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REACTION KINETICS FOR CHEMICAL ENGINEERS

STANLEY M. WALAS

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PREFACE

The design of equipment for conducting chemical reactions is one of the most important and difficult tasks facing the engineer. For—in addition to the purely kinetic aspects—the chemical reactor may possess characteristics of a fluid transport device or heat exchanger or mass-transfer device; it may require agitation, catalysts, and extreme temperatures or pressures; it may involve contacting of gas, liquid, and solid phases; it may impose severe control problems; and above all, it demands a careful economic balance so that the most product of acceptable quality is made with the least expenditure of funds.

So complex a problem defies a completely rational solution. The design approach becomes, usually, a composite of theoretical background, direct work on a pilot-plant scale, experience, judgment, and imagination. As in every engineering field, however, the scientific and mathematical background of reactor design has been growing steadily, so that today a novice can do some of the things that yesterday required the artist.

Into the present book has been gathered from many sources much material essential to the process design of chemical reactors. Some of it has been in the province of physical chemistry for a long time, but a sizable portion dates back only a few years. Since the needs of the undergraduate chemical engineer have been kept foremost in mind, the treatment has been made as concise and as little demanding of advanced methods and refinements as possible. Nevertheless, no important useful topic has been shirked, and a determined effort has been made to present, clearly and simply, enough material that will enable the engineer as well as the student to analyze kinetic data, to interpret recent literature, and to process design reactors with some facility. Adequate reference is made to the literature for more sophisticated design techniques when available. It must be recognized, however, that reactors must be designed and built even when data or rigorous design procedures are not available. The abundant numerical illustrations and problems and descriptions of industrial equipment and processes that are included in this text may suggest to the reader possible approaches to such situations.

Following a brief survey of the terminology and theory of chemical kinetics, the topics include homogeneous reactions, nonisothermal systems,

flow reactors, heterogeneous processes, granular beds, catalysis, and scale-up methods. Descriptive chapters on industrial catalytic processes and on types of reactors are presented in conclusion. Virtually no consideration is given to most of the topics engaging the interest of the modern physical chemist, such as elucidation of mechanism, free radicals, chain reactions, and absolute-reaction-rate theory. These topics cannot be treated adequately in brief space; they are adequately treated in several fine recent books devoted especially to these matters, and they are not of immediate value to the practical design of industrial reactors. The brief treatment of theory in the first chapter merely points up the barest ideas and does little more than call the reader's attention to the existence of these topics.

At the University of Kansas, it has been found desirable to begin the semester's work with about one week of mathematical review, roughly the topics in Chapter 12. Principally, this covers the differential equations occurring most commonly in reaction kinetics and a few of the simpler numerical techniques for differential and other equations. Approximate methods of problem solution are widely employed wherever they save time and effort and are probably as accurate as experimental data justify. Here they are also used to preserve the elementary character of the book whenever rigorous methods are so involved in derivation or application that they may distract the beginner from an understanding of the kinetic principles.

Many illustrative problems have been solved in the text. Often these have been simplified numerically to emphasize the principle. Problems for the student are amply supplied. They range from the handling of simple data and numerical substitution into formulas to some that demand organizing ability, a degree of ingenuity, and considerable labor. Mostly these problems are based on data appearing in recent periodicals widely read by chemical engineers, to assure the student of the liveness of the subject and to encourage use of original sources; occasionally a reward may be found there in the form of a solution of the problem.

All my colleagues, both academic and industrial, have influenced this work for the better. Professor James G. Knudsen, Dean W. L. McCabe, and Professor Max S. Peters kindly reviewed portions of the manuscript and provided welcome constructive criticism. I wish especially to express my appreciation to Professor J. O. Maloney of the University of Kansas and to C. W. Nofsinger of The C. W. Nofsinger Company, Engineers & Constructors, for many opportunities to put design calculations into iron and steel. I owe much to my wife, Suzy Belle, for her secretarial abilities and her sympathy.

Stanley M. Walas

NOTATION

Symbols used only locally and defined there, such as constants, are not included in this list. Certain subscripts used only infrequently are not shown in the table as such, but the complete subscripted item is listed. For more complete explanations, references to the text are cited in some instances. Typical units are shown in a few cases. Chapter 6 has its own table of notation.

- a activity
- a interfacial area, sq ft/cu ft
- A component A ; also, amount or concentration of component A
- A area
- A_p area of a single particle
- B component B (see A)
- C component C (see A)
- C concentration, lb moles/cu ft
- C_p specific heat at constant pressure
- d vessel diameter
- D_a diffusivity of A
- D_b diffusivity of B
- D_e effective diffusivity in a packed bed
- D_p particle diameter; in a mixture, the surface average diameter
- D_t vessel diameter
- D_v diffusivity, sq ft/hr
- E energy of activation
- f fractional conversion = $(n_{a0} - n_a)/n_{a0} = x_a/n_{a0}$
- f friction factor
- f fugacity
- f functional symbol, as in $f(x)$, function of x
- F volumetric flow rate, cu ft/hr
- g functional symbol, as in $g(x)$, function of x
- g_c gravitational constant
- G superficial mass flow rate, lb/(hr)(sq ft)
- G_f superficial mass flow rate under fluidizing conditions, lb/(hr)(sq ft)
- G_m molal superficial mass flow rate, lb moles/(hr)(sq ft)
- G_{mf} superficial mass flow rate at onset of fluidization, lb/(hr)(sq ft)
- h heat-transfer coefficient
- h increment of independent variable in numerical solution of differential equations (Sec. 78)
- h_e heat-transfer coefficient at external surface (wall) of fluidized bed
- h_i heat-transfer coefficient at internal surface of fluidized bed
- H enthalpy
- ΔH_r heat of reaction; negative for exothermic, positive for endothermic reactions
- ΔH_{r0} heat of reaction at initial or inlet conditions
- I integrand, as in $\int I \, dx$
- j_d mass-transfer factor (Eqs. 6-4, 6-6, and 8-15)
- j_h heat-transfer factor (Eq. 8-16)
- k specific reaction rate (Eqs. 1-5 and 1-8)

k	thermal conductivity
k_c	specific reaction rate, concentration units (Sec. 5)
k_e	effective thermal conductivity in bed of particles
k_N	specific reaction rate, mole fraction units (Sec. 5)
k_p	specific reaction rate, partial-pressure units (Sec. 5)
K	reaction equilibrium constant (Eq. 2-36)
K_a	adsorption equilibrium constant of A ; similarly for K_b , K_c , etc.
L	depth of packed bed
L	distance along a reactor
L_f	depth of fluidized bed
M	molecular weight
n	in batch reactors, the number of moles present
n	in flow reactors, the number of moles present per unit of feed
n	order of reaction
N	mole fraction
N_f	expansion ratio of fluidized bed
p	partial pressure, atm
p_{bm}	partial pressure of nondiffusing component
P	total pressure, atm
Pe	Peclet number, $D_p G_s / k$
r	rate of reaction = $-(1/V)dn/dt$, lb moles/(hr)(cu ft)
r	rate of solid-catalyzed reaction = $-(1/w_c)dn/dt$, lb moles/(hr)(lb catalyst)
r_c	reaction rate (used to emphasize distinction from mass-transfer rate)
r_d	rate of diffusive mass transfer
R	gas constant = PV/T for ideal gases
R	radial position
Re	Reynolds number, $du \rho / \mu$
s	specific heat or heat capacity
S	entropy
S	interfacial surface
t	time
$t_{1/2}$	half time, or the time required to achieve 50 per cent conversion
T	temperature, °F, °C, °R, or °K
T_m	temperature of heat-transfer medium
u	linear velocity
U	over-all heat-transfer coefficient
V	in batch reactors, the volume of the system
V	in flow reactors, the volume of the system per unit quantity of the feed
V_r	volume of the reactor
W	mass flow rate, lb/hr
x	amount of substance converted = $n_0 - n$; usually component A
x_e	amount of substance converted at equilibrium conditions

Greek Symbols

α	frequency factor in Arrhenius equation
α	group defined by Eq. 5-22
γ	activity coefficient
δ_a	increase in moles of system per mole of A converted (Eq. 2-7)
Δ	differencing operator, as in $\Delta T = T_1 - T_2$
ϵ	fractional voidage or fraction of volume unoccupied by solid particles
ϵ_f	fractional voidage under fluidizing conditions
ϵ_{mf}	fractional voidage at onset of fluidization

- η fluidization efficiency (Eq. 8-38)
 θ residence time V_r/F
 θ_a fraction of surface covered by adsorbate A ; similarly with θ_b , θ_c , etc.
 θ_v fraction of surface *not* covered by adsorbate = $1 - \theta_a - \theta_b - \dots$
 λ shape factor of a particle, equal to the ratio of the surface of a sphere of the same volume as the particle to the surface of the particle
 μ viscosity
 π total pressure
 ρ density
 ρ_B bed density, including both fluid and solid
 σ active site of solid surface
 ϕ_f porosity function under fluidization conditions (Eq. 8-31)

Subscripts

- a component A
 b component B
 c component C
 e effective, as in k_e , effective thermal conductivity
 f fluid
 f fluidized condition
 g gas
 i interfacial, as in p_{ai} , partial pressure of A at the interface
 i i th member of a group, as in $\Sigma C_i = C_a + C_b + \dots$
 L liquid
 m component m
 m minimum, as in G_{mf} , minimum fluidizing mass flow rate
 m molal, as in ρ_m , molal density, lb moles/cu ft
 p particle, as in D_p , diameter of particle
 s solid, as in k_{es} , effective thermal conductivity of the solid
 t total, as in n_t , total number of moles present
 0 initial or inlet

Abbreviations

- CSTR continuous stirred-tank reactor
 DE differential equation
 ODE ordinary differential equation
 PDE partial differential equation
 SRR specific reaction rate
 SV space velocity
 VHSV volumetric hourly space velocity, volumes of feed measured at 60°F and 14.7 psia/(hr)(vol of reactor)
 WHSV weight hourly space velocity, wt of feed/(hr)(wt of catalyst)

Units

- A angstroms
 atma absolute pressure, atmospheres
 atm_g gauge pressure, atmospheres
 bpsd barrels per stream day
 cfh cubic feet per hour
 fps feet per second
 gpm gallons per minute
 psia pounds per square inch absolute
 psig pounds per square inch gauge

CHAPTER 1

FUNDAMENTALS

1. Introduction

Two questions about a chemical reaction are of paramount importance to engineers engaged in research, design, or operation involving chemical reaction:

1. How far can the reaction proceed, or what is the equilibrium condition?
2. How rapidly is it possible to attain some desirable approach to the equilibrium condition?

Proper answers are rather complex since many properties and conditions of a chemical system affect both equilibrium and rate. Though the questions are related, as yet no unified quantitative treatment exists and to a large extent they are handled separately by the sciences of thermodynamics and reaction kinetics.

Among other matters, thermodynamics is concerned with the study of equilibrium. Fortunately, in the present state of this science, question 1 can be answered for a great many reactions with the aid of data and generalizations obtained by way of thermal, spectroscopic, and equation-of-state measurements.

Though thermodynamics may predict a favorable conversion under specified conditions of temperature and pressure, there is no assurance that the reaction will even proceed at a measurable rate. Indeed, many instances exist where the equilibrium state is virtually complete conversion yet the potential reactants remain unconverted. For example, thoroughly dry oxygen and hydrogen can be maintained in admixture indefinitely, carbon does not react with air appreciably, aluminum does not normally react with water—but in each of these cases the equilibrium condition is virtually complete conversion. Also, rapid chilling of nitrogen oxides formed at high temperatures or of magnesium produced by reduction of the oxide with carbon can prevent reversal to the thermodynamically stable state. Finding the conditions under which thermodynamically feasible reactions will proceed at a sufficient speed is one of the main tasks of the science and art of reaction kinetics.

Rate of a chemical reaction may be influenced by such factors as flow

conditions, interphase boundaries, and presence of foreign substances, in addition to certain factors also influencing the equilibrium, such as temperature, pressure, and relative amounts of the participants. Because of the complexity of the problem, as yet no theory has been developed nor correlations of data achieved which enable advance prediction of even the order of magnitude of a reaction of industrial interest. In every new case, consequently, resort must be had to direct test, often over the entire range of possible operating conditions, though frequently some extrapolation can be made safely on the basis of theory.

At least from the engineer's point of view, reaction kinetics has these principal functions:

1. Establishing the chemical mechanism of reaction
2. Collecting experimental rate data
3. Correlating rate data by mathematical equation or otherwise
4. Designing suitable reactors
5. Specifying operating conditions, methods of control, and auxiliary equipment

The ultimate objective of the engineer working in this field is to design processes and equipment for conducting reactions on an industrial scale or to modify as needed existing equipment or designs. The functions of kinetics just listed may be commented upon briefly from the point of view of this objective.

Knowledge of the chemical mechanism may lead to the formulation of proper mathematical equations in terms of which rate data may be correlated and thus extrapolated outside the range of experimental conditions. This is a topic more suited to pursuit by chemists, but some indication of the spirit of such investigations is given in this book.

Though the chemical engineer will not ordinarily carry out experimental rate work himself, he may need to plan some aspects of it and he must have an appreciation of the methods used by others in order to weigh and use such data properly. Also, industrial reactors are often merely scale-ups of pilot-plant or laboratory units. Rate data may be obtained in either batch or flow equipment. In the former case, the reactants are charged in bulk to a stirred vessel and observations are made of the course of the reaction, whereas in the latter type, reactants are charged continuously at measured rates through a comparatively long, narrow tube or through one or more stirred vessels and observations are made when a steady state obtains. The tubular-flow reactor may be a *differential* type, which is so short that only a small though necessarily measurable amount of conversion takes place, thus affording direct evaluation of the instantaneous rate; or it may be *integral*, in which comparatively large conversion may take place. Both types have their utility.

It is generally desirable to express rate data in the form of a mathematical equation, in order to achieve compactness and to simplify design

calculations. The technique followed to this purpose is to assume a type of equation or a mechanism for which the mathematical equation can be developed, then to test the fit of the data to the equation. If the first attempt is unsuccessful, the procedure is repeated with other equations until a fit is obtained. When only limited use of the test data is to be made or if the system is very complex, various plottings and cross plottings of the data may be adequate for design purposes.

As already emphasized, a process design is the final step. This is to be distinguished from a mechanical design which is concerned with such features of a plant as vessel thicknesses, piping details, insulation, structures, and foundations. A process design involves the preparation of a flowsheet that shows the principal equipment, operating conditions, flow quantities, and major control instruments; a heat and material balance; utilities requirements; sketches showing the sizes and internals of the reactors and other major process equipment; and an estimate of the cost of the plant. Not all these aspects can be stressed in this book, but the engineer should always keep the ultimate goal in mind.

Rather constant use of mathematics is made throughout this subject, though the breadth of mathematical knowledge required of the reader of this book does not extend much beyond the most elementary differential equations and some numerical techniques. Some of the needed material is summarized in Chap. 12 for review or study. In all fields of engineering, approximations often must be considered "good enough." Data may not always be complete or accurate, or the mathematical difficulties may be too great for a truly rigorous solution in the time available. Consequently, numerical methods for obtaining approximate solutions of mathematics of kinetics are often used. Even when rigorous solutions are possible, it may be more convenient to use approximation, since any amateur can apply such methods to a great variety of problems whereas the expert mathematician is often needed to make the analytical solution. Though usually simple in concept, approximation methods have the disadvantage of being tedious in application. Fortunately, increasing use of electronic computers is relieving this burden on the engineer. Also, by making the use of short intervals feasible, computers can obtain solutions fully as accurate as any obtained by analytical methods.

2. Classification of Reactions

Reactions may be classified in several ways. On the basis of *mechanism* they may be, for example:

1. Irreversible
2. Reversible
3. Simultaneous
4. Consecutive

A further classification from the point of view of mechanism is with respect to the number of molecules actually participating in the reaction, the so-called *molecularity*:

5. Unimolecular
6. Bimolecular

Related to the preceding is the classification with respect to *order*. This is fundamentally a mathematical concept. As brought out later, the rate of a simple reaction is proportional to the products of certain powers of the concentrations or active masses, as in the equation rate = $kC_a^pC_b^q$. The exponent to which the concentration of any particular reactant is raised is called the order with respect to that substance, p or q , and the sum of all the exponents, $p + q$, is the order of the reaction. At times the order is identical with molecularity, but there are many reactions which appear on experimental grounds to have zero or fractional orders. To continue the classification, there are reactions of:

7. Integral orders, such as first, second, etc.
8. Fractional or zero order

With respect to operating *conditions*, there are the principal types:

9. Isothermal at constant volume
10. Isothermal at constant pressure
11. Adiabatic
12. Nonadiabatic and nonisothermal (programmed or heat-regulated)

Reactions may be classified according to the *phases* involved:

13. Homogeneous, gaseous or liquid or solid
14. Heterogeneous
 - a. Controlled by diffusive mass transfer
 - b. Controlled by chemical resistance

Furthermore, it is important to distinguish between:

15. Uncatalyzed
16. Catalyzed

Equipment type is also a basis for differentiation, namely:

17. Stirred tank or tank battery
18. Single- or multiple-tubular reactor
19. Reactor filled with solid particles, inert or catalytic
 - a. Fixed bed
 - b. Moving bed
 - c. Fluidized bed, dense phase or dilute phase

Finally there are the broad types:

20. Batch
21. Flow
22. Semibatch or semiflow

Clearly, these groupings are not mutually exclusive. Thus a reaction may be irreversible-second-order, taking place under adiabatic and approximately constant pressure conditions in a flow reactor loaded with a solid catalyst in particle form. From the engineer's point of view, the principal distinctions are drawn between homogeneous and heterogeneous and between batch and flow reactions. These most influence the choice of equipment and operating conditions as well as the design methods.

3. The Rate of a Chemical Reaction

A chemical reaction produces a rearrangement of the atoms of which molecules are composed. The rate at which this occurs depends on the natures of the participants and the circumstances. The more important factors have been mentioned in Sec. 1.

Quantitatively, the reaction rate is expressed as the number of units of mass of some participant that is formed or transformed per unit of time t per unit of volume V of the system. When the system volume remains constant, the rate becomes the change in concentration C per unit of time. Mathematically, these definitions are

$$r = -\frac{1}{V} \frac{dn}{dt} \quad \text{in general} \quad (1-1)$$

$$r = -\frac{d(n/V)}{dt} = -\frac{dC}{dt} \quad \text{at constant volume only} \quad (1-2)$$

where n is the number of moles of reactant present at time t . In terms of amount of reactant that has been transformed in this time, $x = n_0 - n$, the rate is

$$r = +\frac{1}{V} \frac{dx}{dt} \quad (1-3)$$

For some types of reactions, it is possible to segregate the effects of the amounts n_i from those of the other variables. In formal terms, accordingly, the rate equation may be written

$$r = -\frac{1}{V} \frac{dn}{dt} = kf(n_a, n_b, \dots) \quad (1-4)$$

Here the term k is variously called the specific reaction rate (SRR), or the rate coefficient, or the rate constant. By definition it is independent of the masses of the participants but is influenced by all the other variables which influence the rate of reaction. However, when operating conditions

are such that the gases or solutions concerned do not behave ideally, k as defined by Eq. 1-4 develops a dependence on the concentrations. From thermodynamic considerations, in such instances activities should be substituted for concentrations, so that

$$r = kf(a_a, a_b, \dots) \quad (1-5)$$

In still other instances, specifically reactions involving ions, a further correction is necessary to assure a constant k . Thus

$$r = k\beta f(a_a, a_b, \dots) \quad (1-6)$$

where β depends on the concentration. An interpretation of β due to Brønsted is that it is the reciprocal of the activity coefficient of an intermediate complex [Sec. 18 and Denbigh (57)].

The nature of the function f is established by the law of mass action, discussed later in this chapter. However, it must be emphasized that these equations apply only to simple reactions. When a reaction is a composite of several chemical or physical processes, more than one parameter k may be required to characterize the rate, and often it is not possible to segregate them from the concentrations or related quantities as stated by Eqs. 1-4ff.

4. The Law of Mass Action

The law of mass action states that the rate of a chemical reaction is proportional to the active masses of the participants. It was first obtained on experimental grounds by Guldberg and Waage in 1864 to 1867 [Leicester and Klickstein (132), for example] and was subsequently derived from the theory of molecular collisions in gases and liquids. In the original development, "active mass" meant concentration, mass per unit volume, but other interpretations have been ventured from time to time. Among early investigators, Arrhenius suggested osmotic pressure and van't Hoff thought that the solubility as well as the concentration had a bearing on the active mass.

From a study of reversible processes (Sec. 15) it appears that thermodynamic activity should be regarded as the active mass. As mentioned in Sec. 3, however, even this requires a modification in the case of ionic reactions. Moreover, it has not been possible to show experimentally that thermodynamic and kinetic activities are the same, neglecting the case of ionic reactions just referred to. Reactions for which deviations from ideality might be significant are frequently heterogeneous catalytic, and it has not been possible in these cases to dissociate the activity coefficients from other parameters of the rate equations. Also, the accuracy of kinetic data is generally poor, so that relatively large deviations from ideality can go undetected.

Nevertheless, it is theoretically satisfying to recognize that both the collision process (as determined by concentrations) and the forces between

molecules (partly accounted for by activity coefficients) affect the rate of reaction. Several kinds of activity coefficients are commonly used, related to the activity a and the fugacity f , as follows:

$$a = \gamma C, \text{ where } C \text{ is the concentration, say, lb moles/cu ft solution}$$

$$a = \gamma m, \text{ where } m \text{ is the molality, say, lb moles/cu ft of solvent}$$

$$a = \gamma N, \text{ where } N \text{ is the mole fraction}$$

$$f = \gamma p, \text{ where } p \text{ is the partial pressure, say, atm}$$

For the most part, rate equations in this text are expressed in terms of concentrations. When activity data are available, substitution can be made from the above relations or as developed in Secs. 5 and 13.

5. The Rate Equation

Mathematically, the law of mass action is a differential equation. Consider the reaction between three substances represented by this chemical equation:



Let n_{a0} , n_{b0} , and n_{c0} be the initial amounts of these substances, and let $x = n_{a0} - n_a$ be the decrease in the moles of reactant A at time t . The rate of disappearance of substance A is then expressed by the equation

$$\begin{aligned} r_a &= \frac{1}{V} \frac{dx}{dt} = -\frac{1}{V} \frac{dn_a}{dt} = k \left(\frac{n_a}{V} \right)^p \left(\frac{n_b}{V} \right)^q \left(\frac{n_c}{V} \right)^r \\ &= k \left(\frac{n_{a0} - x}{V} \right)^p \left(\frac{n_{b0} - bx/a}{V} \right)^q \left(\frac{n_{c0} - cx/a}{V} \right)^r \end{aligned} \quad (1-8)$$

Order and molecularity. Reactions may be identified according to the number of molecules in the stoichiometric equation; or according to the number of molecules, the molecularity, involved at one time in the rate-determining step; or according to the order. In Eq. 1-8, the sum of the exponents, $n = p + q + r$, is the order of the reaction; p is the order with respect to substance A , and so on. Order is strictly an empirical concept applicable only to rate equations of the form of Eq. 1-8. When the stoichiometric equation truly represents the mechanism of the reaction, the order and molecularity both are $n = a + b + c$ and individually $p = a$, $q = b$, and $r = c$; in such cases, a unimolecular reaction is first-order, a bimolecular is second-order, and so on. Table 1-1 includes some examples for which this is not true. How this may come about is considered in Sec. 9. As a simple example, when one of the reactants, say A , is present in large excess, its concentration does not change appreciably during the course of reaction, so the order with respect to A is apparently $p = 0$; for the reaction as a whole, the *apparent*, or pseudo, order is $n = q + r$.

TABLE 1-1. REACTIONS AT CONSTANT VOLUME AND TEMPERATURE

Reaction: $aA + bB + cC \rightarrow$ productsRate equation: $\frac{dx}{dt} = k(n_{a0} - x)^p(n_{b0} - bx/a)^q(n_{c0} - cx/a)^r$

Order	Reaction	Rate equation	Units of k	Integral
0	$A \rightarrow$ products	$\frac{dx}{dt} = k$	$t^{-1}C$	$x - x_0 = k(t - t_0)$
	$A \rightarrow$ products	$\frac{dx}{dt} = k(n_{a0} - x)^{\frac{1}{2}}$	$t^{-1}C^{\frac{1}{2}}$	$(n_{a0} - x_0)^{\frac{1}{2}} - (n_{a0} - x)^{\frac{1}{2}} = \frac{k(t - t_0)}{2}$
1	$A \rightarrow$ products	$\frac{dx}{dt} = k(n_{a0} - x)$	t^{-1}	$\ln \frac{n_{a0} - x_0}{n_{a0} - x} = k(t - t_0)$
	$2A \rightarrow$ products	$\frac{dx}{dt} = k(n_{a0} - x)^2$	$t^{-1}C^{-1}$	$\frac{1}{n_{a0} - x} - \frac{1}{n_{a0} - x_0} = k(t - t_0)$
2	$A + B \rightarrow$ products	$\frac{dx}{dt} = k(n_{a0} - x)(n_{b0} - x)$	$t^{-1}C^{-1}$	$\frac{1}{n_{b0} - n_{a0}} \ln \frac{(n_{b0} - x_0)(n_{a0} - x)}{(n_{b0} - x_0)(n_{a0} - x)} = k(t - t_0)$
	$3A \rightarrow$ products	$\frac{dx}{dt} = k(n_{a0} - x)^3$	$t^{-1}C^{-2}$	$\left(\frac{1}{n_{a0} - x}\right)^2 - \left(\frac{1}{n_{a0} - x_0}\right)^2 = 2k(t - t_0)$
3	$A + B + C \rightarrow$ products	$\frac{dx}{dt} = k(n_{a0} - x)(n_{b0} - x)(n_{c0} - x)$	$t^{-1}C^{-2}$	$\frac{n_{b0} - n_{a0}}{\phi} \ln \frac{n_{a0} - x_0}{n_{a0} - x} + \frac{n_{c0} - n_{a0}}{\phi} \ln \frac{n_{a0} - x_0}{n_{a0} - x}$
				$+ \frac{n_{a0} - n_{b0}}{\phi} \ln \frac{n_{c0} - x_0}{n_{c0} - x} = k(t - t_0)$

 C = units of concentration, for example, lb/cu ft $\phi = n_{a0}n_{b0}(n_{a0} - n_{b0}) + n_{a0}n_{c0}(n_{c0} - n_{a0}) + n_{b0}n_{c0}(n_{b0} - n_{c0})$

Note: For convenience, because the volume is assumed constant in the rate equations of this table, the volume term $V^{1-p-q-r}$ is included in the constant k .

Rates of transformation or formation of the other participants are related to that of A by the stoichiometric coefficients. Thus

$$\frac{r_a}{a} = \frac{r_b}{b} = \frac{r_c}{c} = -\frac{r_1}{1} = -\frac{r_m}{m} = \dots \quad (1-9)$$

In terms of concentrations,

$$r_a = -\frac{1}{V} \frac{dn_a}{dt} = k(C_a)^p(C_b)^q(C_c)^r \quad (1-10)$$

At constant volume, Eq. 1-10 becomes

$$r_a = -\frac{dC_a}{dt} = k(C_a)^p(C_b)^q(C_c)^r \quad (1-11)$$

Partial pressures are often used to define the rates of gas reactions. Thus

$$r_a = -\frac{1}{V} \frac{dn_a}{dt} = k_p(p_a)^p(p_b)^q(p_c)^r \quad (1-12)$$

In terms of the various activity coefficients,

$$r_a = -\frac{1}{V} \frac{dn_a}{dt} = k_{aC}(\gamma_a C_a)^p(\gamma_b C_b)^q(\gamma_c C_c)^r \quad (1-13)$$

$$r_a = -\frac{1}{V} \frac{dn_a}{dt} = k_{aN}(\gamma_a N_a)^p(\gamma_b N_b)^q(\gamma_c N_c)^r \quad (1-14)$$

$$r_a = -\frac{1}{V} \frac{dn_a}{dt} = k_{ap}(\gamma_a p_a)^p(\gamma_b p_b)^q(\gamma_c p_c)^r \quad (1-15)$$

The k 's in these equations differ in their units and in their dependence on temperature and pressure. A comparison for first-order reactions is shown in Table 1-2. With ideal gases, since

$$C_i = \frac{p_i}{RT} = \frac{\pi}{RT} N_i \quad (1-16)$$

the following relations hold for a reaction of order n :

$$k_c = (RT)^n k_p = \left(\frac{RT}{\pi} \right)^n k_N \quad (1-17)$$

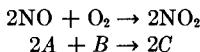
TABLE 1-2. FIRST-ORDER RATE EQUATIONS

Variable	Rate equation	Typical units of k
Concentration.....	$r = k_c C$	sec^{-1}
Partial pressure.....	$r = k_p p$	lb moles/(cu ft)(sec)(atm)
Mole fraction.....	$r = k_N N$	lb moles/(cu ft)(sec)
Activity.....	$r = k_{aC} \gamma C$	sec^{-1}
Activity.....	$r = k_{ap} \gamma p$	lb moles/(cu ft)(sec)(atm)
Activity.....	$r = k_{aN} \gamma N$	lb moles/(cu ft)(sec)

When there is no possibility of confusion, subscripts are not ordinarily appended to the k 's. Mostly, rate equations in this text are written in terms of concentrations.

Other relations between rate equations in terms of C , p , and N are developed in Sec. 13, for instance, expressions for such derivatives as dp/dt and dN/dt . The equations of Table 1-1 are basic to the study of homogeneous kinetics. Later chapters will illustrate their application and how the proper one is found to fit experimental data on particular reactions. The handling of a rate equation is shown in the following illustration.

Illustration 1-1. Consider the third-order reaction



taking place at constant volume at approximately atmospheric pressure. The specific reaction rate at 30°C is $2.65(10^4)$ liters 2 /(g mole) 2 (sec). Find the composition, after 10 sec, of a mixture with initial composition 9 per cent NO, 8 per cent O_2 , and 83 per cent N_2 .

Solution. At constant volume, Eq. 1-8 may be applied as follows:

$$\begin{aligned} r_b = \frac{dx}{dt} &= k(n_{a0} - 2x)^2(n_{b0} - x) = 4k \left(\frac{n_{a0}}{2} - x\right)^2(n_{b0} - x) \\ &= 2.65(10^4) \left(\frac{n_{a0}}{2} - x\right)^2(n_{b0} - x) \end{aligned}$$

Integrating,

$$4kt = \frac{1}{(n_{b0} - 0.5n_{a0})^2} \left[\frac{(n_{b0} - 0.5n_{a0})x}{(0.5n_{a0} - x)(0.5n_{a0})} + \ln \frac{(0.5n_{a0} - x)n_{b0}}{(n_{b0} - x)(0.5n_{a0})} \right]$$

From the data,

$$0.5n_{a0} = \frac{p_{\text{NO}}}{2RT} = \frac{9}{2(8.21)(303)} = 1.81(10^{-3})$$

$$n_{b0} = \frac{p_{\text{O}_2}}{RT} = \frac{8}{8.21(303)} = 3.22(10^{-3})$$

Substituting into the integral,

$$2.65(10^4)(10) = \frac{10^6}{(3.22 - 1.81)^2} \left[\frac{(0.00322 - 0.00181)x}{(0.00181 - x)(0.00181)} + \ln \frac{(0.00181 - x)(0.00322)}{(0.00322 - x)(0.00181)} \right]$$

$$\text{or } \frac{0.779x}{0.00181 - x} + \ln \frac{1.779(0.00181 - x)}{0.00322 - x} = 0.525$$

Solving by trial, with the method of Eq. 12-17,

$$x = 0.00100 \text{ g mole/liter}$$

The fractional conversion of NO is

$$f = \frac{0.00100}{0.00181} = 0.554, \text{ or } 55.4\%$$

With x known, the final composition is readily seen to be NO = 4.1 per cent, NO_2 = 5.1 per cent, O_2 = 5.6 per cent, and N_2 = 85.2 per cent.

A nomogram has been prepared to facilitate repeated solutions of this industrially important problem (Besskow, 21).

6. Variables Other than Mass or Concentration

Any property of the reacting system that changes regularly as the reaction proceeds can be formulated in a rate equation. In fact, it may often be more convenient to work directly with the measured variables rather than convert them to corresponding units of mass or concentration. Several examples of such variables may be cited: in a gas-phase reaction under some conditions, the variation in total pressure is related to the extent of reaction; liquid-phase reactions may be accompanied by slight though measurable changes in volume as the reaction progresses; properties such as turbidity, electrical conductivity, optical rotation, pH, and octane number may vary with conversion; temperature changes may be used to follow the course of a reaction accompanied by only slight though measurable heat effects, though it is not usually desirable to conduct rate measurements in nonisothermal systems, for reasons that will be brought out later.

A mathematical rate equation probably can be fitted to data in terms of any of the properties mentioned, though if the choice of property is poor, the equation may be complicated. It is desirable to relate the constants of any such equation to the fundamental definition of rate in terms of mass or concentration, specifically the order and the specific reaction rate. A few examples will indicate how this may be done.

Illustration 1-2. Suppose that the rate equation is of the form $-dC/dt = kC$, but measurements have been made of the optical rotation R , which is a linear function of the concentration; thus $R = R_\infty + aC$. In terms of the new variable, the differential equation clearly becomes

$$-\frac{dR}{dt} = -\frac{d(R - R_\infty)}{dt} = k(R - R_\infty)$$

which possesses the same mathematical form as the equation in terms of C , when $R - R_\infty$ is regarded as the variable, but not when R alone is so regarded.

Illustration 1-3. A gas-phase reaction, $2A \rightarrow B$, occurring at constant volume and temperature, has a rate equation

$$r = -\frac{1}{V} \frac{dn}{dt} = \frac{kn^2}{V^2}$$

Rate equations will be derived in terms of the partial pressure p of substance A and in terms of the total pressure π . Since

$$\pi = \frac{n_1\pi_0}{n_{10}} = \frac{(n + n_0)\pi_0}{2n_0}$$

and $n = \frac{pV}{RT} = \frac{V(2\pi - \pi_0)}{RT}$

$$-\frac{dn}{dt} = -\frac{V}{RT} \frac{dp}{dt} = -\frac{2V}{RT} \frac{d\pi}{dt} = \frac{k}{V} \left(\frac{V}{RT} \right)^2 p^2 = \frac{k}{V} \left(\frac{V}{RT} \right)^2 (2\pi - \pi_0)^2$$

Rearranging,

$$-\frac{dp}{dt} = \frac{kp^2}{RT}$$

$$-\frac{d(2\pi - \pi_0)}{dt} = -2 \frac{d\pi}{dt} = \frac{k}{RT} (2\pi - \pi_0)^2$$

which are the relations sought.

Illustration 1-4. The volume of a certain liquid-phase system is related to the amount of reactant present by the equation $V = V_\infty + a\sqrt{n}$, and the rate equation is

$$-\frac{dn}{dt} = \frac{kn^2}{V}$$

Differentiating,

$$dV = \frac{a}{2\sqrt{n}} dn = \frac{a^2}{2(V - V_\infty)} dn$$

Substituting,

$$-\frac{dV}{dt} = \frac{k}{2a^2} \frac{(V - V_\infty)^3}{V}$$

These illustrations emphasize that some care must be exercised when seeking the true order or specific reaction rate from data other than mass or concentration, particularly when the test variables are not related linearly to the fundamental quantities. In Illustration 1-4, for instance, though the reaction is second-order with respect to n , it is not second-order with respect to V .

7. Effect of Temperature

Chemical-reaction rates are markedly influenced by temperature. Several kinds of behavior occur, some of which are represented in Fig. 1-1.

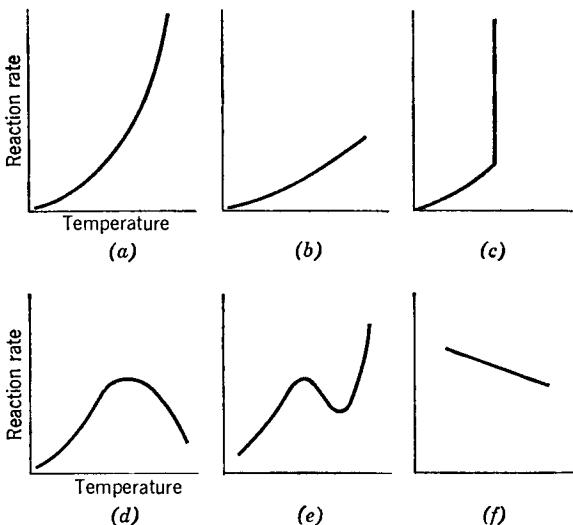


FIG. 1-1. Effect of temperature on reaction rate. [After Frost and Pearson (72). Courtesy John Wiley & Sons, Inc., New York.]

Complex reactions or those limited by physical factors such as diffusion or adsorption or the special behavior of catalysts exhibit unusual behavior. Some comments may be made about the types shown in Fig. 1-1:

- a. Normal behavior, that is, a comparatively rapid increase in rate with rising temperature
- b. The behavior of certain heterogeneous reactions dominated by resistance to diffusion between phases, a rather slow increase in rate with rising temperature
- c. Typical of explosions, where the rapid rise takes place at the ignition temperature
- d. Catalytic reactions controlled by the rate of adsorption (in which the amount of adsorption decreases at elevated temperatures) and enzyme reactions (where high temperatures destroy the enzyme)
- e. Some reactions, oxidation of carbon for example, complicated by side reactions which become significant as the temperature rises
- f. Diminishing rate with increasing temperature, for example, the reaction between oxygen and nitric oxide where the equilibrium conversion is favored by lower temperatures and the rate appears to depend on the displacement from equilibrium

To emphasize, behavior of type *a* is characteristic of simple reactions; the others are behaviors of composite reactions or of reactions influenced by physical rate processes.

The striking effect of temperature on rate was noted at an early date, with relations of the form $r = aT^m$, where m ranged from 6 to 8, and of the form $r = ae^{-b/T}$ being proposed (Hood in 1878). Arrhenius in 1889 was able to rationalize the simple exponential form, which is still regarded as generally adequate. In an attempt to explain the effect of temperature on the rate of inversion of sucrose by acids, he was led to assume that a tautomeric form of the sugar was continually formed, was more sensitive to attack than the normal form, had a definite heat of formation, and existed in equilibrium with the normal form. To this equilibrium he applied the thermodynamic equation

$$\frac{\partial(\ln K)}{\partial T} = \frac{\Delta E}{RT^2} \quad (1-18)$$

where K is the equilibrium constant and is equal to the ratio of the forward and reverse reaction rates; thus $K = k_1/k_2$ (Sec. 15). Consequently,

$$\frac{\partial(\ln k_1)}{\partial T} - \frac{\partial(\ln k_2)}{\partial T} = \frac{E_1}{RT^2} - \frac{E_2}{RT^2} \quad (1-19)$$

Arrhenius noted from experimental data that the individual specific reaction rates followed relations of the form suggested by Eq. 1-19, or

$$\frac{\partial(\ln k)}{\partial T} = \frac{E}{RT^2} \quad (1-20)$$

which integrates to the following when E is taken constant over the temperature range of interest:

$$k = \alpha e^{-E/RT} \quad (1-21)$$

This is called the Arrhenius equation; E is called the energy of activation, and α the frequency factor. It represents the effect of temperature so accurately that when deviations occur they are usually taken as evidence that the reaction is a composite one.

The frequency factor has the units of specific reaction rate, usually based on the units of concentration, and thus dependent on the order of the reaction. Though the relation between k_c and k_p or k_N involves a factor of T^n (Eq. 1-17), the effect of the exponential is so great that over normal temperature ranges, k_p and k_N likewise follow Eq. 1-21 and the effect of T^n is submerged in the frequency factor. For example, in Fig. 1-2 the open circles are plots of $\log kT^2$ against $1/T$. Clearly, they are fully as collinear as the plot of $\log k$ against $1/T$ over the full range from 0 to 60°C, for which these particular data hold. Note Eq. 1-17.

Other equations have been proposed, some empirical, some theoretical. One of these derives by similar reasoning from the thermodynamic equation $\Delta F^\circ = \Delta H^\circ - T \Delta S^\circ = RT \ln K$ and is

$$k = e^{\Delta S^\circ/R} e^{-\Delta H^\circ/RT} \quad (1-22)$$

The transition-state theory (Sec. 12) predicts this equation:

$$k = T^m e^{\Delta S^\circ/R} e^{-\Delta H^\circ/RT} \quad (1-23)$$

From the theory, m is always some integral multiple of 0.5. The exponential with the entropy term is identified with a steric hindrance factor.

For all practical purposes, the Arrhenius equation is a sufficiently accurate representation of data. Trotman-Dickenson (218) states, "Even today, there are no results on either unimolecular or bimolecular gas reactions which cannot be adequately represented by the Arrhenius equation, if due allowance is made for experimental errors." This statement probably holds equally well for liquid-phase reactions.

8. Energy of Activation

Energy of activation is obtained from measurements of the effect of temperature on the specific reaction rate. When such data are plotted as $\ln k$ against $1/T$, the slope of the resulting straight line is $-E/R$. Such a plot is shown in Fig. 1-2 for the unimolecular decomposition of acetone-carboxylic acid in aqueous solution, with the equation

$$k = 7(10^{20})e^{-55,400/T} \quad \text{sec}^{-1}$$

The calculation need not be graphical, as shown by the following illustration.

Illustration 1-5. At temperatures of 32 and 68°F, specific reaction rates are 2.46 and 47.5 sec⁻¹. The activation energy and the frequency factor are therefore obtained by simultaneous solution of the equations

$$2.46 = \alpha e^{-E/(1.99)(492)}$$

with the results $E = 42,300$ Btu/lb mole and $\alpha = 1.42(10^{19})$ sec $^{-1}$.

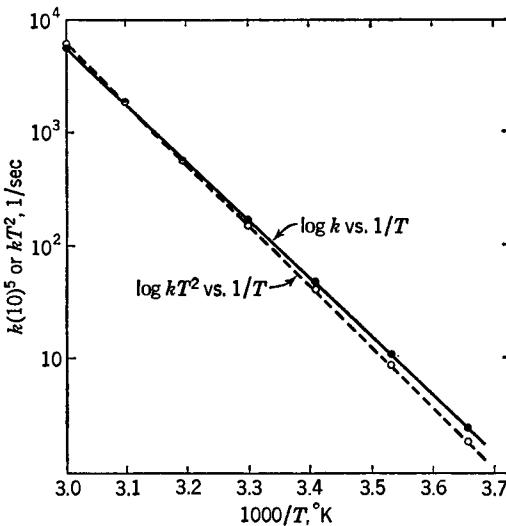


FIG. 1-2. Temperature dependence of rate of decomposition of acetonedicarboxylic acid in aqueous solution. [Data cited by Moelwyn-Hughes (162).]

Over the moderate-temperature ranges in which kinetic measurements are usually made, the activation energy appears to be independent of temperature. This can be interpreted by considering that the activation energy is the heat of formation of an intermediate compound, since the variation with temperature of the difference in sensible heats between products and reactants is usually quite small, over a moderate-temperature interval. However, in a few instances an effect of temperature has been believed detected. For example, a careful reexamination of the original data on which Arrhenius based his theory and more recent data on the same system reveals the effect of temperature shown here (Moelwyn-Hughes, 161):

<i>T</i> , °C.....	20	35	50
<i>E</i> , cal/g mole.....	25,430	24,470	22,950

In this evaluation the Arrhenius equation was assumed.

Other variables have been found to influence the activation energy.

For example, in the reaction $2\text{NO}_2 \rightarrow \text{N}_2 + 2\text{O}_2$, pressure has the following effect (Hinshelwood, 89):

P , atm.....	0.03	0.79	36.3
E , cal/g mole.....	54,500	58,700	65,000

Catalysts change the energy of activation, presumably by changing the mechanism of reaction; examples are in Tables 2-8 and 2-9. A selection of energies of activation is shown in Table 1-3. Further mention of activation energy is in Secs. 10 and 12.

