

# **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 ( $\text{m}^2/\text{m}^3$ ), 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 ( $\text{m}^2$ ), see Chapter 20
A, B, ...	reactants
<b>A, B, C, D,</b>	Geldart classification of particles, see Chapter 20
$C$	concentration ( $\text{mol}/\text{m}^3$ )
$C_M$	Monod constant ( $\text{mol}/\text{m}^3$ ), see Chapters 28-30; or Michaelis constant ( $\text{mol}/\text{m}^3$ ), 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
<b>D</b>	axial dispersion coefficient for flowing fluid ( $\text{m}^2/\text{s}$ ), see Chapter 13
$\mathcal{D}$	molecular diffusion coefficient ( $\text{m}^2/\text{s}$ )
$\mathcal{D}_e$	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 <sup>3</sup> ), see Chapter 27
$E$	dimensionless output to a pulse input, the exit age distribution function (s <sup>-1</sup> ), 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 <sup>3</sup> solid/m <sup>3</sup> 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 <sup>2</sup> ·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 <sup>3</sup> /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
$\Delta H_r$	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 <sup>3</sup> ) <sup>1-n</sup> s <sup>-1</sup> , 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
$k_{\text{eff}}$	effective thermal conductivity (W/m·K), see Chapter 18
$k_g$	mass transfer coefficient of the gas film (mol/m <sup>2</sup> ·Pa·s), see Eq. 23.2
$k_l$	mass transfer coefficient of the liquid film (m <sup>3</sup> liquid/m <sup>2</sup> 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
<b>R</b>	ideal gas law constant, = 8.314 J/mol·K = 1.987 cal/mol·K = 0.08206 lit·atm/mol·K
<b>R</b>	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**

$\alpha$	$m^3$ wake/ $m^3$ bubble, see Eq. 20.9
$\delta$	volume fraction of bubbles in a BFB
$\delta$	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 $t_0$ ( $s^{-1}$ )
$\varepsilon_A$	expansion factor, fractional volume change on complete conversion of A, see Eq. 3.64
$\epsilon$	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
$\mu$	viscosity of fluid (kg/m·s)
$\mu$	mean of a tracer output curve, (s), see Chapter 15
$\pi$	total pressure (Pa)
$\rho$	density or molar density (kg/ $m^3$ or mol/ $m^3$ )
$\sigma^2$	variance of a tracer curve or distribution function ( $s^2$ ), see Eq. 13.2
$\tau$	$V/v = C_{A0}V/F_{A0}$ , space-time (s), see Eqs. 5.6 and 5.8
$\tau$	time for complete conversion of a reactant particle to product (s)
$\tau'$	$= C_{A0}W/F_{A0}$ , 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
$\Phi$	overall fractional yield, see Eq. 7.8
$\phi$	sphericity, see Eq. 20.6
$\varphi$	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
$\theta$	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

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## Overview of Chemical Reaction Engineering

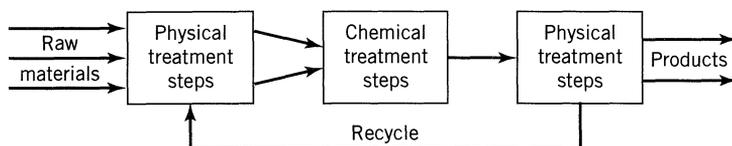
Every industrial chemical process is designed to produce economically a desired product from a variety of starting materials through a succession of treatment steps. Figure 1.1 shows a typical situation. The raw materials undergo a number of physical treatment steps to put them in the form in which they 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.

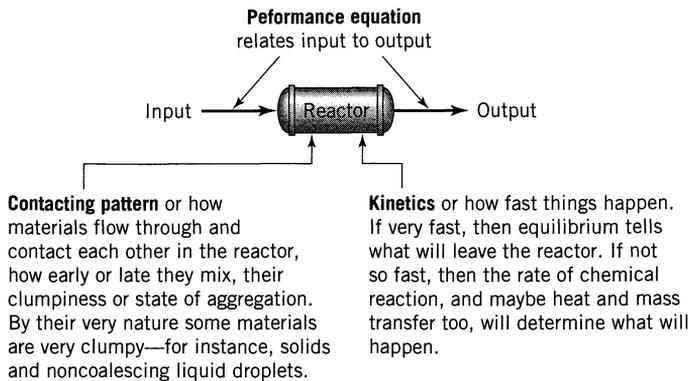
Design of the reactor is no routine matter, and many alternatives can be proposed for a process. In searching for the optimum it is not just the cost of the reactor that must be minimized. One design may have low reactor cost, but the materials leaving the unit may be such that their treatment requires 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 $\text{SO}_2$ to $\text{SO}_3$

