_R = 4$

30.7. . . . $C_R = 9$

30.8. The microbial fermentation of A produces R as follows



and experiments in a mixed flow reactor with $C_{A0} = 250 \text{ mol/m}^3$ show that

$$C_R = 24 \text{ mol/m}^3 \text{ when } \tau = 1.5 \text{ hr}$$

$$C_R = 30 \text{ mol/m}^3 \text{ when } \tau = 3.0 \text{ hr}$$

In addition, there seems to be a limiting upper value for C_R at 36 mol/m^3 for any τ_m , C_A , or C_C .

From this information determine how to maximize the fractional yield of R, or (R/A) , from a feed stream of $10 \text{ m}^3/\text{hr}$ of $C_{A0} = 350 \text{ mol/m}^3$. Cell or product separation and recycle are not practical in this system, so only consider a once-through system. Present your answer as a sketch showing reactor type, reactor volume, C_R in the exit stream, and the moles of R produced/hr.

In spring the fermentation of fruit flies proceeds with $n = 1$ kinetics, as shown in Example 30.1. However, in winter or summer, maybe because of a difference in temperature, the poisoning proceeds differently. So repeat Example 30.1 with one change:

30.9. in winter, $n = \frac{1}{2}$

30.10. in summer, $n = 2$

Note: To tell how the value of n affects the reactor performance, compare your answers here with the answer in Example 30.1.

30.11. Shredded chemical reactor textbooks are degraded to glucose in a pilot plant well stirred fermenter ($V_m = 50 \text{ lit}$) under the action of a word gobbling bug. With a large excess of these shredded incomprehensible words, the presence of glucose becomes the rate limiting factor. We summarize the findings as follows

$$\begin{array}{ll} \text{when } v = 16 \text{ books/hr} & C_R = 54 \mu\text{mol/liter} \\ \text{when } v = 4 \text{ books/hr} & C_R = 75 \mu\text{mol/lit} \\ \text{when } v \rightarrow 0 & C_R \rightarrow 90 \mu\text{mol/lit} \end{array}$$

Determine the flow rate of books which maximizes glucose production per word gobbled up, and find this production rate.

- 30.12.** Professor Microbe has submitted a paper for publication in which he studied the growth of a new strain of bug in a mixed flow fermenter ($V_m = 46.4$) using a pure substrate feed ($C_{A0} = 150$, $C_{R0} = C_{C0} = 0$). His raw data is as follows

v	C_A	
4.64	5	
20.0	125	with $\textcircled{R/A} = 0.5$
22.0	150 (washout)	

He asserts, without giving details, that this data clearly represents poison-limiting kinetics with rate constants

$$k = 0.50, \quad C_R^* = 90.6, \quad n = 1.0$$

The reviewer of the paper, Dr. Ferment, counters that Microbe is quite wrong, that the data in fact represents substrate limiting Monod kinetics with

$$C_M = 20, \quad k = 0.50$$

But, out of orneriness, he didn't present the details of his calculations either. The editor can't determine who is right (this is not his field), so he sends the paper and the review to duWayne Zuelhsdorff. What is duWayne's answer? Is Microbe, or Ferment, or both, or neither, right?

Appendix—Miscellany

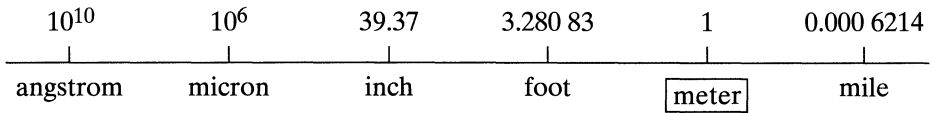
A. Newton's Law

at earth's surface $a = g = 9.806 \text{ m/s}^2$

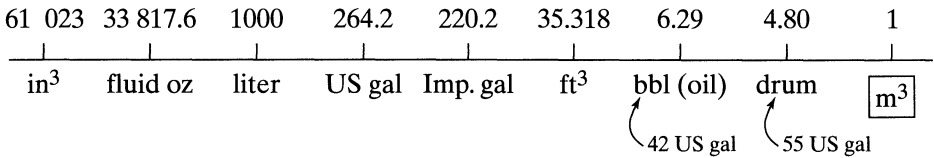
$$F = \frac{ma}{g_c} \quad \dots \quad 1\text{N} = \frac{(1 \text{ kg})(1 \text{ m/s}^2)}{(1 \text{ kg}\cdot\text{m/s}^2\cdot\text{N})}$$

conversion factor: $g_c = \frac{1 \text{ kg}\cdot\text{m}}{\text{s}^2\cdot\text{N}}$