TABLE 1-3. SOME ENERGIES OF ACTIVATION*

System	Energy of activation, kcal/g mole
First-order gaseous decompositions:	
Nitrogen tetroxide.....	13.9
Ethyl chlorocarbonate.....	29.1
Ethyl peroxide.....	31.5
Ethyl nitrite.....	37.7
Methyl iodide.....	43.0
Nitromethane.....	50.6
Dimethylethyl acetic acid.....	60.0
Trimethyl acetic acid.....	65.5
Second-order gaseous reactions between stable molecules:	
$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	2.5
$i\text{-C}_4\text{H}_9 + \text{HBr} \rightarrow$	22.5
$2\text{NOCl} \rightarrow 2\text{NO} + \text{Cl}_2$	24.0
$i\text{-C}_4\text{H}_9 + \text{HCl} \rightarrow$	28.8
$\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$	40.0
$2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$	44.0
$\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow$	43.2
Second-order reactions involving atoms or radicals:	
$\text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br}$	1.2
$\text{H} + \text{Br}_2 \rightarrow \text{HBr} + \text{Br}$	1.2
$\text{CH}_3 + i\text{-C}_4\text{H}_{10} \rightarrow$	7.6
$\text{CH}_3 + n\text{-C}_4\text{H}_{10} \rightarrow$	8.3
$\text{CH}_3 + \text{C}_2\text{H}_6 \rightarrow$	10.4
Third-order gaseous reactions:	
$2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$	0 or negative
$\text{H} + \text{H} + \text{H} \rightarrow \text{H}_2 + \text{H}$	0
$2\text{NO} + \text{Br}_2 \rightarrow 2\text{NOBr}$	~ 4
$2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$	~ 4

* From Frost and Pearson (72).

9. Mechanism and Stoichiometry

A chemical or stoichiometric equation shows the proportions in which substances eventually react with each other. Only comparatively infrequently, it seems, however, does a reaction take place in the manner implied by such an equation. For example, the statement $H_2 + Br_2 \rightarrow 2HBr$ implies simply that a molecule of hydrogen collides and reacts with a molecule of bromine, resulting directly in the formation of 2 molecules of hydrogen bromide. The actual facts are much more complex, as shown later. Why mechanism and stoichiometry often differ appears to be involved with energy considerations. Nature gains her ends with a minimum expenditure of energy. Frequently this involves what may appear to be devious routes, but it must be recognized that the reaction easiest to write is not necessarily the one taking place most easily.

Knowledge of the true mechanism of a reaction is the surest basis for extrapolation beyond test conditions, provided that the mechanism remains the same under the extrapolated conditions. Though this assumption is unfortunately not true, it must usually be made. Practically, the mechanism is established by trial, whereby various mechanisms are postulated, then over-all rate equations developed and checked against test data.

In cases where the stoichiometric equation does not at the same time represent the mechanism, the law of mass action cannot of course be applied directly but must be restricted to the elementary reactions which go to make up the reaction described by the over-all chemical equation. The principle is maintained that for the elementary reactions the rate equation and the chemical equation do correspond. The burden thus is placed on the investigator to find the elementary reactions which fit the test data in accordance with the law of mass action.

Several examples may be treated in some detail, though the method of combining the rate equations in a complex system is treated more completely in later sections. First, consider the formation of HBr already mentioned. At about $300^{\circ}C$, this reaction apparently takes place in the following steps:



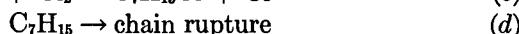
Experimentally, it is known that the equilibrium represented by reactions *a* and *e* is attained rapidly and that only a small amount of atomic hydrogen

is present in the reaction mixture. On this basis, the following rate equation can be derived (Sec. 17):

$$\frac{d(\text{HBr})}{dt} = \frac{k_1(\text{H}_2)(\text{Br}_2)^{1/2}}{1 + k_2 \frac{(\text{HBr})}{(\text{Br}_2)}}$$

Here the parentheses signify concentrations and k_1 and k_2 are constants made up of the specific reaction rates of the five elementary reactions. Clearly, this rate equation would not be given by direct application of the law of mass action to the over-all reaction, but it does fit the experimental facts closely.

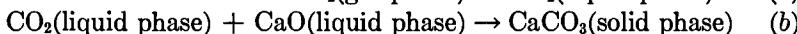
As another example, consider the reaction between *n*-heptane and chlorine when they are irradiated in carbon tetrachloride solution. This series of elementary reactions appears to fit the rate data:



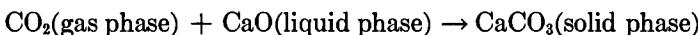
The amounts present of Cl and C_7H_{15} are found experimentally to be very small. Accordingly, the rate of disappearance of chlorine is represented by the equation

$$-\frac{d(\text{Cl}_2)}{dt} = \frac{k_1 k_3}{k_4} (\text{Cl}_2)^2$$

Many reactions involve substances in different phases. In such cases, purely physical intermediate steps occur and affect the over-all rate. Consider the reaction of CO_2 mixed with air and an aqueous solution of lime. Before these substances can react, the CO_2 must diffuse to at least the surface of the aqueous phase. The mechanism of reaction may then be represented by these equations:



and over-all:



Physical intermediate steps such as diffusion in this example enter into all heterogeneous reactions, which, incidentally, comprise the bulk of industrial reactions. Such reactions are treated in detail in Chaps. 6 and 7. The method of deriving the over-all rate equation for a complex set of reactions is treated in Sec. 16.

10. Theory of Reaction; Collision Theory

Molecules or atoms react only upon collision. At the moment of impact, they are visualized to form a short-lived intermediate compound, so-called

"complex," that eventually dissociates to the over-all reaction product. Two fruitful theories exist which emphasize different aspects of this view of the reaction mechanism, namely:

1. The collision theory, which is based on the kinetic theory of gases, or on statistical mechanics
2. The activated-complex theory, also called the transition-state theory, or the absolute-reaction-rate theory, which is based on atomic-structure theory and quantum mechanics

Derivations of quantitative results by either of these theories are somewhat lengthy and involved, so for the most part they cannot be presented here, but some of the more interesting and useful conclusions can be noted.

Collision theory stresses the fact that the molecules must collide before they can react, and no reference is made to the structures of the participating molecules. The number of collisions between unlike molecules per unit time and unit volume is given by

$$N = C_a C_b \sigma_{ab}^2 \left[8\pi RT \left(\frac{1}{M_a} + \frac{1}{M_b} \right) \right]^{1/2} \quad (1-24)$$

where σ_{ab} is the mean of the two molecular diameters. Thus frequency of collision is proportional to the product of the concentrations or to the square of the pressure of a gaseous system when two types of molecules are involved, and also to the square root of the absolute temperature. It is a very large number, of the order of $10^{28} \text{ ml}^{-1} \text{ sec}^{-1}$.

Since the rate of collision is so large, yet many reactions proceed slowly, clearly not every collision leads to reaction. It is believed that only those molecules possessing energies in excess of a critical amount, called the activation energy, react upon impact. Ordinarily, these active molecules constitute only a small fraction of the whole.

For several reasons, it is believed that the individual molecules of a gas differ from each other in their velocities and consequently in their kinetic energies. This must be so if molecules collide more or less elastically, for after collision some molecules will slow down and others speed up. The mathematical law governing the distribution of velocities and energies was derived by Maxwell and by Boltzmann. A derivation is given later in this chapter. According to this law, the fraction $\Delta N/N$ of molecules having velocities in excess of u , or kinetic energies in excess of $\frac{1}{2}mu^2$, is

$$\frac{\Delta N}{N} = e^{-mu^2/2k'T} = e^{-E/RT} \quad (1-25)$$

This equation is commonly given in the differentiated form

$$\frac{1}{N} \frac{dN}{dE} = \frac{2\pi}{(\pi RT)^{3/2}} e^{-\frac{E}{RT}} E^{1/2} \quad (1-26)$$

When E is the activation energy, the fraction of collisions leading to reaction is therefore

$$N_{\text{effective}} = C_a C_b \sigma_{ab}^2 \left[8\pi RT \left(\frac{1}{M_a} + \frac{1}{M_b} \right) \right]^{\frac{1}{2}} e^{-(E_a + E_b)/RT} \quad (1-27)$$

Figure 1-3a is a plot of Eq. 1-26. The fractional number of molecules having energies within a certain range is given by the area under the curve between the appropriate ordinates. Both the range of energies of significant amount and the proportion of molecules having high energies increase rapidly with temperature, as indicated in Fig. 1-3b. For example, doubling

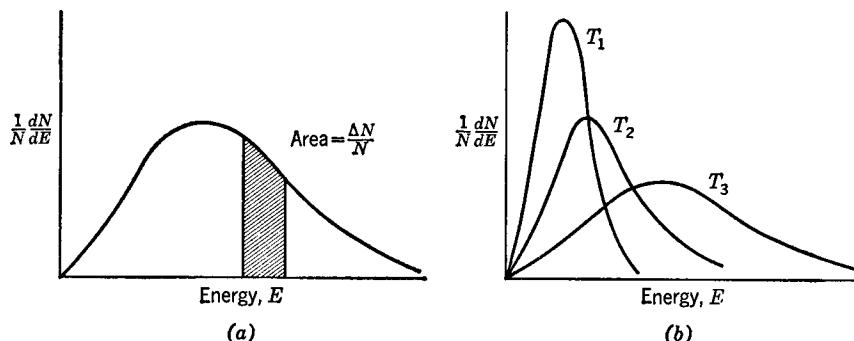


FIG. 1-3. Maxwell-Boltzmann distribution of molecular energies. (a) Distribution function; (b) effect of temperature, $T_3 > T_2 > T_1$.

the absolute temperature of a gas, say, from 1000 to 2000°K, merely doubles the average kinetic energy of its molecules, but the fraction having energies in excess of 20 kcal/g mole is increased 150-fold.

In summary, these principal interrelations exist between reaction kinetics and the kinetic theory of gases:

1. Equation 1-24 resembles the law of mass action, in so far as the effect of concentration is concerned.
2. Since the effect of temperature on the exponential in Eq. 1-27 is much greater than on the $T^{\frac{1}{2}}$ term, this equation resembles the Arrhenius equation for the dependence of reaction rate on temperature.

Thus the kinetic theory provides a reasonable interpretation of some important features of the mechanics of reaction, but it is of limited utility with regard to specific reactions. More modern theories are able to predict the rates of specific reactions, though only very roughly.

11. Energy Distribution

Wherever random assemblages occur, individual members differ in various characteristics. This common statistical observation applies fully to the energies of molecules. From kinetic theory, the *average energy* of a

group of identical molecules is a function of the temperature. However, some molecules possess a great deal more than the average and others much less. This energy distribution can be evaluated by the laws of mathematical probability.

Consider a total of N molecules, of which N_i have individual energies ϵ_i . Many combinations of the numerical values of N_1, N_2, \dots , are possible, subject to the condition $\Sigma N_i = N$. The probability W of any particular combination is

$$W = \frac{N!}{N_1! N_2! \dots} \quad (1-28)$$

which can be written in logarithmic form:

$$\ln W = \ln N! - \Sigma \ln N_i! \quad (1-29)$$

For large values of N , approximately,

$$\ln N! = N \ln N - N \quad (1-30)$$

$$\text{so that} \quad \ln W = N \ln N - N - \Sigma (N_i \ln N_i - N_i) \quad (1-31)$$

The most likely distribution is the one with the greatest numerical value of W , or of $\ln W$ for that matter; the latter function has been introduced because it is easier to handle mathematically in what follows.

Differentiating for a maximum,

$$d(\ln W) = -d(\Sigma N_i \ln N_i) = -\Sigma (\ln N_i + 1) dN_i = 0 \quad (1-32)$$

Since N and the total energy E are fixed numbers under specified conditions:

$$dN = \Sigma dN_i = 0 \quad (1-33)$$

$$dE = \Sigma \epsilon_i dN_i = 0 \quad (1-34)$$

These three simultaneous differential equations may be solved by the *method of undetermined multipliers*, with the result

$$\frac{N_i}{N} = \alpha e^{-\beta \epsilon_i} = \alpha e^{-\epsilon_i/k' T} \quad (1-35)$$

where α and β are integration constants. Further work shows that $\beta = 1/k' T$ and accounts for the last term in the equation. The name frequency factor is applied to α ; k' is the Boltzmann constant.

This is one form of the Maxwell-Boltzmann distribution law. It is a statistical relation, with its most distinctive feature the exponential form in which the temperature occurs.

The energy of a molecule is due to its motion and to the motions of its component atoms and subatomic particles. The several possible types of motion are:

1. Translation of the molecule as a whole, which may be resolved into three components along the coordinate axes of any reference frame
2. Rotation of the molecule as a whole or of any of the component atoms

3. Vibration of the component atoms
4. Electronic motions of various types

The total energy of a molecule is the sum of its energies of translation, rotation, and vibration and that due to electronic motion. Thus

$$\epsilon_i = t_i + r_i + v_i + e_i \quad (1-36)$$

The probability that the molecule possesses a certain value, indicated by a subscript i of any of the energy components, is expressed by the distribution law. Thus

$$f_t = \Sigma g_i e^{-t_i/RT} \quad (1-37)$$

$$f_r = \Sigma g_i e^{-r_i/RT} \quad (1-38)$$

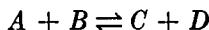
$$f_v = \Sigma g_i e^{-v_i/RT} \quad (1-39)$$

$$f_e = \Sigma g_i e^{-e_i/RT} \quad (1-40)$$

These equations are written for 1 mole, whereas Eq. 1-35 is for 1 molecule. The quantities f are called partition functions, and g_i the statistical weight. The total partition function is similarly defined. Thus

$$F = f_t f_r f_v f_e = \Sigma g_i e^{-\epsilon_i/RT} \quad (1-41)$$

Partition functions are widely useful throughout chemistry. For instance, the ratio of concentrations is equal to the ratio of the probabilities of existence of the two types of molecules. Consequently, in these terms, for the reaction



the equilibrium constant is

$$K = \frac{F_c F_d}{F_a F_b} e^{-E_0/RT} \quad (1-42)$$

where E_0 is the energy change accompanying the reaction at the absolute zero of temperature. This energy term occurs because the same zero of energy is not used for each species; instead, the lowest energy level of each species is taken as its individual zero. Thus E_0 is a correction for the difference in reference states.

12. Activated Complex

Theory. In this theory, emphasis is placed on the nature and energy properties of the momentary combination of reacting molecules which necessarily exists between the time of impact of reactants and the subsequent breakup into the products. Thus the reaction is of the type



where X is the intermediate complex. Virtually all applications of the theory have assumed that the complex is always in equilibrium with both reactants and products. On this premise, the rate of reaction is identical with the rate of dissociation of the complex, which is in turn fixed by its

energy content. Energies of all participants in the reaction, including the complex, are expressible in terms of partition functions.

For molecules of known structure, partition functions are calculable by the methods of atomic physics. Formulas for the various forms of energy are

$$f_t = \frac{(2\pi mk'T)^{1.5}}{h^3} \quad \text{for 3 degrees of translational freedom} \quad (1-43)$$

$$f_r = \frac{8\pi^2 I k' T}{h^2 \sigma} \quad \text{for linear molecule with 2 degrees of rotational freedom} \quad (1-44)$$

$$f_v = \frac{1}{1 - e^{-\hbar\nu/k' T}} \quad \text{for diatomic molecule with 1 degree of vibrational freedom} \quad (1-45)$$

$$f_e = \frac{k' T}{\hbar\nu} \quad \text{for small values of frequency} \quad (1-45a)$$

$$f_e = \Sigma g_i e^{-\epsilon_i/k' T} \quad \text{must be calculated for all the electronic-energy levels} \quad (1-46)$$

Numerical order-of-magnitude values per degree of freedom are

$$f_t = 10^8-10^9$$

$$f_r = 10^1-10^2$$

$$f_v = 10^0-10^1$$

By Eq. 1-42, the equilibrium constant for the reaction is

$$K = \frac{(X)}{(A)(B)} = \frac{F_x}{F_a F_b} e^{-E_0/RT} \quad (1-47)$$

Since the complex is unstable, one of the terms in its partition function corresponds to a very loose vibration which allows the complex to dissociate into the products of the reaction. As given by Eq. 1-45a, this value is

$$f_v = \frac{k' T}{\hbar\nu} \quad (1-48)$$

Here ν is the frequency of decomposition; its product with the concentration of the complex is the rate of reaction. Therefore Eq. 1-47 may be transformed to

$$\text{Rate} = (X)\nu = (A)(B) \frac{k' T}{h} \frac{F'_x}{F_a F_b} e^{-E_0/RT} \quad (1-49)$$

where the substitution

$$F_x = F'_x \frac{k' T}{\hbar\nu}$$

also has been made. Clearly, the specific reaction rate is

$$k = \frac{k' T}{h} \frac{F'_x}{F_a F_b} e^{-E_0/RT} \quad (1-50)$$

At least in principle, the partition functions of all molecules can be calculated from their structures. This is also true of the activation energy E_0 . Thus the problem of the rate of a chemical reaction has been reduced to the determination of the molecular structure of the activated complex.

Order-of-magnitude values of the frequency factors of typical reactions have been calculated from the equation

$$\alpha = \frac{k'T}{h} \frac{F'_x}{F_a F_b} \quad (1-51)$$

and listed in Table 1-4. In this calculation, it was assumed that all partition functions of like type are numerically equal; that is, the f_i 's were assumed equal for all participants and degrees of freedom, and similarly the f_r 's and f_v 's. Consequently, the values in Table 1-4 are only order-of-magnitude figures.

TABLE 1-4. CALCULATED FREQUENCY FACTORS*

No.	Reaction	Frequency factor	
		Formula	Value †
1	2 atoms	$\frac{k'T}{h} \frac{f_r^2}{f_t^3}$	$10^{-10}-10^{-9}$
2	Atom + linear molecule, linear complex	$\frac{k'T}{h} \frac{f_v^3}{f_t^3}$	$10^{-12}-10^{-11}$
3	Atom + linear molecule, nonlinear complex	$\frac{k'T}{h} \frac{f_v f_r}{f_t^3}$	$10^{-11}-10^{-10}$
4	Atom + nonlinear molecule, linear complex	$\frac{k'T}{h} \frac{f_v^2}{f_t^3}$	$10^{-12}-10^{-11}$
5	2 linear molecules, linear complex	$\frac{k'T}{h} \frac{f_v^4}{f_t^3 f_r^2}$	$10^{-14}-10^{-13}$
6	2 linear molecules, nonlinear complex	$\frac{k'T}{h} \frac{f_v^3}{f_t^3 f_r}$	$10^{-13}-10^{-12}$
7	1 linear + 1 nonlinear molecule, nonlinear complex	$\frac{k'T}{h} \frac{f_v^4}{f_t^3 f_r^2}$	$10^{-14}-10^{-13}$
8	2 nonlinear molecules, nonlinear complex	$\frac{k'T}{h} \frac{f_v^5}{f_t^3 f_r^3}$	$10^{-15}-10^{-14}$
9	3 atoms, linear complex	$\frac{k'T}{h} \frac{f_r^2 f_v^4}{f_t^6}$	10^{-33}

* Frost and Pearson (72).

† Concentrations are in molecules per cubic centimeter, and time is in seconds.

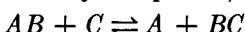
Energy and mechanism. To complete the estimation of the specific reaction rate, the energy of activation also must be determined. For this purpose, the theoretical principles are well understood. Because of the great mathematical labor required, however, no precise calculations have yet been made. Various simplifications in theory have in some instances

led to activation energies in rough agreement with experiment. Often these simplifications have had to be adjusted to fit the data, thus casting some doubts on the method. Table 1-5 lists several of the reactions that have been treated theoretically. For references, see Trotman-Dickenson (217).

TABLE 1-5. CALCULATED ACTIVATION ENERGIES

Reaction	kcal/g mole
ortho-H + H ₂ → para-H + H ₂	14
C ₂ H ₄ + HCl → CH ₃ CH ₂ Cl.....	63
C ₂ H ₄ + C ₄ H ₆ → CH ₂ (CH ₂) ₃ CH=CH.....	15-18
[
ortho-H + CH ₄ → para-H + CH ₄	37
H ₂ + I ₂ → 2HI.....	50

The reaction classically treated is that in which an atom replaces another atom in a binary compound; that is,



The process may be followed by observing the variation in potential energy of the system of 3 atoms as the distances between them change. It has been shown that in certain general cases the most stable configuration occurs when the 3 atoms are in line. Representation of this linear system is possible three-dimensionally, wherein the three coordinates are the potential energy and the distances r_1 between A and B and r_2 between B and C . For convenience, this surface is usually represented by contours, as in Fig. 1-4. With the aid of band spectral data, the potential surfaces can be calculated, in principle. A detailed example is shown by Burns and Dainton (36). Though the mathematical process and the physical knowledge are too involved for presentation here, the physical picture can be suggested.

As 2 atoms A and B approach each other, the potential energy of the system decreases until they are so close that repulsive forces come into play. The stable configuration AB corresponds to a minimum potential

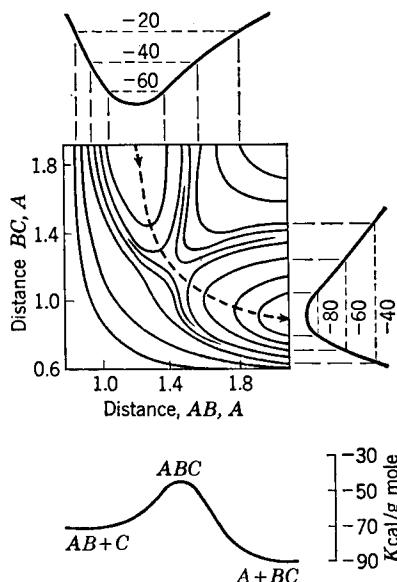


FIG. 1-4. Contour map of potential-energy surface and energy profile of path followed by the reaction $AB + C \rightarrow A + BC$. Zero energy is energy of the system when atoms are infinitely separated. [Trotman-Dickenson (217). Courtesy Academic Press, Inc., New York.]

energy. As a third atom C approaches the compound AB from a great distance, the potential energy of the system remains in a valley substantially parallel to the axis r_2 (Fig. 1-4). This valley rises slowly as C comes close enough for the repulsive forces to act. At a certain position, the 3 atoms are close enough to be regarded as a compound, $X = ABC$. This occurs at a high point at the end of the valley of AB . Dissociation of this complex and movement of A away from BC decrease the system potential energy, which remains in another valley as A moves farther and farther away.

Thus the lowest path—corresponding always to the most stable configuration of the system—from one valley to another has a peak corresponding to the existence of the activated complex ABC . The profile of this path is shown in Fig. 1-4, corresponding to the dashed path on the contour diagram of this same figure. The atom and molecule are able to approach each other against the action of repulsive forces and to raise the potential energy of the system at the expense of other forms of energy, primarily kinetic energy. The elevation of the pass between the valleys, above the valley corresponding to compound AB , is the energy of activation of the reaction $AB + C \rightarrow A + BC$. All other paths between the valleys require greater energies than this.

The complex is not necessarily a union of the reacting molecules in stoichiometric proportions, as perhaps implied in this example. From a

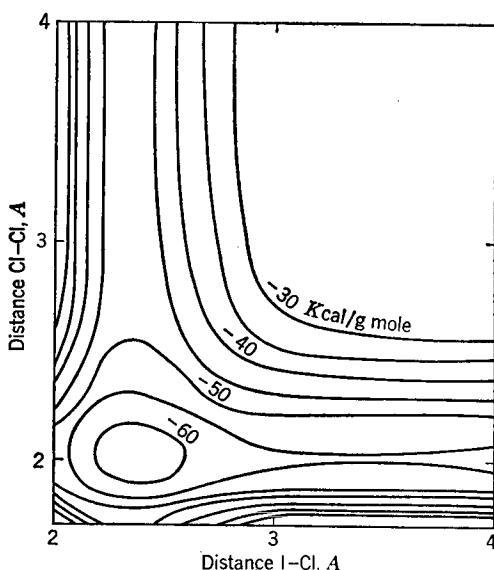


FIG. 1-5. Potential-energy diagram of the reaction $\text{ICl} + \text{Cl} \rightarrow \text{ICl}_2$. [After Burns and Dainton (36).]

physical point of view, it is merely the condition existing at the col. In simpler cases, this condition can be established mathematically. However, most applications of the theory have made guesses of the structure of the complex, based on a general knowledge of similar reactions.

Though it does not appear that the calculation techniques of the activated-complex theory will be of much practical value to chemical engineering in the near future (they were first introduced in 1931), they are of considerable interest as an application of quantum mechanics to a problem of great chemical engineering importance. Many qualitative or semiquantitative results have been obtained. For instance, experiment bears out the prediction by this theory that the reaction rates of complicated molecules are much lower than predicted by collision theory. Also, the negative temperature coefficient of the reaction between nitric oxide and oxygen has been explained (Frost and Pearson, 72).

PROBLEMS

1-1. The specific reaction rate of a first-order reaction is $2.5(10^{-7})$ sec $^{-1}$, and the initial concentration is 0.1 g mole/liter. What is the initial rate, expressed in units of:

- (a) Seconds, liters, gram moles?
- (b) Hours, cubic feet, pound moles?

1-2. The initial rate of a second-order reaction is $5.0(10^{-7})$ g mole/(liter)(sec), and the initial concentrations of the two reactants are each 0.2 g mole/liter. What is the specific reaction rate, expressed in units of:

- (a) Seconds, liters, gram moles?
- (b) Hours, cubic feet, pound moles?

1-3. The third-order gas-phase reaction $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ has a specific reaction rate of

$$k_c = 2.65(10^4) \text{ liters}^2/(\text{g mole})^2(\text{sec})$$

at 30°C and 1 atm. Find k_p and k_N .

1-4. Consider the reaction $A \rightarrow 3B$, with rate equation

$$r = -\frac{1}{V} \frac{dn}{dt} = \frac{k}{V} n$$

Derive a rate equation in terms of the total pressure π , that is, $d\pi/dt = f(\pi)$, at constant volume.

1-5. Rework Illustration 1-4 for a reaction of the first order.

1-6. Determine the activation energy and the frequency factor from the following data for the bimolecular formation of methylethyl ether in ethyl alcoholic solution:

$T, ^\circ\text{C} \dots \dots \dots$	0	6	12	18	24	30
$10^6 k, \text{liters}/(\text{g mole})(\text{sec}) \dots \dots \dots$	5.6	11.8	24.5	48.8	100	208

1-7. Data on the effect of temperature on the reaction between ethanol and acetic acid catalyzed by a cation-exchange resin were obtained by Saletan and White (190).

$T, ^\circ\text{C} \dots \dots \dots$	30	40	50	60	70
$k, \text{liters}/(\text{g mole})(\text{hr}) \dots \dots \dots$	0.5	1.1	2.2	4.0	6.0

Find the energy of activation.

1-8. The effect of temperature on the rates of pyrolysis of various alkylbenzenes was determined by Rase (186), with the results shown below for the specific reaction rates. Find the energies of activation.

$T, ^\circ\text{F}$	k			
	Tertiary amyl	Isopropyl	<i>n</i> -Butyl	Ethyl
750				
850	0.15	0.13	0.016	
900	0.023	
950	0.30	0.21	0.033	0.018
1000	0.023
1050	0.50	0.38	...	0.030

1-9. The statement is commonly made that the rate of a chemical reaction is approximately doubled for each 10°C rise in temperature. Referring to the Arrhenius equation, derive a general relation between absolute temperature and activation energy which must hold if the above statement is to be true. Complete the following table accordingly.

$T, ^\circ\text{K} \dots \dots \dots$	300	400	600	800	1000
$E, \text{kcal/g mole} \dots \dots \dots$					

1-10. Find the constants a , b , and E of the equation

$$k = aT^b e^{-E/RT}$$

using these data on the mutarotation of alpha-glucose:

$T, ^\circ\text{K} \dots \dots \dots$	273.32	298.06	323.13
$(10^8)k \dots \dots \dots$	1.052	14.36	129.6

1-11. Oxygen has a molecular diameter of $2(10^{-8})$ cm. Also, the gas constant is $R = 8.3(10^7)$ ergs and $n = 2.7(10^{19})$ molecules/ml at 0°C and 1 atm. Find the frequency of collisions between oxygen molecules at:

- (a) 1 atm and 0°C .
- (b) 1 atm and 100°C .
- (c) 2 atm and 100°C .

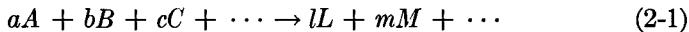
1-12. The initial rate of reaction between two kinds of molecules at 0°C and 1 atm is $5(10^{-7})$ g mole/(sec)(liter), and the initial amounts are equal. At these conditions, the frequency of collision between the unreacted molecules is $1.7(10^{28})$ collisions per second per milliliter. What fraction of the collisions is resulting in reaction?

CHAPTER 2

HOMOGENEOUS ISOTHERMAL REACTIONS

13. Simple Reactions at Constant Volume or Pressure

For present purposes a simple reaction is defined as one whose mechanism corresponds to a single stoichiometric equation, or one that is uncomplicated by side, consecutive, or reverse reactions or by physical resistances. As shown in Sec. 4, the simple reaction



has the rate equation

$$r_a = -\frac{1}{V} \frac{dn_a}{dt} = \frac{1}{V} \frac{dx}{dt} = k(C_a)^a(C_b)^b(C_c)^c \dots \quad (2-2)$$

Before integration can proceed, some of the variables must be eliminated from this equation. By definitions and by material balance, the following relations hold:

$$\begin{aligned} C_a &= \frac{n_a}{V} = \frac{n_{a0} - x}{V} \\ C_b &= \frac{n_{b0} - bx/a}{V} \\ C_c &= \frac{n_{c0} - cx/a}{V} \end{aligned} \quad (2-3)$$

Also

$$\begin{aligned} C_b &= C_{b0} - \frac{b}{a} (C_{a0} - C_a) \\ C_c &= C_{c0} - \frac{c}{a} (C_{a0} - C_a) \end{aligned} \quad (2-4)$$

Upon substitution of these equivalents, Eq. 2-2 can be integrated directly under constant-volume conditions, in terms of either moles or concentrations.

Also of interest are conditions other than constant volume and units other than moles or concentrations. Often the volume changes with the course of a reaction because of changes in pressure or in the total number of moles present. The composition of a reacting system may be expressed

in terms of the mole fraction N or the partial pressure p of a gaseous system. Interrelations between these units are

$$n_i = VC_i = n_t N_i = \frac{n_t p_i}{\pi} \quad (2-5)$$

where the subscript t denotes total. For ideal gases,

$$n_i = \frac{n_t RT}{\pi} C_i = \frac{n_t}{\pi} p_i = \frac{V}{RT} p_i = \frac{\pi V}{RT} N_i \quad (2-6)$$

Designating δ_a as the increase in the number of moles per mole decrease of substance A ,

$$\delta_a = \frac{(l + m + \dots) - (a + b + c + \dots)}{a} \quad (2-7)$$

The total number of moles present is

$$n_t = n_{t0} + \delta_a (n_{t0} - n_a) = n_{t0} + \delta_a x_a = n_{t0} + \delta_b x_b = n_{t0} + \delta_c x_c \quad (2-8)$$

It then follows that

$$-\frac{dn_t}{dt} = \delta_a \frac{dn_a}{dt} = \delta_b \frac{dn_b}{dt} = \delta_c \frac{dn_c}{dt} \quad (2-9)$$

At constant volume,

$$\frac{dn_i}{dt} = V \frac{dC_i}{dt} = \frac{V}{RT} \frac{dp_i}{dt} = n_t \frac{dN_i}{dt} + N_i \frac{dn_t}{dt} \quad (2-10)$$

At constant pressure, for ideal gases,

$$\frac{dn_i}{dt} = \frac{RT}{\pi} \left(n_t \frac{dC_i}{dt} + C_i \frac{dn_t}{dt} \right) = \frac{n_t (dC_i/dt)}{\pi/RT + \delta_i C_i} \quad (2-11)$$

$$\frac{dn_i}{dt} = \frac{1}{\pi} \left(n_t \frac{dp_i}{dt} + p_i \frac{dn_t}{dt} \right) = \frac{n_t (dp_i/dt)}{\pi + \delta_i p_i} \quad (2-12)$$

$$\frac{dn_i}{dt} = n_t \frac{dN_i}{dt} + N_i \frac{dn_t}{dt} = \frac{n_t (dN_i/dt)}{1 + \delta_i N_i} \quad (2-13)$$

With the aid of these relations, the rate equation can be transformed into any desired units. Tables 2-1 and 2-2 show some of these derivations.

Illustration 2-1. A mixture containing 1 lb mole each of propylene and propane is polymerized at 700°F and a constant pressure of 30 atm. For present purposes the reaction may be taken simply as $2C_3H_6 \rightarrow C_6H_{12}$. When the reaction is 75 per cent complete, the partial pressure of the propane is changing at the rate of 1.5 atm/sec. For propylene, what is the rate of change of (a) partial pressure, (b) pound moles, (c) concentration, and (d) mole fraction?

Solution. Let A be the propylene and B the propane. At 75 per cent completion,

$$n_a = 0.25$$

$$n_t = n_{t0} + \delta(n_{t0} - n_a) = 2 - 0.5(1 - 0.25) = 1.625$$

$$p_a = \frac{n_a \pi}{n_t} = \frac{0.25(30)}{1.625} = 4.61 \text{ atm}$$

$$V = \frac{n_t RT}{\pi} = \frac{1.625(0.73)(1,160)}{30} = 45.9 \text{ cu ft}$$

$$C_a = \frac{n_a}{V} = \frac{0.25}{45.9} = 0.00545 \text{ lb mole/cu ft}$$

$$N_a = \frac{n_a}{n_t} = \frac{0.25}{1.625} = 0.154 \text{ mole fraction}$$

Also $p_a = \frac{n_a \pi}{n_t} = \frac{2n_a \pi}{3 + n_a}$

$$p_b = \frac{n_b \pi}{n_t} = \frac{2\pi}{3 + n_a}$$

TABLE 2-1. RATE EQUATIONS AT CONSTANT VOLUME

$$\begin{aligned} -\frac{dn_a}{dt} &= kV\Pi(C_i)^i \\ &= kV\Pi\left(\frac{n_i}{V}\right)^i \\ &= k\left(\frac{1}{V}\right)^{q-1}\Pi(n_i)^i \end{aligned} \quad (2-14)$$

$$\begin{aligned} -\frac{dC_a}{dt} &= -\frac{1}{V}\frac{dn_a}{dt} \\ &= k\Pi(C_i)^i \end{aligned} \quad (2-15)$$

$$\begin{aligned} -\frac{dp_a}{dt} &= -\frac{RT}{V}\frac{dn_a}{dt} \\ &= RTk\Pi(C_i)^i \\ &= RTk\Pi\left(\frac{p_i}{RT}\right)^i \\ &= \left(\frac{1}{RT}\right)^{q-1}k\Pi(p_i)^i \end{aligned} \quad (2-16)$$

$$\begin{aligned} -\frac{dN_a}{dt} &= -\frac{1}{n_t}\left(\frac{dn_a}{dt} + \delta_a N_a \frac{dn_a}{dt}\right) \\ &= \frac{1}{n_t}(1 + \delta_a N_a)\frac{dn_a}{dt} \\ &= \frac{1}{n_t}(1 + \delta_a N_a)Vk\Pi(C_i)^i \\ &= \frac{V}{n_t}(1 + \delta_a N_a)\Pi\left(\frac{n_i}{V}N_i\right)^i \\ &= \left(\frac{n_t}{V}\right)^{q-1}(1 + \delta_a N_a)k\Pi(N_i)^i \end{aligned} \quad (2-17)$$

where

$$\begin{aligned} q &= a + b + c + \dots \\ \Pi(C_i)^i &= (C_a)^a(C_b)^b(C_c)^c \dots \end{aligned}$$

and similarly for other products.

TABLE 2-2. RATE EQUATIONS AT CONSTANT PRESSURE (IDEAL GASES)

$$\begin{aligned}
 -\frac{dn_a}{dt} &= kV\Pi(C_i)^i \\
 &= kV\Pi \left(\frac{n_i}{V}\right)^i \\
 &= k \left(\frac{1}{V}\right)^{q-1} \Pi(n_i)^i
 \end{aligned} \tag{2-18}$$

$$\begin{aligned}
 -\frac{dC_a}{dt} &= -\frac{1}{n_t} \left(\frac{\pi}{RT} + \delta_a C_a\right) \frac{dn_a}{dt} \\
 &= \frac{1}{n_t} \left(\frac{\pi}{RT} + \delta_a C_a\right) kV\Pi(C_i)^i \\
 &= \left(1 + \frac{\delta_a V C_a}{n_t}\right) k\Pi(C_i)^i \\
 &= \left(1 + \frac{RT\delta_a C_a}{\pi}\right) k\Pi(C_i)^i
 \end{aligned} \tag{2-19}$$

$$\begin{aligned}
 -\frac{dp_a}{dt} &= -\frac{1}{n_t} (\pi + \delta_a p_a) \frac{dn_a}{dt} \\
 &= \frac{1}{n_t} (\pi + \delta_a p_a) kV\Pi(C_i)^i \\
 &= \frac{V}{n_t} (\pi + \delta_a p_a) k\Pi \left(\frac{p_i}{RT}\right)^i \\
 &= \left(1 + \frac{\delta_a p_a}{\pi}\right) \left(\frac{1}{RT}\right)^{q-1} k\Pi(p_i)^i
 \end{aligned} \tag{2-20}$$

$$\begin{aligned}
 -\frac{dN_a}{dt} &= -\frac{1}{n_t} (1 + \delta_a N_a) \frac{dn_a}{dt} \\
 &= \frac{1}{n_t} (1 + \delta_a N_a) kV\Pi \left(\frac{n_t}{V} N_i\right)^i \\
 &= (1 + \delta_a N_a) \left(\frac{n_t}{V}\right)^{q-1} k\Pi(N_i)^i \\
 &= (1 + \delta_a N_a) \left(\frac{\pi}{RT}\right)^{q-1} k\Pi(N_i)^i
 \end{aligned} \tag{2-21}$$

Solving simultaneously,

$$p_a + 3p_b = 2\pi$$

Hence $\frac{dp_a}{dt} = -3 \frac{dp_b}{dt} = -3(1.5) = -4.5 \text{ atm/sec}$

From Eq. 2-12,

$$\frac{dn_a}{dt} = \frac{n_t}{\pi + \delta p_a} \frac{dp_a}{dt} = \frac{1.625(-4.5)}{30 - 0.5(4.61)} = -0.264 \text{ lb mole/sec}$$

$$\begin{aligned}
 \frac{dC_a}{dt} &= \frac{1}{n_t} \left(\frac{\pi}{RT} + \delta C_a\right) \frac{dn_a}{dt} = \frac{1}{1.625} \left[\frac{30}{0.73(1,160)} - 0.5(0.00545)\right](-0.264) \\
 &= -0.00531 \text{ lb mole/(cu ft)(sec)}
 \end{aligned}$$

$$\begin{aligned}
 \frac{dN_a}{dt} &= \frac{1}{n_t} (1 + \delta N_a) \frac{dn_a}{dt} = \frac{1}{1.625} [1 - 0.5(0.154)](-0.264) \\
 &= -0.150 \text{ mole fraction/sec}
 \end{aligned}$$

14. Constants of the Rate Equation

Kinetic data usually consist of measurements of the concentrations of some of the reactants, or of some quantities related to the concentrations, as a function of time, under controlled conditions, often isothermal. The problem is to fit a mathematical equation to these data, thus achieving a correlation, and consequently a method of translation to other than the experimental conditions. Generally such an equation is found by trial. Most often the stoichiometry of the reaction suggests the form of rate equation to try first. If this proves incorrect, each reaction then presents a unique problem, and success in fitting a rate equation to the data depends on individual ingenuity.

Consider the reaction $aA + bB \rightarrow cC + \dots$ under constant-volume and constant-temperature conditions. The rate equation is

$$\frac{dx}{dt} = k(n_{a0} - x)^p \left(n_{b0} - \frac{bx}{a} \right)^q \quad (2-22)$$

where, for convenience, the factor of volume is included in k . In this equation, k , p , and q are constants to be evaluated from the experimental data. The procedures for this may be described more clearly by taking the special case wherein $p = q$ and the initial amounts of the reactants are the same. This rate equation is

$$\frac{dx}{dt} = k(n_{a0} - x)^n \quad (2-23)$$

1. Method of differentiation. By graphical or numerical means (Sec. 77), the derivative dx/dt may be evaluated from the data. Since

$$\log \frac{dx}{dt} = n \log (n_{a0} - x) + \log k \quad (2-24)$$

k and n are determined from a log-log plot of the rate versus $n_{a0} - x$ (Fig. 2-1). In terms of the coordinates of two points on this straight line,

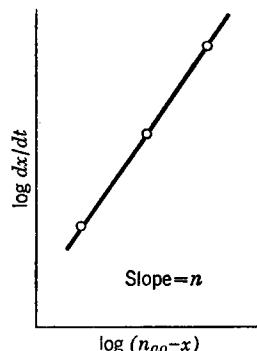


FIG. 2-1. Method of differentiation.

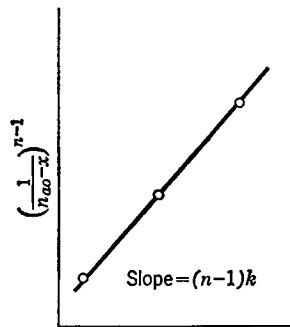


FIG. 2-2. Method of integrated equation.

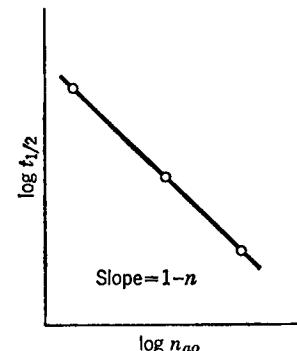


FIG. 2-3. Method of half times.

$$n = \frac{\log (dx/dt)_2 - \log (dx/dt)_1}{\log (n_{a0} - x_2) - \log (n_{a0} - x_1)} \quad (2-25)$$

$$k = \frac{(dx/dt)_1}{(n_{a0} - x_1)^n} \quad (2-26)$$

If the line is not straight though the data may be known to be accurate, the reaction is probably a complex one. Such cases are covered later.

2. Method of the integrated equation. Except when $n = 1$, the integral of Eq. 2-23 is

$$\left(\frac{1}{n_{a0} - x}\right)^{n-1} - \left(\frac{1}{n_{a0}}\right)^{n-1} = (n-1)kt \quad (2-27)$$

There is no direct way of plotting this equation as a straight line from whose slope and intercept the constants k and n may be obtained. It is necessary to assume some value for n , then to plot $[1/(n_{a0} - x)]^{n-1}$ against t . If this plot is a straight line, the correct value for n had been chosen; k may then be calculated from the slope of the line. This method is ordinarily feasible for identifying an integral order of reaction or the more common half orders. Observe that when $n = 1$, $\log (n_{a0} - x)$ is plotted against t .

Instead of making the plot described, values of k may be calculated for individual data points from the integrated equations for assumed orders. The order which gives a nearly constant set of k 's is the correct one. If there is a drift in k for all orders tried, a complex reaction is indicated.