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

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

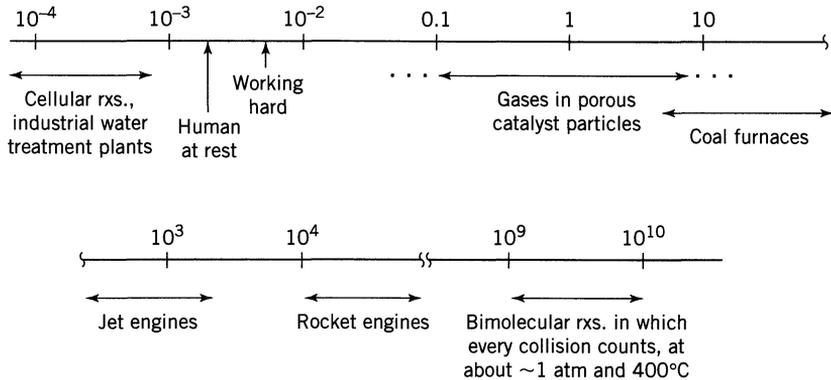
## Speed of Chemical Reactions

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

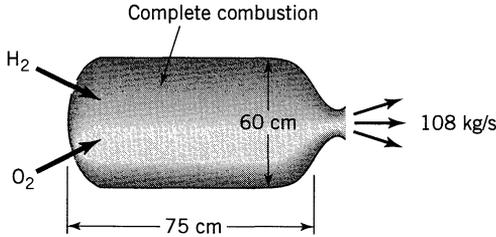
## Overall Plan

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**

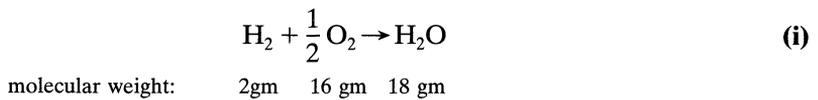
We want to evaluate

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

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

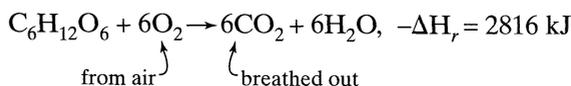
$$\underline{\underline{-r_{\text{H}_2}}} = -\frac{1}{0.2121 \text{ m}^3} \cdot \frac{6 \text{ kmol}}{\text{s}} = \underline{\underline{2.829 \times 10^4 \frac{\text{mol used}}{(\text{m}^3 \text{ of rocket}) \cdot \text{s}}}}$$

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

**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 m<sup>3</sup> 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

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

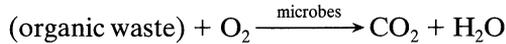
Inserting into Eq. (i)

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

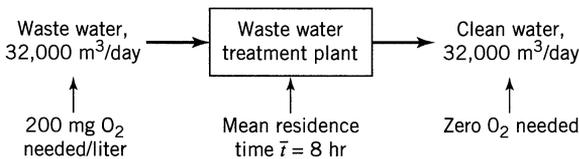
**Note:** Compare this value with those listed in Figure 1.3.

## 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 m<sup>3</sup>/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

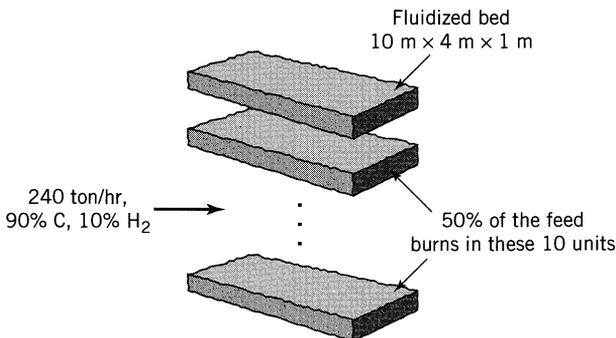


A typical entering feed has a BOD (biological oxygen demand) of 200 mg O<sub>2</sub>/liter, while the effluent has a negligible BOD. Find the rate of reaction, or decrease in BOD in the treatment tanks.