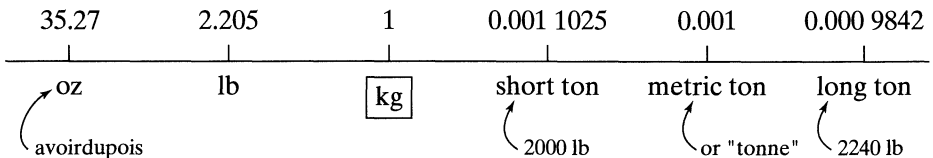
B. Length



C. Volume



D. Mass



E. Pressure

$$\text{The Pascal: } 1 \text{ Pa} = 1 \frac{\text{N}}{\text{m}^2} = 1 \frac{\text{kg}}{\text{m} \cdot \text{s}^2} = 10 \frac{\text{dyne}}{\text{cm}^2}$$

$$1 \text{ atm} = 760 \text{ mm Hg} = 14.696 \frac{\text{lb}_f}{\text{in}^2} = 29.92 \text{ in Hg} = 33.93 \text{ ft H}_2\text{O} = 101\,325 \text{ Pa}$$

1 bar = 10^5 Pa . . . close to 1 atm, sometimes called a *technical atmosphere*

$$1 \text{ inch H}_2\text{O} = 248.86 \text{ Pa} \cong 250 \text{ Pa}$$

F. Work, Energy, and Heat

$$\text{The joule: } 1 \text{ J} = 1 \text{ N} \cdot \text{m} = 1 \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2}$$

10^{13}	10^6	737 562	238 846	101 972	9869	947.8	238.85	0.372 51	0.277 778	
erg	J	ft · lb _f	cal	kg _f · m	lit · atm	Btu	kcal	Hp · hr	kW · hr	

↖ 778 ft · lb_f

G. Molecular Weight

In SI units: $(mw)_{\text{O}_2} = 0.032 \frac{\text{kg}}{\text{mol}}$

$$(mw)_{\text{air}} = 0.0289 \frac{\text{kg}}{\text{mol}} \dots \text{etc.}$$

H. Ideal

$$pV = nRT \quad \dots \text{ or } \frac{p}{\rho} = \frac{RT}{(mw)} \quad \dots \text{ or } C_A = \frac{n_A}{V} = \frac{p_A}{RT}$$

the gas constant ↗

↖ kg/m³

↖ m³/mol

$$R = \boxed{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}} = 1.987 \frac{\text{cal}}{\text{mol} \cdot \text{K}} = 0.7302 \frac{\text{ft}^3 \cdot \text{atm}}{\text{lb mol} \cdot ^\circ\text{R}}$$

$$= 0.082\,06 \frac{\text{liter} \cdot \text{atm}}{\text{mol} \cdot \text{K}} = 1.987 \frac{\text{Btu}}{\text{lb mol} \cdot ^\circ\text{R}} = 82.06 \times 10^{-6} \frac{\text{m}^3 \cdot \text{atm}}{\text{mol} \cdot \text{K}}$$

$$= \boxed{8.314 \frac{\text{Pa} \cdot \text{m}^3}{\text{mol} \cdot \text{K}}} = 8314 \frac{\text{Pa} \cdot \text{liter}}{\text{mol} \cdot \text{K}}$$

I. Viscosity (μ)

The poiseuille: $1 \text{ Pl} = \frac{\text{kg}}{\text{m} \cdot \text{s}}$

$$1 \text{ Pl} = 1 \frac{\text{kg}}{\text{m} \cdot \text{s}} = 10 \text{ poise} = 1000 \text{ cp} = 0.672 \frac{\text{lb}_m}{\text{ft} \cdot \text{s}} = 2420 \frac{\text{lb}_m}{\text{ft} \cdot \text{hr}}$$