3. Method of half times. At 50 per cent conversion, that is, when $x = 0.5n_{a0}$, the integrated equations assume particularly simple forms, for example:

$$\frac{dx}{dt} = k(n_{a0} - x) \quad t_{1/2} = \frac{\ln 2}{k} \quad (2-28)$$

$$\frac{dx}{dt} = k(n_{a0} - x)^2 \quad t_{1/2} = \frac{1}{kn_{a0}} \quad (2-29)$$

$$\frac{dx}{dt} = k(n_{a0} - x)^n \quad t_{1/2} = \frac{2^{n-1} - 1}{k(n-1)n_{a0}^{n-1}} \quad (n \neq 1) \quad (2-30)$$

Since the half time $t_{1/2}$ is a function of the initial quantity n_{a0} , data must be available from experiments performed with several initial amounts in order to evaluate both k and n by this scheme. Rewriting the last equation,

$$\log t_{1/2} = \log \frac{2^{n-1} - 1}{k(n-1)} - (n-1) \log n_{a0} \quad (2-31)$$

Therefore a plot of $\log t_{1/2}$ against $\log n_{a0}$ should be a straight line whose slope is $1 - n$; k is then determined from

$$k = \frac{2^{n-1} - 1}{t_{1/2}(n-1)n_{a0}^{n-1}} \quad (2-32)$$

This method is of perhaps greatest utility when the same reaction is investigated at several temperatures or under other variations of conditions which cause a change in k but preserve the order. Once the order has been established, k is readily evaluated for the different tests.

4. Method of reference curves. The integral (Eq. 2-27) can be transformed into a generalized form which does not contain k by taking the ratio of the time at conversion x to the time needed for reaching a particular percentage conversion. A convenient reference conversion is 90 per cent. On this basis,

$$\frac{t}{t_{90\%}} = \frac{(n_{a0} - x)^{1-n} - n_{a0}^{1-n}}{(n_{a0} - 0.9n_{a0})^{1-n} - n_{a0}^{1-n}} = \frac{(1 - x/n_{a0})^{1-n} - 1}{(0.1)^{1-n} - 1} \quad (n \neq 1) \quad (2-33)$$

Clearly, the shape of the plot of this equation, as x/n_{a0} against $t/t_{90\%}$, is uniquely determined by n . Such a family of curves is shown in Fig. 2-4.

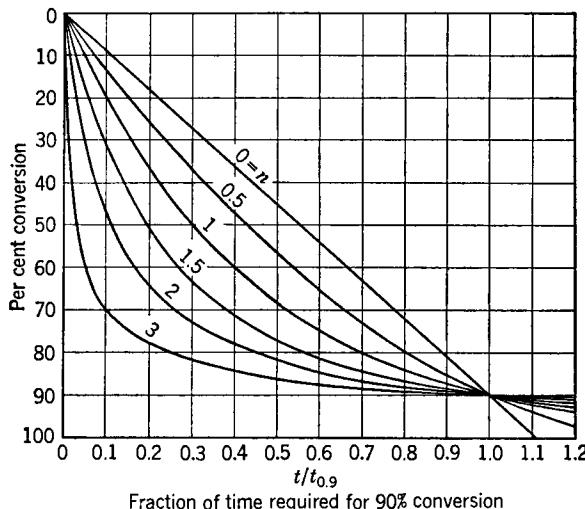


FIG. 2-4. Generalized curves for determining order of reaction. [After Noddings (170).]

When using this method, the data are plotted in the same way as on the reference plot and on the same scale. Superimposing the two plots will then reveal the correct order of reaction.

Equations for complex reactions, such as systems of simultaneous or consecutive ones, are often difficult to analyze and require individual treatment. For example, the constants of the rate equation

$$\frac{dx}{dt} = k_1(n_{a0} - x) + k_2(n_{a0} - x)(n_{b0} - x)$$

can be evaluated from the straight-line plot of $(dx/dt)/(n_{a0} - x)$ against $n_{b0} - x$.

It is always possible to evaluate any number of constants in a rate equation by substituting a corresponding number of experimental points and solving the resulting set of equations simultaneously. For greater accuracy, this can be done for several different sets of points and the results averaged.

Sometimes it is advantageous to plan the experimental program so that the subsequent handling of the data will be simplified. Take Eq. 2-22, for instance. Since in general $n_{a0} \neq n_{b0}$, three constants, k , p and q need be evaluated. Two experiments can be performed, in the first of which such a large excess of substance B is used that its percentage conversion is nil; in the second, a large excess of A is similarly used. These data enable the separate evaluation of the exponents a and b . Alternatively one of the experiments can be made with $n_{a0} = n_{b0}$; analysis of these data will establish the sum of the exponents $p + q$ and the other experiment with a large excess of either A or B will determine either p or q separately.

Writing Eq. 2-22 in the form

$$\log \frac{dx}{dt} = \log k + p \log (n_{a0} - x) + q \log (n_{b0} - \frac{b}{a} x) \quad (2-33a)$$

all three constants can be evaluated at once by the method of least squares. An example of this is Illustration 7-2, Sec. 50.

Illustration 2-2. In the dimerization of butadiene, measurements were made of the total pressure as the reaction proceeded at 326°C and constant volume (Vaughan, 223). These data have been replotted, and the first two columns of Table 2-3 prepared; the other columns are calculated in the course of this problem. A rate equation of the following form will be assumed:

$$-\frac{dp}{dt} = kp^n$$

and the constants k and n will be found by several methods. $p = 2\pi - \pi_0$ is the partial pressure of butadiene.

Method 1. The derivatives $-dp/dt$ are evaluated by the three-point formula (Sec. 77). Calculating the first group of points with $h = \Delta t = 5$,

$$\left(\frac{dp}{dt}\right)_0 = 0.1[-3(632) + 4(590) - 552] = -8.8$$

$$\left(\frac{dp}{dt}\right)_1 = 0.1(-632 + 552) = -8.0$$

$$\left(\frac{dp}{dt}\right)_2 = 0.1[632 - 4(590) + 3(552)] = -7.2$$

and so forth, for the other points shown in the table. From the plot of $\log (-dp/dt)$ against $\log p$ (Fig. 2-5),

$$\frac{\log (-dp/dt) - \log 10}{\log p - \log 663} = \frac{\log 10 - \log 2}{\log 663 - \log 296} = 2.00$$

whence

$$-\frac{dp}{dt} = 2.28(10^{-5})p^2$$

Note from the irregularity of the plotted data that measurements should have been available in tenths of millimeters for accurate determination of the derivatives.

Method 2. Assuming a second-order equation, the integral is

$$\frac{1}{p} - \frac{1}{632} = kt$$

The plot of $1/p$ against t is a straight line (Fig. 2-6), verifying the assumption. The slope of this line is

$$k = \frac{3.50 - 1.58}{84 - 0} (10^{-3}) = 2.28(10^{-6})(\text{mm Hg})^{-1} \text{ min}^{-1}$$

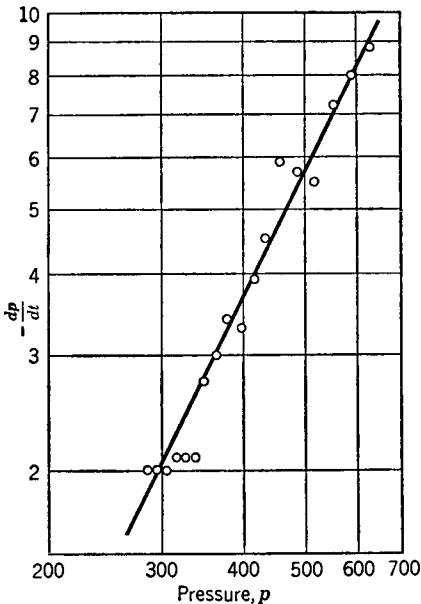


FIG. 2-5. Rate plot for Illustration 2-2.

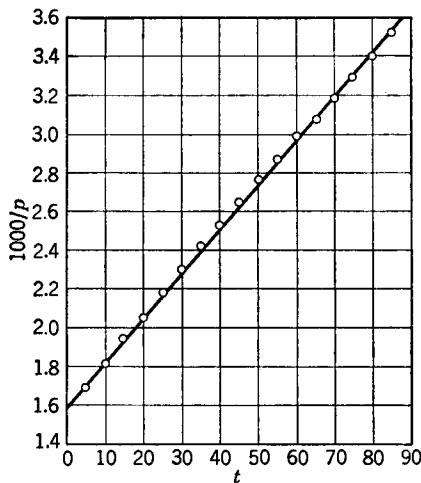


FIG. 2-6. Plot for method 2, Illustration 2-2.

Method 3. When the partial pressure has fallen to half its original value, $t_{1/2} = 69$. Consequently, for second order (Eq. 2-29),

$$k = \frac{1}{t_{1/2} p_0} = \frac{1}{69(632)} = 2.28(10^{-6})(\text{mm Hg})^{-1} \text{ min}^{-1}$$

Also, comparing the equations

$$-\frac{dC}{dt} = k_c C^2 \quad \text{and} \quad -\frac{dp}{dt} = kp^2$$

it follows that

$$k_c = kRT = 2.28(10^{-6})(62.4)(599) = 0.85 \text{ liter (g mole)}^{-1} \text{ min}^{-1}$$

TABLE 2-3. DATA FOR ILLUSTRATION 2-2

t , min	π , mm Hg	$p = 2\pi - \pi_0$	$-\frac{dp}{dt}$	$\frac{1,000}{p}$
0	632	632	8.8	1.58
5	611	590	8.0	1.695
10	592	552	7.2	1.81
15	573.5	515	6.3	1.94
20	558.5	485	5.7	2.05
25	545	458	5.1	2.18
30	533.5	435	4.5	2.30
35	523	414	3.9	2.42
40	514	396	3.3	2.525
45	505	378	3.4	2.645
50	497	362	3.0	2.76
55	490	348	2.6	2.87
60	484	336	2.2	2.98
65	478.5	325	2.2	3.07
70	473	314	2.2	3.18
75	468	304	2.0	3.29
80	463	294	2.0	3.40
85	458	284	2.0	3.52
90	453	274	...	3.65

15. Reversible Reactions

When the products of a reaction are able to recombine and form the original reactants, they do so until a state of dynamic equilibrium is reached in which the initial reactants are decomposing and again reforming from the products at equal rates. Theoretically, all reactions could be considered reversible, but frequently the amount of reverse reaction is very small or even undetectable. For the moment, the fact of reversibility has a particular interest in that it brings out an interrelation between kinetics and thermodynamics. Take the reactions



The net rate of decomposition of substance A which participates in both reactions is

$$-\frac{1}{V} \frac{dn_a}{dt} = -\frac{1}{V} \left(\frac{dn_a}{dt} \right)_1 + \frac{1}{V} \left(\frac{dn_a}{dt} \right)_2 = k_1 \frac{n_a}{V} \frac{n_b}{V} - k_2 \frac{n_c}{V} \frac{n_d}{V} \quad (2-34)$$

At equilibrium the net rate of decomposition is zero, so that

$$k_1 \left(\frac{n_a}{V} \right)_e \left(\frac{n_b}{V} \right)_e - k_2 \left(\frac{n_c}{V} \right)_e \left(\frac{n_d}{V} \right)_e = 0 \quad (2-35)$$

$$\text{or } \frac{k_1}{k_2} = \frac{\left(\frac{n_c}{V}\right)_e \left(\frac{n_d}{V}\right)_e}{\left(\frac{n_a}{V}\right)_e \left(\frac{n_b}{V}\right)_e} = K_c \quad (2-36)$$

where K_c is the equilibrium constant expressed in terms of concentrations and the subscript e refers to equilibrium conditions. In nonideal systems, K_c is properly expressed in terms of activities rather than concentrations. Thus it appears that thermodynamic activity is the *active-mass* terms of the law of mass action, as discussed in Sec. 4; but note the qualifications given there.

Continuing with Eq. 2-34, introducing the equilibrium constant and calling it simply K ,

$$-\frac{1}{V} \frac{dn_a}{dt} = k_1 \left(\frac{n_a n_b}{V^2} - \frac{1}{K} \frac{n_c n_d}{V^2} \right) \quad (2-37)$$

In terms of x , the decrease in amount of substance A , this becomes

$$\begin{aligned} \frac{dx}{dt} &= \frac{k_1}{V} \left[(n_{a0} - x)(n_{b0} - x) - \frac{(n_{c0} + x)(n_{d0} + x)}{K} \right] \\ &= \frac{k_1}{KV} [(K - 1)x^2 - (Kn_{a0} + Kn_{b0} + n_{c0} + n_{d0})x + Kn_{a0}n_{b0} - n_{c0}n_{d0}] \end{aligned} \quad (2-38)$$

which may be written

$$\frac{dx}{dt} = (\alpha x^2 - \beta x + \gamma) \frac{k_1}{KV} \quad (2-39)$$

When $q^2 = \beta^2 - 4\alpha\gamma$ is positive, the integral is

$$\frac{k_1(t - t_0)}{KV} = \frac{1}{q} \ln \frac{(2\alpha x - \beta - q)(2\alpha x_0 - \beta + q)}{(2\alpha x - \beta + q)(2\alpha x_0 - \beta - q)} \quad (2-40)$$

Other reversible rate equations in which at least one of the directions is of the second order may have their solutions expressed by Eq. 2-40, with appropriate values of α , β , and γ . Table 2-4 summarizes these results for the more common reactions of this type.

The reaction of first order in both directions, $A \xrightleftharpoons[k_2]{k_1} B$, with rate equation

$$\frac{dx}{dt} = k_1(n_{a0} - x) - k_2(n_{b0} + x) \quad (2-41)$$

has the integral

$$t - t_0 = \frac{1}{k_1 + k_2} \ln \frac{k_1(n_{a0} - x_0) - k_2(n_{b0} + x_0)}{k_1(n_{a0} - x) - k_2(n_{b0} + x)} \quad (2-42)$$

The substitution $K = k_1/k_2$ can be made to simplify the form slightly. For the important special case when $n_{b0} = 0$ and $x_0 = 0$, Eq. 2-42 becomes

$$t - t_0 = \frac{x_e}{k_1 n_{a0}} \ln \frac{x_e}{x_e - x} \quad (2-43)$$

TABLE 2-4. REVERSIBLE SECOND-ORDER REACTIONS

$$\frac{k(t - t_0)}{KV} = \frac{1}{q} \ln \frac{(2\alpha x - \beta - q)(2\alpha x_0 - \beta + q)}{(2\alpha x - \beta + q)(2\alpha x_0 - \beta - q)}$$

$$q = \sqrt{\beta^2 - 4\alpha\gamma}$$

Reaction	$\frac{dx}{dt}$	α	β	γ
$A \rightleftharpoons C + D$	$\frac{k}{KV} [KV(n_{a0} - x) - (n_{e0} + x)(n_{d0} + x)]$	-1	$KV + n_{e0} + n_{d0}$	$KVn_{a0} - n_{e0}n_{d0}$
$2A \rightleftharpoons C$	$\frac{k}{KV} \left[K(n_{a0} - x)^2 - V \left(n_{e0} + \frac{x}{2} \right) \right]$	K	$2Kn_{a0} + \frac{V}{2}$	$Kn_{a0}^2 - Vn_{e0}$
$2A \rightleftharpoons C + D$	$\frac{k}{KV} \left[K(n_{a0} - x)^2 - \left(n_{e0} + \frac{x}{2} \right) \left(n_{d0} + \frac{x}{2} \right) \right]$	$K - \frac{1}{4}$	$2Kn_{a0} + \frac{n_{e0} + n_{d0}}{2}$	$Kn_{a0}^2 - n_{e0}n_{d0}$
$A + B \rightleftharpoons C$	$\frac{k}{KV} [K(n_{a0} - x)(n_{b0} - x) - V(n_{e0} + x)]$	K	$K(n_{a0} + n_{b0}) + V$	$Kn_{a0}n_{b0} - Vn_{e0}$
$A + B \rightleftharpoons C + D$	$\frac{k}{KV} [K(n_{a0} - x)(n_{b0} - x) - (n_{e0} + x)(n_{d0} + x)]$	$K - 1$	$K(n_{a0} + n_{b0}) + n_{e0} + n_{d0}$	$Kn_{a0}n_{b0} - n_{e0}n_{d0}$

A few other reversible reactions, in combination with consecutive and simultaneous processes, are cited in Sec. 17.

When experimental rate data are examined, the occurrence of oncoming equilibrium may be indicated by a gradual decrease in the specific reaction rate, for all possible irreversible reaction orders that may be tried. The equations in this section are most conveniently used with the equilibrium constant K or with the equilibrium conversion x_e of substance A . The latter can be obtained by extrapolating the experimental rate data to zero rate, or it may be calculated from the equilibrium constant if that is known.

Thermodynamic consistency. As previously indicated, a reversible reaction, say $aA + bB \rightleftharpoons cC$, may have a forward reaction rate

$$r_1 = k_1(C_a)^p(C_b)^q$$

where p and q are not necessarily identical with the corresponding stoichiometric coefficients a and b . For the thermodynamic equilibrium constant to apply (Eq. 2-36), the reverse reaction rate must therefore be

$$r_{-1} = k_{-1}(C_c)^s$$

where s is determined by

$$(C_c)^s = (C_c)^c(C_a)^{p-a}(C_b)^{q-b}$$

For example, in the case of the reaction $\text{CO} + \text{Cl}_2 \rightleftharpoons \text{COCl}_2$ the forward rate has been determined as

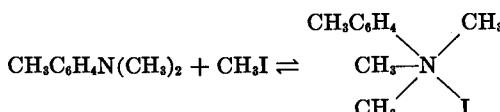
$$\frac{d(\text{COCl}_2)}{dt} = k_1(\text{CO})(\text{Cl}_2)^{\frac{3}{2}}$$

Consequently the reverse rate must be

$$-\frac{d(\text{COCl}_2)}{dt} = k_{-1}(\text{COCl}_2)(\text{Cl}_2)^{\frac{1}{2}}$$

which has been verified experimentally (Bodenstein). Some reversible rate equations have been derived experimentally which are not thermodynamically sound in that Eq. 2-36 is not satisfied. Illustration 2-3 is such an example. Such empirical equations may serve a practical end, but they should be extrapolated only with caution.

Illustration 2-3. Data of Table 2-5 are cited (Laidler, 127) for the reaction between methyl iodide and dimethyl-*p*-toluidine in nitrobenzene solution. The stoichiometric equation is



with equilibrium constant $K = x_e/(a - x_e)^2 = 69.8$. The initial concentration of each reactant is 0.05 g mole/liter, and the products are initially absent. These four rate equations will be checked in the effort to establish the correct one:

$$\frac{dx}{dt} = k_1(a - x) \quad (I)$$

$$\frac{dx}{dt} = k_2(a - x)^2 \quad (II)$$

$$\frac{dx}{dt} = k_3(a - x)^2 - k_{-3}x = k_3 \left[(a - x)^2 - \frac{x}{K} \right] \quad (III)$$

$$\frac{dx}{dt} = k_4(a - x)^2 - k_{-4}x^2 = k_4 \left[(a - x)^2 - \frac{x^2}{K} \right] \quad (IV)$$

The integrals of these equations are

$$k_1 = \frac{1}{t} \ln \frac{1}{1 - x/a}$$

$$k_2 = \frac{1}{t} \frac{x/a}{a(1 - x/a)}$$

$$k_3 = \frac{\frac{x_e}{a}}{at \left[1 - \left(\frac{x_e}{a} \right)^2 \right]} \ln \frac{\frac{x}{a} \left(1 - \frac{x_e x}{a^2} \right)}{a^2 \left(\frac{x_e}{a} - \frac{x}{a} \right)}$$

$$k_4 = \frac{\frac{x_e}{a}}{2at \left(1 - \frac{x_e}{a} \right)} \ln \frac{\frac{x_e}{a} + \frac{x}{a} \left(1 - \frac{2x_e}{a} \right)}{\frac{x_e}{a} - \frac{x}{a}}$$

Since

$$K = \frac{x_e}{(0.05 - x_e)^2} = 69.8$$

$$x_e = 0.02946$$

$$\frac{x_e}{a} = \frac{0.02946}{0.05} = 0.589$$

Calculating the first point by each equation,

$$k_1 = \frac{1}{10.2} \ln \frac{1}{1 - 0.175} = 0.0187$$

$$k_2 = \frac{1}{10.2} \frac{0.175}{0.05(1 - 0.175)} = 0.415$$

$$k_3 = \frac{0.589}{10.2(0.05)[1 - (0.589)^2]} \ln \frac{0.175[1 - 0.589(0.175)]}{(0.05)^2(0.589 - 0.175)} = 8.89$$

$$k_4 = \frac{0.589}{2(10.2)(0.05)(1 - 0.589)} \ln \frac{0.589 + 0.175[1 - 2(0.589)]}{0.589 - 0.175} = 0.421$$

These results and also the ones for the remaining data points are shown in Table 2-5. Clearly, rate equation IV, corresponding to second order in both directions, appears to fit the data best, though Eq. III corresponds to the stoichiometry. The downward drift of k_2 is typical when an irreversible mechanism is postulated for a reversible reaction.

TABLE 2-5. DATA AND RESULTS FOR ILLUSTRATION 2-3

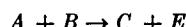
t	$\frac{x}{a}$	k_1	k_2	k_3	k_4
10.2	0.175	0.0187	0.415	8.89	0.421
26.5	0.343	0.0158	0.394	4.15	0.412
36.0	0.402	0.0143	0.373	3.25	0.405
78.0	0.523	0.0096	0.281	1.78	0.371

16. Material Balance in Complex Reactions

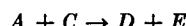
In simple cases, the relations between the conversions of the several participants can be found readily by inspection, but in complex ones a systematic procedure is helpful. The reactions of a group can be numbered, and the initial and final amounts of the participants identified for each reaction. For those substances which participate in more than one reaction, the initial amount for a particular reaction is the same as the final amount from the last preceding reaction in which this substance participated. It is convenient to subscript the final amount from any reaction with the number of that reaction. Then all possible material balances are written down, between initial, intermediate, and final amounts. The balances may then be combined and rearranged to eliminate the intermediate amounts, leaving only the initial and final amounts for the complete reaction. Several examples may be presented.

Illustration 2-4

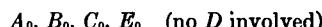
Reaction 1:



Reaction 2:



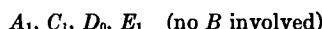
Reaction 1, initial amounts:



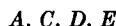
Reaction 1, final amounts:



Reaction 2, initial amounts:



Reaction 2, final amounts:



Reaction 1, balance:

$$A_0 - A_1 = B_0 - B = C_1 - C_0 = E_1 - E_0$$

Reaction 2, balance:

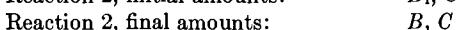
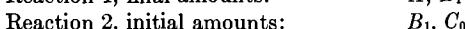
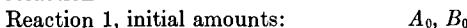
$$A_1 - A = C_1 - C = E - E_1 = D - D_0$$

Upon algebraic elimination of the quantities with subscript 1, the material balance is expressed in these three relations:

$$A_0 - 2B_0 - C_0 = A - 2B - C$$

$$B_0 + C_0 + D_0 = B + C + D$$

$$A_0 + E_0 = A + E$$

Illustration 2-5

$$\text{Reaction 1, balance: } \frac{A_0 - A}{2} = B_1 - B_0$$

$$\text{Reaction 2, balance: } \frac{B_1 - B}{2} = C - C_0$$

Upon eliminating B_1 , the final balance is

$$A_0 + 2B_0 + 4C_0 = A + 2B + 4C$$

17. Consecutive and Simultaneous Reactions

As already indicated in Sec. 9, most chemical transformations are not simple but are the results of several elementary reactions. Thus the

reversible processes just discussed are examples of complex reactions. Other broad types are (1) simultaneous or side or parallel reactions, for example, the chlorination of a mixture of benzene and toluene; (2) consecutive reactions, for example, the chlorination of benzene to the monochlor and subsequent chlorination of the latter to the dichlor and higher. Many combinations of these basic types occur. Because of their importance or special interest, some of them are given special names such as chain reactions, coupled reactions, and solid-catalyzed reactions, which are usually found to involve the formation of intermediate complexes.

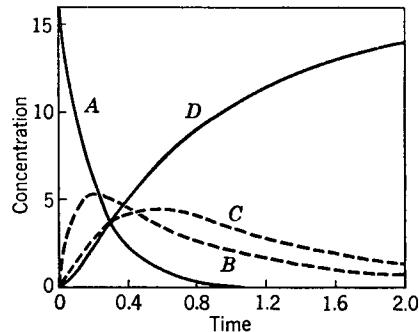
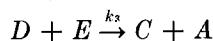
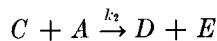
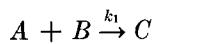


FIG. 2-7. Concentrations in a complex reacting system. $A \xrightarrow{k_1} B; B \xrightleftharpoons[k_3]{k_2} C; B \xrightarrow{k_4} D$; $k_1 = 5, k_2 = 4, k_3 = k_4 = 3; C_{a0} = 16, C_{b0} = C_{c0} = C_{d0} = 0$. [Wall (226). Courtesy Interscience Publishers, Inc., New York.]

When a substance participates in several reactions at the same time, its net rate of formation or decomposition is the algebraic sum of its rates in the elementary reactions. The rates of the elementary steps may be identified with subscripts, thus: $(dx/dt)_1, (dx/dt)_2$, and so forth. Take this group of reactions:



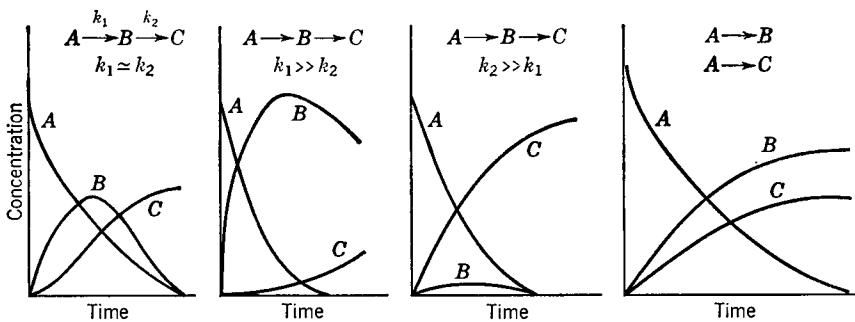


FIG. 2-8. Typical concentration curves for complex reactions.

The over-all rates of the several participants are

$$r_a = (r_a)_1 + (r_a)_2 + (r_a)_3 = -k_1 C_a C_b - k_2 C_a C_c + k_3 C_d C_e \quad (2-44)$$

$$r_b = -k_1 C_a C_b \quad (2-45)$$

$$r_c = k_1 C_a C_b - k_2 C_a C_c + k_3 C_d C_e \quad (2-46)$$

$$r_d = k_2 C_a C_c - k_3 C_d C_e \quad (2-47)$$

$$r_e = k_2 C_a C_c - k_3 C_d C_e \quad (2-48)$$

To integrate such rate equations, some of the variables may be eliminated with the aid of material balances. The procedure is shown by the following examples.

Illustration 2-6

Reactions:



Rate equations:

$$\frac{dn_a}{dt} = -k_1 n_a \quad (2-49)$$

$$\frac{dn_b}{dt} = k_1 n_a - k_2 n_b \quad (2-50)$$

Material balance: $n_{a0} + n_{b0} + n_{c0} = n_a + n_b + n_c$

The solution of the first rate equation is direct:

$$n_a = n_{a0} e^{-k_1 t} \quad (2-51)$$

Substitution into the other rate equation results in a linear differential equation of the first order:

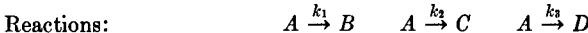
$$\frac{dn_b}{dt} + k_2 n_b = k_1 n_{a0} e^{-k_1 t} \quad (2-52)$$

of which the solution is (Sec. 76)

$$n_b = n_{b0} e^{-k_2 t} + \frac{k_1 n_{a0}}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad (2-53)$$

Also $n_c = n_{a0} + n_{b0} + n_{c0} - n_a - n_b$

$$= n_{a0} + n_{b0} + n_{c0} - n_{a0} e^{-k_1 t} - n_{b0} e^{-k_2 t} - \frac{k_1 n_{a0}}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad (2-54)$$

Illustration 2-7

The rate equations are

$$-\frac{dn_a}{dt} = (k_1 + k_2 + k_3)n_a = kn_a \quad (2-55)$$

$$\frac{dn_b}{dt} = k_1 n_a \quad (2-56)$$

$$\frac{dn_c}{dt} = k_2 n_a \quad (2-57)$$

$$\frac{dn_d}{dt} = k_3 n_a \quad (2-58)$$

Integration of the first rate equation is direct and of the others after substitution of Eq. 2-59:

$$n_a = n_{a0}e^{-kt} \quad (2-59)$$

$$n_b = n_{b0} + \frac{k_1 n_{a0}}{k} (1 - e^{-kt}) \quad (2-60)$$

$$n_c = n_{c0} + \frac{k_2 n_{a0}}{k} (1 - e^{-kt}) \quad (2-61)$$

$$n_d = n_{d0} + \frac{k_3 n_{a0}}{k} (1 - e^{-kt}) \quad (2-62)$$

Interestingly, it appears that the amounts produced are in the ratios of the specific reaction rates:

$$(n_b - n_{b0}):(n_c - n_{c0}):(n_d - n_{d0}) = k_1:k_2:k_3 \quad (2-63)$$

The derivation of over-all rate equations corresponding to complex mechanisms has been mentioned in Sec. 9. Examples of HBr formation and of the chlorination of *n*-heptane were cited. The equation for the former process will be obtained by the methods of this chapter.

Illustration 2-8. To derive the rate equation for the formation of HBr from its elements according to the mechanism postulated in Sec. 9, first note that the equilibrium of dissociation of Br₂ represented by Eqs. *a* and *e* of Sec. 9 is attained rapidly, so that

$$\frac{d(\text{Br}_2)}{dt} = -k_1(\text{Br}_2) + k_5(\text{Br})^2 = 0 \quad (A)$$

Also, it is observed experimentally that only a small amount of atomic hydrogen is present at any time, so that its net rate of formation is zero, or

$$\frac{d(\text{H})}{dt} = k_2(\text{Br})(\text{H}_2) - k_3(\text{H})(\text{Br}_2) - k_4(\text{H})(\text{HBr}) = 0 \quad (B)$$

The net rate of formation of HBr is

$$\frac{d(\text{HBr})}{dt} = k_2(\text{Br})(\text{H}_2) + k_3(\text{H})(\text{Br}_2) - k_4(\text{H})(\text{HBr}) \quad (C)$$

Solving Eqs. *A* and *B* for (Br) and (H),

$$(\text{Br}) = \sqrt{\frac{k_1(\text{Br}_2)}{k_5}} \quad (D)$$

$$(H) = \frac{k_2(\text{Br})(\text{H}_2)}{k_3(\text{Br}_2) + k_4(\text{HBr})} = \frac{k_2(\text{H}_2) \sqrt{\frac{k_1(\text{Br}_2)}{k_5}}}{k_3(\text{Br}_2) + k_4(\text{HBr})} \quad (E)$$

Substituting into Eq. C,

$$\begin{aligned} \frac{d(\text{HBr})}{dt} &= k_2(\text{H}_2) \sqrt{\frac{k_1(\text{Br}_2)}{k_5}} + [k_3(\text{Br}_2) - k_4(\text{HBr})] \frac{k_2(\text{H}_2) \sqrt{\frac{k_1(\text{Br}_2)}{k_5}}}{k_3(\text{Br}_2) + k_4(\text{HBr})} \\ &= \frac{2k_2k_3 \sqrt{\frac{k_1}{k_5}} (\text{H}_2)(\text{Br}_2)^{0.5}}{k_3 + k_4 \frac{(\text{HBr})}{(\text{Br}_2)}} \end{aligned} \quad (F)$$

A general rule to be followed in derivations such as this one is that the net rates of formation of intermediate substances are zero, as was assumed in the case of atomic hydrogen in the present example. In chain reactions, generally, it is to be observed that the specific reaction rate of the chain-terminating step is negligible in comparison with those of the chain-propagating steps.

Some comparatively simple combinations of reactions lead to mathematical equations which it is not always possible to solve analytically. Consider, for example, the reactions



where

$$n_{b0} = n_{d0} = 0$$

$$n_{a0} = n_{c0}$$

The material balance is

$$\begin{aligned} n_{a0} - n_a &= n_b + n_d \\ n_c &= n_{c0} - n_d = n_{c0} - n_{a0} + n_a - n_b = n_a - n_b \end{aligned}$$

The rate equations are

$$-\frac{dn_a}{dt} = k_1 n_a \quad (2-64)$$

$$\frac{dn_b}{dt} = k_1 n_a - \frac{k_2}{V} n_b n_c = \left(k_1 - \frac{k_2 n_b}{V} \right) n_{a0} e^{-k_1 t} + \frac{k_2 n_b^2}{V} \quad (2-65)$$

upon substitution from the material balance and the solution for n_a . An analytical solution for n_b may not be possible.

Another difficulty encountered with complex reactions, even when integration is possible, is that the integral may be so complex that the specific reaction rates cannot be evaluated from experimental data by any kind of plotting of the data. In such cases it is best to work with the differential equation rather than the integral. Using Eq. 2-65 as an example, say that the experimental data are measurements of n_b as a function of time. From such data the derivative dn_b/dt can be evaluated. When two sets of data (dn_b/dt , n_b and t) are substituted into the differential equation, the unknowns k_1 and k_2 can be evaluated by simultaneous

solution of the resulting equations. In the present example, the numerical solution is not simple but it can be obtained by successive approximation (Sec. 77, Eq. 12-17).

By modifying the experimental program, evaluation of the k 's often may be simplified. For instance, if one of the reactions of a set is of the second order, perhaps it can be made into a pseudo first order by employing a large excess of one of the reactants. Or if one of the steps is reversible, it may be possible to utilize only the initial data, when the system is so far displaced from equilibrium that the reverse reaction is inappreciable. Individual cases may suggest other approaches. A few complex systems are summarized in Table 2-6. Reference may be made to Frost and Pearson (72) for several other examples.

Illustration 2-9. For the pair of reactions



these conditions are given:

$$k_1 = 0.10 \text{ cu ft/(lb mole)(min)}$$

$$k_2 = 0.05 \text{ cu ft/(lb mole)(min)}$$

$$A_0 = 3B_0 = 0.9 \text{ lb mole/cu ft}$$

$$C_0 = D_0 = 0$$

Concentrations of the four participants will be calculated as a function of time. The material balance is

$$C = 3(B_0 - B) - (A_0 - A) = A - 3B$$

$$D = (A_0 - A) - (B_0 - B) = 0.6 + B - A$$

and the rate equations are

$$-\frac{dA}{dt} = k_1AB + k_2AC = k_1AB + k_2A(A - 3B) = 0.1AB + 0.05A(A - 3B)$$

$$-\frac{dB}{dt} = k_1AB = 0.1AB$$

These simultaneous differential equations will be solved numerically by the method of Sec. 78. Results are summarized in Table 2-7. Let the increment of time be

$$h = \Delta t = 1 \text{ min}$$

Then

$$\left(\frac{dA}{dt}\right)_0 = -0.1(0.9)(0.3) - 0.05(0.9)[0.9 - 3(0.3)] = -0.0270$$

$$\left(\frac{dB}{dt}\right)_0 = -0.1(0.9)(0.3) = -0.0270$$

$$\left(\frac{d^2B}{dt^2}\right)_0 = -0.1 \left(A \frac{dB}{dt} + B \frac{dA}{dt} \right)_0 = -0.1[0.9(-0.027) + 0.3(-0.027)] = 0.00324$$

$$\begin{aligned} \left(\frac{d^2A}{dt^2}\right)_0 &= -0.1 \left(A \frac{dB}{dt} + B \frac{dA}{dt} \right)_0 - 0.05 \left[A \left(\frac{dA}{dt} - 3 \frac{dB}{dt} \right) + (A - 3B) \frac{dA}{dt} \right]_0 \\ &= -0.1[0.9(-0.027) + 0.3(-0.027)] - 0.05[0.9(-0.027) + 0.081] + 0 \\ &= 0.0008 \end{aligned}$$

TABLE 2-6. RATE EQUATIONS OF SOME COMPLEX REACTIONS

I. Reactions.....	$A \xrightarrow{k_1} C$	$B \xrightarrow{k_2} C$		
Rate equation.....	$\frac{dn_c}{dt} = k_1 n_a + k_2 n_b = k_1 n_{a0} e^{-k_1 t} + k_2 n_{b0} e^{-k_2 t}$			
II. Reactions.....	$2A \xrightarrow{k_1} B$	$B \xrightarrow{k_2} C$		
Rate equations.....	$-\frac{dn_a}{dt} = \frac{k_1 n_a^2}{V}$	$\frac{dn_b}{dt} = \frac{k_1 n_a^2}{2V} - k_2 n_b = \frac{k_1}{2V} \left(\frac{n_{a0}}{1 + k_1 n_{a0} t/V} \right)^2 - k_2 n_b$		
III. Reactions.....	$2A \xrightarrow{k_1} B$	$2B \xrightarrow{k_2} C$		
Material balance.....	$n_{b0} = n_{c0} = 0$	$n_{a0} = n_a + 2n_b + 4n_c$		
Rate equations.....	$\frac{dn_a}{dt} = -\frac{k_1 n_a^2}{V}$	$\frac{dn_b}{dt} = \frac{k_1 n_a^2}{2V} - \frac{k_2 n_b^2}{V}$		
		$\frac{dn_c}{dt} = \frac{k_2 n_b^2}{V} = \frac{k_2}{V} \left(\frac{n_{a0} - n_a - 4n_c}{2} \right)^2$		
		$= \frac{k_2}{4V} \left(n_{a0} - \frac{n_{a0}}{1 + k_1 n_{a0} t/V} - 4n_c \right)^2$		
IV. Reactions.....	$A \xrightarrow{k_1} B$	$B \xrightarrow{k_2} A$	$B \xrightarrow{k_3} C$	$C \xrightarrow{k_4} B$
Material balance.....	$n_{b0} = n_{c0} = 0$	$n_{a0} = n_a + n_b + n_c$		
Rate equations.....	$\frac{dn_a}{dt} = -k_1 n_a + k_2 n_b$	$\frac{dn_b}{dt} = k_1 n_a - k_2 n_b - k_3 n_b + k_4 n_c$		
		$= (k_1 - k_4) n_a - (k_2 + k_3 + k_4) n_b + k_4 n_{a0}$		
		$\frac{dn_c}{dt^2} + (k_1 + k_2 + k_3 + k_4) \frac{dn_a}{dt}$		
		$+ (k_1 k_3 + k_1 k_4 + k_2 k_4) n_a - k_2 k_4 n_{a0} = 0$		
V.* Reactions.....	$A + B \xrightarrow{k_1} C + E$	$A + C \xrightarrow{k_2} D + E$		
Material balance.....	$n_{e0} = n_{d0} = n_{e0} = 0$	$n_a - n_b + n_d = n_{a0} - n_{b0} + n_{d0}$		
		$n_b + n_c + n_d = n_{b0} + n_{c0} + n_{d0}$		
		$n_a + n_e = n_{a0} + n_{e0}$		
Rate equations.....	$\frac{dn_a}{dt} = -k_1 n_a n_b - k_2 n_a n_c$	$\frac{dn_b}{dt} = -k_1 n_a n_b$		
		$\frac{dn_c}{dt} = k_1 n_a n_b - k_2 n_a n_c$		
		$\frac{dn_d}{dt} = k_2 n_a n_c$		

* See Frost and Pearson (72) for an approximate solution of this system of equations.

TABLE 2-7. DATA FOR ILLUSTRATION 2-9

<i>t</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	$-\frac{dA}{dt}$	$-\frac{dB}{dt}$
0	0.9000	0.3000	0	0	0.0270	0.0270
1	0.8734	0.2746	0.0532	0.0012	0.0262	0.0241
2	0.8476	0.2518	0.0930	0.0042	0.0253	0.0214
3	0.8228	0.2318	0.1274	0.0090	0.0244	0.0191
4	0.7988	0.2136	0.1580	0.0148	0.0233	0.0170
5	0.7762	0.1978	0.1828	0.0216	0.0223	0.0154
6	0.7542	0.1828	0.2064	0.0286	0.0216	0.0138
7	0.7330	0.1702	0.2224	0.0372	0.0207	0.0125
8	0.7128	0.1578	0.2396	0.0430	0.0197	0.0112
9	0.6936	0.1478	0.2502	0.0542	0.0189	0.0102
10	0.6750	0.1374	0.2628	0.0624	0.0182	0.0093
11	0.6572	0.1292	0.2696	0.0720	0.0174	0.0085
12	0.6402	0.1204	0.2790	0.0802		

Applying Taylor's theorem,

$$A_1 = 0.9 + (-0.027) + 0.5(0.0008) + \dots = 0.8734$$

$$B_1 = 0.3 + (-0.027) + 0.5(0.0032) + \dots = 0.2746$$

Therefore

$$\left(\frac{dA}{dt}\right)_1 = -0.1(0.8734)(0.2746) - 0.05(0.8734)[0.8734 - 3(0.2746)] = -0.0262$$

$$\left(\frac{dB}{dt}\right)_1 = -0.1(0.8734)(0.2746) = -0.0241$$

$$A_2 = A_1 + 2\left(\frac{dA}{dt}\right)_1 = 0.9000 + 2(-0.0262) = 0.8476$$

$$B_2 = 0.3 + 2(-0.0241) = 0.2518$$

$$\left(\frac{dA}{dt}\right)_2 = -0.1(0.8476)(0.2518) - 0.05(0.8476)[0.8476 - 3(0.2518)] = -0.0253$$

$$\left(\frac{dB}{dt}\right)_2 = -0.1(0.8476)(0.2518) = -0.0214$$

$$A_3 = 0.8734 + 2(-0.0253) = 0.8228$$

$$B_3 = 0.2746 + 2(-0.0214) = 0.2318$$

and so forth, for the other points. This system of equations could be solved in perhaps a less tedious manner. By eliminating *t* from the rate equations, the result is

$$\frac{dA}{dB} = \frac{k_2 A}{k_1 B} + \frac{k_1 - 3k_2}{k_1}$$

This is a linear equation, solvable directly to give a relation between *A* and *B*. Then the equation $-dB/dt = 0.1AB$ can be integrated numerically or graphically to bring in the relation of *A* and *B* to time.

18. Homogeneous Catalysis

A catalyst is a substance which influences the rate of a reaction. During the process it may or may not become altered itself. When it does alter, the substance is regarded as a catalyst only when no stoichiometric whole-number relationship exists between its amount and the amounts of reactants converted. Trace amounts of catalysts are often extremely effective. The turnover ratio is the number of molecules converted per molecule of catalyst; this number may be in the millions. If a reaction is reversible, the reverse process is accelerated to the same extent as the forward. When the reaction can proceed by more than one irreversible path, the catalyst may favor one path over another and thus can lead to a product distribution different from that of the uncatalyzed reaction.

Catalytic processes are excellent examples of complex reactions. The catalyst is regarded as combining with some of the reactants to form an intermediate compound which subsequently reacts to form the products of the main reaction, with release of the catalyst so that it can react further. Evidence is quite conclusive that the catalyzed path requires a lower activation energy and thus can proceed more easily. Examples are provided by Tables 2-8 and 2-9.

TABLE 2-8. DECOMPOSITIONS CATALYZED BY IODINE*

Decomposition of	Activation energy, kcal/g mole	
	Uncatalyzed	Catalyzed
Dipropyl ether.....	60.5	28.5
Diethyl ether.....	53.5	34.3
Methylethyl ether.....	47.0	38.0
Acetaldehyde.....	45.5	32.5

* Hinshelwood (89).

TABLE 2-9. DECOMPOSITION OF HYDROGEN PEROXIDE*

Catalyst	Activation energy, kcal/g mole
None.....	18.0
Iodide ion.....	13.5
Colloidal platinum.....	11.7
Liver catalase.....	5.5

* Moelwyn-Hughes (161).

Two broad classes of catalytic reactions are recognized, homogeneous and heterogeneous. Known homogeneous catalytic reactions are either gas- or liquid-phase, preponderantly the latter; existence of solid-phase reactions of this type is considered doubtful. Solid catalysts are widely employed for fluid-phase reactions. These are the most important heterogeneous type and are considered at length in later chapters, where also general characteristics of catalysis and catalysts are discussed further.

Since a catalyst participates chemically, the rates of such reactions are influenced by the same kinds of variables as ordinary reactions, such as the concentration and chemical nature of the catalyst. In the majority of cases, the rate of a catalyzed reaction is first-order in the catalyst concentration. However, since the rate may be finite in the complete absence of the catalyst, a more nearly correct statement is that the rate is proportional to $a + b(C_{\text{catalyst}})^n$, where a , b , and n are constants. Figure 2-9 on the acid catalysis of the mutarotation of glucose illustrates this.