**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%

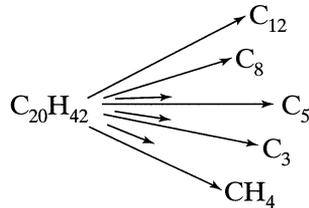


**Figure P1.2**

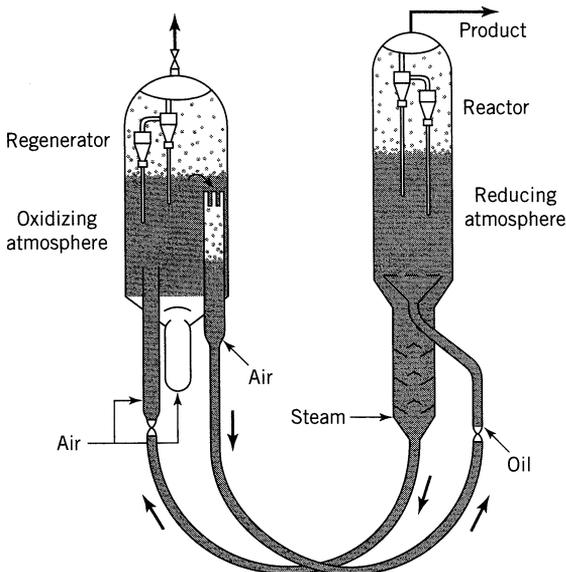
$H_2$ ), 50% of which would burn within the battery of primary fluidized beds, the other 50% elsewhere in the system. One suggested design would use a battery of 10 fluidized beds, each 20 m long, 4 m wide, and containing solids to a depth of 1 m. Find the rate of reaction within the beds, based on the 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  $\cdot$  s) and as  $r'''$  (mols reacted/ $\text{m}^3$  cat  $\cdot$  s)?



**Figure P1.3** The Exxon Model IV FCC unit.



# Part I

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## Homogeneous Reactions in Ideal Reactors

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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

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

rate of disappearance of A

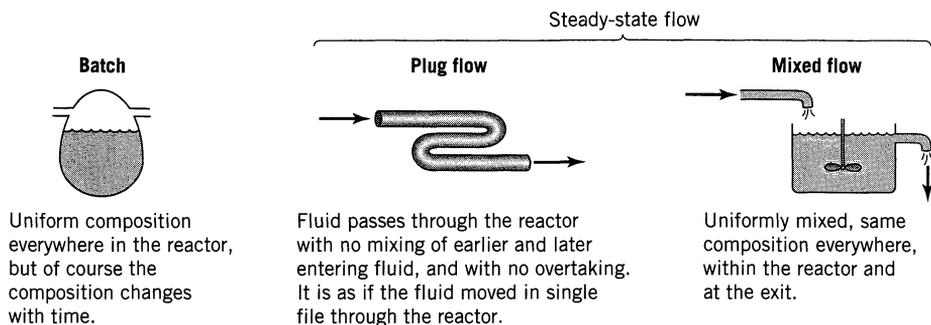
note that this is an intensive measure

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.

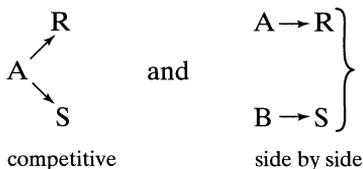
When a single stoichiometric equation and single rate equation are chosen to represent the progress of the reaction, we have a *single reaction*. When more than one stoichiometric equation is chosen to represent the observed changes,

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

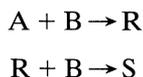
Multiple reactions may be classified as:  
*series reactions*,



*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

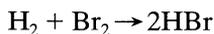


If we postulate that the rate-controlling mechanism involves the collision or interaction of a single molecule of A with a single molecule of B, then the number of collisions of molecules A with B is proportional to the rate of reaction. But at a given temperature the number of collisions is proportional 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  $k$ .

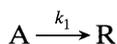
For brevity, elementary reactions are often represented by an equation showing both the molecularity and the rate constant. For example,



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,

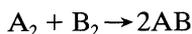


Rate: 
$$r_{\text{NH}_3} = k_1 \frac{[\text{N}_2][\text{H}_2]^{3/2}}{[\text{NH}_3]^2} - k_2 \frac{[\text{NH}_3]}{[\text{H}_2]^{3/2}}$$

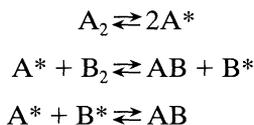
This nonmatch shows that we must try to develop a multistep reaction model to explain the kinetics.