↖ 1 gm/cm·s
↖ centipoise

for water: $\mu_{20^\circ\text{C}} = 10^{-3} \text{ Pl}$

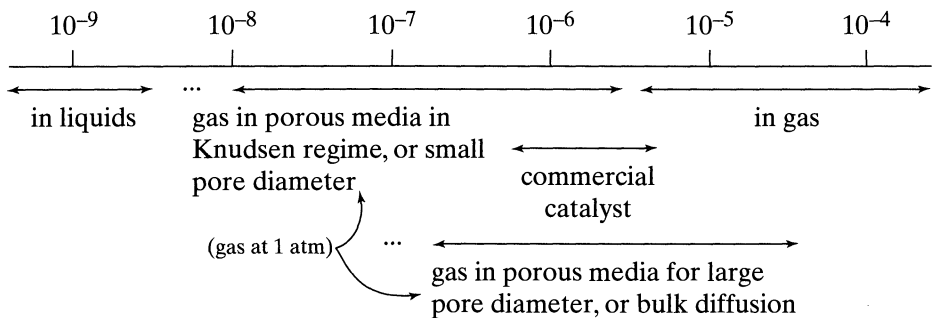
for gases: $\mu \cong 10^{-5} \text{ Pl}$

for air: $\mu_{20^\circ\text{C}} = 1.8 \times 10^{-5} \text{ Pl}$

J. Density $\rho = \left[\frac{\text{kg}}{\text{m}^3} \right]$

for water: $\rho \cong 1000 \frac{\text{kg}}{\text{m}^3}$

for ideal gas: $\rho = \frac{p(mw)}{RT} \stackrel{\text{air}}{20^\circ\text{C}} \frac{(101\,325)(0.0289)}{(8.314)(293)} = 1.20 \frac{\text{kg}}{\text{m}^3}$

K. Diffusivity \mathcal{D} and $\mathcal{D}_{\text{eff}} = \left[\frac{\text{m}^2}{\text{s}} \right]$ 

$$1 \frac{\text{m}^2}{\text{s}} = 3.875 \times 10^4 \frac{\text{ft}^2}{\text{hr}}$$

\mathcal{D} independent of π ... for liquids

$\mathcal{D} \propto T^{3/2}$, $\mathcal{D} \propto \frac{1}{\pi}$... for bulk diffusion of gases

$\mathcal{D} \propto T^{1/2}$, \mathcal{D} independent of π ... for Knudsen diffusion of gases

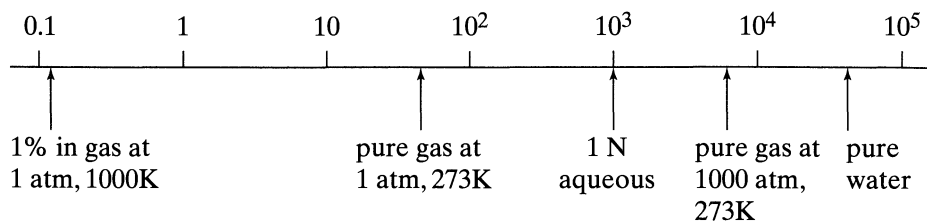
In a tube of diameter d Knudsen diffusion occurs when $\pi d < 0.01$, Pa·m.

In this situation,

$$\mathcal{D} = 1.534d \sqrt{T/(mw)}$$

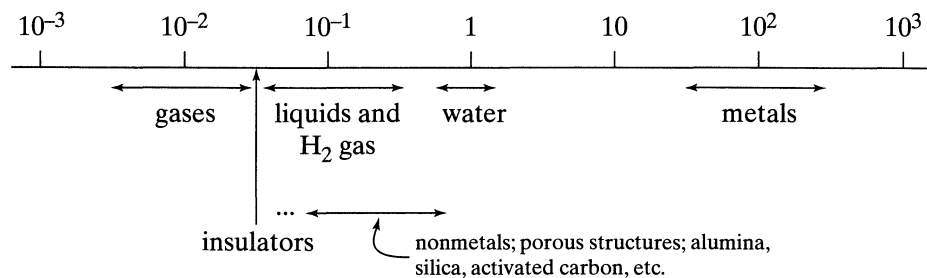
$$\text{Dimensions: } \begin{cases} \text{In gas or any fluid: } \mathcal{D} = \left[\frac{\text{m}^2 \text{ fluid}}{\text{s}} \right] \\ \text{In a porous structure: } \mathcal{D} = \left[\frac{\text{m}^3 \text{ fluid}}{\text{m solid} \cdot \text{s}} \right] \end{cases}$$