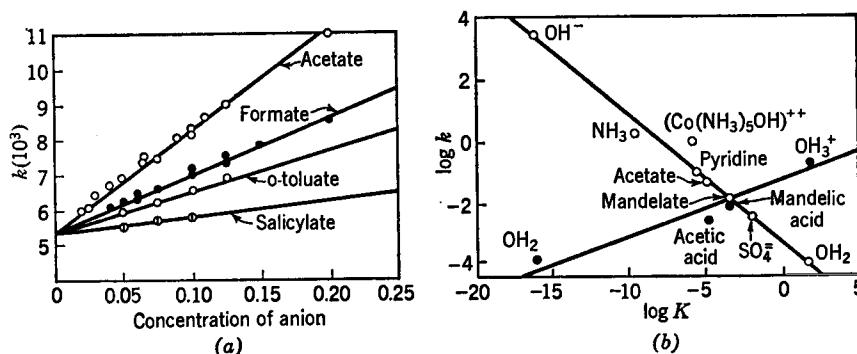
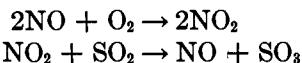


FIG. 2-9. Specific reaction rates of the mutarotation of glucose. (a) Effect of concentration; (b) effect of ionization constant. [After Brønsted and Guggenheim (35).]

Homogeneous catalysis in the gas phase is comparatively rare, but a few examples may be noted.

1. Nitric oxide is an industrial catalyst for the oxidation of sulfur dioxide. Here it has been shown that the reaction proceeds much more rapidly by the sequence

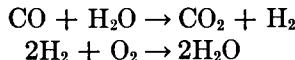


than by direct combination. Incidentally, the first of these is purportedly one of the very few known instances of a termolecular reaction.

2. Decompositions of acetaldehyde, various ethers, and nitrous oxide are strongly catalyzed by iodine in the gas phase (Table 2-8).

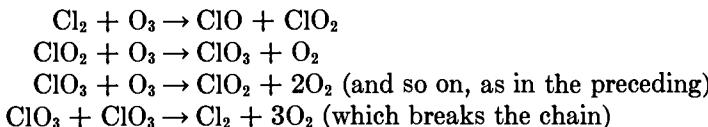
3. Formation of hydrogen chloride from its elements is catalyzed by sodium or potassium vapor. Several thousand molecules of HCl result from the reaction of a single metallic atom.

4. The positive catalytic effect of water on the reaction between carbon monoxide and oxygen has been interpreted in accordance with the mechanism



and so forth.

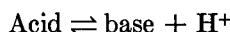
Most gas reactions which appear homogeneous really take place on the vessel wall and are therefore heterogeneous-catalyzed. Thus water exhibits a negative catalytic effect in some cases, but this has been interpreted as due to adsorption of water, with resultant poisoning of the container wall, which is really a catalyst. Those few reactions which appear to be homogeneous-catalyzed are really chain reactions. Substances which initiate chain reactions are sometimes called sensitizers rather than catalysts. An example is the decomposition of ozone, which proceeds slowly by itself but is strongly accelerated by chlorine according to the chain



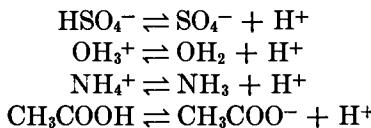
When simple rate equations do not appear to fit data, heterogeneous effects or a chain mechanism are indicated. Thus the chain reaction just mentioned has the relatively complex rate equation cited in Prob. 2-19.

Liquid-phase homogeneous catalysis is common. Most widely investigated has been catalysis by ions, of which the most important type is acid and base catalysis. Processes catalyzed by acids and bases include esterification, saponification, inversion, mutarotation, enolization, and many oxidations and reductions.

Rates of such reactions are expressed in terms of the generalized concept of acid and base. According to this definition, molecules able to furnish a proton are called acids, and those able to combine with a proton are called bases; these molecules may be ions or neutral. Thus acids and bases are related by the equation



Specific examples are



Specific reaction rates are correlated in terms of ionization constants by empirical equations of the form

$$k = aK^b$$

where K = ionization constant

a and b = empirical constants

In numerical value, b ranges from 0.3 to 0.9. Some idea of the order of magnitude of these effects is indicated by Fig. 2-9.

Neutral salts in solution influence reactivity. It is to be expected that collisions of ions will be influenced by the ionic atmospheres, which are in turn affected by the presence of salts. Collisions between oppositely charged ions are increased by salts which favor electrostatic attraction and decreased by salts which modify the ionic atmosphere so that electrostatic attraction is decreased. This effect is correlated in terms of the ionic strength of the solution; its order of magnitude is rather less than that of most catalytic effects.

Nature of the solvent sometimes may affect the kinetics of a process. This may possibly be regarded as an example of catalysis. In some cases this effect is due to the influence of the solvent on the thermodynamic activity of the reactants. Solvating power and dielectric constant are pertinent properties. Where neutral molecules are concerned, reactions yielding products more polar than the reactants proceed better in polar solvents, while those with products less polar than the reactants proceed better in nonpolar solvents.

PROBLEMS

2-1. Under certain conditions, the product from the thermal cracking of butane has the following composition:

Component	Wt %
Hydrogen.....	0.2
Methane.....	10.8
Ethylene.....	25.0
Ethane.....	10.0
Propylene.....	20.0
Propane.....	3.0
Butene.....	21.0
Butane.....	10.0

What is the increase in the number of moles of the system per mole of butane converted?

2-2. The reaction $C_4H_{10} \rightarrow 2C_2H_4 + H_2$ takes place at $1300^{\circ}F$ and 2 atm. At a time when the reaction is 50 per cent complete, the partial pressure of the butane is changing at the rate of 2.4 atm/sec. The weight of the system is 116 lb. At what rates are the following items changing:

- Partial pressure of ethylene?
- Number of pound moles of hydrogen present?
- Mole fraction of butane?

2-3. Find k and n for the following reactions occurring at constant volume:

(a) Thermal decomposition of nitrous oxide in the gas phase at 1030°K. $2\text{N}_2\text{O} = 2\text{N}_2 + \text{O}_2$

p_0 , mm Hg.....	52.5	139	290	360
$t_{\frac{1}{2}}$, sec.....	860	470	255	212

(b) Thermal decomposition of nitrous oxide on gold at 990°C and initial pressure of 200 mm Hg.

t , min.....	30	53	100
% decomposition.....	32	50	73

(c) Reaction between nitric oxide and hydrogen at 826°C with equal initial amounts. P_0 is the total initial pressure. $\text{NO}_2 + \text{H}_2 = \text{products}$

P_0 , mm Hg.....	354	340.5	288	202
$t_{\frac{1}{2}}$, sec.....	81	102	140	224

(d) Thermal decomposition of dimethyl ether at 504°C (Wolfenden, 241). $(\text{CH}_3)_2\text{O} = \text{CH}_4 + \text{CO} + \text{H}_2$

P , mm Hg.....	312	408	488	562	779	931
t , sec.....	0	210	717	1,195	3,155	∞

2-4. Given the following data, determine k and n by each of the first two methods of Sec. 14. Taking the correct value of n as thus established, determine k by the third method.

t	0	5.4	21.6	25.5	32.9	∞
x	0	0.624	1.298	1.376	1.474	2.000

2-5. The rates of decomposition of acetaldehyde, expressed as millimeters of mercury per minute, corresponding to various per cent decompositions, are as follows: $\text{CH}_3\text{CHO} = \text{CH}_4 + \text{CO}$

%.....	0	5	10	15	20	25	30	35	40	45	50
Rate....	8.53	7.49	6.74	5.90	5.14	4.69	4.31	3.75	3.11	2.67	2.29

Determine the order of the reaction.

2-6. Hexamethylenetetramine was made at 0°C from aqueous ammonia and formaldehyde. The volume of the reactor was 1 liter. Find the order of the reaction with respect to NH_3 (Meissner, 153).

Wt % NH_3 present.....	0.8	0.6	0.41	0.20	0.016
Moles NH_3 converted per minute....	0.025	0.020	0.010	0.002	0.00002

2-7. Condensation of formaldehyde (F) with sodium paraphenolsulfonate (M) was effected by Stults, Moulton, and McCarthy (207). Rate data for the formation of a monomer (MA) are as follows at 100°C and pH = 8.35. Equal quantities of F and M were initially present. Determine whether the data correspond more nearly to first- or second-order kinetics.

F, g moles/liter.....	0.131	0.125	0.121	0.117	0.111	0.104
t, min.....	0	10	20	30	40	60

2-8. The rate equation

$$\frac{dx}{dt} = 1.5k_1e^{-k_1t} - k_2x$$

has the solution

$$x = \frac{1.5k_1}{k_2 - k_1} (e^{-k_1t} - e^{-k_2t})$$

Given the following data, find the numerical values of k_1 and k_2 .

t.....	20	30	40	50
x.....	0.699	0.515	0.286	0.225

2-9. Write the integrals of the rate equations of Table 2-4 for the special case when the products are initially absent. Do this in terms of the specific reaction rate of the forward reaction and the equilibrium amount x_e of substance A.

2-10. One solution contains substance A in concentration 1.6 lb moles/cu ft, and another contains substance B in concentration 1.0 lb mole/cu ft. Equal amounts of these solutions are mixed quickly, and measurements of C_a versus t are made. The reaction is believed to be reversible of first order in both directions. Find the specific reaction rates. The reaction is $A \rightleftharpoons B$.

t, min.....	0	0.5	1.0	1.5	2.0	3.0	4.0	5.0	10.0
C_a , lb moles/cu ft...	0.800	0.670	0.600	0.563	0.543	0.527	0.522	0.520	0.520

2-11. The following data refer to a reaction that is believed to be of the second order in the forward direction and of the first order in reverse. Initial concentrations of the two reactants were each 1.2 lb moles/cu ft, and there was no product initially.

(a) Find the specific reaction rates.

(b) What is the equilibrium constant?

(c) How long does it take to convert 60 per cent of the reactants?

Pound moles A converted per cubic foot	Rate, lb moles/(cu ft)(min)
0	2.16
0.05	1.96
0.10	1.79
0.15	1.60
0.20	1.44
0.30	1.12
0.40	0.84
0.50	0.59
0.60	0.38
0.70	0.17
0.80	0.00

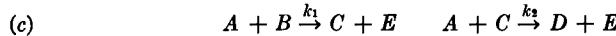
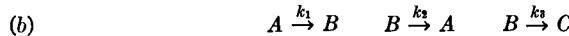
2-12. Write material balances for the groups of reactions:



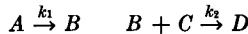
2-13. Set up and integrate wherever possible the rate equations for the following groups of reactions:



where substance *B* exerts a catalytic effect on the reaction in proportion to its concentration.



2-14. For the set of reactions



with $A_0 = C_0 = 1$ and $B_0 = D_0 = 0$, preliminary calculations indicate that the specific reaction rates are approximately $k_1 = 0.18$ and $k_2 = 0.12$. Given these data, evaluate the *k*'s more accurately:

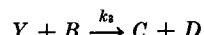
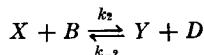
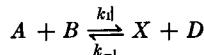
<i>t</i>	<i>B</i>	dB/dt
0	0	
10	0.2	0.028
20	0.4	0.019

2-15. In one experiment dinitrobenzene was prepared from mononitrobenzene by the addition of three equivalents of nitric acid. After 20 min the mononitrobenzene was half used up and the *o*-, *m*-, and *p*- forms of the dinitrobenzene were present in the proportions of 6.4, 93.5, and 0.1, respectively. The reaction for the formation of each of these substances is of the second order. Find the three specific reaction rates.

2-16. Show that in a pair of consecutive first-order processes the first product rises to a maximum and then falls off toward zero. Find expressions in terms of the specific reaction rates for the maximum amount of this first product and for the time when this maximum is reached.

2-17. For the set of reactions $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, the value of $k_1 = 0.35 \text{ hr}^{-1}$, $k_2 = 0.13 \text{ hr}^{-1}$, $C_{a0} = 4 \text{ lb moles/cu ft}$, and $C_{b0} = C_{c0} = 0$. Plot the concentrations of *A*, *B*, and *C* against the time (Corrigan, 48).

2-18. Consider the reaction $A + 3B \rightarrow C + D$, for which the mechanism is



where *X* and *Y* are unstable intermediates. Show that the over-all rate of reaction is

$$r = -\frac{dA}{dt} = \frac{k_1 k_2 k_3 A B^3}{k_2 k_3 B^2 + k_{-1} k_3 B D + k_{-1} k_{-2} D^2}$$

Also, show that the limiting cases when each of the three reactions control individually are, respectively,

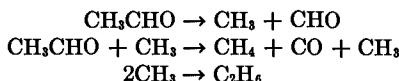
$$r = \frac{k_1 k_2 k_3 A B^3}{k_{-1} k_{-2} D^2}$$

2-19. In Sec. 18, a mechanism for the decomposition of ozone in the presence of chlorine was stated, in terms of ClO_2 and ClO_3 functioning as chain carriers. Show that this mechanism is described by the rate equation

$$-\frac{d(O_3)}{dt} = 2k_3 \sqrt{\frac{k_1}{k_4}} (Cl_2)^{0.5} (O_3)^{1.5}$$

The ClO appearing in the mechanism decomposes into its elements without chain action (Schwab, Taylor, and Spence, 196).

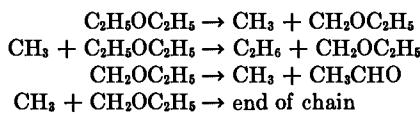
2-20. Thermal decomposition of acetaldehyde is postulated (Hinshelwood, 90) to proceed by the chain mechanism



Observing that the rate of the first reaction is small in comparison with the second when the chains are long, show that

$$-\frac{d(\text{CH}_3\text{CHO})}{dt} = k_2 \sqrt{\frac{k_1}{k_2}} (\text{CH}_3\text{CHO})^{1.5}$$

2-21. Thermal decomposition of diethyl ether is postulated (Hinshelwood, 90) to proceed by the chain mechanism

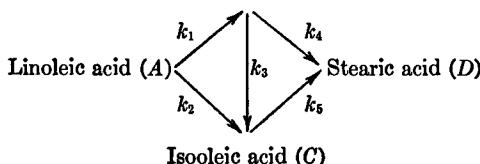
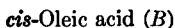


Show that the rate equation is

$$-\frac{d(C_2H_5OC_2H_5)}{dt} = k_2 \sqrt{\frac{k_1 k_3}{k_2 k_4}} (C_2H_5OC_2H_5)$$

2-22. The hydrolysis of methyl acetate is catalyzed by the reaction product acetic acid. In one experiment, when the initial concentration of the acetate was 0.5 and that of the acid was 0.05 g mole/liter, 60 per cent conversion was attained in 1 hr. Find the time at which the reaction velocity becomes a maximum and also the value of this maximum.

2-23. For the hydrogenation of cottonseed oil, these main reactions are postulated (Eldib and Albright, 59):



If all the reactions are of the first order, show that the amount of component *C* is given by

$$n_c = n_{c0}e^{-k_5t} + n_{a0} \frac{k_1k_3}{(k_3 + k_4 - k_1 - k_2)(k_5 - k_3 - k_4)} (e^{-k_5t} - e^{-(k_3+k_4)t}) \\ + n_{a0} \frac{k_2(k_3 + k_4 - k_1 - k_2) + k_1k_3}{(k_3 + k_4 - k_1 - k_2)(k_5 - k_1 - k_2)} (e^{-(k_1+k_2)t} - e^{-k_5t}) \\ + n_{b0} \frac{k_3}{k_5 - k_3 - k_4} (e^{-(k_3+k_4)t} - e^{-k_5t})$$

2-24. Some measurements of the rate of depolymerization of trioxane at 20°C in the presence of sulfuric acid as catalyst are given in the following table (Walker and Chadwick, 225):

Normality of acid	Time required for liberating indicated % of formaldehyde			
	10%	50%	75%	99%
8	12.3 hr	3.4 days	6.8 days	22.5 days
12	55 min	6.1 hr	12.2 hr	40 hr
16	4.4 min	29 min	58 min	190 min

Find the order of the reaction with respect to (a) the trioxane when using 8 *N* sulfuric acid and (b) the sulfuric acid.

2-25. Lauroyl peroxide was used as a catalyst for the polymerization of vinyl chloride at 50°C with the results shown (Bankoff and Shreve, 9). Find the order with respect to catalyst concentration, which is given as parts lauroyl peroxide per 316 parts of catalyst-free mixture.

Catalyst concentration	Time of run, hr	% conversion of monomer
0.3	3	6.0
0.6	3	12.9
1.2	3	25.5
1.5	3	33.2
0.3	5	12.2
0.6	5	24.4
0.9	5	30.1
1.2	5	50.1
1.5	5	62.4
0.113	14.7	26.4
0.150	14.7	40.6
0.200	14.7	54.7
0.267	14.7	89.0

2-26. The reaction between formaldehyde (F) and sodium paraphenolsulfonate (M) involves eight second-order reactions, namely:

No.	Reaction	k , liters/(g mole)(min)
1	$F + M \rightarrow MA$	0.16
2	$F + MA \rightarrow MDA$	0.50
3	$MA + MDA \rightarrow DDA$	0.15
4	$M + MDA \rightarrow DA$	0.14
5	$MA + MA \rightarrow DA$	0.03
6	$MA + M \rightarrow D$	0.058
7	$F + D \rightarrow DA$	0.50
8	$F + DA \rightarrow DDA$	0.50

The various symbols are identified in the original literature (Stults, Moulton, and McCarthy, 207) but are of no concern here. When the initial concentrations of F and M are each 0.1 g mole/liter and all others are zero, find the concentrations of all participants at the end of 60 min.

CHAPTER 3

ADIABATIC AND PROGRAMMED REACTIONS

19. Nonisothermal Conditions

Almost invariably, chemical reactions are accompanied by thermal effects, and the temperature tends to change as the reaction progresses. In experimental work it is desirable to maintain as nearly as possible isothermal conditions so that the tests are not complicated by the variation of the specific reaction rate with temperature. The latter effect, if desired, is determined by separate experiments carried out at several different constant temperatures. In the laboratory it is not difficult to maintain substantially isothermal conditions, because of the large amount of surface per unit volume that is associated with small equipment and because the economics of heat transfer is not important on a small scale. In large equipment, on the other hand, severe limitations exist to the attainable rates of heat transfer. Industrial reactions thus raise problems in heat transfer as well as kinetics. Sometimes, in fact, the heat-transfer aspect is so dominant that the equipment can be regarded more as a heat exchanger than as a reactor.

Adiabatic reaction is practicable when the resulting temperatures stay in a workable range, that is, when they do not drop so that the rate becomes too small or rise until the rate becomes uncontrollable. The following conditions are favorable to adiabatic operation:

1. When the heat of reaction is small
2. When it is possible to adjust the initial temperature so that the changes will not take the system out of the workable range
3. When the heat capacity of the equipment or of the solvent or of any inert materials that may be present is sufficient to moderate the temperature effect
4. When an inert material is present or can be introduced without harm and can moderate temperature changes by vaporization or condensation

For the design of nonisothermal operation, these basic data are needed:

1. The specific reaction rate as a function of temperature
2. The thermal data of the system, such as the heat capacities and sensible and latent enthalpies of all participants and inert materials present, as functions of temperature

3. The heat of reaction at some base or reference temperature
4. Heat fluxes or heat-transfer coefficients

Fundamentally, the design procedure involves first of all the making of a heat balance which relates the temperature to the degree of conversion. Since the temperature is in turn related to the specific reaction rate, this balance indirectly affords a relation between x and k . In effect, k is thus eliminated from the rate equation, which can then be integrated, numerically or graphically, in order to relate the conversion to the time.

Reactions employing heat transfer according to a definite plan are called *programmed*, or heat-regulated, reactions.

The energy balance is expressed by the first law of thermodynamics; that is,

$$\Delta H = q - w_s + \frac{\Delta u^2}{2g} + \Delta z \quad \text{for flow processes}$$

$$\Delta E = q - w \quad \text{for batch processes}$$

In processes such as those in gas turbines, where combustion continues during the passage of the fluid through the machine, the shaft work and other mechanical-energy effects must be taken into account. Such problems are treated by Penner (item C12 in Sec. 81). In most other cases of industrial interest there are no such mechanical-energy effects, so that

$$\Delta H = q \quad \text{flow process}$$

$$\Delta E = q \quad \text{batch process}$$

Gas-phase reactions are more generally conducted in flow reactors. For liquids, the difference between enthalpy and internal energy is numerically so small that an enthalpy balance is adequate even for liquid-phase reactions at constant volume. In the great bulk of industrial reactions, therefore,

$$\Delta H = q \quad \text{for most processes, sufficiently accurately}$$

This, then, is the complete energy statement for reacting systems.

20. The Adiabatic Reaction

As a basis, take the reaction $A + B \rightarrow C + D$, whose rate equation is

$$r = \frac{1}{V} \frac{dx}{dt} = \frac{k}{V^2} (n_{a0} - x)(n_{b0} - x) \quad (3-1)$$

Refer the heat of reaction ΔH_r , Btu/lb mole of A converted, and the enthalpies of all participants to some base temperature T_b . Clearly, then, the total heat of reaction $x(\Delta H_r)_{T_b}$ equals the change in enthalpy of the system, as measured by heat capacities and latent heats of phase change; or the change in chemical enthalpy equals the change in physical enthalpy.

In equation form (Fig. 3-1),

$$-(\text{Enthalpy change of reaction}) = \text{enthalpy of unconverted reactants} + \text{enthalpy of products formed} - \text{enthalpy of initial reactants}$$

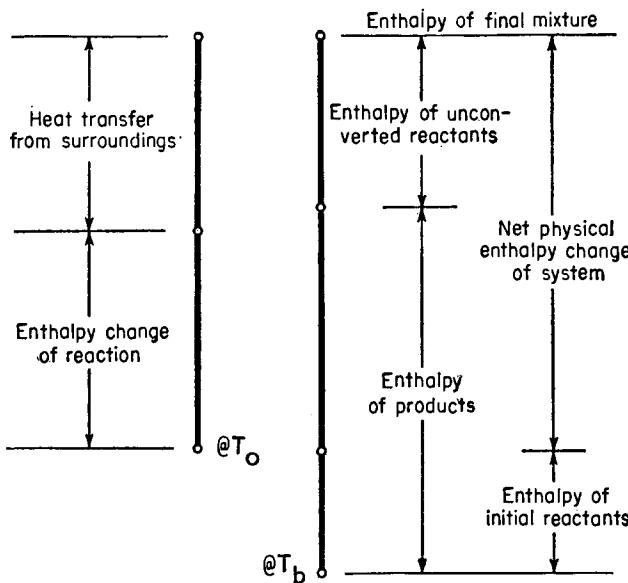


FIG. 3-1. Enthalpy balance on chemically reacting system (Eqs. 3-2 and 3-12).

Mathematically,

$$-x(\Delta H_r)_{T_b} = (n_{a0} - x)(H_a)_T + (n_{b0} - x)(H_b)_T + (n_{c0} + x)(H_c)_T + (n_{d0} + x)(H_d)_T - n_{a0}(H_a)_{T_0} - n_{b0}(H_b)_{T_0} - n_{c0}(H_c)_{T_0} - n_{d0}(H_d)_{T_0} \quad (3-2)$$

When there is no phase change, the heat balance can be written in terms of heat capacities and rearranged as follows:

$$\begin{aligned} & \int_{T_b}^{T_0} (n_{a0}s_a + n_{b0}s_b + n_{c0}s_c + n_{d0}s_d) dT \\ &= (n_{a0} - x) \int_{T_b}^T s_a dT + (n_{b0} - x) \int_{T_b}^T s_b dT \\ &+ (n_{c0} + x) \int_{T_b}^T s_c dT + (n_{d0} + x) \int_{T_b}^T s_d dT + x(\Delta H_r)_{T_b} \quad (3-3) \end{aligned}$$

Furthermore, when the capacities are constant and the initial and base temperatures are the same, $T_0 = T_b$, the heat balance simplifies to

$$[(n_{a0} - x)s_a + (n_{b0} - x)s_b + (n_{c0} + x)s_c + (n_{d0} + x)s_d](T - T_0) + x(\Delta H_r)_{T_0} = 0 \quad (3-4)$$

The plausibility of these heat balances is apparent from the last equation. For instance, say that the reaction is exothermic and consequently the

enthalpy change is negative. Then Eq. 3-4 states that the temperature will rise, which is of course intuitively correct.

Integration of the rate equation (Eq. 3-1) is conveniently done in tabular form, as follows:

T	k	x	$\frac{V}{k(n_{a0} - x)(n_{b0} - x)}$
(Assumed values)	(Data)	(Calculated from Eqs. 3-2ff.)	(Calculated)

The first two columns record experimental data, which may be in tabular or graphical form originally or in the form of the Arrhenius equation; the values of x are obtained from the heat balance; and the last column is obtained with the aid of the previously tabulated k and x at each temperature. The relation between time and conversion is obtained by integration of

$$t = \int_0^x \frac{V}{k(n_{a0} - x)(n_{b0} - x)} dx \quad (3-5)$$

Only graphical or numerical integration is usually feasible. Over limited ranges, however, a linear relation between temperature and k may sometimes hold, say, $T = a + bk$. In that case, Eq. 3-4 becomes

$$T = a + bk = T_0 - \frac{x(\Delta H_r)_{T_0}}{(n_{a0} - x)s_a + (n_{b0} - x)s_b + (n_{c0} + x)s_c + (n_{d0} + x)s_d} \quad (3-6)$$

whence

$$k = k_0 - \frac{x(\Delta H_r)_{T_0}}{b[(n_{a0} - x)s_a + (n_{b0} - x)s_b + (n_{c0} + x)s_c + (n_{d0} + x)s_d]} \quad (3-7)$$

which is of the form

$$k = \frac{\alpha + \beta x}{\gamma + \delta x} \quad (3-8)$$

Consequently, Eq. 3-5 becomes

$$t = \int_0^x \frac{\gamma + \delta x}{\alpha + \beta x} \frac{V}{(n_{a0} - x)(n_{b0} - x)} dx \quad (3-9)$$

which can be integrated by the method of partial fractions. Over a wide temperature range, however, the Arrhenius equation must be used, and in most cases the integration cannot be done analytically.

When the heat capacities vary appreciably with temperature, Eq. 3-2 or 3-3 must be used. Should phase changes occur, latent heats must be taken into account. These heat balances have not taken into account the heat capacities of the equipment, solvents, and inert materials; in general, these heat capacities cannot be neglected, so terms for them should be included in the heat balances.

Illustration 3-1. On the basis that the cracking of ethane proceeds entirely according to the simplified equation $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$, establish the relation between the degree of conversion and the temperature under adiabatic conditions, given the enthalpy data of Table 3-1 and the net heats of combustion following. Initial conditions are 1500°F and 45 psia.

Solution. The heat of reaction at 60°F is

$$\Delta H_r = -30.048(20,420) + 28.032(20,290) + 2.016(72,970) = 102,296 \text{ Btu/lb mole}$$

Heat balance with final temperature of 1475:

$$30.048(1417 - 318) = 30.048(1391 - 318)(1 - x)$$

$$+ [28.032(1199 - 305) + 2.016(5570 - 670) + 102,296]x$$

$$\text{whence } x = \frac{782}{104,990} = 0.00745$$

and similarly at other temperatures. The last column of Table 3-1 shows the conversions calculated over the entire temperature range. Note that the rapid drop in temperature, and consequently in reaction rate, makes it impractical to crack ethane under adiabatic conditions.

TABLE 3-1. DATA FOR ILLUSTRATION 3-1

Temperature, °F	Enthalpy, Btu/lb			Fractional conversion <i>x</i>
	Ethane	Ethylene	Hydrogen	
60	318	305	670	0.323
1400	1,312	1,135	5,310	0.030
1425	1,348	1,152	5,400	0.020
1450	1,365	1,178	5,490	0.015
1475	1,391	1,199	5,570	0.0075
1500	1,417	1,220	5,670	0
Heat of combustion at 60°F.....	20,420	20,290	72,970	

Illustration 3-2. The ideal-gas decomposition $A \rightarrow B + C$ takes place with initial conditions 600°R, 5 atma, and 8.75 cu ft. The enthalpy change of reaction is -2500 Btu/lb mole at 600°R, the heat capacity of A is 30, and those of B and C are each 25 Btu/(lb mole)(°R). The variation of specific rate with temperature is shown in Table 3-2. Calculate the relations between conversion and time under (a) adiabatic conditions and (b) isothermal conditions.

Solution. From the ideal-gas law,

$$n_{a0} = \frac{5(8.75)}{(0.73)(600)} = 0.1 \text{ lb mole}$$

Since the rate equation is $dx/dt = k(0.1 - x)$, under isothermal conditions the integral is

$$x = n_{a0}(1 - e^{-kt}) = 0.1(1 - e^{-1.2t})$$

Numerical values are shown in Table 3-3. With 600°R as the base temperature, the heat balance is

$$0 = [(0.1 - x)(30) + x(25 + 25)](T - 600) - 2500x$$

or $T = 600 + \frac{2500x}{3 + 20x}$

The time is obtained by graphical integration of the equation

$$t = \int_0^x \frac{dx}{k(0.1 - x)}$$

Calculations are summarized in Table 3-3.

TABLE 3-2

$T, {}^{\circ}\text{R.} \dots$	600	610	620	630	640	650	660
$k, \text{hr}^{-1} \dots$	1.20	1.68	2.33	3.28	4.61	7.20	9.41

TABLE 3-3. DATA AND RESULTS FOR ILLUSTRATION 3-2

x	T	k	$\frac{1}{k(0.1 - x)}$	Time t	
				Adiabatic	Isothermal
0	600	1.20	8.33	0	0
0.02	614.7	1.93	6.46	0.142	0.186
0.04	626.3	2.90	5.75	0.262	0.428
0.06	635.7	3.94	6.35	0.378	0.763
0.08	643.5	5.30	9.42	0.528	1.34
0.09	646.9	6.18	16.18	0.648	1.92
0.095	648.5	6.70	29.8	...	2.50
0.10	650.0	7.20	∞	∞	∞

21. Rate of Heat Input

In order to maintain adequate control of a reaction, the temperature must be held within at least moderate limits. This is accomplished by appropriate heat exchange. With industrial equipment it is not always practicable to maintain truly isothermal conditions, but adequate control at a satisfactory rate of reaction can be achieved by heat transfer together with adjustment of initial temperatures and concentrations and the use of catalysts or inhibitors.

Several ways of exchanging heat with a reacting system can be employed to approximate isothermal conditions. These are governed by the amount of heat-transfer surface available or economical, by the heat-transfer coefficient (which can be regulated within limits by factors such as the intensity of agitation), and by the complexity of the control system that is economically or otherwise feasible. Some of the possibilities are the following:

1. Heat may be exchanged with the reactor at a constant rate. Such an operation is achieved, for example, in a tubular reactor heated with

flames and hot flue gases. Here the variation in heat-transfer coefficient is small and the temperature difference is large so that changes in reactant temperature have only a small effect on the ΔT .

2. A constant heat-transfer coefficient may be obtained, and the temperature of the heat source may also remain constant. For instance, in a steam-jacketed agitated reactor, the heat-transfer coefficient is affected mostly by the degree of agitation and therefore can be maintained reasonably constant. In this case, the rate of heat input will vary as the temperature of the reactants changes.

3. The heat transfer is adjusted automatically to maintain a constant temperature by regulating the flow of heat-transfer medium or by regulating the condensing temperature of a vapor heat-transfer medium.

Figure 3-2 illustrates these three operations. Method 3 of course is the

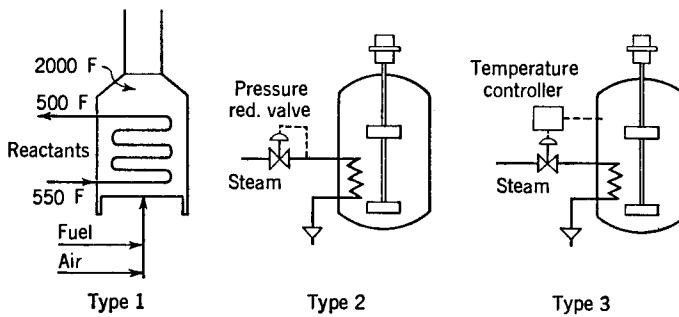


FIG. 3-2. Representative heat-transfer operations.

ideal system, but plant conditions may not permit it or the expense may not be justifiable. By either of the other two methods it is clearly not possible to maintain constant temperatures, but only a suitable range may be realizable. Typical heat-transfer and temperature behaviors are shown in Fig. 3-3. Speaking for the moment of endothermic reactions and

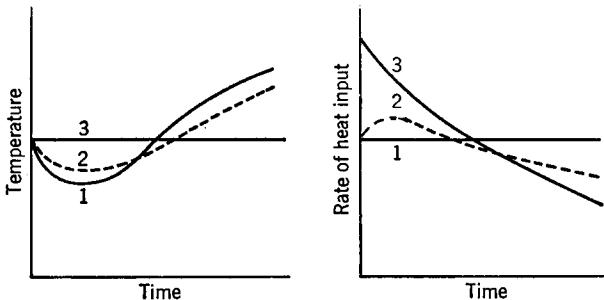


FIG. 3-3. Typical time-temperature variation for the three methods of operation of Fig. 3-2.

FIG. 3-4. Typical time versus rate of heat input for the three methods of operation of Fig. 3-2.

referring to this figure, initially the rate of reaction is high because of high reactant concentrations, and consequently the temperature will drop because the rate of heat transfer will not be sufficient to compensate for the endothermic heat of reaction. As the temperature drops, the reaction rate also falls off, until eventually the rate of heat input may exceed the heat of reaction rate. Toward the end of the process, the constant rate of heat input by method 1 will raise the temperature above the ideal isothermal value, thus compensating for the loss in reaction rate at the beginning of the process. By method 2, the rate of heat transfer increases as the reaction temperature falls because the ΔT for heat transfer increases. Accordingly, the variation in temperature is less pronounced in method 2 than in method 1.

For all methods of operation, the problem is to calculate the correct rate of heat transfer and how it may have to be adjusted during the course of reaction. The amount of heat-transfer surface and the properties of the heat-transfer medium are variables to be considered. Several cases will be treated now, taking the general reaction $A + B \rightarrow C + D$.

As in the adiabatic case, the energy balance affords the relation between temperature T and conversion x , but now involves the heat transfer as well as the heat of reaction. A differential energy balance may be made. Consider what happens in the system in the element of time dt . The reaction rate is $r = (1/V) dx/dt$ and, say, the rate of heat input is $R = dQ/dt$, which is defined as positive when heat is absorbed by the system. In time dt the conversion will be dx and the temperature change dT . Differential conversion and time are related by

$$dx = rV dt \quad (3-10)$$

The reaction heat at the initial temperature plus the heat input from the outside will raise the temperature of the products and the remaining reactants by dT . In terms of heat capacities,

$$-\Delta H_{r0} dx + R dt = \left(-\Delta H_{r0} + \frac{R}{rV} \right) dx = n_t s_t dT \quad (3-11)$$

$$= [(n_{a0} - x)s_a + (n_{b0} - x)s_b + (n_{c0} + x)s_c + (n_{d0} + x)s_d] dT \quad (3-11)$$

$$\text{or } \left(-\Delta H_{r0} + \frac{R}{rV} \right) dx = (n_{a0}s_a + n_{b0}s_b + n_{c0}s_c + n_{d0}s_d + x \Delta s) dT \quad (3-12)$$

where $\Delta s = s_c + s_d - s_a - s_b$. Since

$$r = \frac{k}{V^2} (n_{a0} - x)(n_{b0} - x) \quad (3-13)$$

upon substituting into Eq. 3-12,

$$\begin{aligned} \frac{dT}{dx} &= \frac{-\Delta H_{r0} + R/rV}{n_{a0}s_a + n_{b0}s_b + n_{c0}s_c + n_{d0}s_d + x \Delta s} \\ &= \frac{-\Delta H_{r0} + RV/[k(n_{a0} - x)(n_{b0} - x)]}{n_{a0}s_a + n_{b0}s_b + n_{c0}s_c + n_{d0}s_d + x \Delta s} \end{aligned} \quad (3-14)$$

The heat capacities and the specific reaction rate are known functions of T . Therefore, whenever R can be related to the temperature, integration can proceed. For the three methods of operation mentioned:

Method 1: $R = \text{constant}$.

Method 2: $R = UA(T_m - T)$, with both UA and T_m , the temperature of the heat-transfer medium, constant.

Method 3: $R = rV \Delta H_{r,T} = \Delta H_{r,T}(k/V)(n_{a0} - x)(n_{b0} - x) = UA(T_m - T)$.

Here the reaction temperature stays constant, but both U and T_m (principally the latter) vary as the reaction proceeds. Note that the heat of reaction $\Delta H_{r,T}$ is evaluated at the reaction temperature.

Clearly, integration is simplest in method 1. However, the problem remains of how to select the proper value of the heat-transfer rate so that the reaction will proceed satisfactorily. This may be established only by trial. In case 2, only the variables T and x occur. However, the variables in the differential equation are not separable, so an approximate method of solution is called for. Since case 3 is isothermal, there is no difficulty in integrating the rate equation, but there does exist the problem of establishing how R is to be varied as the reaction proceeds and what provisions must be made in the way of heat-transfer surface, heat-transfer-medium temperature, and possibly its flow rate.

22. Constant Rate of Heat Input

Equation 3-12 may be written

$$-\Delta H_{r0} dx + R dt = (n_{a0}s_a + n_{b0}s_b + n_{c0}s_c + n_{d0}s_d + x \Delta s) dT \quad (3-15)$$

When the heat-transfer rate is constant, this may be integrated term by term, with the result

$$-\Delta H_{r0} x + Rt = \int_{T_0}^T (n_{a0}s_a + n_{b0}s_b + n_{c0}s_c + n_{d0}s_d + x \Delta s) dT \quad (3-16)$$

The temperature integral always can be evaluated when the heat capacities are known as functions of temperature. When they are constant,

$$-\Delta H_{r0}x + Rt = (n_{a0}s_a + n_{b0}s_b + n_{c0}s_c + n_{d0}s_d + x \Delta s)(T - T_0) \quad (3-17)$$

Solving for T ,

$$T = T_0 + \frac{-\Delta H_{r0}x + Rt}{n_{a0}s_a + n_{b0}s_b + n_{c0}s_c + n_{d0}s_d + x \Delta s} \quad (3-18)$$

Note that for the exothermic reaction ΔH_{r0} is negative and R is positive when heat is added to the reactor.

In the rate equation

$$r = \frac{1}{V} \frac{dx}{dt} = \frac{k}{V^2} (n_{a0} - x)(n_{b0} - x) \quad (3-19)$$

k is a function of temperature, which is, in turn, by Eq. 3-18, a function

of t and x . For the solution, the numerical-integration method of Sec. 78 will be followed. This employs the approximate relation

$$t_{n+1} = t_{n-1} + 2h \left(\frac{dt}{dx} \right)_n \quad (3-20)$$

where $h = \Delta x$. Two successive sets of values of t and x are needed to start the solution. The initial conditions are usually known, so the value of t_1 at $x_1 = x_0 + h$ must be determined. Two methods may be used:

1. A convenient, though sometimes quite rough, method is based on the assumption that the tangent $(dt/dx)_0$ at x_0 coincides with the curve up to the point at x_1 , thereby allowing t_1 to be evaluated either graphically or numerically. This estimate can be improved, as shown in Illustration 3-3.

2. An improved value of t_1 can be obtained by use of Taylor's theorem. Thus

$$t_1 = t_0 + h \left(\frac{dt}{dx} \right)_0 + \frac{h^2}{2!} \left(\frac{d^2t}{dx^2} \right)_0 + \dots \quad (3-21)$$

The various derivatives are obtained by differentiation of the rate equation.

Once t_1 has been evaluated, the successive use of Eq. 3-18, the empirical relation between k and T for the particular reaction, and Eq. 3-19 will enable calculation of $(dt/dx)_1$. Then from Eq. 3-20, t_2 can be evaluated. This procedure is continued until the desired conversion is attained. The accuracy of the computations is governed by the length of the interval h . When greater accuracy is desirable, the improved methods in the references cited in Sec. 78 may be consulted. Though these methods are all more complex in principle, they may be less laborious because larger increments can be used for the same accuracy.

Illustration 3-3. Given the data of Illustration 3-2, find what constant rate of heat transfer will require the same reaction time for 90 per cent conversion as the isothermal operation.

Solution. The energy balance is

$$[50x + 30(0.1 - x)](T - 600) = 2,500x - Rt$$

or

$$T = 600 + \frac{2500x - Rt}{3 + 20x}$$

The rate equation is $r = k(0.1 - x)$. Integration will be carried out numerically for three trial values of R , namely, 150, 200, and 250 Btu/hr, with the interval $h = 0.01$. Over this short interval, t_1 may be evaluated from the average rate during the interval. For $x_1 = 0.01$, assume $r_1 = 0.120$, from which $t_1 = 0.0833$. Taking $R = 150$,

$$T_1 = 600 + \frac{2500(0.01) - 150(0.0833)}{3 + 20(0.01)} = 604$$

$$k_1 = 1.34 \quad (\text{from plot of data})$$

$$r_1 = 1.34(0.10 - 0.01) = 0.1206$$

With this corrected value of r_1 , the new estimate of t_1 becomes

$$t_1 = \frac{2(0.01)}{0.120 + 0.1206} = 0.0831$$

which is close enough to the previous value. Applying Taylor's theorem as a check,

$$\left(\frac{dt}{dx}\right)_0 = \frac{1}{(1.2)(0.1)} = 8.33$$

$$\left(\frac{d^2t}{dx^2}\right)_0 = \frac{1}{(1.2)(0.1)^2} = 83.3$$

$$t_1 = 0 + 0.01(8.33) + 0.00005(83.3) + \dots = 0.0875$$

This is a fairly good check.

Continuing,

$$t_2 = t_0 + 2h \left(\frac{dt}{dx}\right)_1 = 0 + 2(0.01)(1.34)(0.1 - 0.01) = 0.167$$

$$T_2 = 600 + \frac{2500(0.02) - 150(0.167)}{3 + 20(0.02)} = 607.3$$

$$k_2 = 1.50$$

$$\left(\frac{dt}{dx}\right)_2 = \frac{1}{(1.50)(0.1 - 0.02)} = 8.33$$

$$t_3 = t_1 + 2h \left(\frac{dt}{dx}\right)_2 = 0.083 + 2(0.01)(8.33) = 0.247$$

and so forth. Table 3-4 summarizes the work for the case when $R = 150$. Similar calculations are made for the other rates of heat transfer mentioned, and the results are plotted in Fig. 3-5, as time versus temperature up to 90 per cent conversion except when

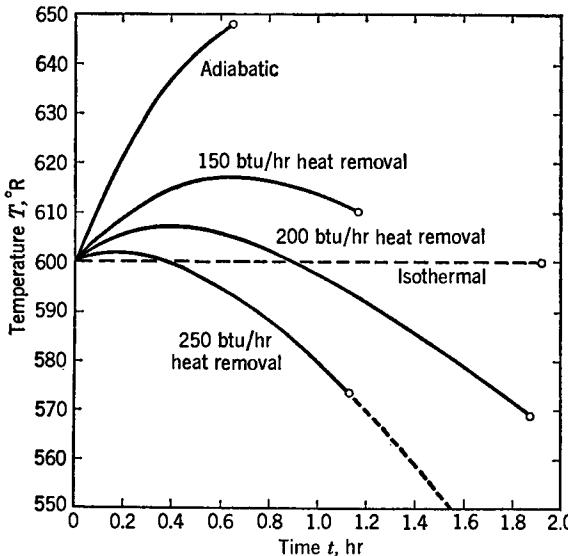


FIG. 3-5. Data and results for Illustration 3-3. Terminals of curves correspond to time required for 90 per cent conversion, except in the case of the bottom curve where the terminal corresponds to 70 per cent.