## 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



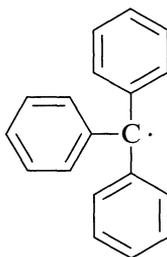
indicates that the reaction is nonelementary, we may postulate a series of elementary steps to explain the kinetics, such as



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.

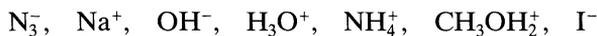
**Free Radicals.** Free atoms or larger fragments of stable molecules that contain one or more unpaired electrons are called free radicals. The unpaired electron is designated by a dot in the chemical symbol for the substance. Some free radicals are relatively stable, such as triphenylmethyl,



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

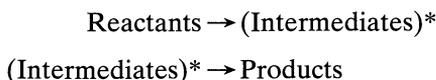


Ordinarily these are treated as multiple reactions. However, if the intermediate R is highly reactive its mean lifetime will be very small and its concentration in the reacting mixture can become too small to measure. In such a situation R may not be observed and can be considered to be a reactive intermediate.

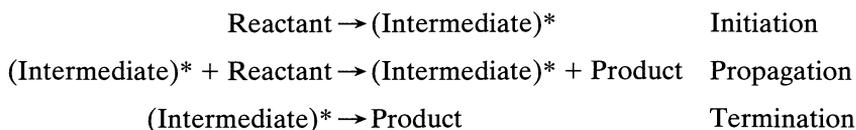
**Transition Complexes.** The numerous collisions between reactant molecules result in a wide distribution of energies among the individual molecules. This can result in strained bonds, unstable forms of molecules, or unstable association of molecules which can then either decompose to give products, 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,



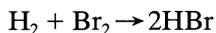
**Chain Reactions.** In chain reactions the intermediate is formed in a first reaction, called the *chain initiation step*. It then combines with reactant to form product and more intermediate in the chain propagation step. Occasionally the intermediate is destroyed in the chain termination step. Thus,



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.

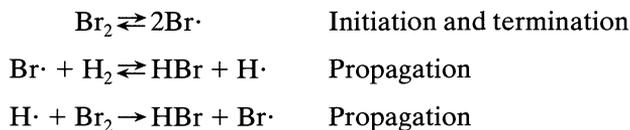
**1. Free radicals, chain reaction mechanism.** The reaction



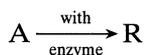
with experimental rate

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

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

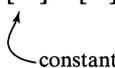


2. **Molecular intermediates, nonchain mechanism.** The general class of enzyme-catalyzed fermentation reactions

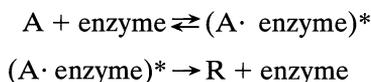


with experimental rate

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


  
constant

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

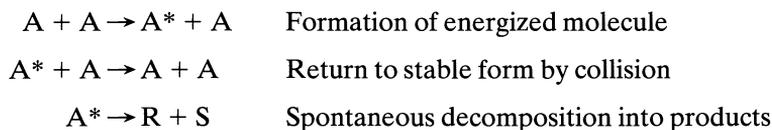


In such reactions the concentration of intermediate may become more than negligible, in which case a special analysis, first proposed by Michaelis and Menten (1913), is required.

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.

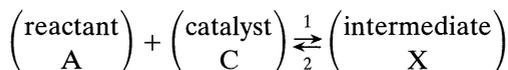
**Type 2.** Where a homogeneous catalyst of initial concentration  $C_0$  is present in two forms, either as free catalyst C or combined in an appreciable extent to form intermediate X, an accounting for the catalyst gives

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

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?

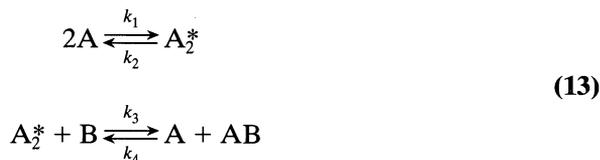
### SOLUTION

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

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

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.