L. Concentration $C_A = \left[\frac{\text{mol}}{\text{m}^3 \text{ fluid}} \right]$



$$1 \frac{\text{mol}}{\text{m}^3} = 6.24 \times 10^{-5} \frac{\text{lb mol}}{\text{ft}^3}$$

M. Thermal Conductivity k and $k_{\text{eff}} = \left[\frac{\text{W}}{\text{m} \cdot \text{K}} \right]$



$$1 \frac{\text{W}}{\text{m} \cdot \text{K}} = 0.239 \frac{\text{cal}}{\text{m} \cdot \text{K} \cdot \text{s}} = 0.578 \frac{\text{Btu}}{\text{hr} \cdot \text{ft} \cdot ^\circ\text{F}}$$

k and k_{eff} are independent of π

$$\text{Dimensions: } \begin{cases} \text{In gas or liquid: } k = \left[\frac{\text{W}}{\text{m fluid} \cdot \text{K}} \right] \\ \text{In porous structures: } k_{\text{eff}} = \left[\frac{\text{W}}{\text{m structure} \cdot \text{K}} \right] \end{cases}$$

N. Heat Transfer Coefficient $h = \left[\frac{W}{m^2 \cdot K} \right]$

$$1 \frac{W}{m^2 \cdot K} = 0.239 \frac{\text{cal}}{m^2 \cdot K \cdot s} = 0.176 \frac{\text{Btu}}{\text{hr} \cdot \text{ft}^2 \cdot ^\circ\text{F}}$$

Gas to particle: $h = 8 \sim 1200$

Gas to fine entrained particles (fast fluidized systems, FCC, etc.) $h \cong 1000\text{--}1200$

Liquid to particle: $h = 80 \sim 1200$

$$\text{In packed beds: } Nu = \frac{hd_p}{k} = 2 + 1.8(Re_p)^{1/2} (Pr)^{1/3} \quad \dots Re_p > 100$$

$\left\{ \begin{array}{l} \cong 1 \text{ for gases} \\ \cong 10 \text{ for liquids} \end{array} \right.$

O. Mass Transfer Coefficient $k_g = \left[\frac{m^3 \text{ gas}}{m^2 \text{ surface} \cdot s} \right]$

Gas to particle: $k_g = 0.02 \sim 2$

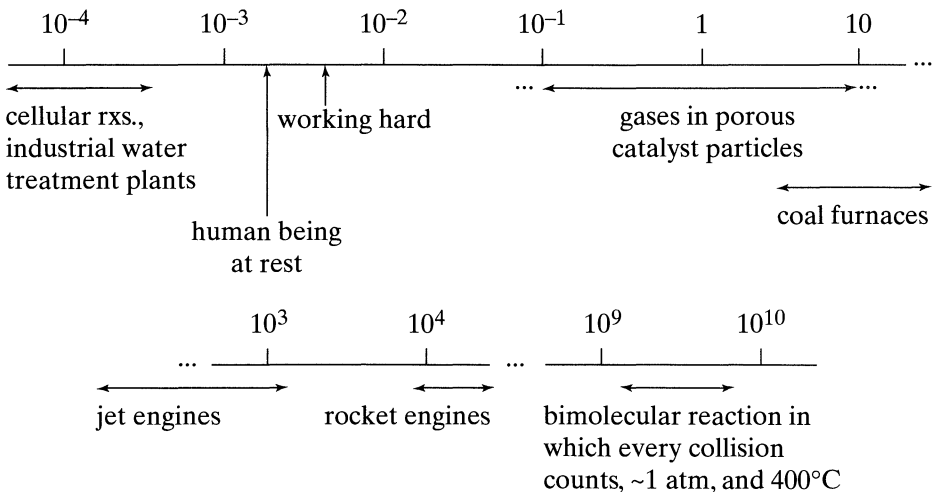
Liquid to particle: $k_g = 2 \times 10^{-7} \sim 2 \times 10^{-5}$

$$\text{In packed beds: } Sh = \frac{k_g d_p}{\mathcal{D}} = 2 + 1.8(Re_p)^{1/2} (Sc)^{1/3} \quad \dots Re_p > 80$$