$R = 250$. In this case the calculations were discontinued at 70 per cent conversion because the rate falls off so rapidly. It appears from this work that a heating rate of 200 Btu/hr requires approximately the same reaction time for 90 per cent conversion as does isothermal operation.

TABLE 3-4. DATA FOR ILLUSTRATION 3-3

x	t	T	k	$\frac{dx}{dt}$
0	0	600	1.20	0.120
0.01	0.083	604	1.34	0.120
0.02	0.167	607.3	1.50	0.120
0.03	0.247	610.6	1.68	0.118
0.04	0.337	613.0	1.83	0.110
0.05	0.429	615.2	1.98	0.099
0.06	0.539	616.5	2.05	0.082
0.07	0.673	616.8	2.05	0.062
0.08	0.862	615.4	1.96	0.040
0.09	1.173	610.2	1.66	0.0166

23. Constant Heat-transfer Coefficient

Upon substituting the rate of heat transfer,

$$R = UA(T_m - T) \quad (3-22)$$

into Eq. 3-11, the heat balance becomes

$$-\Delta H_{r0} dx + UA(T_m - T) dt = (n_{a0}s_a + n_{b0}s_b + n_{c0}s_c + n_{d0}s_d + x \Delta s) dT \quad (3-23)$$

Integrating,

$$+\Delta H_{r0} x + (n_{a0}s_a + n_{b0}s_b + n_{c0}s_c + n_{d0}s_d + x \Delta s)(T - T_0) = \int_0^t UA(T_m - T) dt = \int_0^x \frac{UA(T_m - T)}{rV} dx = \int_0^x I dx \quad (3-24)$$

where the integrand is designated by

$$I = \frac{UA(T_m - T)}{rV} \quad (3-25)$$

In the above, the heat capacities have been assumed constant, but this restriction need not be made. When integrating with respect to temperature, x is regarded as constant since the enthalpy change is a function of the terminal conditions only.

When UA is constant, Eq. 3-24 may be solved according to this procedure:

1. Choose uniform increments, $h = \Delta x$.
2. Evaluate the integrand I_0 from Eq. 3-25, using x_0 and T_0 .

3. For x_1 , assume a value of T_1 , look up the value of k_1 , and calculate I_1 .
 4. The integral may be evaluated by the trapezoidal rule (Sec. 77):

$$\int_{x_0}^{x_1} I \, dx = \frac{I_0 + I_1}{2} h$$

If this satisfies Eq. 3-24, the correct value of T_1 had been assumed. Otherwise, try another one.

5. Once T_1 has been established, proceed similarly for T_2 at x_2 , and so on. With three points available, integration may be carried out with the more accurate Simpson's rule (Sec. 77):

$$\int_{x_0}^{x_2} I \, dx = \frac{h}{3} (I_0 + 4I_1 + I_2)$$

In this way, the relation between T , k , and x is established. Then by integration of

$$t = \int_0^x \frac{V}{k(n_{a0} - x)(n_{b0} - x)} \, dx \quad (3-26)$$

time may be related to these variables.

Ordinarily, what is sought is the amount of heat-transfer surface needed to keep the reaction temperature within appropriate limits. This can be established only by trial. An approximation to the needed surface may be made first by estimating, on the assumption of an isothermal process, the time required for the desired conversion, and hence the average rate of heat evolution or absorption. With the surface A calculated from this heat-transfer rate, integration of Eq. 3-24 may proceed as described. If need be, another estimate of A can be made and the solution repeated. Figure 3-6 shows schematically the effect of surface on the time-temperature curve.

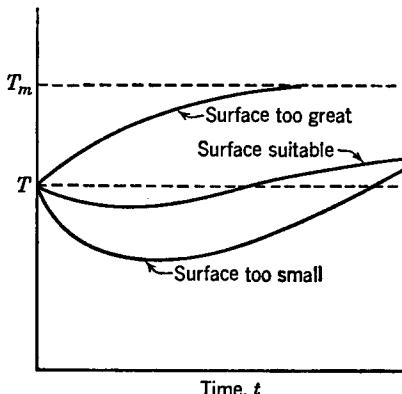


FIG. 3-6. Typical effect of amount of heat-transfer surface on reaction temperature. T_m is temperature of heat-transfer medium.

Illustration 3-4. The reaction of Illustration 3-2 is to be controlled within the range 590 to 610°F up to 90 per cent conversion. Cooling water is available in such large quantities that its temperature remains substantially constant at 80°F. The heat-transfer coefficient is 3 Btu/(hr)(sq ft)(°F). Find the amount of surface needed.

Solution. A preliminary estimate may be made from isothermal operation:

$$t = \frac{1}{1.2} \ln \frac{0.1}{0.1 - 0.09} = 1.92 \text{ hr}$$

$$A = \frac{Q}{tU \Delta T} = \frac{0.09(2,500)}{1.92(3)(600 - 540)} = 0.65 \text{ sq ft}$$

Use $A = 1$ sq ft for the nonisothermal operation. Proceeding,

$$n_{a0}s_a + x \Delta s = 0.1(30) + 20x = 3 + 20x$$

Equation 3-24 becomes

$$2,500x - (3 + 20x)(T - 600) = \int_0^x \frac{3(T - 540)}{k(0.1 - x)} dx$$

$$\text{When } x = 0, T_0 = 600, I_0 = \frac{3(600 - 540)}{1.2(0.1)} = 1,500.$$

$$\text{When } x_1 = 0.01, \text{ try } T_1 = 603 \text{ and } I_1 = \frac{3(603 - 540)}{1.32(0.09)} = 1,590. \text{ Checking,}$$

$$2,500(0.01) - [3 + 20(0.01)](603 - 600) \stackrel{?}{=} \frac{0.01}{2} (1,500 + 1,590)$$

$$15.4 \neq 15.45$$

$$\text{Try } T_1 = 602.5, I_1 = \frac{3(602.5 - 540)}{1.30(0.09)} = 1,600:$$

$$2,500(0.01) - 3.2(602.5 - 600) \stackrel{?}{=} \frac{0.01}{2} (1,500 + 1,600)$$

$$17.0 \neq 15.5$$

Interpolating, $T_1 = 602.9, I_1 = 1,591$.

$$\text{When } x_2 = 0.02, \text{ try } T_2 = 605, I_2 = \frac{3(65)}{(1.41)(0.08)} = 1,730.$$

$$2,500(0.02) - 3.4(605 - 600) \stackrel{?}{=} \frac{0.01}{3} [1,500 + 4(1,591) + 1,730]$$

$$33 \neq 31.98$$

$$\text{Try } T_2 = 605.3, I_2 = \frac{3(65.3)}{(1.43)(0.08)} = 1,720.$$

$$2,500(0.02) - 3.4(5.3) \stackrel{?}{=} \frac{0.01}{3} [1,500 + 4(1,591) + 1,720]$$

$$32.0 \simeq 31.95 \quad \text{Check}$$

The calculations up to 90 per cent conversion are summarized in Table 3-5. Simpson's rule was employed to evaluate the time t from the equation

$$t = \int_0^x \frac{dx}{k(0.1 - x)}$$

At about 85 per cent conversion, the temperature is somewhat below that specified as the lower limit. The calculations could be repeated with a slightly smaller heat-transfer surface.

TABLE 3-5. DATA FOR ILLUSTRATION 3-4

x	T	k	I	\int_0^x	$\frac{1}{k(0.1 - x)}$	t
0	600	1.20	1,500		8.33	0
0.01	602.9	1.30	1,591	15.4	8.55	0.084
0.02	605.3	1.43	1,720	32.0	8.75	0.171
0.03	607.0	1.51	1,900	49.9	9.45	0.177
0.04	607.9	1.56	2,180	70.1	10.68	0.191
0.05	608.0	1.56	2,620	93.0	12.80	0.217
0.06	606.4	1.48	3,360	123.5	16.88	0.263
0.07	602.9	1.30	4,760	162.4	25.20	0.352
0.08	594.8	1.03	7,980	224.8	48.50	0.554
0.09	570.0	0.57	15,800	370.7	175.5	1.316

24. Rate of Heat Transfer to Isothermal Systems

When the rate of heat transfer is sufficient to maintain isothermal conditions, it is equal at any moment to the rate at which heat of reaction is occurring; that is,

$$R = UA(T_m - T) = rV \Delta H_r = \frac{k}{V} (n_{a0} - x)(n_{b0} - x) \Delta H_r T \quad (3-27)$$

for the reaction $A + B \rightarrow C + D$.

With a specified amount of heat-transfer surface, control of reaction temperature is achieved primarily by varying the temperature of the heat-transfer medium, by changing its rate of flow or its condensing or vaporizing pressure. When the temperature of the medium is restricted within specified limits, the required amount of surface may be calculated from Eq. 3-27.

Illustration 3-5. Given the following data for a first-order reaction, find the amount of surface needed to hold the temperature constant at 120°F, for conversion up to 70 per cent. Heating is with steam whose temperature may range from 350 to 230°F.

$$\Delta H_r = 5000 \text{ Btu/lb mole}$$

$$k = 80 \text{ hr}^{-1}$$

$$n_{a0} = 5 \text{ lb moles}$$

$$U = 90 \text{ Btu/(hr)(sq ft)(°F)}$$

Solution. The rate of heat transfer is greatest at the beginning, when the reaction rate is greatest. Consequently, the minimum surface needed at this time is

$$A = \frac{k(n_{a0} - x) \Delta H_r}{U(T_m - T)} = \frac{80(5 - 0)(5,000)}{90(350 - 120)} = 96.5 \text{ sq ft}$$

With this surface, at 70 per cent conversion,

$$T_m = 120 + \frac{80(5 - 3.5)(5,000)}{(90)(96.5)} = 189^\circ\text{F}$$

which is lower than attainable with the steam of this illustration. The conversion corresponding to the lowest attainable temperature, 230°F, is

$$x = 5 - \frac{90(96.5)(230 - 120)}{80(5,000)} = 2.61 \text{ lb moles}$$

With 230°F, at 70 per cent conversion,

$$A = \frac{80(5 - 3.5)(5,000)}{90(230 - 120)} = 60.6 \text{ sq ft}$$

and when $x = 2.61$, with this area,

$$T_m = 120 + \frac{80(5 - 2.61)(5,000)}{90(60.6)} = 295^\circ\text{F}$$

Therefore it appears that the heating coil must be constructed in two portions, one of 60.6 sq ft and the other of $96.5 - 60.6 = 35.9$ sq ft. When the temperature of the me-

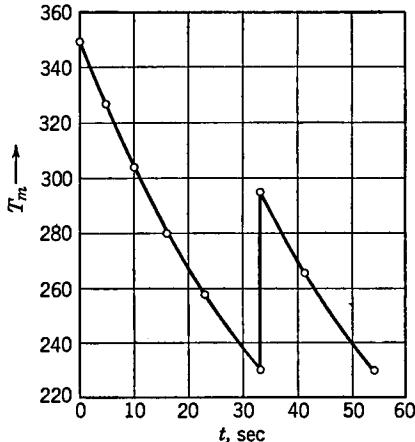


FIG. 3-7. Data for Illustration 3-5.

dium drops to 230°F, the smaller coil must be shut off. Figure 3-7 shows the time-temperature profile calculated from the equations

$$t = 45 \ln \frac{5}{5-x}$$

$$\begin{aligned} T_m &= 120 + 46(5-x) && \text{when } x < 2.61 \\ T_m &= 120 + 73.2(5-x) && \text{when } x > 2.61 \end{aligned}$$

Illustration 3-6. A reaction is conducted isothermally at 180°F in a jacketed batch reactor. The rate equation is

$$r = -\frac{dC}{dt} = 40C^2 \quad \text{lb moles/(hr)(gal)}$$

Temperature is controlled by regulating the rate of water supply which enters at 90°F. Other data are:

$$\Delta H_r = -5000 \text{ Btu/lb mole at } 180^\circ\text{F}$$

$$V = 100 \text{ gal}$$

$$U = 80 \text{ Btu/(hr)(sq ft)}(^\circ\text{F})$$

$$A = 125 \text{ sq ft}$$

$$C_0 = 0.2 \text{ lb mole/gal}$$

It is sufficiently accurate to take the logarithmic mean-temperature difference. Establish the exit-water temperature and flow rate as functions of the concentration and the time.

Solution. The rate of heat evolution by reaction equals the rate of heat pickup by the water and also the rate of heat transfer. Thus

$$\begin{aligned} \phi &= Vr \Delta H_r = V k C^2 \Delta H_r = 100(40)(5,000)C^2 = 20(10^6)C^2 \\ &= w(T_2 - T_1) = w(T_2 - 90) \\ &= UA \Delta T = \frac{80(125)(T_2 - 90)}{\ln [90/(180 - T_2)]} \end{aligned}$$

TABLE 3-6. RESULTS FOR ILLUSTRATION 3-6

T_2	$\phi/1,000$	w	C	t
110	797	39,900	0.1998	0.0045
120	740	24,600	0.1923	0.180
130	680	17,000	0.1844	0.380
140	617	12,350	0.1757	0.622
150	545	9,080	0.1651	0.951
160	466	6,660	0.1525	1.40
170	364	4,550	0.1350	2.17
175	294	3,460	0.1212	2.93
177	256	2,940	0.1130	3.46
179	198	2,220	0.0995	4.55
179.9	132	1,470	0.0813	6.57
179.99	99	1,100	0.0703	8.31

These equations are solved by assuming values of T_2 and then calculating corresponding values of ϕ , w , C , and t . The solution equations are

$$w = \frac{\phi}{T_2 - 90} \text{ lb/hr water rate}$$

Results are summarized in Table 3-6.

PROBLEMS

3-1. A spent catalyst is contaminated with 2 wt % of carbon which is to be burned off in a reactivating operation. Operating pressure is 50 psig. The catalyst enters the reactivator at 900°F. A 25 per cent excess of air is used, entering at 100°F. Heat capacity of the catalyst is 0.2, and that of the gas is 0.28 Btu/(lb)(°F) on an average. In order to maintain operating temperature below 1200°F, liquid water at 100°F is injected into the burning zone. How much water must be injected, pounds per 100 lb of reactivated catalyst?

3-2. In Illustration 3-2, if the initial temperature is 625°R and adiabatic conditions prevail, find the time for attaining 90 per cent conversion.

3-3. The following data hold for the gas-phase reaction $A + B \rightarrow C$, which takes place adiabatically at a constant pressure of 2 atm:

$$\begin{aligned}
 T_0 &= 560^{\circ}\text{R} \\
 n_{a0} &= n_{b0} = 1 \text{ lb mole} \\
 n_{c0} &= 0 \\
 s_a &= s_b = 30 \text{ Btu/(lb mole)}(^{\circ}\text{F}) \\
 s_c &= 40 \text{ Btu/(lb mole)}(^{\circ}\text{F}) \\
 \Delta H_r &= -5000 \text{ Btu/lb mole at } 600^{\circ}\text{R} \\
 k &= 4.4 + 0.08(T - 600) \quad \text{cuft/(1bmol)} \text{ (hr)}
 \end{aligned}$$

When the temperature has risen 50°F, what will be the percentage conversion, and how long will it take to attain this conversion?

3-4. The reaction $2A \rightarrow B$ takes place under adiabatic, constant-volume conditions. Make a plot of time against pound moles of A converted up to 70 per cent, starting at 600°R , given these data:

$$\begin{aligned}
 n_{a0} &= 2 \text{ lb moles} \\
 n_{b0} &= 0 \\
 s_a &= 20 \text{ Btu/(lb mole)(}^{\circ}\text{F)} \\
 s_b &= 30 \text{ Btu/(lb mole)(}^{\circ}\text{F)} \\
 \Delta H_r &= -2000 \text{ Btu/lb mole of } A \text{ reacted, at } 600^{\circ}\text{R}
 \end{aligned}$$

3-5. An endothermic reaction proceeds in accordance with the equation $A + B \rightarrow C$. The heat of reaction at 500°F is 4000 Btu/lb mole; inlet temperature is 800°F; the charge is 50 lb moles. The vessel is made of steel and weighs 1,200 lb. Other data are:

Material	Mole % in the feed	Heat capacity, Btu/(lb mole)(°F)
<i>A</i>	40	10
<i>B</i>	40	8
<i>C</i>	10	12
Inerts	10	6

Find the temperature of the system as a function of the conversion.

3-6. Given the following data for the reaction $A + B \rightarrow C$, taking place at constant volume and 120°F:

$$\Delta H_r = 5000 \text{ Btu/lb mole}$$

$$n_{a0} = n_{b0} = 5 \text{ lb moles}$$

$$V = 10 \text{ cu ft}$$

$$\Delta s = 0 \text{ Btu/(lb mole)(°F)}$$

$$U = 90 \text{ Btu/(hr)(sq ft)(°F)}$$

In a separate test at a constant temperature of 120°F, 90 per cent conversion was attained in 1.5 hr. Maximum temperature of heat medium is $T_m = 350°F$.

(a) Find the minimum surface needed to maintain isothermal conditions up to 75 per cent conversion and make a plot of T_m against time.

(b) When the lowest usable temperature of the heating medium is 230°F, again establish T_m as a function of time and determine how the amount of surface must be adjusted stepwise during the course of the reaction.

3-7. Direct combination of nitrogen and oxygen occurs at elevated temperatures. In one commercial process (Ermenc, 63) reaction is conducted at about 4000°F until equilibrium is attained; then the gases are chilled quickly to retard reversal. The reaction is second-order in both directions with the rate equation

$$r = \frac{dp_{NO}}{dt} = k \left(p_{N_2} p_{O_2} - \frac{p_{NO}^2}{K} \right)$$

The equilibrium constant K is tabulated following. The specific reaction rate is represented by the equation

$$\log \frac{k}{3} = \frac{T - 3800}{300}$$

where T is in degrees Fahrenheit and k is in reciprocal atmosphere-seconds.

For a rate of cooling of 30,000°F/sec, starting at 4040°F, make a plot of mole fraction of NO present versus time and temperature. Assume that the air consists of 79 mole % nitrogen and the balance oxygen and that the operating pressure is atmospheric. *Suggestion:* Take increments of 0.001 sec and integrate numerically.

$$^{\circ}F \quad K = (p_{NO})/(p_{N_2})^{1/2}(p_{O_2})^{1/2}$$

1700	0.000526
2060	0.001918
2420	0.005078
2780	0.010816
3140	0.019815
3500	0.032513
3860	0.049120
4040	0.058880

CHAPTER 4

CONTINUOUS STIRRED REACTORS

25. Types of Flow Processes

Reactions are often conducted in such a manner that some or all of the participants are in flow during the process. When the reaction time is comparatively short, when the production rate is high, when the reactants are gaseous, when high concentrations lead to poor control or undesirable product distribution—these are possible reasons for adopting a flow process. Most such processes are operated in the steady state—though transient conditions must be considered during start-up and shutdown—and are usually conducted on a much larger scale than batch reactors. Some types of flow reactors are shown in Figs. 4-1 and 4-2. Typical concentration curves are shown in Fig. 4-3; note the differences in abscissas on these plots.

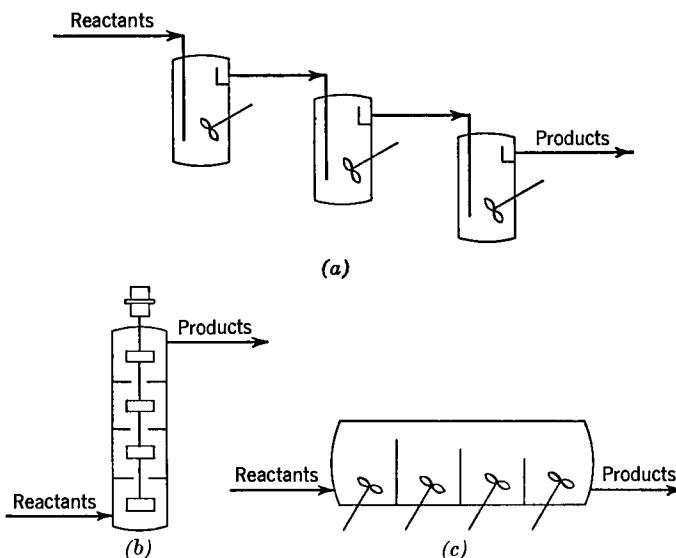


FIG. 4-1. Types of staged reactors. (a) Reactor battery; (b) vertically staged; (c) compartmented.

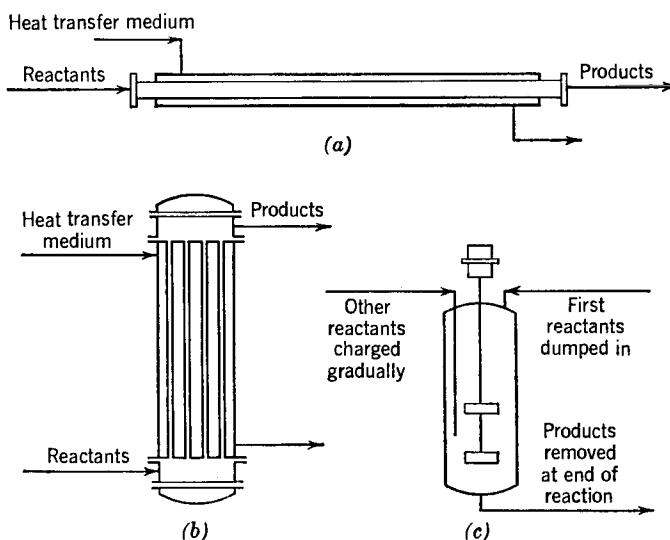


FIG. 4-2. Other types of flow reactors. (a) Tubular flow (jacketed); (b) multitubular flow; (c) semibatch or semiflow process.

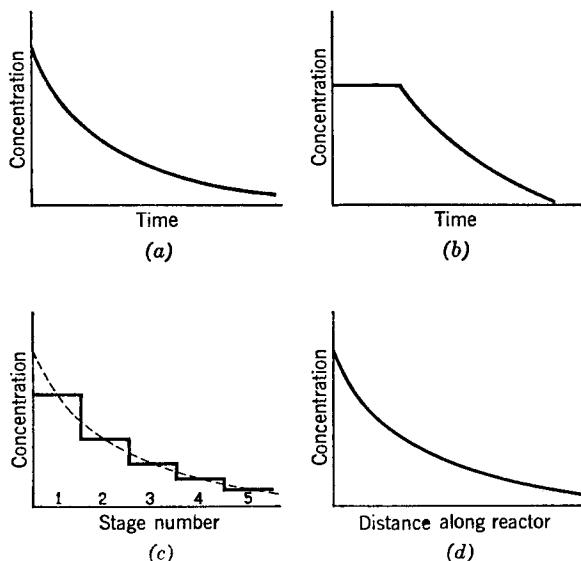


FIG. 4-3. Progression of concentration in reactors. (a) Batch; (b) semibatch or semi-flow; (c) staged; (d) tubular flow.

Continuous stirred-tank reactors are frequently employed in multiple and in series. Reactants are fed continuously to the first tank, from which they overflow through the other reactors in succession, all the while being thoroughly mixed in each tank. An attempt is made to attain uniform compositions within individual reactors. In the system as a whole, a stepped concentration gradient exists. Instead of being in several vessels, the several stages of a continuous stirred-tank reactor (CSTR) battery may be in a single vessel. If horizontal, the multistage reactor is compartmented with vertical weirs at different heights, over which the reacting mixture cascades. When the reactants are of limited miscibility and have a sufficient density difference, the vertical reactor lends itself to counter-current operation, a fact of considerable importance with reversible reactions. In a large fluidized-bed reactor, the fluid and solid phases are of substantially uniform composition, so this type of unit may be regarded as a stirred reactor. Pilot-plant-size fluidized-bed units in which the bed height is several times its diameter also exhibit substantially uniform solids composition, but generally have very little backmixing of the fluid phase, thus exhibiting plug flow (Sec. 59).

Tubular-flow reactors are characterized by a continuous concentration gradient in the direction of flow, in contrast to the stepped-gradient characteristic of the CSTR battery, and are made of one or several pipes or tubes in parallel. The reactants are charged continuously at one end, and the products are removed at the other. Normally, a steady state exists, a fact of considerable value to automatic control and to experimental work. Either horizontal or vertical orientation is common. When heat transfer is required, a jacketed tube or a construction like that of a shell-and-tube heat exchanger is utilized. In the latter case the reactants may be on either the tube or shell side. The reactant side may be filled with solid particles, either catalytic, if required, or inert to improve heat transfer by increased turbulence or to improve interphase contact in heterogeneous reactions.

Semiflow or semibatch or batch-flow operations usually employ a single stirred tank. Some of the reactants are loaded into the reactor as a single charge, and the remaining ones are then fed in gradually. This method of operation is especially favored when large heat effects occur, since exothermic reactions may be slowed down or endothermic rates maintained by limiting the concentration of one of the reactants, and the reaction thus may be kept within controllable limits with heat transfer. Other situations making this sort of operation desirable occur when high concentrations may result in the formation of undesirable side products, or when one of the reactants is a gas of limited solubility so that it may be fed only at the dissolution rate.

Relative advantages and fields of application of stirred and tubular

reactors may be indicated briefly. A reaction battery is a highly flexible system, though perhaps more expensive and more complicated both mechanically and operationally than the tubular reactor. Relatively slow reactions are best conducted in a reaction battery, which is usually cheaper than a single reactor for moderate production rates. The tubular reactor is especially well adapted to cases where considerable heat transfer is needed, where high pressures and very high or very low temperatures occur, and when relatively short reaction times suffice. Exceptions always occur. Thus the relatively slow reaction between monochlorobenzene and caustic soda resulting in the formation ultimately of phenol is conducted in a single pipe more than a mile long, in one known plant.

A word of caution: In modern industry with its great emphasis on mass production, the continuous process is highly favored. Because the continuous process is modern, because it lends itself easily to automatic control, and because it involves interesting design calculations, it possesses such a fascination for chemical engineers that the economic superiority of batch operations in some instances may be overlooked. A careful evaluation of both schemes must always be made.

26. Material Balance in Flow Problems

In flow situations, the law of the conservation of matter may be stated simply:

$$\text{Input} + \text{Source} = \text{Output} + \text{Sink} + \text{Accumulation}$$

As applied to chemically reacting systems in flow, this law is formulated in terms of differential quantities and results in a differential equation, with concentration, time, and position as variables. When the steady state exists, at any point in the apparatus the concentration is independent of time; then only two variables are of concern, that is, concentration and either time or position. The transient state requires partial differential equations for its description.

As a basis for setting up the material-balance equations, a differential unit of time, dt , may be taken. What happens to each of the terms in the conservation law during this time interval is then expressed in mathematical terms. Representative examples of this procedure may be given.

Illustration 4-1. A vessel contains V_0 gal of a solution of concentration C_0 . Another solution of concentration C_1 flows into this vessel at a rate R_1 and solution overflows at a rate R_2 . The vessel is well stirred, so that the concentration is uniform and that of the overflow is the same as that in the tank. The solute undergoes a chemical reaction according to the rate equation $r = kC^n$.

In element of time dt the several terms in the material balance become

$$\text{Input} = C_1 R_1 dt \quad (A)$$

$$\text{Output} = CR_2 dt + rV dt = (CR_2 + kVC^n) dt \quad (B)$$

$$\text{Accumulation} = d(CV) = [V_0 + (R_1 - R_2)t] dC + C(R_1 - R_2) dt \quad (C)$$

Hence

$$C_1 R_1 dt = (CR_2 + kVC^n) dt + [V_0 + (R_1 - R_2)t] dC + C(R_1 - R_2) dt \quad (D)$$

Rearranging,

$$\frac{dC}{dt} + \frac{R_1}{V_0 + (R_1 - R_2)t} C - \frac{R_1 C_1}{V_0 + (R_1 - R_2)t} = -kC^n \quad (E)$$

Though not a case of much practical value, when $C_1 = 0$, Eq. E reduces to a Bernoulli type; upon substitution of $z = C^{1-n}$, it is transformed to

$$\frac{dz}{dt} + \frac{R_1(1-n)z}{V_0 + (R_1 - R_2)t} = (1-n)k \quad (F)$$

which is linear with constant coefficients and easily integrated. Another readily integrable form occurs when the reaction is of the first order and $R_1 = R_2$. Thus

$$\ln \frac{C_1 R - (R + kV_0)C_0}{C_1 R - (R + kV_0)C} = \frac{R + kV_0}{V_0} t \quad (G)$$

Illustration 4-2. A reacting mixture is flowing through a pipe of cross section A at a constant velocity u . By reason of the concentration gradient there is also present diffusion of the reactant in the axial direction, in accordance with Fick's law:

$$\text{Rate} = -DA \frac{dC}{dL} \quad (A)$$

Over an element of length dL in time dt , under steady-state conditions,

$$\text{Input} = uAC dt - DA \frac{dC}{dL} dt \quad (B)$$

$$\text{Output} = uA(C + dC) dt - DA \left[\frac{dC}{dL} + d \left(\frac{dC}{dL} \right) \right] dt \quad (C)$$

$$\text{Sink} = -kC^n dV dt = -kC^n A dL dt \quad (D)$$

$$\text{Hence} \quad u dC - D d \left(\frac{dC}{dL} \right) - kC^n dL = 0 \quad (E)$$

$$\text{or} \quad D \frac{d^2C}{dL^2} - u \frac{dC}{dL} + kC^n = 0 \quad (F)$$

If $n = 1$, the resulting second-order linear differential equation with constant coefficients has the solution

$$C = Ae^{-m_1 L} + Be^{-m_2 L} \quad (G)$$

where m_1 and m_2 = roots of auxiliary equation

$$Dm^2 - um + k = 0 \quad (H)$$

A and B = integration constants which can be evaluated from initial conditions

27. Stirred Reactor Batteries; Graphical Method

The effectiveness of a reactor battery depends on the number of stages, the sizes of the individual stages, and the thoroughness of the mixing. When the mixing is perfect, the concentration is uniform throughout the stage and the effluent concentration is the same as that in the stage; this is called a theoretical, or ideal, stage. The ideal can only be approached, the closeness depending on economics and the peculiarities of individual systems. A certain amount of short circuiting always takes place, with

reduced residence time for that portion of material. Though other portions reside longer than the mean, on an average the effluent conversion is less than ideal. The ratio of the concentration difference between entering and leaving streams under actual conditions to that with complete mixing is defined as the stage efficiency. Reasonably well stirred reactors have efficiencies from 60 to 90 per cent; however, no generalized correlations in terms of operating variables have been made of this important quantity.

For the most part, the discussion here will be confined to theoretical stages. The number of these needed for a given separation may be calculated by several methods, of which a graphical method and an algebraic one of wider applicability will be described. Initially, only steady-state operation is considered. In liquid systems to which reactor batteries are primarily restricted, density changes due to reaction or thermal effects are small, so that the volumetric rate of flow between stages becomes substantially uniform when the steady state is attained. Corrections may be applied readily to other cases.

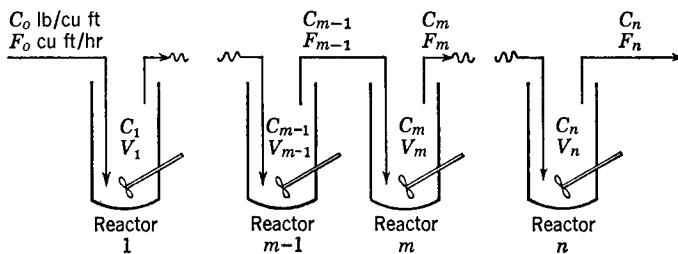


FIG. 4-4. Battery of n stages.

Referring to Fig. 4-4, the material balance on the m th reactor is

$$F_{m-1}C_{m-1} = (F_mC_m + r_mV_m) + \frac{dC_mV_m}{dt} \quad (4-1)$$

or

Input rate = output rate + accumulation rate

where F = volumetric rate of flow

V = volume of stage

In the steady state, the volume of material in each stage becomes constant and the rate of accumulation becomes zero; that is,

$$\frac{dC_mV_m}{dt} = 0 \quad (4-2)$$

Assuming uniform overflow F ,

$$r_m = -\frac{F}{V_m}C_m + \frac{F}{V_m}C_{m-1} \quad (4-3)$$

Often the rate of reaction can be expressed as a function of the concentration of one of the reactants alone; that is,

$$r = kf(C) \quad (4-4)$$

or in any particular stage,

$$r_m = kf(C_m) \quad (4-5)$$

For a given inlet concentration to a particular stage, simultaneous solution of Eqs. 4-3 and 4-5 will evaluate the concentration in that stage.

Before going on to this solution, however, it will be instructive to derive Eq. 4-3 in another way. Since the reaction rate in vessel m is constant, it may be written as the ratio of finite increments of concentration and time. Observe the progress of a slug of liquid entering stage m . On an average its residence time θ_m is equal to the ratio of the tank holdup and the volumetric flow rate:

$$\theta_m = \frac{V_m}{F_{m-1}} \quad (4-6)$$

During this time the concentration of the slug changes from C_{m-1} to C_m . Therefore the rate of reaction is

$$r_m = -\frac{\Delta C}{\Delta t} = -\frac{C_m - C_{m-1}}{V_m/F_{m-1}} = \frac{C_{m-1} - C_m}{\theta_m} \quad (4-7)$$

which is the same as Eq. 4-3.

A graphical method of solution has been devised (Jones, 116). Rearranging Eq. 4-7,

$$r_m = -\frac{C_m}{\theta_m} + \frac{C_{m-1}}{\theta_m} \quad (4-8)$$

For a given inlet concentration C_{m-1} this equation is a linear relation between the effluent concentration and the rate. The straight line cuts the abscissa at C_{m-1} and has a slope of $-1/\theta_m$. However, not all the sets of values of r_m and C_m given by this equation are pertinent, but only those also consistent with the rate equation 4-5. Thus the intersection of this straight line with the plot of rate against concentration determines C_m . Figure 4-5 illustrates the method. Once C_m has been determined, the subscripts in Eq. 4-8 are advanced by 1 and the graphical solution repeated to determine the effluent concentration C_{m+1} of the next stage. Most conveniently, the procedure begins with one of the terminal concentrations, either inlet or outlet to the battery, and continues until the other terminal is reached. When the sizes of the stages are all the same, the residence times also will be equal and the straight lines represented by Eq. 4-8 will be parallel. In case the number of stages and the terminal concentrations are specified, a solution by trial is needed for the residence time; various slopes of the straight lines are assumed until one is found that fits the requirements.

This method is applicable only to cases where the rate of reaction is expressible as a function of a single variable (Eq. 4-5). For complex reactions, the algebraic method described next is suitable.

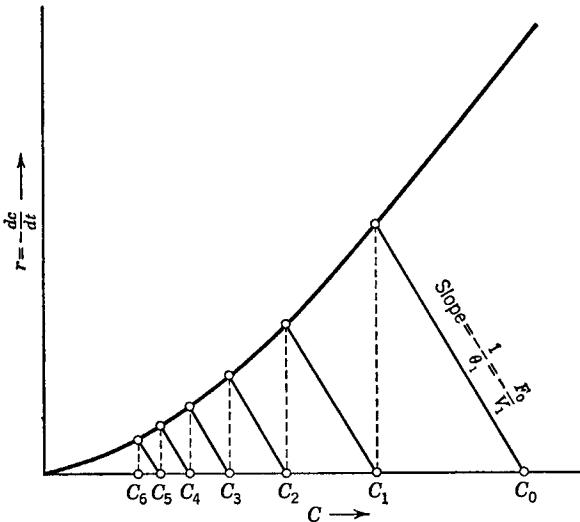


FIG. 4-5. Construction for reaction battery of six stages with equal residence times.

Illustration 4-3. The reaction $2A \rightleftharpoons C + D$ is to be conducted in a continuous stirred reactor battery at a flow rate of 100 cfh. Initially the concentration of A is 1.5 lb moles/cu ft and those of C and D are zero. The specific reaction rate in the forward direction is $10 \text{ cu ft}/(\text{lb mole})(\text{hr})$, and the thermodynamic equilibrium constant is $K_c = 16.0$. It is desired to attain 80 per cent of equilibrium conversion.

- (a) What size vessel is needed if only one is used?
 (b) If vessels are limited to one-tenth the capacity of the one calculated in part *a*, how many such vessels are needed when operated in series?

Solution. Let x_e be the equilibrium amount formed of C or D . Then

$$K_c = \frac{x_e^2}{(1.5 - 2x_e)^2} = 16$$

whence $x_e = 0.667$. Accordingly,

$$x_2 = 0.8(0.667) = 0.533$$

$$C_{a2} = 1.5 - 2(0.533) = 0.433$$

The rate equation is

$$-\frac{dC_a}{dt} = k \left(C_a^2 - \frac{C_a C_d}{K_c} \right) = 10 \left[(1.5 - 2x)^2 - \frac{x^2}{16} \right]$$

Corresponding values of $C_a = 1.5 - 2x$ and $-dC_a/dt$ are plotted in Fig. 4-6a and b upon calculation from the last equation.

For a single stage,

$$r = 10 \left\{ [1.5 - 2(0.533)]^2 - \frac{(0.533)^2}{16} \right\} = 1.70$$

$$= \frac{\Delta C}{\Delta t} = \frac{\Delta C}{V_r/F} = \frac{100(1.5 - 0.433)}{V_r}$$

whence

$$V_r = 62.7 \text{ cu ft}$$

With V_r for each vessel only one-tenth this size, or 6.27 cu ft, the slope of the material balance line in Fig. 4-6b is

$$\text{Slope} = -\frac{1}{\theta} = -\frac{F}{V_r} = -\frac{100}{6.27} = -15.9$$

From Fig. 4-6b,

$$\text{At three stages: } C_{a3} = 0.52$$

$$\text{At four stages: } C_{a4} = 0.42$$

Interpolating to $C_a = 0.433$,

$$\text{Stages} = 3 + \frac{0.52 - 0.433}{0.52 - 0.42} = 3.9$$

As an alternative to the above algebraic calculation of the single-stage vessel size, Fig. 4-6a shows the graphical construction, from which

$$\text{Slope} = -1.60$$

$$\text{and } V_r = -\frac{F}{\text{slope}} = \frac{100}{1.60} = 62.5 \text{ cu ft}$$

which is a close check.

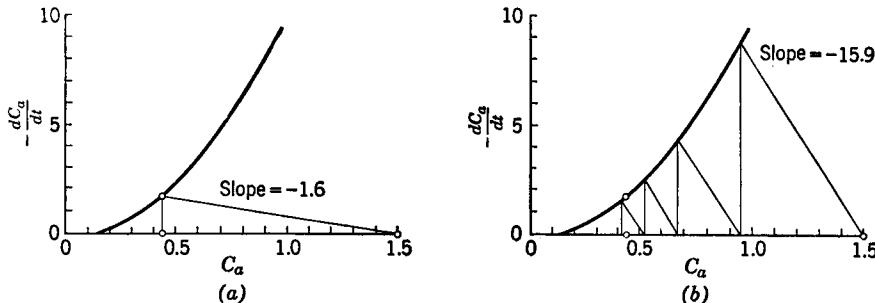


FIG. 4-6. Construction for (a) single-stage reactor, (b) multistage reactor (Illustration 4-3).

28. Algebraic Method

Generally speaking, algebraic methods are capable of greater accuracy than graphical ones, particularly in situations like the present, where a graphical or numerical differentiation with all its inaccuracies must precede the graphical reactor calculation itself. On the other hand, algebraic methods require the specific reaction rate to have been determined whereas the graphical can use the raw data. When both are usable, the choice of method is largely one of personal preference.

Equation 4-8 may be written

$$C_m + r_m \theta_m = C_{m-1} \quad (4-9)$$

By algebraic iteration, this equation may be solved for particular rate equations. For instance, take the first-order rate equation $r = kC$. Then

$$C_m + k\theta_m C_m = C_m(1 + k\theta_m) = C_{m-1} \quad (4-10)$$

or
$$C_m = \frac{C_{m-1}}{1 + k\theta_m} \quad (4-11)$$

Specifically,

$$C_1 = \frac{C_0}{1 + k\theta_1} \quad (4-12)$$

$$C_2 = \frac{C_1}{1 + k\theta_2} = \frac{C_0}{(1 + k\theta_1)(1 + k\theta_2)} \quad (4-12a)$$

and so forth. When holdup times are equal in all vessels,

$$C_m = \frac{C_0}{(1 + k\theta)^m} \quad (4-13)$$

For other than first-order rate equations, an explicit expression for C_m in terms of C_0 is quite complicated, but numerical calculations are not difficult to make for practicable numbers of stages. Take, for instance, the rate equation $r = kC^2$. Then

$$C_m + kC_m^2\theta_m = C_{m-1} \quad (4-14)$$

or
$$C_m = \frac{-1 + \sqrt{1 + 4k\theta_m C_{m-1}}}{2k\theta_m} \quad (4-15)$$

Therefore

$$C_1 = \frac{-1 + \sqrt{1 + 4k\theta_1 C_0}}{2k\theta_1} \quad (4-16a)$$

$$C_2 = \frac{-1 + \sqrt{1 + 4k\theta_2} \frac{-1 + \sqrt{1 + 4k\theta_1 C_0}}{2k\theta_1}}{2k\theta_2} \quad (4-16b)$$

and so forth. Clearly, a general expression for C_m would be impractical. For small numbers of stages, numerical solutions have been worked out (Eldrige and Piret, 60) for the second-order rate equation $r_a = kC_a(C_a + E)$, where E is the excess of reactant B over reactant A . Figure 4-7 presents some of these results.

Even more complex situations can be handled algebraically, for example, this set of reactions:



with $C_{b0} = C_{c0}$. The rate equations are

$$r_a = k_1 C_a \quad (4-17a)$$

$$r_b = k_2 C_b^2 - k_1 C_a \quad (4-17b)$$

The relations between the concentrations of successive stages are obtained by substitution into Eq. 4-9. Thus:

$$(C_a)_m = \frac{(C_a)_{m-1}}{1 + k_1 \theta_m} \quad (4-18a)$$

$$(C_b)_m + [k_2(C_b)_m^2 - k_1(C_a)_m]\theta_m = (C_b)_{m-1} \quad (4-18b)$$

Following Eq. 4-13, all values of $(C_a)_m$ can be expressed in terms of the initial

$$(C_a)_m = \frac{(C_a)_0}{(1 + k_1 \theta)^m} \quad (4-19)$$

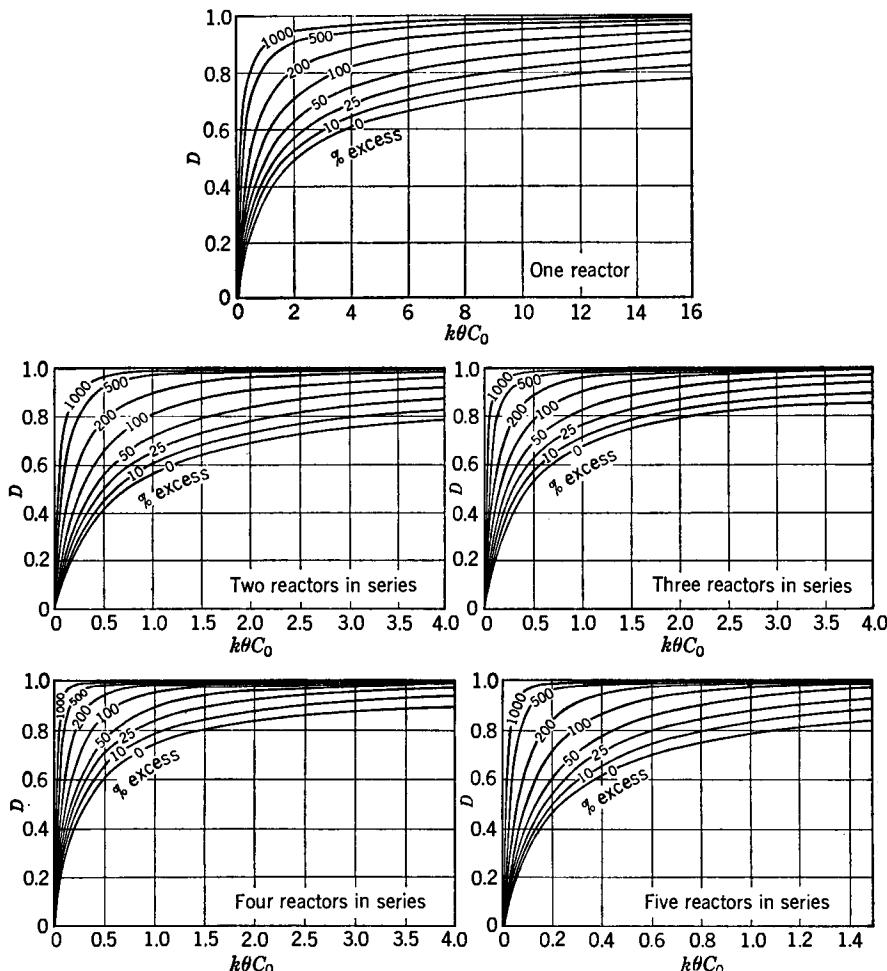


FIG. 4-7. Degree of completion, $D = 1 - C_n/C_0$, of second-order reaction $A + B \rightarrow$ products, with rate equation $r = kC_a(C_a + E)$, where E designates the excess of the concentration of B above that of A . Equal-volume reactors. [Eldridge and Piret (60). Courtesy Chemical Engineering Progress.]