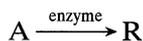
**Model 2.** First note that the stoichiometry of Eq. 10 is symmetrical in A and B, so just interchange A and B in Model 1, put  $k_2 = 0$  and we will get  $r_{AB} = k[B]^2$ , which is what we want. So the mechanism that will match the second-order rate equation is



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

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

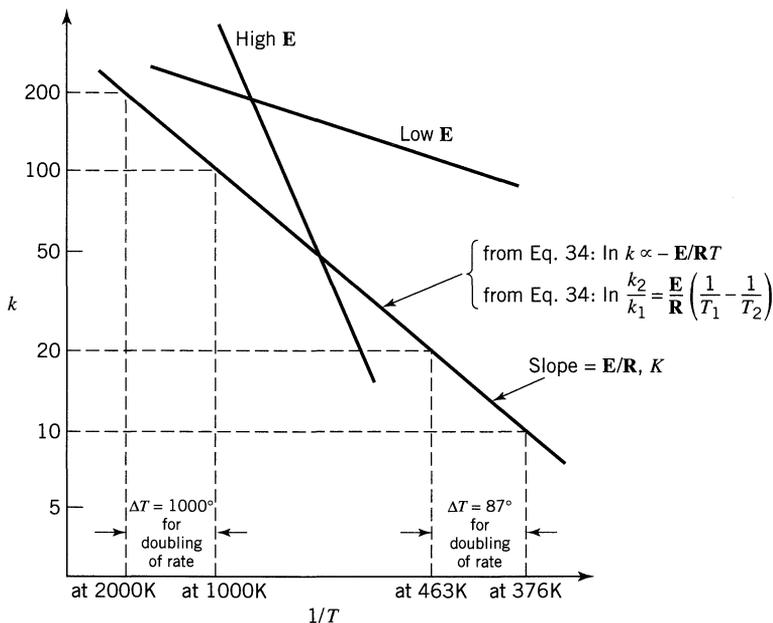
summarizes the predictions of the simpler versions of the collision and transition state theories for the temperature dependency of the rate constant. For more complicated versions  $m$  can be as great as 3 or 4. Now, because the exponential term is so much more temperature-sensitive than the pre-exponential 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<sup>a</sup>

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

<sup>a</sup> 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.

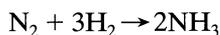
Although we cannot delve into the many aspects of this problem, a number of clues that are often used in such experimentation can be mentioned.

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



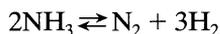
or one that changes with reaction conditions or extent of reaction is clear evidence of multiple reactions.

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.

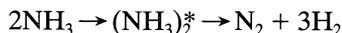
3. A comparison of the stoichiometric equation with the experimental kinetic expression can suggest whether or not we are dealing with an elementary reaction.
4. A large difference in the order of magnitude between the experimentally found frequency factor of a reaction and that calculated from collision 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



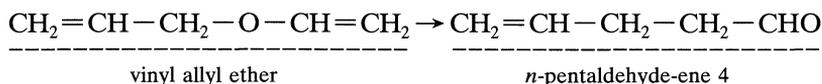
At a first sight this could very well be an elementary bimolecular reaction with two molecules of ammonia combining to yield directly the four product molecules. From this principle, however, the reverse reaction would then also have to be an elementary reaction involving the direct combination of three 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

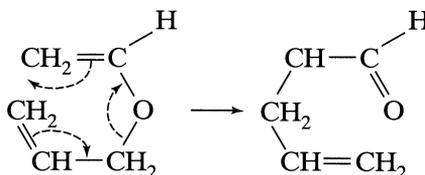
time, each then being an elementary step in the mechanism. From this point of view, the simultaneous splitting of the complex into the four product molecules in the reaction



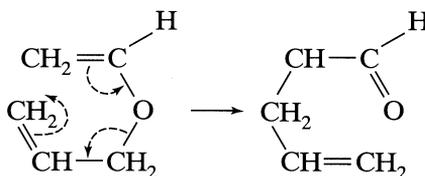
is very unlikely. This rule does not apply to changes that involve a shift in electron density along a molecule, which may take place in a cascade-like manner. For example, the transformation