$\left\{ \begin{array}{l} \cong 1 \text{ for gases} \\ \cong 1000 \text{ for liquids} \end{array} \right.$

For gases: $k_g \propto 1/\pi$

P. Rate of Reaction $-r''_A = \left[\frac{\text{moles of A disappearing}}{m^3 \text{ of thing} \cdot s} \right]$



Q. Dimensionless Groups

$$\boxed{\text{Sc}} = \frac{\mu}{\rho \mathcal{D}} = \frac{\text{molecular momentum transfer}}{\text{molecular mass transfer}} \dots \text{Schmidt number}$$

viscous effects
diffusion effects

$$\cong \frac{10^{-5}}{(1)(10^{-5})} = 1 \dots \text{for gases}$$

$$\cong \frac{10^{-3}}{(10^3)(10^{-9})} = 10^3 \dots \text{for liquids}$$

$$\boxed{\text{Pr}} = \frac{C_p \mu}{k} = \frac{\text{molecular momentum transfer}}{\text{molecular heat transfer}} \dots \text{Prandtl number}$$

viscous effects
heat conduction

$$\cong 0.66 \sim 0.75 \text{ for air, A, CO}_2, \text{CH}_4, \text{CO, H}_2, \text{He, N}_2, \text{ and other common gases}$$

$$\cong 1.06 \text{ for steam}$$

$$= 10 \sim 1000 \text{ for most liquids}$$

$$= 0.006 \sim 0.03 \text{ for most liquid metals}$$

$$\boxed{\text{Re}} = \frac{du\rho}{\mu} = \frac{\text{total momentum transfer}}{\text{molecular momentum transfer}} \dots \text{Reynolds number}$$

inertial effects
viscous effects

$$\boxed{\text{Nu}} = \frac{hd}{k} = \frac{\text{total heat transfer}}{\text{molecular heat transfer}} \dots \text{Nusselt number}$$

turbulent and laminar, conduction and convection
heat conduction alone

$$\boxed{\text{Sh}} = \frac{k_g d}{\mathcal{D}} = \frac{\text{total mass transfer}}{\text{molecular mass transfer}} \dots \text{Sherwood number}$$

$$\boxed{\text{Pe}} = \frac{du\rho C_p}{k} = (\text{Re})(\text{Pr}) = \frac{\text{total momentum transfer}}{\text{molecular heat transfer}} \dots \text{Peclet number}$$

$$\boxed{\text{Bo}} = \frac{ud}{\mathcal{D}} = (\text{Re})(\text{Sc}) = \frac{\text{total momentum transfer}}{\text{molecular mass transfer}} \dots \text{Bodenstein number}$$

$$\boxed{\frac{\mathbf{D}}{ud} \text{ and } \frac{\mathbf{D}}{uL}} = \frac{\text{movement by longitudinal dispersion}}{\text{movement by bulk flow}} \dots \text{dispersion groups}$$

fluid overtaking caused by molecular diffusion, velocity differences, turbulent eddies, etc.

This is a new and different type of dimensionless group introduced by workers in chemical reaction engineering. Unfortunately someone started calling the reciprocal of this group the Peclet number—this is wrong. It is neither the Peclet number nor its mass transfer analog, which is widely called the Bodenstein number in Europe. The difference rests in the use of **D** in place of \mathcal{D} ; hence, these groups have completely different meanings.

A name is needed for this group. Until one is chosen let us use:

$\frac{\mathbf{D}}{ud}$... intensity of axial dispersion

$\frac{\mathbf{D}}{uL}$... vessel dispersion number.

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