Values calculated from this equation may be substituted into the series of equations for C_b , of which this is the first:

$$k_2\theta(C_b)_1^2 + (C_b)_1 = (C_b)_0 + k_1(C_a)_1\theta \quad (4-20)$$

This quadratic is readily solvable for $(C_b)_1$; the other concentrations of reactant B are obtained similarly.

Illustration 4-4. Nitration of benzene with mixed aqueous nitric and sulfuric acids was conducted in a five-stage stirred reactor (Pope, 182). The operating conditions are noted in Fig. 4-8. The temperature was maintained at 86°F with a water jacket. Specific volume of the system remained substantially constant as the reaction progressed. Corresponding to the flow rates shown, the aqueous phase was 31.414 g moles/liter mixture and the organic phase was 2.5151 g moles/liter mixture. The volume of each stage was 103 ml.

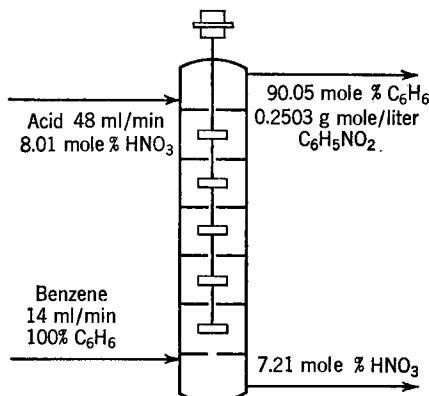


FIG. 4-8. Nitration of benzene in a five-stage reactor (Illustration 4-4).

For a given sulfuric acid concentration, the reaction rate is determined by the nitric acid concentration in the aqueous phase and the benzene concentration in the organic phase. Figure 4-9 presents the results of batch experiments with acid of 20.5 mole % sulfuric acid content.

For a given sulfuric acid concentration, the reaction rate is determined by the nitric acid concentration in the aqueous phase and the benzene concentration in the organic phase. Figure 4-9 presents the results of batch experiments with acid of 20.5 mole % sulfuric acid content.

Find the stage efficiency and compare the performance of this reactor with a single stage.

Solution. Let A represent the nitric acid and B the benzene. In each stage the reaction time is

$$\theta = \frac{103}{62} = 1.661 \text{ min}$$

Terminal concentrations are shown in Fig. 4-7; those in intermediate stages will be determined by trial. In stage 1,

$$C_{b1} = 90.05 \text{ mole \%}$$

$$C_{a0} = 8.01 \text{ mole \%} = 0.0801(31.414) = 2.5162 \text{ g moles/liter mixture}$$

$$\text{Try } C_{a1} = 7.80 \text{ mole \%} = 0.078(31.414) = 2.4503 \text{ g moles/liter mixture}$$

From Fig. 4-9,

$$r_1 = 0.0422 \text{ g mole/(liter)(min)}$$

$$r_1\theta = 0.0422(1.661) = 0.0701 \text{ g mole/liter}$$

Therefore

$$C_{a1} = C_{a0} - r_1\theta = 2.5162 - 0.0701 = 2.4461$$

which does not quite check the assumed value of $C_{a1} = 2.4503$. Other trials are summarized as follows:

$$\begin{array}{ll} \text{Try} & C_{a1} = 7.79 \\ & = 2.4472 \\ & r_1 = 0.0419 \\ & r_1\theta = 0.0696 \\ & C_{a1} = 2.4466 \end{array}$$

$$\begin{array}{ll} \text{Try} & 7.78 \text{ mole \%} \\ & 2.4440 \text{ g moles/liter mixture} \\ & 0.0416 \text{ g mole/(liter)(min)} \\ & 0.0691 \text{ g mole/liter mixture} \\ & 2.4471 \text{ g moles/liter mixture} \end{array}$$

Interpolating,

$$C_{a1} = 7.788, \text{ say } 7.79 \text{ mole \%}$$

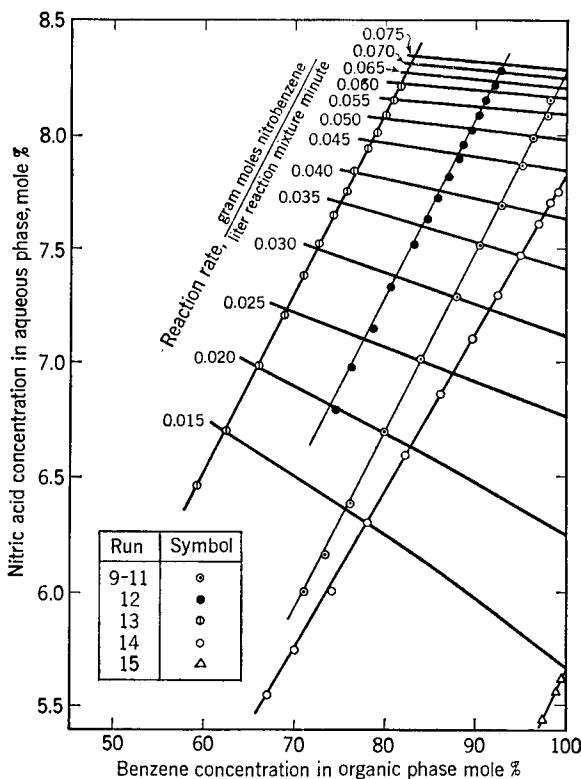


FIG. 4-9. Nitration of benzene with mixed acid containing 20.5 mole % sulfuric acid. Lines of constant rate of reaction at 30°C. [Pope (182).]

TABLE 4-1. DATA FOR ILLUSTRATION 4-4

Stage	Nitric acid			Benzene		Con- version, moles/liter mixture	Nitro- benzene, moles/liter mixture
	Mole %, aqueous phase	Moles/liter mixture	Rate <i>r</i>	Mole %, organic phase	Moles/liter mixture		
0	8.01	2.5162					
1	7.79	2.4466	0.0419	90.05	2.2648	0.0696	0.2503
2	7.59	2.3846	0.0373	92.82	2.3344	0.0620	0.1807
3	7.41	2.3180	0.0341	95.56	2.3934	0.0566	0.1187
4	7.24	2.2656	0.0315	97.80	2.4530	0.0524	0.0621
5	7.09	2.2165	0.0294	99.88	2.5054	0.0491	0.0097
6	100.0	2.5151	0

Also $C_{b2} = \frac{2.2648 + 0.0696}{2.5151} (100) = 92.82 \text{ mole \% benzene}$

Similarly for the remaining theoretical stages. The calculation for the fifth theoretical

stage shows $C_{a5} = 7.09$ mole %, which is less than the measured value of 7.21. Therefore the theoretical stages for the measured conversion are

$$N = 4 + \frac{C_{a4} - C_{a5}}{C_{a4} - C_{a5}^*} = 4 + \frac{7.24 - 7.21}{7.24 - 7.09} = 4.2$$

and the over-all stage efficiency is therefore 84 per cent.

In order to compare the performance of a single stage with this reactor, the volume needed to effect the same conversion will be calculated.

$$\text{Conversion} = (0.0801 - 0.0721)(31.414) = 0.2413 \text{ g mole/liter}$$

$$C_a = 7.21 \text{ mole \%}$$

$$C_b = 90.05 \text{ mole \%}$$

$$r = 0.029 \text{ g mole/(liter)(min)}$$

$$V_r/F = V_r/0.062$$

Therefore volume of single-stage reactor is (@ 84% efficiency)

$$V_r = \frac{\text{conversion}}{\eta r F} = \frac{0.2413(0.062)}{0.84(0.029)} = 0.615 \text{ liters}$$

compared with the actual amount of $5(0.103) = 0.515$ liter of the five-stage reactor.

In complex reactions, the product distribution is affected by the method of operation, sometimes seriously enough to determine the choice of method. Following is a study of a complex reaction.

Illustration 4-5. For the consecutive reactions $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, numerical values are $k_1 = 0.35 \text{ hr}^{-1}$, $k_2 = 0.13 \text{ hr}^{-1}$, $C_{a0} = 4 \text{ lb moles/cu ft}$, and $C_{b0} = C_{c0} = 0$. Find the maximum concentration attained by B when operating as (a) batch reactor, (b) single-stage continuous stirred reactor, (c) two-stage continuous stirred reactor.

Solution. The rate equations are

$$r_a = -\frac{dC_a}{dt} = k_1 C_a \quad (A)$$

$$r_b = -\frac{dC_b}{dt} = k_2 C_b - k_1 C_a \quad (B)$$

The integral of Eq. B is given by Eq. 2-53 (with $C_{b0} = 0$); thus

$$C_b = \frac{k_1 C_{a0}}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \quad (C)$$

Differentiating for a maximum,

$$\frac{dC_b}{dt} = \frac{k_1 C_{a0}}{k_2 - k_1} (-k_1 e^{-k_1 t} + k_2 e^{-k_2 t}) = 0 \quad (D)$$

$$\text{whence} \quad t = \frac{\ln(k_1/k_2)}{k_1 - k_2} = \frac{\ln(0.35/0.13)}{0.35 - 0.13} = 4.55 \quad (E)$$

$$\text{and} \quad (C_b)_{\text{max}} = \frac{0.35(4)}{0.35 - 0.13} (e^{-0.13(4.55)} - e^{-0.35(4.55)}) = 2.23$$

This is the answer to part a. For a single-stage continuous reactor, substitute Eq. A into Eq. 4-13 and Eq. B into Eq. 4-10.

$$C_{a1} = \frac{C_{a0}}{1 + k_1 \theta} \quad (F)$$

$$C_{b1} + (k_2 C_{b1} - k_1 C_{a1})\theta = C_{b0} = 0 \quad (G)$$

$$\text{or} \quad C_{b1} = \frac{k_1 C_{a0} \theta}{(1 + k_1 \theta)(1 + k_2 \theta)} \quad (H)$$

Upon differentiating for a maximum,

$$(1 + k_1\theta)(1 + k_2\theta) - \theta[k_1(1 + k_2\theta) + k_2(1 + k_1\theta)] = 0 \quad (I)$$

whence

$$\theta = \sqrt{\frac{1}{k_1 k_2}} = \sqrt{\frac{1}{(0.35)(0.13)}} = 4.7 \quad (J)$$

and

$$(C_{b1})_{\max} = \frac{(0.35)(4)(4.7)}{[1 + (0.35)(4.7)][1 + (0.13)(4.7)]} = 1.54$$

For the two-stage reactor, again applying Eqs. 4-10, 4-13, and H ,

$$C_{b2}(1 + k_2\theta) - \frac{k_1 C_{a0}\theta}{(1 + k_1\theta)^2} = \frac{k_1 C_{a0}\theta}{(1 + k_1\theta)(1 + k_2\theta)} \quad (K)$$

or

$$C_{b2} = \frac{k_1 C_{a0}\theta[2 + (k_1 + k_2)\theta]}{[(1 + k_1\theta)(1 + k_2\theta)]^2} \quad (L)$$

The maximum is conveniently found by trial as shown in this tabulation:

$\theta \dots \dots$	0	0.5	1.0	1.5	2.0	2.5	3.0	5	10
$C_{b2} \dots \dots$	0	1.003	1.500	1.725	1.815	1.820	1.782	1.505	0.892

from which it appears that $(C_{b2})_{\max} = 1.82$.

The performance of an infinite number of stages approaches that of a batch reactor, so it is possible to interpolate the calculations thus far made for any number of stages, as shown in Fig. 4-10, where the maximum concentration is plotted against the reciprocal of the number of stages, $1/m$. Clearly, when a maximum concentration of substance B is desired, the batch reactor is the best type of equipment to use.

29. Unsteady-state Conditions

Whenever a reaction battery is started up or shut down or changed to another set of conditions, the concentrations of individual reactors change as time goes on. It is often of interest to know how long it takes for a steady state to develop, or how long it takes for the individual reactors to reach concentrations suitable for dumping.

Such variable or transient conditions are covered by Eq. 4-1, which may be rewritten in terms of θ_m and for constant overflow between stages as

$$\frac{dC_m}{dt} + \frac{C_m}{\theta_m} + r = \frac{C_{m-1}}{\theta_m} \quad (4-21)$$

This equation has been solved in general terms for a number of cases in-

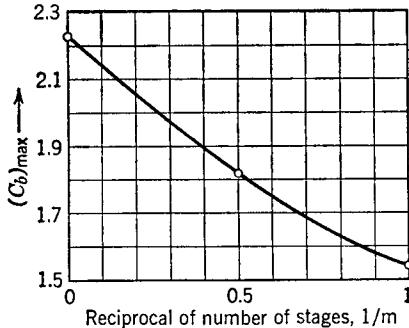


FIG. 4-10. Data for Illustration 4-5.

volving first-order reactions. Figure 4-11 shows the fractional approach of the transient to the steady state for a first-order irreversible reaction with zero initial concentrations in all reactors and with all residence times equal (Mason and Piret, 147).

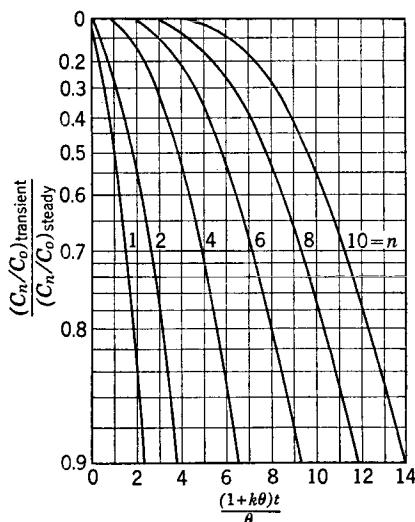


FIG. 4-11. Transient behavior in continuous stirred reactors. Rate $r = kC$; initial concentrations in all reactors, zero; feed concentration, C_0 .

For more general conditions, a system of differential equations like Eq. 4-21, one for each reactor, can be set up and solved simultaneously. Take the case of a three-reactor battery, each reactor of which is filled with a solution of its own concentration. Let C_0 be the fresh inlet concentration and x , y , and z the concentrations in the individual reactors. Equation 4-21 becomes, for the first reactor,

$$\frac{dx}{dt} + \frac{x}{\theta_1} + k_1 x = \frac{C_0}{\theta_1} \quad (4-22)$$

or

$$\frac{dx}{dt} + ax = \frac{C_0}{\theta_1} \quad (4-22a)$$

where $a = k_1 + 1/\theta_1$. Similarly for the other reactors,

$$\frac{dy}{dt} + by = \frac{x}{\theta_2} \quad (4-23)$$

$$\frac{dz}{dt} + cz = \frac{y}{\theta_3} \quad (4-24)$$

These are all linear differential equations with constant coefficients. The solution of Eq. 4-22a is

$$x = \frac{C_0}{\theta_1 a} + A_1 e^{-at} \quad (4-25)$$

and

$$A_1 = x_0 - \frac{C_0}{\theta_1 a} \quad (4-26)$$

Substituting into Eq. 4-23,

$$\frac{dy}{dt} + by = \frac{C_0}{\theta_1 \theta_2 a} + \frac{A_1}{\theta_2} e^{-at} \quad (4-27)$$

Illustration 4-6. When $\theta = 10$ min, $k = 0.4 \text{ min}^{-1}$, and the number of reactors is 4, find the time for the effluent from the last reactor to attain 90 per cent of the steady-state concentration.

Solution. From Fig. 4-11,

$$\frac{(1 + k\theta)t}{\theta} = \frac{[1 + 0.4(10)]t}{10} = 6.4$$

$$\text{whence } t = 12.8 \text{ min.}$$

For more general conditions, a system of differential equations like Eq. 4-21, one for each reactor, can be set up and solved simultaneously. Take the case of a three-reactor battery, each reactor of which is filled with a solution of its own concentration. Let C_0 be the fresh inlet concentration and x , y , and z the concentrations in the individual reactors. Equation 4-21 becomes, for the first reactor,

The solution is

$$y = \frac{C_0}{\theta_1 \theta_2 a b} + \frac{A_1}{\theta_2(b-a)} e^{-at} + A_2 e^{-bt} \quad (4-28)$$

$$A_2 = y_0 - \frac{C_0}{\theta_1 \theta_2 a b} - \frac{A_1}{\theta_2(b-a)} \quad (4-28a)$$

For the last reactor,

$$\frac{dz}{dt} + cz = \frac{C_0}{\theta_1 \theta_2 \theta_3 abc} + \frac{A_1}{\theta_2 \theta_3 (b-a)} e^{-at} + \frac{A_2}{\theta_3} e^{-bt} \quad (4-29)$$

$$z = \frac{C_0}{\theta_1 \theta_2 \theta_3 abc} + \frac{A_1}{\theta_2 \theta_3 (b-a)(c-a)} e^{-at} + \frac{A_2}{\theta_3 (c-b)} e^{-bt} + A_3 e^{-ct} \quad (4-30)$$

$$A_3 = z_0 - \frac{C_0}{\theta_1 \theta_2 \theta_3 abc} - \frac{A_1}{\theta_2 \theta_3 (b-a)(c-a)} - \frac{A_2}{\theta_3 (c-b)} \quad (4-31)$$

When the θ 's and k 's are the same for all reactors, $a = b = c$ and the solutions become

$$x = \frac{C_0}{\theta a} + B_1 e^{-at} \quad (4-32)$$

$$y = \frac{C_0}{\theta^2 a^2} + \left(\frac{B_1 t}{\theta} + B_2 \right) e^{-at} \quad (4-33)$$

$$z = \frac{C_0}{\theta^3 a^3} + \left(\frac{B_1 t^2}{2\theta^2} + \frac{B_2 t}{\theta} + B_3 \right) e^{-at} \quad (4-34)$$

$$B_1 = x_0 - \frac{C_0}{\theta a} \quad (4-35)$$

$$B_2 = y_0 - \frac{C_0}{\theta^2 a^2} \quad (4-36)$$

$$B_3 = z_0 - \frac{C_0}{\theta^3 a^3} \quad (4-37)$$

For reactions of order higher than the first, formal solution of the differential equations may not be possible. In that event, suitable procedures are typified by the following illustration.

Illustration 4-7. A second-order reaction will be conducted in a two-stage battery. Let x and y be the concentrations in the reactors. Initially they contain solutions of concentrations $C_0 = x_0 = y_0 = 1$, the same as the running charge. The reactors are the same size, $\theta = 1$ and $k = 0.5$. Accordingly, the rate equations are

$$\frac{dx}{dt} + x + 0.5x^2 = 1 \quad (A)$$

$$\frac{dy}{dt} + y + 0.5y^2 = x \quad (B)$$

Equation A may be rewritten

$$t = \int_0^{\infty} \frac{dx}{1 - x - 0.5x^2} \quad (C)$$

Integration is direct; the results are plotted in Fig. 4-12. Equation *B* must be integrated by the method of Sec. 78. To obtain the first point with Taylor's theorem,

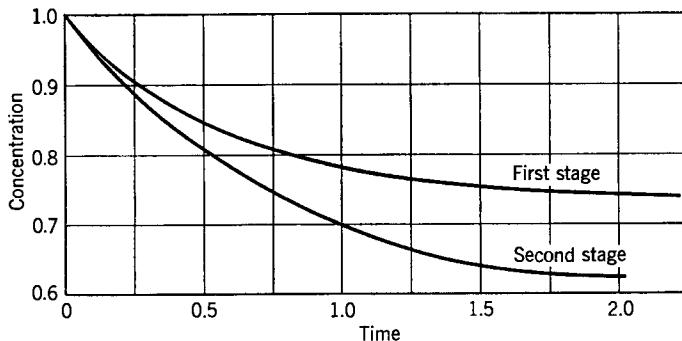


FIG. 4-12. Transient conditions in a two-stage reactor battery (Illustration 4-7).

$$x_0 = 1$$

$$x'_0 = 1 - x_0 - 0.5x_0^2 = -0.5$$

$$x''_0 = -x'_0 - x_0x'_0 = 1$$

$$x'''_0 = -x''_0 - x_0x''_0 - (x'_0)^2 = -0.75$$

$$x^{(4)}_0 = -x'''_0 - x_0x'''_0 - (x''_0)^2 - 2x'_0x''_0 = 1.5$$

$$y_0 = 1$$

$$y'_0 = x_0 - y_0 - 0.5y_0^2 = -0.5$$

$$y''_0 = x'_0 - y'_0 - y_0y'_0 = 0.5$$

$$y'''_0 = x''_0 - y''_0 - y_0y''_0 - (y'_0)^2 = 0.25$$

$$y^{(4)}_0 = x^{(4)}_0 - y^{(4)}_0 - y_0y^{(4)}_0 - (y''_0)^2 - 2y'_0y''_0 = -1$$

TABLE 4-2. RESULTS FOR ILLUSTRATION 4-7

<i>t</i>	<i>x</i>	<i>y</i>	$-y^1$
0	1.000	1.000	0.500
0.1	0.962	0.953	0.445
0.2	0.928	0.911	0.398
0.3	0.896	0.873	0.358
0.4	0.869	0.839	0.321
0.5	0.846	0.809	0.290
0.6	0.829	0.781	0.257
0.7	0.815	0.758	0.230
0.8	0.802	0.735	0.203
0.9	0.791	0.717	0.183
1.0	0.782	0.699	0.161
1.2	0.767	0.671	0.129
1.4	0.758	0.647	0.098
1.6	0.752	0.632	0.080
1.8	0.746	0.615	0.042
2.0	0.743	0.616	

Taking $h = \Delta t = 0.1$,

$$\begin{aligned}
 y_1 &= 1 + 0.1(-0.5) + \frac{0.01}{2} (0.5) + \frac{0.001}{6} (0.25) + \frac{0.0001}{24} (-1) + \dots \\
 &= 0.953 \\
 y'_1 &= 0.962 - 0.953 - 0.5(0.953)^2 = -0.445 \\
 y_2 &= y_0 + 2hy'_1 = 1 + 2(0.1)(-0.445) = 0.911 \\
 y'_2 &= 0.928 - 0.911 - 0.5(0.911)^2 = -0.398 \\
 y_3 &= 0.953 + 2(0.1)(-0.398) = 0.873
 \end{aligned}$$

and so forth. The results are summarized in Table 4-2 and plotted in Fig. 4-12. Substantially steady operation obtains by the time $t = 2$.

PROBLEMS

4-1. Given the following numerical data for Illustration 4-1, and assuming the density of the solution to remain constant, find how long it will take for the amount of solute in the tank to fall to 25 per cent of its original value.

$$\begin{array}{ll}
 n = 1 & C_1 = 0 \\
 k = 0.75 \text{ min}^{-1} & R_1 = 1.8 \text{ gpm} \\
 V_0 = 200 \text{ gal} & R_2 = 2.0 \text{ gpm} \\
 C_0 = 1.5 \text{ lb/gal} &
 \end{array}$$

4-2. A tank contains 100 gal of brine, with 50 lb of dissolved salt. The bottom of the tank is covered with a cake of undissolved salt whose surface may be assumed to remain substantially constant. The salt dissolves at a rate proportional to the difference between the concentration of the solution and that of a saturated solution which is 3.0 lb/gal. If the water in the tank were fresh, the rate of solution would be 1.0 lb/min. Fresh water is allowed to run into the tank at the rate of 3 gpm, and brine overflows at the same rate. The solution is kept uniform by agitation. Assuming that the volume of the brine does not vary as its concentration changes, how much salt will be in solution in the tank at the end of 1 hr?

4-3. Brine containing C_0 lb/gal of dissolved salt flows at the rate of R gpm into a tank of volume V_1 gal, which is initially full and contains x_0 lb of dissolved salt. Overflow at R gpm passes into a second tank of volume V_2 gal, which is also full initially and contains y_0 lb of dissolved salt. Overflow from this tank is also at rate R gpm. Both tanks are well stirred. Express the instantaneous amounts x and y as functions of time.

4-4. A solution containing 0.5 lb mole/cu ft of a reactive component is to be treated at the rate of 25 cfh. Kinetic data obtained in a batch laboratory reactor are as follows:

C , lb moles/cu ft	r , lb moles/(hr)(cu ft)
0.50	0.850
0.45	0.675
0.40	0.530
0.35	0.405
0.30	0.310
0.25	0.240
0.20	0.180
0.15	0.128
0.10	0.081
0.05	0.040

(a) If the filling and draining time per batch is negligible, what size batch reactor is needed for 90 per cent conversion? How many batches are made in a 24-hr day?

(b) What percentage conversion is attained with a two-stage reactor battery, each vessel being 50 cu ft?

(c) For 90 per cent conversion, tabulate the total reactor volumes required with one stage, two stages, three stages, and four stages.

4-5. The hydrolysis of acetic anhydride is conducted in a reaction battery consisting of four vessels. The temperature of the first reactor is maintained at 10°C, the second at 15°C, the third at 25°C, and the fourth at 40°C. The reaction is of the first order, with specific reaction rates as follows:

Temperature, °C.....	10	15	25	40
$k, \text{min}^{-1}.....$	0.0567	0.0806	0.1580	0.380

The inlet composition is 1.5 lb moles/gal, the feed rate is 25 gpm, the vessels are all the same size, and the desired conversion is 95 per cent.

(a) What size of vessel is needed?

(b) If all reactors are maintained at 15°C, how many reactors of the size calculated in part a will be needed?

4-6. It is desired to find the least expensive continuous stirred reactor battery for converting 2,000 lb moles/24 hr of a reactant. Inlet concentration is 1.25 lb moles/cu ft, and the outlet is to be 0.15 lb mole/cu ft. Batch reaction data are given below. Approximate cost data are:

Reactors: Assembled cost is \$0.85 per lb. Dished bottoms, open tops, height equal to diameter, bottom surface equals 1.5 times the surface of a flat bottom of the same diameter. Tanks of over 1,500 gal capacity are made of $\frac{1}{4}$ -in. plate; smaller ones are of $\frac{3}{16}$ -in. plate. Freeboard equals volume of the dished head.

Agitators: The cost in dollars = $150V^{0.3}$, where V is the volume of the straight side of the tank, in cubic feet.

Batch reaction data:

Time, min	Concentration, lb moles/cu ft
0	1.25
1	1.11
2	1.01
3	0.910
4	0.825
5	0.770
6	0.715
7	0.670
8	0.625
9	0.590
10	0.555
15	0.435
20	0.357
25	0.303
30	0.264
40	0.208
50	0.172

4-7. Alkylation of toluene and acetylene in the presence of sulfuric acid is accomplished in a four-stage reactor as shown in Fig. 4-13. The retention time in each stage is 10 min, agitation is extremely vigorous, the temperature is maintained at 41°F, and the pressure at 50 psig. On the assumption that the liquid is always saturated with acetylene, the reaction is first-order with respect to toluene. Under the conditions shown, the reaction is estimated 95 per cent complete. Find the specific reaction rate.

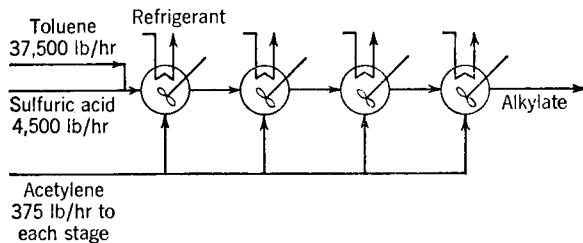


FIG. 4-13. Alkylation of toluene (Prob. 4-7).

4-8. A reaction with rate equation $r = kC^2$ is carried out in a four-stage reactor. When $k\theta C_0 = 1.2$, find the fractional conversion by the algebraic method.

4-9. Several reactors, each of capacity 25 cu ft, are available for conducting the reaction $A + B \rightarrow$ products. These data apply:

$$C_{a0} = 1.5 \text{ lb moles/cu ft}$$

$$C_{b0} = 2.25 \text{ lb moles/cu ft}$$

$$k = 0.08 \text{ cu ft}/(\text{lb mole})(\text{min})$$

Required conversion of A is 80 per cent. Find the allowable charge rates for one reactor, three reactors in series, and five reactors in series.

4-10. The reaction $A \rightarrow B \rightarrow C$ has the rate equations

$$r_a = 0.4C_a$$

$$r_b = 0.3C_b - 0.4C_a$$

Three tanks of different sizes are available for conducting this reaction. At the desired production rate, their sizes correspond to residence times of 5, 10, and 15 min. The initial amounts are $C_{a0} = 0.9$, $C_{b0} = 1.2$, and $C_{c0} = 0$. Find the concentrations of all three substances in the effluents from each tank when:

- (a) The solution is pumped in succession through the 15-min, 10-min, and 5-min tanks.
- (b) The solution is pumped in the reverse direction.

4-11. A process is to be conducted in a two-stage battery whose total volume is fixed at $V_1 + V_2 = V_0$. Show that the relative sizes of the two reactors which give the maximum conversion are as tabulated (Denbigh, 56):

Rate equation	Optimum value of V_2/V_1
$r = k(a - x)/V$	1
$r = k(a - x)^2/V^2$	2
$r = k(a - x)^3/V^3$	3

4-12. A first-order reaction is conducted in a battery of four reactors each of which has a residence time of 8 min. The rate equation is $r = 0.27C$. What is the steady-state value of C_2/C_0 ? How long does it take to reach 95 per cent of the steady-state value?

4-13. For a first-order reaction with $k = 0.12$, make a plot of the number of reactors, up to 10, against the time required for C_n/C_0 to reach 0.20. The combined residence time of all the reactors is 1 hr.

4-14. A two-stage battery is being used to obtain 80 per cent conversion under the following conditions:

$$F = 75 \text{ cu ft of total solution/hr}$$

$$C_0 = 1.5 \text{ lb moles/cu ft}$$

$$r = 0.2C \text{ lb moles/(min)(cu ft)}$$

After several days of operation, flow is stopped. The two reactors are dumped when the average of their concentrations is the same as the steady-state effluent from the last reactor under normal operating conditions. How soon after flow is stopped can the material be discharged? Instantaneous discharge is to be assumed.

4-15. A variation in the usual technique of operating a CSTR battery was practiced by Fontana, Herold, Kinney, and Miller* for making high-molecular-weight polyolefins. They charged fresh butene at equal rates to each of four stages operated in series. Catalyst was charged to the first stage. Overflow between stages was continuous. In this work the successive stages were increased in size to maintain approximately constant residence times. However, develop equations or a construction for a battery of four equal-sized reactors operated with equally split flow rates to each reactor, for a first-order reaction.

* *Ind. Eng. Chem.*, **44**: 2955 (1952).

CHAPTER 5

HOMOGENEOUS FLOW REACTIONS

30. Tubular-flow Reactors

Ease of control, labor saving, mechanical simplicity, adaptability to heat transfer and high pressure, unvarying product quality, high capacity—these are some of the good points of tubular-flow reactors. In the laboratory, flow reaction is especially well suited to the study of rapid reactions. Thus once steady-state conditions have been attained in an experiment, the extent of conversion often can be observed by some physical means without disturbing the course of the reaction. Measurements in the steady state can be more accurate than those of the rapidly changing state of a batch reaction. The conversion is regulated by the length of the reactor or by the charge rate.

The rate of a reaction, of course, does not depend on whether it is conducted in batch or in flow. However, flow reactions do not ordinarily occur at constant volume, so there is a problem in defining the time of reaction. The simplest picture assumes that plug flow exists; that is, movement of each particle is always forward and no backmixing takes place. Visualize a small element of feed to be confined between two pistons sliding through the reactor. When there is no change in the density of the reacting mixture, the time of reaction is (Fig. 5-1)

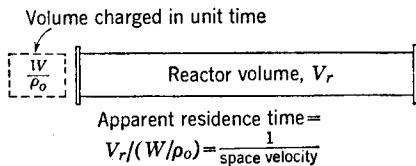


FIG. 5-1. Residence time in flow reactor at constant system density (Eq. 5-1).

$$t = \frac{V_r}{W/\rho} \quad (5-1)$$

where V_r = reactor volume

W = mass flow rate

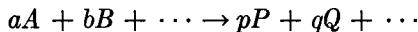
ρ = density

The reciprocal of this quantity, of interest even when the density varies, is called the space velocity SV ; that is,

$$SV = \frac{W/\rho}{V_r} \quad (5-2)$$

Usually the density is that of the inlet material; for gases, the density is usually that at standard conditions of temperature and pressure, 32°F and 14.7 psia.

Particularly with gases, serious density changes do occur, so in general the reaction time depends on the conversion. Consider the gas-phase reaction



Let δ be the increase in the number of moles of the system per mole of substance A converted. It will be convenient to express all quantities per unit of feed; thus n_a is the moles of A per unit of feed, which may be in moles, cubic feet, pounds, etc. At a point in the reactor where the cross section is S and the length is L , the linear velocity is

$$u = \frac{W(n_{a0} + \delta x)}{S} \frac{RT}{\pi} \quad (5-3)$$

Accordingly, the time for traversing a differential length dL is

$$dt = \frac{dL}{u} = \frac{S dL}{W(n_{a0} + \delta x)RT/\pi} = \frac{dV_r}{W(n_{a0} + \delta x)RT/\pi} \quad (5-4)$$

As this expression stands, it cannot be integrated for the reaction time, unless some of the variables are eliminated. It proves most convenient to eliminate the time. From the definition of rate,

$$dt = \frac{dx}{rV} = \frac{dx}{r(n_{a0} + \delta x)RT/\pi} \quad (5-5)$$

Substituting into Eq. 5-4 and rearranging,

$$\frac{V_r}{W} = \int_0^{V_r} \frac{dV_r}{W} = \int_{x_0}^x \frac{dx}{r} \quad (5-6)$$

This is the *basic flow-reactor equation*. In view of its importance, it will be derived also in another manner.

Referring to Fig. 5-2, consider the element of reactor volume, dV_r , in

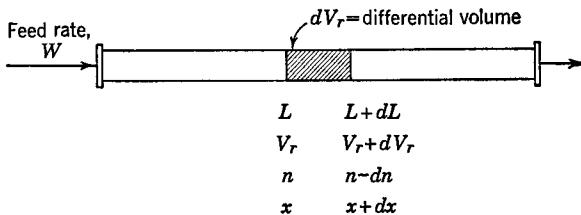


FIG. 5-2. Differential element of tubular-flow reactor.

which the rate of reaction is r . The conversion in this space is $r dV_r$, since r is the rate of change per unit volume. Applying the conservation law,

Accumulation = input - output

$$\begin{aligned} r dV_r &= W n_a - W(n_a + dn_a) \\ &= -W dn_a \\ &= W dx \end{aligned}$$

which can be rearranged to Eq. 5-6. When W is expressed in volumetric units the same as V_r , the left side of Eq. 5-6 is the reciprocal of the space velocity, or an *apparent time of reaction*.

Several examples of flow equations may now be treated. For a first-order reaction, $A \rightarrow (\delta + 1)B$, the rate equation is

$$r = \frac{k(n_{a0} - x)}{V} = \frac{k(n_{a0} - x)}{(RT/\pi)(n_{a0} + \delta x)} \quad (5-7)$$

At constant pressure and temperature, the flow equation becomes

$$\frac{V_r}{W} = \int_0^x \frac{RT(n_{a0} + \delta x)}{k\pi(n_{a0} - x)} dx = \frac{RT}{k\pi} \left[-\delta x + (n_{a0} + \delta n_{a0}) \ln \frac{n_{a0}}{n_{a0} - x} \right] \quad (5-8)$$

The true contact time is obtained from Eq. 5-5. Thus

$$t = \int_0^x \frac{dx}{rV} = \frac{1}{k} \int_0^x \frac{dx}{n_{a0} - x} = \frac{1}{k} \ln \frac{n_{a0}}{n_{a0} - x} \quad (5-9)$$

As another example take the second-order reaction for which

$$r = \frac{kn_a n_b}{V^2} = \frac{k(n_{a0} - x)(n_{b0} - x)}{[(RT/\pi)(n_{a0} + \delta x)]^2} \quad (5-10)$$

Substituting into Eq. 5-6,

$$\begin{aligned} \frac{V_r}{W} &= \frac{1}{k} \left(\frac{RT}{\pi} \right)^2 \left[\delta^2 x - \frac{(n_{a0} + \delta n_{a0})^2}{n_{a0} - n_{b0}} \ln \frac{n_{a0}}{n_{a0} - n_{b0}} \right. \\ &\quad \left. + \frac{(n_{a0} + \delta n_{b0})^2}{n_{a0} - n_{b0}} \ln \frac{n_{b0}}{n_{b0} - x} \right] \quad (5-11) \end{aligned}$$

The true contact time is

$$\begin{aligned} t &= \int_{x_0}^x \frac{dx}{rV} = \frac{RT}{k\pi} \int_{x_0}^x \frac{(n_{a0} + \delta x) dx}{(n_{a0} - x)(n_{b0} - x)} \\ &= \frac{RT}{k\pi(n_{a0} - n_{b0})} \left[n_{a0} \ln \frac{n_{b0} - x}{n_{a0} - x} - \frac{\delta}{n_{a0}} \ln (n_{a0} - x) - \frac{\delta}{n_{b0}} \ln (n_{b0} - x) \right]_{x_0}^x \quad (5-12) \end{aligned}$$

The basic flow equation has been integrated for several other reversible and irreversible reactions of the first, second, and third orders (Hougen and Watson, 102). In that work the rate equations are written in terms of k_p ; so to convert those equations to the concentration units of this chapter, it is necessary to multiply the Hougen equations for V_r/W by $(RT)^n$, where n is the order of the reaction.

Since the integrals are so complicated, it is often preferable to employ

graphical or numerical integration. This is always necessary, of course, when temperature or pressure varies.

Illustration 5-1. The reversible reaction $A \rightleftharpoons 2B$ is conducted at 540°F and 3 atm in a tubular-flow reactor. The feed contains 30 mole % A and the balance inert material, the total being at the rate of 75 lb moles/hr. The rate equation is

$$r_a = k \left[\frac{n_a}{V} - \frac{1}{K_c} \left(\frac{n_b}{V} \right)^2 \right]$$

with $k = 1.6 \text{ sec}^{-1}$ and $K_c = 0.0055$. To accomplish 75 per cent of equilibrium conversion, find (a) the volume of the reactor, (b) the space velocity.

Solution. Refer all quantities to 1 lb mole of feed. Accordingly,

$$n_{a0} = 1$$

$$n_{b0} = 0.3$$

$$n_t = n_{a0} + \delta x = 1 + x$$

$$V = \frac{n_t RT}{\pi} = \frac{0.73(1,000)(1 + x)}{3} = 243(1 + x)$$

At equilibrium,

$$K_c = 0.0055 = \left(\frac{C_b^2}{C_a} \right)_e = \left(\frac{n_b^2}{V n_a} \right)_e = \frac{(2x_e)^2}{243(1 + x_e)(0.3 - x_e)}$$

whence $x_e = 0.20$

$$\begin{aligned} r &= 1.6 \left\{ \frac{0.3 - x}{243(1 + x)} - \frac{1}{0.0055} \left[\frac{2x}{243(1 + x)} \right]^2 \right\} \\ &= 0.0066 \left[\frac{0.3 - x}{1 + x} - 0.747 \left(\frac{2x}{1 + x} \right)^2 \right] \end{aligned}$$

$$\frac{V_r}{W} = \int_0^x \frac{dx}{r} = \int_0^{0.15} \frac{152 dx}{(0.3 - x)/(1 + x) - 0.747[2x/(1 + x)]^2}$$

This is integrated by Simpson's rule, with the integrands shown in Table 5-1.

TABLE 5-1. DATA FOR ILLUSTRATION 5-1

x	Integrand		
0	3.33		
0.025	3.79	
0.05	4.33
0.075	5.15	
0.10	6.36
0.125	8.44	
0.15	12.59		
	15.92	17.38	10.69

$$\frac{V_r}{W} = 152 \left(\frac{0.025}{3} \right) [15.92 + 4(17.38) + 2(10.69)] = 135 \text{ cu ft/(lb mole)} \text{ sec}$$

$$V_r = 135 W = \frac{135(75)}{3,600} = 2.81 \text{ cu ft}$$

$$SV = \frac{\text{feed quantity, std cu ft/sec}}{\text{reactor volume, cu ft}} = \frac{75(359)}{3,600(2.81)} = 2.66 \text{ sec}^{-1}$$

Illustration 5-2. Cracking of an 11.3°API gas oil was conducted experimentally in a coil 150 ft long by 0.209 in. ID, immersed in a lead bath at 850°F. The oil entered at 200°F and 475 psig at the rate of 1.6 gph. The amount converted to gas and gasoline was 12.2 wt %. The heat-transfer coefficient was computed as 31. The density of the mixture is expressed by the equation

$$\frac{1}{\rho} = 0.0229 + 0.317x$$

Hydrocarbon cracking is a first-order reaction. Neglecting pressure drop, find the specific reaction rate.

Solution. Heat-transfer calculations show that when 15 per cent of the reactor has been traversed, the oil temperature is within 5°F of the lead bath. It will be assumed that no significant conversion has occurred in the preheat section and that the reaction is substantially isothermal in the remaining 85 per cent of the reactor volume. S.G. = 0.95

$$W = \frac{8.33(1.6)(0.95)}{3,600} = 0.00347 \text{ lb/sec}$$

$$V_r = 0.85(150) \left(\frac{0.209}{12} \right)^2 (0.785) = 0.0303 \text{ cu ft}$$

$$\begin{aligned} k &= \frac{W}{V_r} \int_0^x \frac{dx}{\rho(1-x)} = \frac{W}{V_r} \int_0^x \frac{0.0229 + 0.317x}{1-x} dx \\ &= \frac{W}{V_r} \left[0.3401 \ln \frac{1}{1-x} - 0.317x \right]_0^{0.122} \\ &= \frac{0.00347}{0.0303} \left[0.3401 \ln \frac{1}{1-0.122} - 0.317(0.122) \right] = 0.00068 \text{ sec}^{-1} \end{aligned}$$

This result may be compared with an approximate solution, taking an average reciprocal density:

$$\text{Inlet } \rho = \frac{1}{0.0229} = 43.7$$

$$\text{Outlet } \rho = \frac{1}{0.0229 + 0.317(0.122)} = 16.2$$

$$\left(\frac{1}{\rho} \right)_m = 0.5 \left(\frac{1}{43.7} + \frac{1}{16.2} \right) = 0.0453$$

$$\text{and } k = \frac{W}{V_r} \left(\frac{1}{\rho} \right)_m \ln \frac{1}{1-x} = \frac{0.00347(0.0453)}{0.0303} \ln \frac{1}{1-0.122} = 0.00063 \text{ sec}^{-1}$$

31. Pressure Drop in Tubular Reactors

Flow in a tubular-flow reactor may be accompanied by appreciable pressure drop, particularly when gases are involved or when mixtures of liquids and gases occur, as in liquid hydrocarbon cracking. One approach to the latter situation has been shown in Illustration 5-5; a more accurate method of handling the pressure drop in mixed-phase flow is given by Chenoweth and Martin (40). Here only single-phase fluids will be considered.