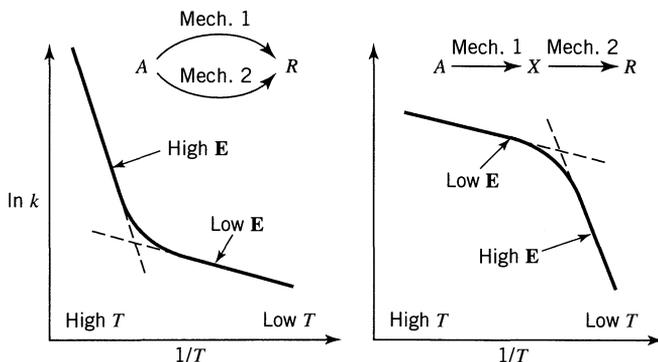
can be expressed in terms of the following shifts in electron density:



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  $E_{\text{obs}}$  rises for reactions or steps in parallel,  $E_{\text{obs}}$  falls for reactions or steps in series. Conversely, for a decrease in temperature  $E_{\text{obs}}$  falls for reactions in parallel,  $E_{\text{obs}}$  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

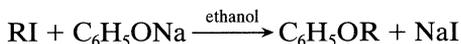
If a reaction has available a number of competing paths (e.g., noncatalytic and catalytic), it will in fact proceed by all of these paths, although primarily by the one of least resistance. This path usually dominates. Only a knowledge of the energies of all possible intermediates will allow prediction 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

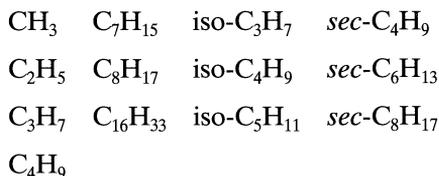
Assuming that we already know the mechanism of reaction and whether or not it is elementary, we may then proceed to the prediction of the frequency factor and activation energy terms of the rate constant.

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.

### REFERENCES

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  $\text{N}_2\text{O}$ , 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

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

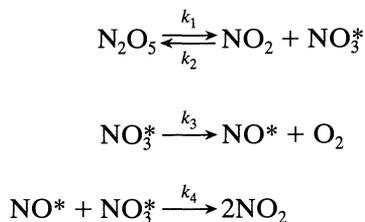
Assuming that the chirping rate is a direct measure of the metabolic rate, find the activation energy in kJ/mol of these crickets in the temperature range 60–80°F.

- 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.

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

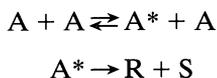
**2.18.** Show that the following scheme



proposed by R. Ogg, *J. Chem. Phys.*, **15**, 337 (1947) is consistent with, and can explain, the observed first-order decomposition of  $\text{N}_2\text{O}_5$ .

**2.19.** The decomposition of reactant A at  $400^\circ\text{C}$  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?

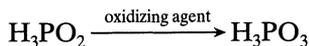
**2.20.** Experiment shows that the homogeneous decomposition of ozone proceeds with a rate

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

(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,

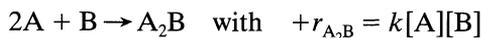
$$r_{\text{H}_3\text{PO}_3} = k[\text{oxidizing agent}][\text{H}_3\text{PO}_2]$$

At a high concentration of oxidizing agent,

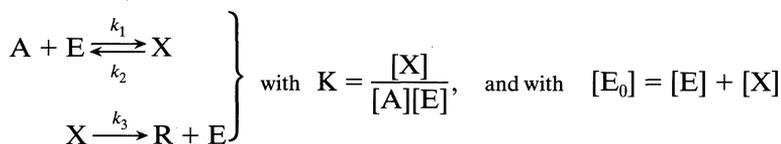
$$r_{\text{H}_3\text{PO}_3} = k'[\text{H}^+][\text{H}_3\text{PO}_2]$$

To explain the observed kinetics, it has been postulated that, with hydrogen ions as catalyst, normal unreactive  $\text{H}_3\text{PO}_2$  is transformed reversibly into an active form, the nature of which is unknown. This intermediate then reacts with the oxidizing agent to give  $\text{H}_3\text{PO}_3$ . 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

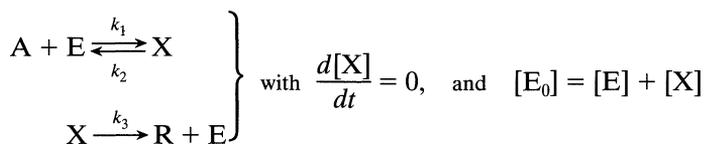


- 2.23.** *Mechanism for enzyme catalyzed reactions.* To explain the kinetics of enzyme-substrate reactions, Michaelis and Menten (1913) came up with the following mechanism, which uses an equilibrium assumption



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?