Regarding the several terms comprised by the mechanical-energy balance, elevation head and shaft work are rarely of significance in reactor

design; and velocity head is also generally negligible. Accordingly, the pressure drop equals the friction loss. Over the element of reactor volume dV_r , or length dL ,

$$d\pi = -f \frac{\rho u^2}{2gD} dL \quad (5-13)$$

Several substitutions can put this equation in a more tractable form. Over the range normally occurring in reactors, $5,000 < \text{Re} < 200,000$, the friction factor is given by the approximate relation (McAdams, 150)

$$f = 0.046(\text{Re})^{-0.2} = 0.044 \left(\frac{\mu D}{W} \right)^{0.2} \quad (5-14)$$

Also, the linear velocity may be eliminated by

$$W = 0.785D^2\rho u \quad \text{lb/hr} \quad (5-15)$$

Now Eq. 5-13 becomes

$$d\pi + \frac{0.036W^{1.8}\mu^{0.2}}{gD^{4.8}\rho} dL = 0 \quad (5-16)$$

The density is variable, depending on both the pressure and the extent of reaction. For ideal gases,

$$\rho = \frac{M}{V} = \frac{\pi M}{RT} = \frac{\pi M_0 n_{\infty}}{RT n_t} = \frac{\pi M_0 n_{\infty}}{RT(n_{\infty} + \delta x)} \quad (5-17)$$

where M_0 is the molecular weight of the charge. Therefore

$$d\pi + \frac{0.036W^{1.8}\mu^{0.2}RT(n_{\infty} + \delta x)}{\pi g D^{4.8} M_0 n_{\infty}} dL = 0 \quad (5-18)$$

This equation holds simultaneously with the flow-reactor equation

$$\frac{W dx}{M_0} = r dV_r = 0.785D^2 r dL \quad (5-19)$$

where x is moles converted per mole of charge. Combining,

$$d\pi + \frac{0.046W^{2.8}\mu^{0.2}RT(n_{\infty} + \delta x)}{\pi g D^{6.8} M_0^2 n_{\infty}} \frac{dx}{r} = 0 \quad (5-20)$$

For convenience this may be written

$$d\pi + \alpha \frac{n_{\infty} + \delta x}{\pi n_{\infty}} \frac{dx}{r} = 0 \quad (5-21)$$

where $\alpha = \frac{0.046W^{2.8}\mu^{0.2}RT}{g D^{6.8} M_0^2}$ (5-22)

The method of solution may be indicated with the example of a first-order rate equation:

$$r = k \frac{n_a}{V} = k \frac{\pi}{RT} \frac{n_{\infty} - x}{n_{\infty} + \delta x} \quad (5-23)$$

Substituting into Eq. 5-21,

$$\pi^2 d\pi + \frac{\alpha RT(n_{t0} + \delta x)^2}{kn_{t0}(n_{a0} - x)} dx = 0 \quad (5-24)$$

or

$$\pi^3 = \pi_0^3 - \frac{3\alpha RT}{kn_{t0}} \int_{x_0}^x \frac{(n_{t0} + \delta x)^2}{n_{a0} - x} dx \quad (5-25)$$

Completing the integration, for isothermal conditions,

$$\pi^3 = \pi_0^3 - \frac{3\alpha RT}{kn_{t0}} \left[-(n_{t0} + \delta n_{a0})^2 \ln(n_{a0} - x) - 0.5 \delta^2(n_{a0} - x)^2 + 2 \delta^2 n_{a0}(n_{a0} - x) - 2 \delta n_{t0} x \right]_{x_0}^x \quad (5-26)$$

When $x_0 = 0$,

$$\pi^3 = \pi_0^3 - \frac{3\alpha RT}{kn_{t0}} \left[-(n_{t0} + \delta n_{a0})^2 \ln \frac{n_{a0}}{n_{a0} - x} - 0.5 \delta^2(n_{a0} - x)^2 + 2 \delta^2 n_{a0}(n_{a0} - x) - 2 \delta n_{t0} x - 1.5 \delta^2 n_{a0} \right] \quad (5-27)$$

These integrals provide the needed relation between pressure and conversion which can be substituted back into Eq. 5-19 to evaluate V_r/W .

For reactions of higher order, Eq. 5-21 is most conveniently integrated numerically or graphically. Such procedures are also necessary in cases where Eq. 5-14 is insufficiently accurate. At small or moderate pressure drop, it may be possible to estimate its value from the average flow in the reactor, thus enabling the use of a mean value of the pressure function in the rate equation. Thus the second-order reaction $A + B \rightarrow$ products will have the flow equation

$$\frac{V_r}{W} = \left(\frac{1}{\pi^2} \right)_{\text{mean}} \int_{x_0}^x \frac{(RT)^2(n_{t0} + \delta x)^2}{k(n_{a0} - x)(n_{b0} - x)} dx \quad (5-28)$$

Illustration 5-3. The gas-phase reaction $A \rightarrow 2B$ is conducted at 600°F in a tubular reactor of diameter 0.2 ft. The feed contains 50 mole % A and the balance inert. Molecular weight of A is 40; that of the inert is 20. Charge rate is 8,800 lb/hr, inlet pressure is 73.5 psia, specific reaction rate is $2,000 \text{ hr}^{-1}$, and viscosity is $0.05 \text{ lb}/(\text{ft})(\text{hr})$. Calculate the relation between conversion, pressure drop, and volume of the reactor.

Solution. Substituting into Eq. 5-22,

$$\alpha = \frac{0.046(8,800)^{2.8}(0.05)^{0.2}(1,540)(600)}{4.18(10^6)(0.2)^{6.8}(30)^2} = 3.73(10^8)$$

Noting that Eq. 5-25 has the pressure units in pounds per square foot,

$$\begin{aligned} \left(\frac{\pi}{144} \right)^3 &= (73.5)^3 - \frac{3(3.73)(10^8)(1,540)(600)}{(144)^3(2,000)} \int_0^x \frac{(1+x)^2}{0.5-x} dx \\ &= 395,000 - 174,000 \int_0^x \frac{(1+x)^2}{0.5-x} dx \end{aligned}$$

The integration is performed numerically and is summarized in Table 5-2. This supplies

the desired relation between pressure and conversion. Applying Eq. 5-19 for the reactor size,

$$V_r = \frac{WRT}{M_0 k} \int_0^x \frac{1+x}{\pi(0.5-x)} dx = \frac{8,800(1,540)(600)}{30(2,000)} \int_0^x \frac{1+x}{\pi(0.5-x)} dx$$

$$= 135,000 \int_0^x \frac{1+x}{\pi(0.5-x)} dx$$

This also is integrated numerically and summarized in Table 5-2.

TABLE 5-2. RESULTS FOR ILLUSTRATION 5-3

x	$\frac{(1+x)^2}{0.5-x}$	\int_0^x	$\frac{\pi}{144}$, psia	$\frac{144(1+x)}{\pi(0.5-x)}$	$144 \int_0^x$	V_r , cu ft
0	2.00	0	73.5	0.0272	0	0
0.05	2.45	0.11	72.1	0.0323	0.0015	1.4
0.10	3.02	0.25	70.6	0.0386	0.0033	3.1
0.15	3.87	0.42	68.7	0.0472	0.0054	5.1
0.20	4.80	0.64	65.7	0.0604	0.0081	7.6
0.25	6.22	0.89	62.1	0.0775	0.0115	10.8
0.30	8.45	1.26	56.1	0.1090	0.0162	15.2
0.35	12.1	1.77	44.4	0.1720	0.0235	22.1

32. Laminar Flow

In tubular-flow reactors where turbulence is not fully developed, differences in residence time exist across the cross section. In true laminar flow, the velocity gradient is parabolic, with a maximum at the center of twice the mean value and gradually falling off to zero at the wall. Though it has been shown (Bosworth, 28) that the mean reaction time in laminar flow is the same as in plug flow, the conversion is not the same; the longer times that some molecules spend in the reactor do not always compensate for the shorter times others spend. The situation is further complicated by diffusion. Because of the longer residence time near the walls, products are formed there in greater concentration and tend to diffuse toward the center, whereas the reactants diffuse toward the walls, the net result being a partial compensation for lack of turbulence. Existence of free convection also favors the approach to plug flow.

Some idea of the order of magnitude of this effect may be obtained by considering a simplified case of first-order reaction that neglects both radial and axial diffusion. The velocity distribution is expressed by Poiseuille's equation for laminar flow:

$$u = 2u_m \left[1 - \left(\frac{r}{R} \right)^2 \right] \quad (5-29)$$

where u_m = mean velocity

R = radius of tube

Consider a differential element at distance r from the center, with cross

section dA and axial length dL . In the steady state, input equals output, so that (Fig. 5-3)

$$uC dA = u \left(C + \frac{dC}{dL} dL \right) dA + kC dA dL \quad (5-30)$$

Upon simplifying and substituting Eq. 5-29,

$$2u_m \left[1 - \left(\frac{r}{R} \right)^2 \right] \frac{dC}{dL} + kC = 0 \quad (5-31)$$

Integrating,

$$\ln \frac{C_0}{C} = \frac{kL}{2u_m [1 - (r/R)^2]} \quad (5-32)$$

This is the concentration at a point r distant from the center of the tube. The average concentration can be evaluated by numerical integration over the cross section.

Numerical calculations have been made (Cleland and Wilhelm, 46) of

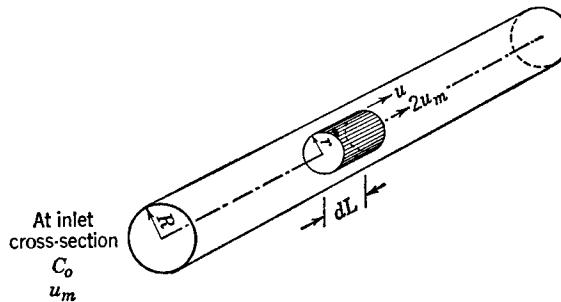


FIG. 5-3. Reaction during laminar flow through cylindrical pipe (Eq. 5-32).

plug and laminar flow with and without diffusion. Table 5-3 shows the comparison for a first-order reaction in the absence of diffusion. The parameter is the term $kL/2u_m$, which appears in Eq. 5-32. Clearly, the extent to which concentrations differ in plug- and laminar-flow reaction depends on the relative values of the specific reaction rate, the flow rate, and the distance from the inlet to the reactor.

In commercial reactors under laminar-flow conditions, sufficient free convection is usually present to enable use of plug-flow equations with little error, but in small-diameter laboratory units the differences may become serious. When obtaining data for scale-up purposes, it is preferable to maintain turbulent conditions in the laboratory test equipment.

Uneven reaction because of flow distribution sometimes may have quite undesirable effects. In polymerization of viscous mixtures, a broadening of the molecular-weight distribution will be obtained in a laminar-flow reactor compared with a thoroughly mixed system, consequently resulting in some differences in physical properties such as a softening range. Or if

there are side or consecutive degradation reactions, the lack of control of the residence times may be so serious as to require going to stirred reactors of some kind.

TABLE 5-3. COMPARISON OF PLUG AND LAMINAR FLOW WITHOUT DIFFUSION

$\frac{kL}{2u_m}$	Average concentration of effluent	
	Laminar flow	Plug flow
0.01	0.9810	0.9802
0.10	0.8328	0.8187
0.50	0.4432	0.3679
1.00	0.2194	0.1353
2.00	0.0603	0.0183

33. Nonisothermal Flow Reactions

Flow reactions taking place at varying temperatures are handled by design methods analogous to those of Chap. 3 on batch processes. Basically, the heat balance is developed to relate the degree of conversion to the temperature and thereby to the specific reaction rate. With this information the flow-reactor equation can be solved. The ensuing discussion will be concerned with the reaction $A + B \rightarrow C + D$, and the heat balances will be expressed in terms of heat capacities.

Over the entire cylindrical tubular reactor, the heat transfer per pound mole of feed is

$$Q = \int \frac{U(T_m - T)}{W} \frac{4}{D} dV_r = \frac{4}{D} \int_0^x U(T_m - T) \frac{dx}{r} \quad (5-33)$$

where T_m = temperature of heat-transfer medium

D = reactor diameter

$(4/D)dV_r$ = element of heat-transfer area

The heat balance then may be written

$$\begin{aligned} \int_{T_b}^{T_0} (n_{a0}s_a + n_{b0}s_b + n_{c0}s_c + n_{d0}s_d) dT &= (n_{a0} - x) \int_{T_b}^T s_a dT \\ &+ (n_{b0} - x) \int_{T_b}^T s_b dT + (n_{c0} + x) \int_{T_b}^T s_c dT + (n_{d0} + x) \int_{T_b}^T s_d dT \\ &+ x(\Delta H_r)_{T_b} - \frac{4}{D} \int_0^x U(T_m - T) \frac{dx}{r} \quad (5-34) \end{aligned}$$

When the heat of reaction is evaluated at the initial temperature T_b ,

$$\begin{aligned} \int_{T_b}^T (n_{a0}s_a + n_{b0}s_b + n_{c0}s_c + n_{d0}s_d) dT + x \int_{T_b}^T \Delta s dT + x(\Delta H_r)_{T_0} \\ - \frac{4}{D} \int_0^x U(T_m - T) \frac{dx}{r} = 0 \quad (5-35) \end{aligned}$$

where

$$\Delta s = s_c + s_d - s_a - s_b \quad (5-36)$$

Several cases may be distinguished, depending on the nature of the heat-transfer term in Eq. 5-34 or 5-35.

Case 1. Adiabatic conditions. The heat-transfer term disappears, the relation between T and x is then directly evaluated, and integration of the flow equation is direct.

Case 2. Constant heat flux. This occurs, for example, in direct-fired furnaces where the heating-fluid temperature is so high that the ΔT for heat transfer is not affected appreciably by changes in reactant temperature and the heat-transfer coefficient is practically constant. For integration, the same type of method is used as in case 3 following.

Case 3. When both the heat-transfer coefficient and T_m are constant, as with a boiling liquid or condensing vapor at constant pressure, only the variables T and x are involved in Eq. 5-34. This may be integrated one increment at a time, but only by trial, according to some procedure like the following:

1. Starting with T_0 and x_0 , choose a definite value of x_1 , a small increment beyond x_0 .
2. Estimate T_1 and thereby evaluate k_1 .
3. Integrate Eq. 5-34 by the trapezoidal rule. If the equation is satisfied, the correct value of T_1 had been chosen; if not, another value must be tried.
4. Once T_1 has been evaluated properly, select x_2 with the same increment of x as before. Proceed with estimates of T_2 as before, and subsequently for all other values of x until the desired conversion is reached. Instead of the trapezoidal rule, the more accurate Simpson's rule may be used as soon as three points become available.

Case 4. Constant U , variable T_m , reacting mixture and heat-transfer medium in concurrent flow. The calculation procedure is similar to case 3: for each value of x and estimated value of T , the corresponding value of T_m is calculated by heat balance over the entire reactor to that point. Then Eq. 5-35 is applied.

Case 5. Like Case 4, but with the reacting mixture and heat transfer medium in countercurrent flow. Here it is necessary to estimate in advance the effluent temperature of either the heat-transfer medium or the reacting mixture, say the former. Starting at the inlet to the reactor, the procedure of case 4 is followed. Correctness of the estimated value of T_m at the outlet is shown when the true inlet is matched. If a match is not obtained, the calculation must be repeated over the entire reactor with another estimate of outlet T_m .

Case 6. Both U and T_m variable. Familiarity with the procedures for solving the other cases will suggest approaches to this most general situation.

ation. Fortunately, the approximations of some one of the other cases are usually adequate.

Several examples of numerical solutions of programmed homogeneous flow reactions have been published. Murdoch and Holland (164) treat an endothermic first-order gas-phase reaction. Perkins and Rase (178) treat the case of vapor-phase propane pyrolysis in a tubular reactor with constant heat flux. A design method in chart form has been devised for endothermic first-order liquid-phase reactions in batch or flow tubular reactors heated with condensing vapors at constant temperature; it is based on a large number of solutions accomplished with a digital computer (Billingsley, McLaughlin, Welch, and Holland, 23).

Illustration 5-4. An ideal-gas mixture is charged to a reactor at the rate of 20 lb moles/hr. Initial temperature is 1500°R, and the pressure remains substantially constant at 5 atm. The reactor is made of 4-in.-ID tubing. The reaction is $A + B \rightarrow D$. These data apply:

$T, ^\circ\text{R.}$	1400	1450	1500	1550	1600
$(10^{-6})k, \text{ cu ft}/(\text{lb mole})(\text{hr.})$	0.078	0.152	0.300	0.585	1.12

Feed composition, mole %: A , 40; B , 40; inert, 20.

Specific heats, Btu/(lb mole)(°F): reactants, 6; products, 10; inert, 5.

$$\Delta H_r = 23,000 \text{ Btu/lb mole } A \text{ at } 500^\circ\text{R}$$

Under these conditions, find:

- (a) Reactor volume versus pound moles A converted under adiabatic conditions
- (b) Reactor volume versus the rate of heat transfer needed to maintain the temperature constant at 1500°R
- (c) Conversion versus reactor volume, when the initial temperature is 1500°R, the heat-transfer coefficient is 5 Btu/(hr)(sq ft)(°F), and T_m is constant at 1600°R

Solution. Base all quantities on 1 lb mole of total charge. The rate equation is

$$\begin{aligned} r &= k \left(\frac{n_a}{V} \right)^2 = k \left[\frac{n_{a0} - x}{\frac{RT}{\pi} (n_{a0} + \delta x)} \right]^2 = k \left[\frac{0.4 - x}{0.73T(1 - x)} \right]^2 \\ &= \frac{k}{(0.146T)^2} \left(\frac{0.4 - x}{1 - x} \right)^2 \end{aligned} \quad (A)$$

Applying Eq. 5-34,

$$\begin{aligned} [0.4(12) + 0.2(5)](1,500 - 500) &= [(0.4 - x)(12) + 10x + 0.2(5)](T - 500) \\ &\quad + 23,000x - \frac{4(5)}{0.333} \int_0^x \frac{(1,600 - T)dx}{r} \end{aligned} \quad (B)$$

$$\text{or } T = 500 + \frac{5,800 - 23,000x + 60 \int_0^x \frac{(1,600 - T)dx}{r}}{5.8 - 2x} \quad (C)$$

(a) Heat transfer is zero, so that

$$T = 500 + \frac{5,800 - 23,000x}{5.8 - 2x} \quad (D)$$

Applying the flow-reactor equation,

$$V_r = W \int \frac{dx}{r} = 20 \int_0^x \frac{(0.146T)^2}{k} \left(\frac{1-x}{0.4-x} \right)^2 dx \quad (E)$$

Accordingly, Table 5-4 is made, in which V_r is evaluated by numerical integration of Eq. E, using the auxiliary Eq. D. Beyond $x = 0.05$ in this case, adiabatic reaction appears to be impractical.

(b) To maintain isothermal conditions, substitute $T = 1500$ into the heat balance and rearrange it to

$$Q = 60 \int_0^x \frac{(1,600 - 1,500) dx}{r} = (5.8 - 2x)(1,500 - 500) - 5,800 + 23,000x \quad (F)$$

$$= 21,000x$$

where Q is the total heat transferred to the system up to the time its conversion becomes x , per pound mole of feed. Since the inside tube surface per cubic foot of reactor is $4/D$, the heat-transfer rate is

$$\text{Btu/(hr)(sq ft)} = \frac{DW}{4} \frac{dQ}{dV_r} = \frac{DW}{4} \frac{dQ}{W(dx)/r} = \frac{rD}{4} \frac{dQ}{dx} = 21,000 \frac{rD}{4}$$

$$= \frac{21,000(0.333)}{4} \frac{300,000}{[0.146(1500)]^2} \left(\frac{0.4-x}{1-x} \right)^2 = 10,920 \left(\frac{0.4-x}{1-x} \right)^2 \quad (G)$$

Furthermore,

$$V_r = W \int \frac{dx}{r} = \frac{20[0.146(1,500)]^2}{300,000} \int_0^x \left(\frac{1-x}{0.4-x} \right)^2 dx = 3.2 \int_0^x \left(\frac{1-x}{0.4-x} \right)^2 dx \quad (H)$$

Corresponding to various assumed values of x , values of heat-transfer rate and V_r are calculated from Eqs. G and H and shown in Table 5-5.

(c) With heat transfer, the procedure described under case 3 will be followed. The increment $\Delta x = 0.02$ will be used; larger increments lead, in this case, to erratic numerical values of the integrals. Calculations for the first two points will be shown.

$$x_0 = 0$$

$$T_0 = 1500$$

$$k_0 = 300,000$$

$$\frac{1}{r_0} = \frac{[0.146(1,500)]^2}{300,000} \left(\frac{1-0}{0.4-0} \right)^2 = 1.00$$

$$I_0 = \frac{1,600 - T_0}{r_0} = \frac{1,600 - 1,500}{1.0} = 100$$

For $x_1 = 0.02$:

Try	$T_1 = 1460$	Try	$T_1 = 1465$
	$k_1 = 188,000$		$k_1 = 174,000$
	$\frac{1}{r_1} = 1.62$		$\frac{1}{r_1} = 1.73$
	$I_1 = 1.62(1,600 - 1,460) = 219$		$I = 1.73(1,600 - 1,465) = 242$
$60 \int I dx = 60(0.02)(0.5)(100 + 219)$		$60 \int I dx = 60(0.02)(0.5)(100 + 242)$	
$= 192$		$= 205$	
$T_1 = 500 + \frac{5800 - 460 + 192}{5.76}$		$T_1 = 500 + \frac{5800 - 460 + 205}{5.76}$	
$= 1460.4$		$= 1462.7$	

Interpolating, $T_1 = 1461$ and $I_1 = 224$.

For $x_2 = 0.04$:

$$\text{Try } T_2 = 1445 \\ k_2 = 142,000$$

$$\frac{1}{r_2} = 2.23$$

$$I_2 = 345$$

$$60 \int I dx = 60 \left(\frac{0.02}{3} \right) [100 + 4(224) + 345] \\ = 537 \\ T_2 = 500 + \frac{5800 - 920 + 537}{5.72} \\ = 1447.0$$

$$\text{Try } T_2 = 1450 \\ k_2 = 151,000$$

$$\frac{1}{r_2} = 2.11$$

$$I_2 = 317$$

$$60 \int I dx = 60 \left(\frac{0.02}{3} \right) [100 + 4(224) + 317] \\ = 525 \\ T_2 = 500 + \frac{5800 - 920 + 525}{5.72} \\ = 1444.9$$

Interpolating, $T_2 = 1446.5$. Continue in this way for the remaining points, with the results shown in Table 5-6. With the aid of this relation between T and x , the reactor volume is evaluated by integration of

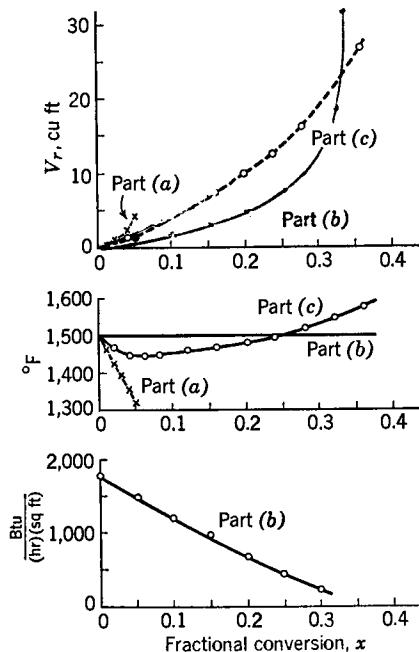


FIG. 5-4. Relation between conversion, reactor volume, temperature, and heat flux (Illustration 5-4).

Given the following additional data, calculate the amount of conversion taking place when (a) all 18 tubes are fired at the rate of 8000 Btu/(hr)(sq ft) and (b) the first 9 tubes are fired at 12,000 and the others at 4000 Btu/(hr)(sq ft).

$$V_r = W \int \frac{dx}{r} \\ = 20 \int_0^x \frac{(0.146T)^2}{k} \left(\frac{1-x}{0.4-x} \right)^2 dx \quad (I)$$

These results are also shown in Table 5-6. Figure 5-4 summarizes the results for parts a, b, and c.

Illustration 5-5. Thermal cracking of a 25°API gas oil is to be accomplished in a tubular furnace at a charge rate of 10,000 bpsd, or 132,000 lb/hr. The furnace has 18 tubes in two groups of 9 each with separate firing controls. Inlet pressure is 775 psia, and inlet temperature is 800°F. Cracked products consist of light hydrocarbons, hydrogen, and gasoline and remain fairly constant in composition over the commercially feasible range of cracking, with an average molecular weight of 71. Under the cracking conditions, the conversion products will be all in the vapor phase, whereas the oil will remain condensed. Pressure drop may be calculated sufficiently accurately from the equation given in this illustration, using a mean density of the two-phase mixture and a constant friction factor of 0.005, though better results could be achieved by the method of Chenoweth and Martin (40).

TABLE 5-4. DATA FOR ILLUSTRATION 5-4a

x	T	$10^{-3}k$	$\frac{1}{r}$	\int_0^x	V_r , cu ft
0	1500	300	1.00	0	0
0.01	1464	185	1.59	0.0129	0.26
0.02	1426	110	2.62	0.0333	0.67
0.03	1391	73	3.88	0.0661	1.32
0.04	1354	42	6.62	0.1158	2.32
0.05	1315	25	10.85	0.2001	4.00

TABLE 5-5. DATA FOR ILLUSTRATION 5-4b

x	$\left(\frac{1-x}{0.4-x}\right)^2$	\int_0^x	V_r , cu ft	$\frac{\text{Btu}}{(\text{hr})(\text{sq ft})}$
0	6.25	0	0	1750
0.05	7.35	0.34	1.09	1490
0.10	9.00	0.75	2.40	1200
0.15	11.55	1.26	4.03	945
0.20	16.0	1.93	6.17	683
0.25	25.0	4.68	15.0	437
0.30	49.0	10.6	31.8	223

TABLE 5-6. DATA AND RESULTS FOR ILLUSTRATION 5-4c

x	T	10^3k	$\frac{1}{r}$	\int_0^x	V_r , cu ft
0	1500	300	1.00		
0.02	1461	178	1.66		
0.04	1446.5	145	2.16	0.0655	1.3
0.06	1448	147	2.32		
0.08	1448	147	2.51	0.1586	3.2
0.10	1454	161	2.52		
0.12	1459.5	173	2.59	0.2599	5.2
0.14	1464.5	185	2.70		
0.16	1468	195	2.89	0.3684	7.4
0.18	1474	211	2.98		
0.20	1481	232	3.22	0.4889	9.8
0.22	1489	260	3.41		
0.24	1494.5	280	3.83	0.6271	12.5
0.26	1505.5	320	4.21		
0.28	1516	370	4.76	0.7971	16.0
0.30	1527.5	430	5.64		
0.32	1541.5	520	7.01	1.0261	20.5
0.34	1557	640	9.75		
0.36	1574.5	820	16.5	1.3441	26.7

Furnace data:

Series flow through all 18 tubes

Tube size: 4 in. ID, 5.5 in. OD, 60 ft long

Effective surface, 84 sq ft per tube; equivalent length, 85 ft per tube; volume including return bend, 5.65 cu ft per tube

Other data:

Vapor density

$$\frac{1}{\rho_a} = \frac{zRT}{MP} = \frac{0.126T}{P} \quad \text{cu ft/lb}$$

Mixture density

$$\frac{1}{\rho_m} = \frac{0.126Tx}{P} + \frac{1-x}{\rho_L} \quad \text{cu ft/lb}$$

Heat of cracking

350 Btu/lb of total conversion (gas and gasoline)

Pressure drop, psi

$$\Delta P = \frac{0.005G^2L}{72gD\rho_m} = \frac{0.005(422)^2L}{72(32.2)(0.333)\rho_m} = \frac{1.153L}{\rho_m}$$

Other data are shown in Table 5-7.

Solution. The rate equation may be written

$$dx = k(1-x) dt = \frac{k\rho(1-x)}{W} dV \quad (A)$$

Over a short interval this may be integrated on the assumption that $1/k\rho$ is constant at the mean value over the interval, with the result

$$\frac{V_{n+1} - V_n}{W} = \int \frac{dx}{k\rho(1-x)} = \left(\frac{1}{k\rho} \right)_m \ln \frac{1-x_{n+1}}{1-x_n} \quad (B)$$

or

$$x_{n+1} = 1 - (1-x_n)e^{-\alpha} \quad (C)$$

where

$$\alpha = \frac{V_{n+1} - V_n}{W(1/k\rho)_m} \quad (D)$$

TABLE 5-7. DATA FOR ILLUSTRATION 5-5

Temperature, °F	$(10^4)k$, sec ⁻¹	Enthalpy, Btu/lb		Liquid density, lb/cu ft
		Liquid	Vapor	
800	7.3	492	581	39.3
820	12.6	507	594	38.8
840	21.2	521	609	38.4
860	35.3	536	625	37.9
880	57.5	550	640	37.5
900	90.0	565	657	37.1

The solution will be carried out by this approximate method, taking a constant-reactor-volume increment, $V_{n+1} - V_n$, corresponding to three tubes. A terminal value of x will be assumed for one increment at a time and then substantiated. Table 5-8 sum-

marizes the results for part *a*. Temperatures and conversions for both cases are plotted in Fig. 5-5. Calculations for the first two points follow.

Try $x_1 = 0.015$. Then

$$\Delta x = 0.015$$

$$H_1 = 492 + \frac{8000(84)(3)}{132,000} - 0.015(350) = 492 + 15.3 - 5.3 = 502.0$$

With the assumed conversion, the mixture enthalpy is

$$H = 0.015(594) + 0.985(507) = 508.3, \text{ at } 820^\circ\text{F}$$

$$H = 0.015(581) + 0.985(492) = 493.3, \text{ at } 800^\circ\text{F}$$

Therefore, by interpolation,

$$T_1 = 812^\circ\text{F}$$

$$k_1 = 10(10^{-4})$$

$$\frac{1}{\rho_1} = \frac{0.126(1,272)(0.015)}{P_1} + \frac{0.985}{39.0} = \frac{2.41}{P_1} + 0.0252$$

$$P_1 = 775 - \frac{1.153(85)(3)}{(39.3 + \rho_1)/2} = 775 - \frac{588}{39.3 + \rho_1}$$

Solving the last two equations simultaneously,

$$P_1 = 767$$

$$\rho_1 = 35.3$$

$$\text{Then } \left(\frac{1}{k\rho}\right)_m = 0.5 \left[\frac{1}{7.3(39.3)} + \frac{1}{10(35.3)} \right] (10^4) = 31.5$$

From Eq. *D*,

$$\alpha = \frac{5.65(3)}{132,000(31.5)/3,600} = \frac{0.462}{31.5} = 0.0147$$

From Eq. *C*,

$$x_1 = 1 - \frac{1 - 0}{1.0148} = 0.0146$$

which is a close check.

Try

$$x_2 = 0.033$$

$$\Delta x = 0.033 - 0.015 = 0.018$$

$$H_2 = 502.0 + 15.3 - 6.3 = 511.0$$

$$H = 0.033(594) + 0.967(507) = 509.8 \text{ at } 820^\circ\text{F}$$

$$H = 0.033(601) + 0.967(514) = 516.9 \text{ at } 830^\circ\text{F}$$

Interpolating,

$$T_2 = 821^\circ\text{F, or } 1281^\circ\text{R}$$

$$k_2 = 13(10^{-4})$$

$$\frac{1}{\rho_2} = \frac{0.126(1,281)(0.033)}{P_2} + \frac{0.967}{38.8} = \frac{5.33}{P_2} + 0.0249$$

$$P_2 = 767 - \frac{588}{35.3 + \rho_2}$$

Solving simultaneously,

$$P_2 = 759$$

$$\rho_2 = 31.4$$

$$\text{Then } \left(\frac{1}{k\rho}\right)_m = 0.5 \left[\frac{1}{10(35.3)} + \frac{1}{13(31.4)} \right] (10^4) = 27.0$$

$$\alpha = \frac{0.462}{27.0} = 0.0171$$

$$x_2 = 1 - \frac{0.985}{1.0172} = 0.0318$$

which is a close check on the assumption. The remaining points are established in the same way and summarized in Table 5-8.

TABLE 5-8. RESULTS FOR ILLUSTRATION 5-5a

	0	1	2	3	4	5	6
T	800	812	821	831	840	846	853
x	0	0.015	0.032	0.051	0.073	0.096	0.120
$10^4 k$	7.3	10.0	13.0	16.9	21.2	25.0	30.0
P	775	767	759	749	738	726	712
H	492.0	502.0	511.0	519.3	527.2	537.4	541.7
Tubes.....	0	3	6	9	12	15	18

Figure 5-5 shows that initially rapid heating gives improved conversion in comparison with uniform heating, at the same over-all average heat input. In this particular example, the choice of heating rates, 12,000 and 4000, was not good because the tempera-

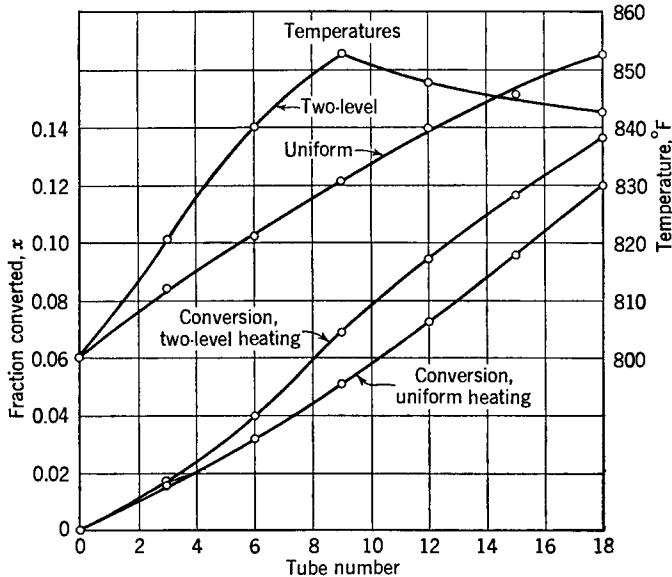


FIG. 5-5. Cracking of gas oil at several heating rates (Illustration 5-5).

ture of the oil decreases in the last section of the furnace. Generally, a negative temperature gradient will lead to coke formation on the tube surface. A combination of 10,000 and 6000 as heating rates probably would keep the temperature rising throughout the furnace and would still give an improvement over uniform heating at a rate of 8000.

34. Semiflow Processes

Types of processes occur in which the several reactants are charged at different rates. In one type, some of the reactants are charged quickly in bulk to the reactor and the others are fed in gradually. Or one reactant

may be charged to the inlet of a flow reactor and the others injected at intervals along the reactor. Examples of the latter are some regenerations of moving-bed catalysts where air is injected at several points in the reactor as the catalyst moves down, to keep down temperature rise, and the polymerization of olefins catalyzed by a film of phosphoric acid distributed over sand particles, where partially spent material is recycled and injected together with some fresh feed at two or three positions into the reactor while the bulk of the charge is flowing through it. As mentioned in Sec. 25, the purpose of such operations may be to limit thermal effects or to improve product distribution; or it may be required by such factors as limited solubilities or the desirability of recycling partially spent materials or diluents.

Such a great variety of situations can occur that only a few representative ones can be described here, enough to indicate the method of approach to such problems.

Illustration 5-6. The reaction $A + B \rightarrow$ products occurs isothermally in a stirred reactor. Reactant A , in solution of concentration C_{a0} , is charged to the reactor to a volume V_0 ; then reactant B is pumped in at the rate F in solution of concentration C_{b0} . There is no overflow and no change in density. Find the relation between the time and the amount of unreacted A present in the tank.

Solution

$$C_a = \frac{n_a}{V} \quad (5-37)$$

$$C_b = \frac{FtC_{b0} - (n_{a0} - n_a)}{V} \quad (5-38)$$

$$V = V_0 + Ft \quad (5-39)$$

Therefore

$$-\frac{dn_a}{dt} = rV = kVC_aC_b = \frac{kn_a(FtC_{b0} - V_0C_{a0} + n_a)}{V_0 + Ft} \quad (5-40)$$

This equation is of the form

$$\frac{dy}{dx} = \frac{y(a + bx + cy)}{d + ex} \quad (5-41)$$

which is an Abel equation of the second type (Kamke, 117); it is best solved by numerical methods.

Illustration 5-7. A stirred reactor of volume V_0 is filled with a reacting mixture of A and B in solution. The reaction is $A + B \rightarrow$ products. A solution of substance B , of concentration C_{b0} , is pumped in at a rate of F cfm, and the solution overflows from the well-stirred tank at the same rate. Determine the progress of the reaction.

Solution. Making a material balance on substance A in time dt :

$$\begin{aligned} \text{Input} &= \text{output} &+ \text{accumulation} \\ 0 &= FC_a dt + rV_0 dt + V_0 dC_a \end{aligned}$$

For substance B ,

$$FC_{b0} dt = FC_b dt + rV_0 dt + V_0 dC_b$$

Consequently,

$$(FC_{b0} - FC_b - kV_0C_aC_b) dt = V_0 dC_b \quad (5-42)$$

$$-(FC_a - kV_0C_aC_b) dt = V_0 dC_a \quad (5-43)$$

Dividing,

$$\frac{dC_a}{dC_b} = - \frac{FC_a - kV_0C_aC_b}{FC_{bf} - FC_b - kV_0C_aC_b} \quad (5-44)$$

This, again, is an Abel equation. It may be integrated numerically to provide a relation between C_a and C_b , and then Eq. 5-43 can be integrated to relate the time to the concentrations.

Illustration 5-8. A gas B is fed to a stirred tank which contains a volume V_0 of a solution of A . The solubility of B is limited but is independent of the presence of dissolved substances. Find the relation between the time and the variable feed rate needed to keep the solution saturated with unreacted substance B .

Solution. Let C_{b0} be the constant concentration of B . The material balance on B is

$$\begin{aligned} \text{Input} &= \text{output} + \text{accumulation} \\ F dt &= kV_0C_aC_{b0} dt + 0 \end{aligned} \quad (5-45)$$

For substance A ,

$$0 = kV_0C_aC_{b0} dt + V_0 dC_a \quad (5-46)$$

Integrating Eq. 5-46,

$$C_a = C_{a0}e^{-kC_{b0}t} \quad (5-47)$$

Substituting into Eq. 5-45,

$$F = kV_0C_aC_{b0} = kV_0C_{a0}C_{b0}e^{-kC_{b0}t} \quad (5-48)$$

which is the desired relation.

PROBLEMS

5-1. The reaction $A \rightarrow B$ is conducted at 1000°R and 3 atm in a tubular-flow reactor. The feed contains 30 mole % A and the balance inert material. Feed rate is 50 lb moles/hr. The rate equation is $r = 48.6n_a/V$.

- (a) What space velocity is needed?
- (b) What volume of reactor is needed?

5-2. For the system of Illustration 5-4 a modified operation is to be tried. A constant rate of heat transfer will be used, 1000 Btu/(hr)(sq ft). The feed will be divided, half entering at the beginning of the reactor, the remainder at the mid-point. The reactor is of sufficient size to give 50 per cent conversion when all the material is charged at the inlet. What conversion is attained by the split-flow arrangement?

5-3. Integrate the flow equation $V_r/W = \int_0^x dx/r$ for the following gas-phase reactions at constant pressure and temperature:

- (a) $2A \rightarrow M$.
- (b) $A + B \rightarrow M$.
- (c) $2A \rightleftharpoons M$.
- (d) $A + B \rightleftharpoons M$.

5-4. An ideal-gas reaction $A \rightarrow 2B$ occurs under adiabatic-flow conditions, starting with pure A at 600°R , at a constant pressure of 2 atm. Given these data:

$$s_a = 20 \text{ Btu}/(\text{lb mole})(^{\circ}\text{F})$$

$$s_b = 15 \text{ Btu}/(\text{lb mole})(^{\circ}\text{F})$$

$$\Delta H_r = -2000 \text{ Btu/lb mole of } A \text{ converted, at } 600^{\circ}\text{R}$$

$$k = 150e^{-3,000/T} \text{ sec}^{-1}$$

Find the space velocity and the true contact time for a conversion of 80 per cent.

5-5. A tubular-flow reactor is to be compared with a continuous stirred tank for a reaction with rate equation $r = -dC/dt = 1.0C$.

- (a) Make a plot of per cent conversion against time for each.

(b) Make a plot of per cent conversion against the ratio of the volumes of the two types needed to achieve equal conversions at equal charge rates.

5-6. The consecutive reactions $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ are to be compared in a tubular-flow reactor and in a continuously stirred tank. Make a plot of time versus concentration of the three participants, given that $C_{a0} = 4$ lb moles/cu ft, $C_{b0} = C_{c0} = 0$, $k_1 = 0.35$ hr^{-1} , and $k_2 = 0.13 \text{ hr}^{-1}$.

5-7. Chlorination of oleic acid dissolved in carbon tetrachloride was tested in a flow reactor (Roper, 188) with the data shown at 12.8°C. Chlorine and oleic acid were dissolved separately in CCl_4 and mixed in the liquid phase at the inlet to the reactor. Show that the reaction is second-order.

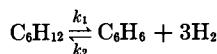
Reactor volume feed volume/sec	C_{a0} , g moles Cl_2 /liter	C_{b0} , g moles acid/liter	C_a , g moles Cl_2 /liter
0.054	0.0208	0.0242	0.0181
0.093	0.0208	0.0242	0.0162
0.258	0.0186	0.0242	0.0097
0.350	0.0186	0.0242	0.0072
0.573	0.0186	0.0242	0.0056

5-8. Conversion of methylcyclopentane (MCP) to benzene is accomplished at 950°F, 300 psig, and ratio $\text{H}_2:\text{MCP} = 4$, with the following results (Heinemann, Mills, Hattman, and Kirsch, 87):

Liquid volumes MCP/hr volume of catalyst	Benzene, % of equilibrium	Conversion of MCP, wt %
1	77.5	90
2	64.0	83.5
3	56.0	79
6	45.0	73.5

Equilibrium conversion of benzene is 92 mole %.

Determine if these data can be represented by a rate equation based on the assumption that the reaction proceeds according to the reversible equation



Bulk density of the catalyst may be assumed as 0.7 g/ml, and that of MCP = 0.754. Space velocity in the table is expressed in terms of liquid volumes of MCP, but the reaction is actually vapor phase. For present purposes, the compressibility factors may be taken unity for all participants.

5-9. Ethylene can be oxidized to ethylene oxide over a silver-alumina catalyst. Experimental data were obtained at 260°C, and atmospheric pressure partly as follows (Wan, 227):

Inlet superficial velocity	30.3 cm/sec
Inlet composition	80% C_2H_4 , 20% O_2
Catalyst bulk density	1.34 g/ml

From these and the following data, evaluate the constants of the rate equation

$$r = \frac{dn_{\text{C}_2\text{H}_4\text{O}}}{dt} = k(p_{\text{C}_2\text{H}_4})^a(p_{\text{O}_2})^b$$

Catalyst bed length, cm	% conversion of C_2H_4 to C_2H_4O	Rate of C_2H_4O production, g moles/(hr)(g catalyst)
30.3	6.50	0.00316
15.2	3.92	0.00387
9.1	2.58	0.00420
6.1	1.77	0.00434
3.0	0.902	0.00442
0	0	0.00457

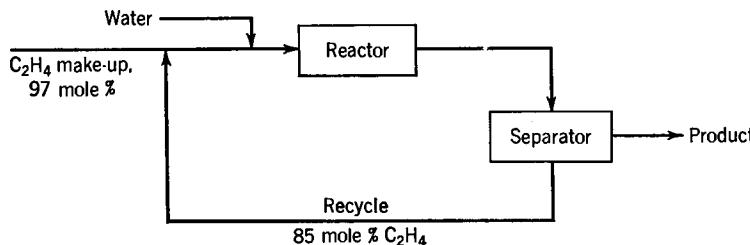
where $n_{C_2H_4O}$ is gram moles ethylene oxide made per gram catalyst, t is in hours, and the partial pressures are in atmospheres. It is sufficiently accurate for the purpose to base a contact time on an average of the inlet and outlet flow rates.

5-10. Direct catalytic hydration of ethylene to ethanol is carried out at 570°F and 1,000 psig, with the ratio of moles water feed/moles total ethylene feed = 0.6, as shown in the flow sketch (Nelson and Courter, 168). These conversion data were obtained:

VMSV.....	54	28	0
% conversion of total ethylene fed.....	3.5	4.5	6.1 (equilibrium)

The space velocity VMSV is volumes of feed at 60°F and 1 atm per minute and per volume of catalyst.

- When VMSV = 54, find the average contact time taking 40% external voids
- When VMSV = 54, find the specific reaction rate, assuming a simple second-order reaction.
- Find the specific reaction rate on the assumption that the reaction is second-order forward and first-order in reverse.



5-11. Pyrolysis of ethylbenzene was carried out at 950°F in a flow reactor (Rase and Kirk, 186) with the following (smoothed) results at low-fractional conversions:

$\frac{W}{F}$, g catalyst g mole feed/hr	Fractional conversion x	
	At 0.97 atm	At 3.15 atm
0	0	0
5	0.009	0.025
10	0.021	0.047
15	0.031	0.068
20	0.040	
25	0.049	

Assuming a linear variation of specific reaction rate with pressure, what is the specific reaction rate at a pressure of 1.5 atm?

5-12. Plant data on the rate of synthesis of ammonia from hydrogen and nitrogen have been correlated in terms of the Temkin and Pyzhev equation (Annable, 3):

$$r = \frac{Fdn_{\text{NH}_3}}{dV_R} = 2 \left(k_1 \frac{p_{\text{N}_2} p_{\text{H}_2}^{1.5}}{p_{\text{NH}_3}} - k_2 \frac{p_{\text{NH}_3}}{p_{\text{H}_2}^{1.5}} \right) \quad \text{kg moles/(hr)(cu m catalyst)}$$

where the partial pressures are in atmospheres. Representative data at 300 atm were

$$k_2 = 30.1, \text{ at } 420^\circ\text{C}$$

$$k_2 = 312.0, \text{ at } 470^\circ\text{C}$$

Also k_2 varied with the pressure, being proportional to $P^{-0.63}$. The forward specific reaction rate k_1 is obtained from equilibrium data; percentage of ammonia at equilibrium from a 3:1 molal mixture of H_2 and N_2 is 32.0 per cent at 250 atm and 450°C .

Given the initial gas composition, mole fractions:

$$\text{NH}_3 = 0.060$$

$$\text{H}_2 = 0.578$$

$$\text{N}_2 = 0.192$$

$$\text{CH}_4 = 0.045$$

$$A = 0.125$$

At a temperature of 450°C and a pressure of 250 atm and a feed rate of 1,000 kg moles/hr, find the volume of reactor needed to achieve 75 per cent of equilibrium content of ammonia.

5-13. Pyrolysis of propane was accomplished by bubbling the gas through molten lead at 1400°F and 4 psig (Fair, Mayers, and Lane, 67). These tests were made in a comparatively shallow depth of lead, so the reactor was considered equivalent to a perfectly mixed tank with substantially no temperature or concentration gradients. The rate equation developed was

$$r = \frac{k\pi(1-x)}{1 + \delta x} = \frac{0.15\pi(1-x)}{1 + 0.95x} \quad \frac{\text{lb moles propane converted}}{(\text{hr})(\text{cu ft lead})(\text{psia})}$$

Consider a reactor with a molten-lead cross section of 4 sq in., filled to a depth of 3 ft, in which there may be considered to be no axial mixing. Lead density is 685 lb/cu ft, temperature is 1400°F , and pressure above the lead surface is 2 psig. Charge rate of pure propane is equivalent to a superficial velocity at the surface of 2 fps at temperature. Calculate the conversion attained, taking into account the variation in static head.

5-14. Polymerization of propylene was conducted in a packed tower with the gas flowing countercurrently to 98 per cent liquid phosphoric acid (Bethea and Karchmer, 22). Composition of the charge was:

Component	Mole %
Propylene.....	58.0
Propane.....	41.0
Butylene.....	0.5
Butane.....	0.5

On an average, 1 mole of polymer required 3.4 moles of propylene. Selected data at 360°F are:

Pressure, psig.....	400	500	702	700
Olefin feed rate, g moles/(hr)(liter of reactor).....	3.25	7.10	7.22	13.12
Olefin conversion, %.....	88.6	70.6	86.6	60.5
Average compressibility factor.....	0.83	0.81	0.67	0.72

The reaction is first-order. Calculate the specific reaction rate per hour for each run.

5-15. Polymerization of propylene is catalyzed by phosphoric acid distributed as a film on quartz particles. An empirical equation is proposed (Langlois and Walkey, 130) for the conversion, namely,

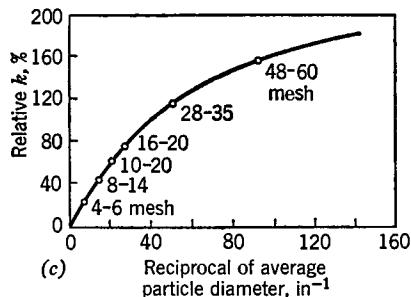
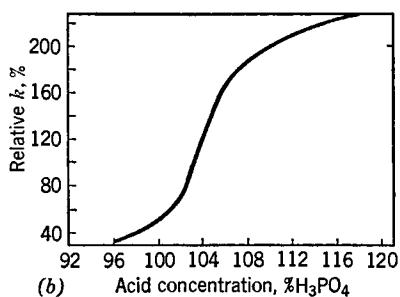
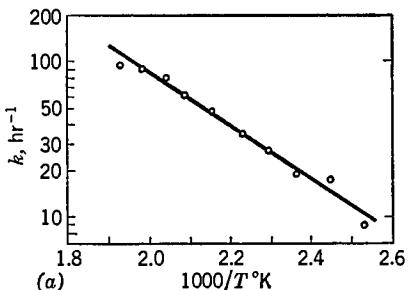


FIG. 5-6. Specific reaction rate of propylene polymerization for Prob. 5-15. (a) Effect of temperature: phosphoric acid concentration, 103 per cent; quartz diameter, 0.025 in.; (b) effect of acid concentration; (c) effect of particle size of quartz. [Langlois and Walkey (130). Courtesy Petroleum Refiner.]

(a) How much A is present in the tank at this time?

(b) What percentage conversion of B has been attained?

5-17. A stirred reactor is charged with 10 cu ft of reactant A . The solubility of

$$\frac{k}{S} = \int_0^x \frac{(1 - Bx)^2}{(1 - x)^2 + 0.3x(1 - x)} dx$$

where B = (mole fraction monomer in feed) $\times \left(1 - \frac{\text{mole wt of monomer}}{\text{mole wt of polymer}}\right)$

k = specific reaction rate, hr^{-1}

S = space velocity = volume of gas feed at reactor temperature and pressure per volume of catalyst voids per hour; voids assumed 42 per cent

x = fractional conversion of monomer

Figure 5-6 presents data on k as a function of temperature, acid concentration, and particle size. Enthalpy data may be found, for example, in Maxwell (149).

Consider a 50:50 mixture of propylene and propane fed at the rate of 100 lb moles/hr initially at 300°F and 350 psig. Phosphoric acid concentration is 104 per cent, and quartz size is 16 to 20 mesh. Pressure drop may be neglected. Conversion of 80 per cent of the propylene is desired, and it may be assumed that a 25:75 mixture of C_6 and C_8 hydrocarbons is made. Calculate the volume of catalyst required when:

(a) Isothermal conditions prevail.

(b) Adiabatic conditions prevail.

(c) The feed is divided into three equal streams. One of these is charged to the inlet of the reactor, the others are cooled to 250°F, then injected individually into the reaction mixture at points one-third and two-thirds of the distance along the reactor.

5-16. In Illustration 5-6, let

$$C_{a0} = 2.5 \text{ lb moles/cu ft}$$

$$C_{b0} = 1.8 \text{ lb moles/cu ft}$$

$$F = 50 \text{ cfh}$$

$$V_0 = 30 \text{ cu ft}$$

At the end of 0.2 hr, the rate of reaction corresponds to

$$\frac{1}{k} \frac{dn_A}{dt} = -13.5$$

reactant B is limited at 0.02 cu ft of B /cu ft of mixture , so it is pumped in just fast enough to keep the solution in the tank saturated. In the concentration range of interest, the reaction may be taken as pseudo-first-order with respect to substance A with $k = 20 \text{ hr}^{-1}$. The molal density of each reactant is 0.5 lb mole/cu ft. After 1.5 hr, at what rate is B being pumped in?

5-18. A mixture is fed at the rate of 100 cfh to a two-stage CSTR battery. The effluent from the second stage continues to react in the line going to the storage tank. This line is 0.864 sq in. cross section and 1,000 ft long. The reaction is $2A \rightleftharpoons C + D$. Initially the concentration of A is 1.5 lb moles/cu ft and those of C and D are zero. The specific reaction rate in the forward direction is $10 \text{ cu ft}/(\text{lb mole})(\text{hr})$, and the thermodynamic equilibrium constant is $K_c = 16.0$. It is desired to have 80 per cent of equilibrium conversion at the inlet to the storage tank. What is the volume of each of the stirred reactors, and what is the concentration of the effluent leaving the second stage?

CHAPTER 6

UNCATALYZED HETEROGENEOUS REACTIONS

35. Heterogeneous Reactions

Many industrial processes involve reactants in more than one phase. Such reactions are complicated by the fact that before substances in different phases can react, they must migrate to at least the interface. Consequently, in addition to chemical affinity, certain physical factors which affect the rate of mass transfer between phases also affect the overall rate of heterogeneous reaction. These factors are as follows:

1. Amount of interfacial surface, to which the rate may be proportional under some conditions. Interfacial surface is created by grinding solids, or dispersion of fluids with spray nozzles or agitators, or dispersion by percolation through beds of solid particles.
2. Rate of diffusion of fluids to and across the interfacial film, which is influenced principally by the relative velocities of the two phases, the pressure of the gas phase, and to a minor extent the temperature of the system, in addition to the physical properties of the reactants and the geometry of the system.
3. Rate of diffusion of the products away from the reaction zone, which is of importance only with reversible reactions, unless the concentrations of the products are sufficient to influence the diffusivities of the reactants.

Particularly noteworthy is induction of turbulence by agitation or other means. Not only may this control the amount of surface available for reaction, but it may eliminate concentration gradients that might otherwise hinder diffusion.

A complete formulation of the rate equation must take into account both the mass-transfer and chemical-reaction rates. This is a special case of an even more complicated situation where adsorption also takes place. Section 48 treats this problem, which leads to some fairly cumbersome equations. A limited degree of success has been attained in the quantitative treatment of gas absorption combined with chemical reaction. This is considered in detail later in the chapter.

In some instances, one of the rates, mass transfer or reaction, is so much smaller than the other that it becomes the controlling one. This is analo-

gous to the situation that prevails in some heat-transfer or pure mass-transfer problems. Experimentally, the dominant mechanism can be detected by observing the effects of certain changes in operating conditions. For example, if the over-all rate increases markedly with temperature in accordance with the Arrhenius law, the chemical rate is controlling. Or the rate may change when the amount of interfacial surface or the flow rate is varied, in a way predicted by correlations for the rate of mass transfer.

When a reaction is studied experimentally, it may be desirable to seek the conditions under which one rate factor at a time is controlling. Though with this information it will not be possible to calculate rigorously the rate for any intermediate condition, in many instances an adequate estimate can be made from the extreme conditions.

The variables influencing chemical-reaction rate have been considered previously; those influencing mass-transfer rate are discussed in this chapter.

36. Examples of Heterogeneous Reactions

Heterogeneous reactions of industrial significance occur between all combinations of gas, liquid, and solid phases. A few examples, chiefly from the inorganic field, are shown in Table 6-1. The most widely investigated class is the reactions between gases and liquids, which is considered at length further on. For the moment, examples of the other classes will be described briefly.

The combustion of carbon in air was investigated by Tu, Davis, and Hottel (219), with temperature and air-flow rate as the principal variables. Figure 6-1 shows that at low temperatures, air velocity had no effect on the rate of reaction, demonstrating that chemical resistance is dominant, whereas at higher temperatures the chemical-reaction rate is so rapid that the rate of air supply is controlling. As a rule, the latter is the case in industrial furnaces. For example, Gumz (83) estimates that at 2192°F the rate of chemical reaction is 150 lb/(hr)(sq ft), but only about 1 per cent of this amount is actually burned because of the limited rate at which oxygen can be supplied to the surface of the coal.

Ion-exchange reactions take place between a solid (the ion-exchange resin) and a substance dissolved in a liquid. Three steps may influence the rate of reaction, namely (1) diffusion in the liquid to the surface of the resin particle, (2) internal diffusion in the particle, and (3) chemical reaction within the solid particle. The chemical-reaction step is relatively fast; in fact, none of the systems thus far studied experimentally appears to be limited by the chemical step, but examples are known where diffusion in either the liquid or the solid is limiting. Cases are known where both these factors are of the same general order of magnitude. Design of

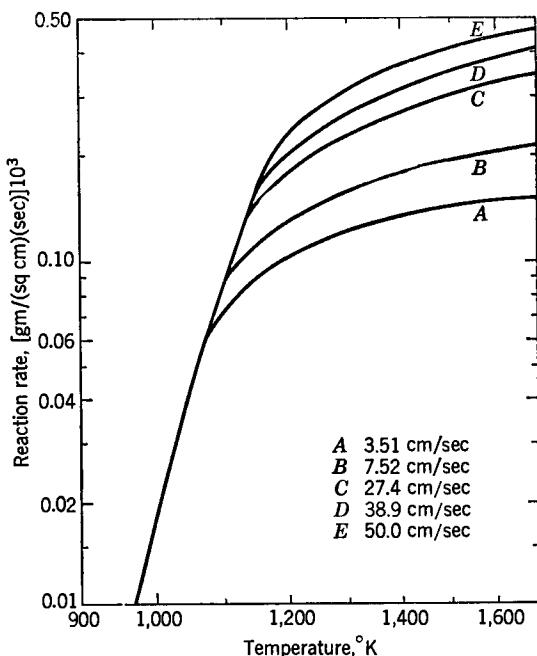


FIG. 6-1. Effect of air velocity on combustion rate of carbon. [Tu, Davis, and Hottel (219). Courtesy *Industrial and Engineering Chemistry*.]

ion exchangers is somewhat complicated by the fact that usually fixed beds are operationally most feasible, in which case an unsteady state exists with its constantly varying concentration gradient throughout (Selke, 197).

A well-known example of reaction between two immiscible liquids is the nitration of benzene by the action of concentrated aqueous nitric acid in the presence of sulfuric acid as catalyst. Reaction takes place in both phases, the rate in the acid phase being several times that in the organic. When the interfacial surface is not sufficient to keep the phases mutually saturated, the rate of reaction drops off sharply. Lewis and Suen (144) measured the reaction rate at constant interfacial area and found it to be a linear function of the rate of stirring, which is roughly consistent with the general observation that diffusion increases approximately as the 0.8 power of the flow rate. The two layers were rotated in opposite directions by individual stirrers. In these experiments the amount of interfacial surface was so small that diffusion remained the limiting factor over the entire range of stirring. In industrial operations, on the other hand, emulsification generally occurs and results in such large interfacial area that the phases are mutually saturated and diffusion no longer controls.

No simple, comprehensive theory describes the behavior of decompo-

TABLE 6-1. SOME INDUSTRIAL HETEROGENEOUS REACTIONS (UNCATALYZED)

Gas-Solid

1. Action of chlorine on uranium oxide to recover volatile uranium chloride
2. Removal of iron oxide impurity from titanium oxide by volatilization by action of chlorine
3. Combustion of coal
4. Manufacture of hydrogen by action of steam on iron
5. Manufacture of blue gas by action of steam on carbon
6. Calcium cyanamide by action of atmospheric nitrogen on calcium carbide
7. Burning of iron sulfide ores with air
8. Nitriding of steel¹

Liquid-Solid

9. Ion exchange
10. Acetylene by action of water on calcium carbide
11. Cyaniding of steel
12. Hydration of lime
13. Action of liquid sulfuric acid on solid sodium chloride or on phosphate rock or on sodium nitrate
14. Leaching of uranium ores with sulfuric acid

Gas-Liquid

15. Sodium thiosulfate by action of sulfur dioxide on aqueous sodium carbonate and sodium sulfide
16. Sodium nitrite by action of nitric oxide and oxygen on aqueous sodium carbonate
17. Sodium hypochlorite by action of chlorine on aqueous sodium hydroxide
18. Ammonium nitrate by action of ammonia on aqueous nitric acid
19. Nitric acid by absorption of nitric oxide in water
20. Recovery of iodine by action of sulfur dioxide on aqueous sodium iodate
21. Hydrogenation of vegetable oils with gaseous hydrogen
22. Desulfurization of gases by scrubbing with aqueous ethanolamines

Liquid-Liquid

23. Caustic soda by reaction of sodium amalgam and water
24. Nitration of organic compounds with aqueous nitric acid
25. Formation of soaps by action of aqueous alkalies on fats or fatty acids
26. Sulfur removal from petroleum fractions by aqueous ethanolamines
27. Treating of petroleum products with sulfuric acid

Solid-Solid

28. Manufacture of cement
29. Boron carbide from boron oxide and carbon
30. Calcium silicate from lime and silica
31. Calcium carbide by reaction of lime and carbon
32. Leblanc soda ash

sition of solids or of solid-solid reactions (Garner, 74). The main theory of the rate of decomposition of a solid is that decomposition begins at positions of strain on the surface, called nuclei or active sites; as the reaction progresses, the number of nuclei increases and the individual nuclei grow. In accordance with this theory, the rate of reaction varies as some power

of the time, that is, as t^n , where n commonly assumes a value of about 6, though the range is from about 1 to 8. The industrially important thermal decomposition of limestone, however, seems to follow a first-order law; it occurs at appreciable rates only above approximately 1650°F, and since it is endothermic, the rate is often limited by the rate of supply of heat. There seems to be no record of a solid decomposition that is limited by the rate of diffusion of a gaseous product away from the reaction zone, probably because in such cases a highly porous structure is made.

Solid-solid reactions could conceivably be controlled by (1) the rate of diffusion of reactants through a gradually thickening husk of product around each particle, and (2) the rate of the phase-boundary process. However, diffusion theory alone has been adequate to describe the experimental results in this field. An example of industrial importance is the manufacture of cement in which the main reaction is solid phase between lime and clay. Reactions between solid phases are very slow. Thus when the ingredients of cement are ground so fine that 95 to 98 per cent passes through a 100-mesh screen, a residence time of 2 to 3 hr is still necessary at temperatures of 1700 to 2200°F. From the point of view of speed of reaction it is desirable to have the smallest possible particles. Practically, such considerations as the cost of grinding and carry-over of fines must be weighed against the cost of a larger reactor and its operation.

37. Diffusive Mass Transfer

According to the widely held two-film theory, the resistance to mass transfer from one fluid to another is concentrated at stagnant films at their interface. Through such a film, the rate of diffusion varies proportionally to the area and to the driving force, which may be expressible in units of pressure or concentration or mole fraction, and inversely to the film thickness, but this is usually incorporated with the proportionality factor. Mathematically,

$$r_d = k_g S(p_g - p_i) = k_L S(C_i - C_L) = k_{0g} S(p_g - p_L) = k_{0L} S(C_g - C_L) \quad (6-1)$$

The various symbols are defined in the table of notation at the end of the chapter and partly in Fig. 6-2.

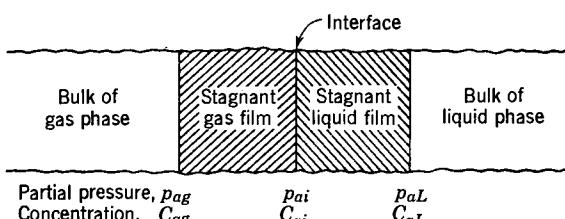


FIG. 6-2. Two-film theory. p_{aL} is partial pressure of diffusing component in equilibrium with solution of concentration C_{aL} , and C_{ag} is concentration of diffusing component in equilibrium with gas of partial pressure p_{ag} .

The proportionality factors k are called the mass-transfer coefficients. They are functions of the physical properties and geometry of the system. Dimensional analysis indicates that these coefficients should be correlatable in terms of these dimensionless groups:

Reynolds:
$$Re = \frac{du\rho}{\mu}$$

Schmidt:
$$Sc = \frac{\mu}{\rho D_v}$$

Sherwood:
$$Sh = \frac{kdM}{\rho D_v}$$

Numerous correlations have been made, for wetted-wall towers, single spheres and cylinders, and packed beds of all kinds. For a complete survey, reference may be made to the standard textbooks (199, 216). Two typical equations may be cited. In wetted-wall towers the Gilliland-Sherwood equation holds:

$$\frac{kdM}{\rho D_v} = 0.023 \left(\frac{du\rho}{\mu} \right)^{0.81} \left(\frac{\mu}{\rho D_v} \right)^{0.44} \quad (6-2)$$

In packed towers, the following correlation (Hobson and Thodos, 92) is useful and comprehensive:

$$\log j_d = 0.7683 - 0.9175 \log Re + 0.0817 (\log Re)^2 \quad (6-3)$$

For liquids:

$$j_d = \frac{k_L C_{bm}}{L_m} \left(\frac{\mu}{\rho D_v} \right)^{2/3} \quad (6-4)$$

For gases:

$$j_d = \frac{k_g p_{bm}}{G_m} \left(\frac{\mu}{\rho D_v} \right)^{2/3} \quad (6-5)$$

The subscript bm designates the mean value of the partial pressure or the concentration, as the case may be, of the nondiffusing components of the gas or liquid phase.

Sometimes the resistance of one only of the films is appreciable. Then, in Eq. 6-1, the interfacial pressure or concentration, p_i or C_i , is known (they are in that case the bulk-phase values) and the mass transfer can be calculated from the individual film coefficients. When two film resistances are comparable, the individual coefficients can be combined into a single over-all coefficient. For example, if a gas film and a liquid film are involved and Henry's law, $p = HC$, holds for the solubility, over-all coefficients are given by

$$\frac{1}{k_{0g}} = \frac{1}{k_g} + \frac{H}{k_L} \quad (6-6)$$

$$\frac{1}{k_{0L}} = \frac{1}{k_L} + \frac{1}{Hk_g} \quad (6-7)$$

When two liquid films are involved and the simple distribution law $C_{\text{phase 1}} = mC_{\text{phase 2}}$ applies, clearly the mass-transfer coefficient on the over-all basis is defined similarly to Eqs. 6-6 and 6-7. In case these simple distribution laws do not hold, the interfacial concentrations must be found as shown in Fig. 6-3.

In addition to the mass-transfer coefficient, the concept of the *height of a transfer unit*, abbreviated HTU, is used widely as a measure of the transferability of mass between phases. The transfer unit is related closely to an equilibrium contact stage and its magnitude is a readily visualized quantity, being usually a few inches or a few feet. The mass-transfer coefficient, on the other hand, is a more complex unit, and its numerical value is less readily translated into the size of equipment needed. Nevertheless, a direct relation exists between the two concepts, which takes the following forms for dilute systems:

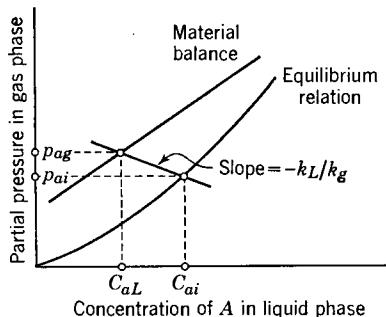


FIG. 6-3. Determination of interfacial concentration C_{ai} .

represent HTUs as well as k 's. Most modern experimental data are expressed in terms of HTUs.

Effect of process variables. It is of importance to be able to identify the mechanism of a process, whether diffusion or chemical reaction is controlling. Flow rate and temperature are two of the principal variables of assistance in this. The correlation of Eq. 6-2 shows the rate of mass transfer to vary almost directly with the flow rate. On the other hand, the rate of a chemical-reaction step is not affected at all by such a change in operating conditions. The influence of temperature on mass transfer is manifested by its effects on the physical properties involved in the dimensionless groups, but the total effect is very small compared with the effect on the rate of chemical reaction as expressed by the Arrhenius equation.

Equipment size. To establish the size of equipment for a desired absorption duty, the cross section and the height of the vessel are established separately. Ultimately, all the methods available for this purpose are strictly empirical in basis and depend on the particular type of vessel internals. The cross sections of packed towers are evaluated from flooding-

$$H_{0g} = \frac{G_m}{k_{0g} a \pi} \quad (6-8)$$

$$H_{0L} = \frac{L_m}{k_{0L} a \rho_m} \quad (6-9)$$

Like the k 's, the HTUs of individual films can be compounded into the over-all ones. Likewise, correlations such as those of Eqs. 6-2 and 6-3

data correlations, those of plate towers from either flooding or entrainment data, and other types from correlations of stage efficiencies; none of these is primarily concerned with rate processes except that the cross section determines the linear velocities of the fluids, which in turn influence the rate of mass transfer.

In a differential height of absorber of unit cross section, the rate of mass transfer is

$$d \left(\frac{G_m p}{\pi} \right) = \frac{G_m}{\pi - p} dp = k_o (p - p_i) dA = k_o a (p - p_i) dh \quad (6-10)$$

$$\text{Also } d \left(\frac{L_m C}{\rho_m} \right) = \frac{L_m}{\rho_m - C} dC = k_L a (C_i - C_L) dh \quad (6-11)$$

These may be integrated directly for the vessel height:

$$h = \frac{G_m}{k_o a} \int \frac{dp}{(\pi - p)(p - p_i)} = \frac{L_m}{k_L a} \int \frac{dC}{(\rho_m - C)(C_i - C)} \quad (6-12)$$

For the important special case of dilute systems,

$$h = \frac{G_m}{k_o a \pi} \int \frac{dp}{p - p_i} = \frac{L_m}{k_L a \rho_m} \int \frac{dC}{C_i - C} \quad (6-13)$$

The quantities outside the integral signs are recognizable as the HTUs defined by Eqs. 6-8 and 6-9; the integrals themselves are defined as the numbers of transfer units, designated N_o and N_L for the above.

These integrals may be evaluated with the aid of a diagram like Fig. 6-3. Here are shown an equilibrium line, obtained experimentally, and a material-balance line, derived as follows: referring to Fig. 6-4, around the upper section of the tower as indicated,

$$\frac{p}{\pi - p} - \frac{p_1}{\pi - p_1} = \frac{L'_m}{G'_m} \left(\frac{C_1}{\rho_{m1} - C_1} - \frac{C}{\rho_m - C} \right) \quad (6-14)$$

$$\text{or } p - p_1 = \frac{L_m \pi}{G_m \rho_m} (C_1 - C) \quad (6-15)$$

The advantage of Eq. 6-14 is the constancy of L'_m/G'_m . In dilute systems, this constancy is also true of L_m/G_m , so Eq. 6-15 is also very useful.

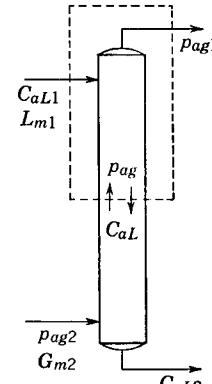
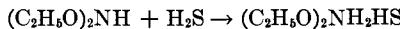


FIG. 6-4. Material balance in mass transfer.

Illustration 6-1. The reaction between hydrogen sulfide and diethanolamine in aqueous solution is thought to be



Much experimental work has been done on this reaction, including evaluation of the effect of chemical-reaction rate on the rate of absorption or extraction of hydrogen

sulfide from solutions in hydrocarbons. However, many aspects of the problem can be treated on the assumption of purely physical absorption or extraction.

In a particular commercial operation, hydrogen sulfide is extracted from a light hydrocarbon mixture with 10 per cent aqueous diethanolamine solution. The tower is 6 ft in diameter and packed with 28 ft of 1.5-in. carbon Raschig rings. Hydrocarbon charge rate is 4,200 bbl/day; inlet H_2S content is 340 grains/gal, and outlet is 2 grains/gal. The solution is at the rate of 1,320 bbl/day. If solution of 20 per cent concentration is used instead, what flow rate is needed to effect the same removal of H_2S ?

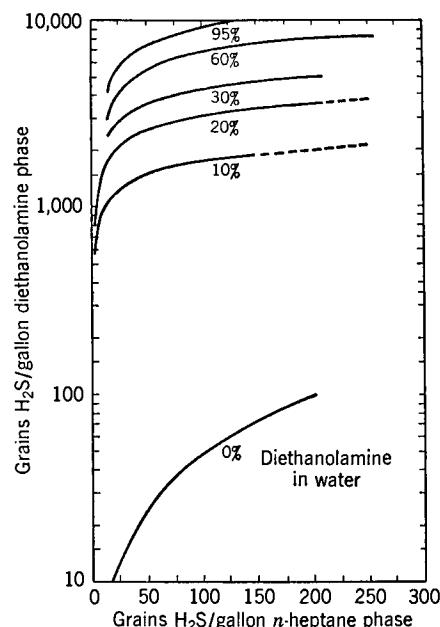


FIG. 6-5. Hydrogen sulfide in *n*-heptane and aqueous solutions of diethanolamine. [Srabian (204).]

Try 20 per cent solution at a charge rate of 660 bbl/day. Then

$$660(C_a - 0) = 4,200(C_b - 2)$$

Values of C_b and C_a^* are evaluated as before. The calculation for the number of transfer units yields the result

$$N = \int_0^{2,150} \frac{dC_a}{C_a^* - C_a} = 1.03 \text{ transfer units}$$

From Eqs. 6-2 and 6-9, for example, the height of a transfer unit increases approximately as the 0.2 power of the flow rate. Hence, at the assumed flow rate for the 20 per cent solution,

$$H = 29.8 \left(\frac{660}{1,320} \right)^{0.2} = 26.9 \text{ ft/transfer unit}$$

Therefore the required tower height is

$$h = NH = 1.03(26.9) = 27.9 \text{ ft}$$

Solution. Data on distribution of H_2S between liquid *n*-heptane and various concentrations of aqueous solutions of diethanolamine at 86°F are shown in Fig. 6-5 (Srabian, 204). Since both phases are dilute, the material balance may be written

$$1,320(C_a - 0) = 4,200(C_b - 2)$$

where subscript *a* refers to the aqueous solution and *b* to the hydrocarbon. Table 6-2 records corresponding values of C_a and C_b from this equation. From the equilibrium diagram, values of C_a^* corresponding to each value of C_b are also recorded. The number of transfer units is then obtained by numerical integration. Thus

$$N = \int_0^{1,075} \frac{dC_a}{C_a^* - C_a} = 0.94 \text{ transfer unit}$$

and

$$H = 28/0.94 = 29.8 \text{ ft/transfer unit}$$

It appears, then, that 20 per cent solution can effect the same removal as 10 per cent at very nearly half the flow rate.

TABLE 6-2. DATA FOR ILLUSTRATION 6-1

10% solution					20% solution				
C_a	C_b	C_a^*	$\frac{1,000}{C_a^* - C_a}$	$\int_0^{C_a}$	C_a	C_b	C_a^*	$\frac{1,000}{C_a^* - C_a}$	$\int_0^{C_a}$
0	2.0	390	2.560	0	0	2.0	520	1.920	0
100	33.4	1,320	0.820		200	33.4	2,310	0.475	
200	64.8	1,600	0.715	0.218	400	64.8	2,800	0.416	0.283
300	96.2	1,790	0.671		600	96.2	3,070	0.405	
400	127.6	1,890	0.671		800	127.6	3,200	0.416	
500	159.0	1,920	0.705	0.419	1,000	159.0	3,380	0.420	0.531
600	190.4	2,000	0.715		1,200	190.4	3,500	0.435	
700	221.8	2,100	0.715		1,400	221.8	3,680	0.439	
800	253.2	2,180	0.725	0.634	1,600	253.2	3,800	0.455	0.753
900	284.6	2,220	0.758		1,800	284.6	3,900	0.475	
1,000	316.8	2,320	0.758		2,000	316.8	4,000	0.500	
1,075	340.0	2,480	0.765	0.936	2,150	340.0	4,050	0.500	1.034

38. Absorption Combined with Chemical Reaction

A gas may be reacted with a liquid for either of two purposes: (1) to make a valuable compound or (2) to remove the active gas from a mixture, either to purify the remainder or to recover the active material in a concentrated form. Recovery of a particular component from a gas mixture may be accomplished by scrubbing with a selective solvent, which may or may not be chemically reactive. The rate and extent of absorption are limited by the back pressure of solute from solution. Therefore, when this back pressure can be reduced by use of a chemically reactive solvent, worthwhile savings in equipment size and possibly some operating costs can be achieved. In order to be economically feasible, the reactive solvent must be either inexpensive or capable of regeneration and the solute must be recoverable if it is of value. Nonregenerable solvents are justifiable ordinarily only for the removal of small quantities of impurities from gases or to recover especially valuable gases.

Industrial examples of gas-liquid reactions are numerous, some of which are listed in Table 6-1. The objectives are varied. Benzene and chlorine produce the end product monochlorobenzene. Aqueous diethanolamine removes the impurity hydrogen sulfide from hydrocarbon gases; the solution is regenerated by heating and stripping with steam, and the recovered hydrogen sulfide is usually disposed of by burning or is treated for recovery of elemental sulfur. Small amounts of hydrogen sulfide are sometimes

washed out of hydrocarbon gases with aqueous sodium hydroxide, and the spent solutions are thrown away.

39. Mass-transfer Coefficients in Chemical Reaction

Through a liquid film, the rate of mass transfer is given by the equation

$$r_d = k_L(C_{ai} - C_{aL}) = k_{0L}(C_{ag} - C_{aL}) \quad (6-16)$$

where the subscript *a* refers to the reactant *A* originally present in the gas phase; *B* is the reactant in the liquid phase. When this equation is applied to absorption combined with reaction, some of its terms need re-interpretation. For irreversible reactions, the concentration of *A* in the bulk of the liquid phase C_{aL} is ordinarily zero; for reversible reactions, C_{aL} must be calculated from the material balance and the chemical-equilibrium constant. When Henry's law applies to the situation prevailing at the interface between the gas and liquid films, the over-all coefficient may be calculated by Eq. 6-7. Henry's-law constant, $H = p/C$, is equal to that in the pure solvent, corrected for decreased solubility due to the presence of dissolved foreign substances; this correction is empirical and usually quite small. Correction for the presence of reactant *B* need not be made since this substance will not ordinarily be present at the interface. In case it does diffuse across the entire liquid film without encountering reactant *A*, this means that the diffusion rate across the gas film is controlling; and the absorption rate can be calculated from the usual absorption correlations, rather than from combined chemical reaction and diffusion.

Data on liquid-film coefficients with reaction are often obtained in the form of correction factors applicable to the corresponding coefficients without reaction. Such factors have been worked out for the main cases of interest involving first- and second-order reactions, both irreversible and reversible.

Specific reaction rate. Determination of the specific reaction rate in a system complicated by diffusion requires an indirect approach. One possible way is to prepare independent solutions of both reactants in the same solvent. These solutions can be mixed very quickly, and the progress of the ensuing homogeneous reaction followed by any of the usual techniques. If it is fairly certain that the solvent itself does not influence the course of the reaction, a different solvent may be used than the one to be used in the absorption process; this technique may be necessary when gas solubility in the primary solvent is small.

40. Empirical Approach to Absorption-Reaction

Much of the work with reactive absorbents has treated the problem like that of purely physical absorption, but with the mass-transfer coefficients and the equilibrium data dependent on the concentration and

nature of the liquid-phase reactant. This is typified by a particular correlation of the absorption of carbon dioxide by sodium carbonate solutions (Sherwood and Pigford, 199). As the absorption proceeds, the carbonate is converted to bicarbonate. The equilibrium in this system is represented by the following highly empirical equation:

$$p_{\text{CO}_2} = \frac{137f^2N^{1.29}}{S(1-f)(365-t)} \quad (6-17)$$

where f = fraction of total base present as bicarbonate

N = sodium normality

p_{CO_2} = equilibrium partial pressure of CO_2 , mm Hg

S = solubility of pure CO_2 in water under a pressure of 1 atm, g moles/liter

t = temperature, °F

The mass-transfer coefficient is given by

$$k_{0g}a = 0.00035f_1f_2f_3L^{0.64} \quad (6-17a)$$

where the correction factors for temperature and composition, f_1 , f_2 , and f_3 , are given by Fig. 6-6. Since the coefficient depends on the extent of conversion, it will vary throughout the equipment, thus necessitating some sort of averaging or integration for determination of equipment size.

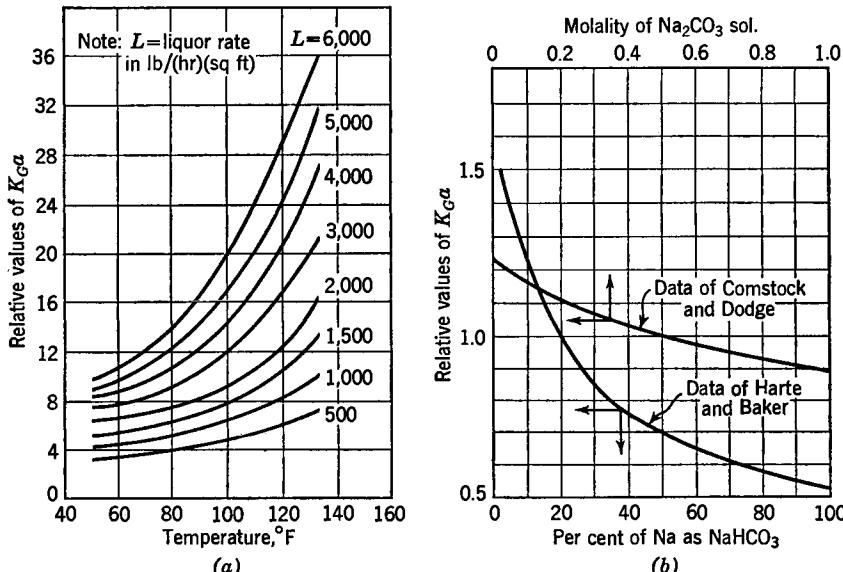


FIG. 6-6. Absorption of CO_2 with carbonate solutions in a tower packed with 1-in. Raschig rings. (a) Correction factor f_1 for temperature and liquid rate; (b) correction factors f_2 and f_3 for composition. [Sherwood and Pigford (199). Courtesy McGraw-Hill Book Company, Inc., New York.]

In the absorption of CO_2 from air by solutions of KOH and NaOH, the gas-film resistance was found negligible (Blum, Stutzman, and Dodds, 26). The rate was correlated by the equation

$$r = 0.0176 L^{0.84} h \frac{(\text{OH}^-)(\text{CO}_3^{2-})}{(\mu')^{1.09}} \quad (6-18)$$

where L = liquid rate

h = tower height

μ' = ionic strength

Also, the rate was found substantially independent of packing size ($\frac{1}{4}$ and $\frac{1}{2}$ in.) and of the partial pressure of CO_2 in the range from 0.03 to 0.28 mole fraction in the gas phase.

These two examples illustrate that data can be fairly successfully correlated by rather arbitrary methods. However, a generalized treatment on rational grounds is desirable to reduce the amount of direct experimental data needed for design and to allow safer extrapolation. Some success has been achieved along these lines, which will be discussed now.

41. Slow Reaction in the Liquid Film

The concept of stagnant films which are assumed to provide all the resistance to mass transfer between phases may serve as a basis for the

theory of reaction combined with absorption. The special case of slow reaction in the liquid film will be considered first. For the moment, discussion is limited to a first-order reaction and to the steady state.

Figure 6-7 illustrates the assumed mechanism of the process. Component A of a gas mixture diffuses through a gas film, enters the liquid film, and there reacts with component B of the solution. Consider a differential

FIG. 6-7. Slow reaction in a liquid film.

element of the liquid film of unit cross section and of thickness dx . Apply to this element the conservation law. The rate of diffusion is in accordance with Fick's law. Thus

$$\text{Input rate} = -D_v \left(\frac{dC_a}{dx} \right) \quad (6-19)$$

At the exit face, the concentration gradient has changed by an amount

$$d \left(\frac{dC_a}{dx} \right) = \frac{d^2C_a}{dx^2} dx$$

so that

$$\text{Output rate} = -D_v \left(\frac{dC_a}{dx} + \frac{d^2C_a}{dx^2} dx \right) \quad (6-20)$$

The accumulation rate is the difference between these two quantities, and furthermore, it equals the rate of reaction since this is the only way that substance *A* can disappear under steady-state conditions. In the differential element, this rate is

$$r = k_c C_a dV = k_c C_a dx \quad (6-21)$$

where the substitution $dV = dx$ has been made since the cross section is unity. Applying the conservation law, therefore,

$$\frac{d^2 C_a}{dx^2} = \frac{k_c}{D_v} C_a \quad (6-22)$$

This linear-differential equation with constant coefficients has the general solution

$$C_a = A_1 e^{bx} + A_2 e^{-bx} \quad (6-23)$$

where $b = \sqrt{k_c/D_v}$.

Upon evaluating the integration constants for the conditions $C_a = C_{ai}$ when $x = 0$ and $C_a = C_{aL}$ when $x = x_L$, Eq. 6-23 becomes

$$C_a = \frac{C_{aL} \sinh bx + C_{ai} \sinh b(x_L - x)}{\sinh bx_L} \quad (6-24)$$

This equation may be differentiated to provide the rate of diffusion r_d into the liquid film, that is, at $x = 0$, with the result

$$r_d = -D_v \left(\frac{dC_a}{dx} \right)_{x=0} = \frac{bD_v (C_{ai} \cosh bx_L + C_{aL})}{\sinh bx_L} \quad (6-25)$$

An especially important situation is that in which the reaction takes place entirely in the liquid film and consequently none of substance *A* reaches the bulk of the liquid phase. Then $C_{aL} = 0$, and Eq. 6-25 becomes

$$r_d = \frac{bD_v \cosh bx_L}{\sinh bx_L} (C_{ai} - 0) = \frac{D_v}{x_L} (\text{Ha}) (C_{ai} - 0) = \frac{D_v}{x_L} (\text{Ha}) (\Delta C_a) \quad (6-26)$$

$$\text{or } r_d = k_L^0 (\text{Ha}) (\Delta C_a) = k_L (\Delta C_a) \quad (6-27)$$

where

$$\text{Ha} = \frac{bx_L}{\tanh bx_L} \quad (6-27a)$$

is the Hatta number, a dimensionless group; $k_L^0 = D_v/x_L$ is the mass-transfer coefficient through a liquid film *without* chemical reaction; and $k_L = (\text{Ha})k_L^0$ is the corresponding coefficient when reaction does take place. Thus the Hatta number is a correction factor for converting liquid-film mass-transfer coefficients for absorption with inert solvent to absorption with chemical reaction.

The following correlation has been developed (Van Krevelen and Hofstijzer, 222):

$$\frac{k_L x_L}{D_v} = 0.015 \left(\frac{L}{a\mu} \right)^{\frac{1}{3}} \left(\frac{\mu}{\rho D_v} \right)^{\frac{1}{3}} \frac{bx_L}{\tanh bx_L} \quad (6-28)$$

or more compactly,

$$\frac{k_L x_L}{D_v} = 0.015 (\text{Re})^{\frac{1}{3}} (\text{Sc})^{\frac{1}{3}} (\text{Ha}) \quad (6-29)$$

For the film thickness, these same investigators substitute

$$x_L = \left(\frac{\mu^2}{g \rho^2} \right)^{\frac{1}{3}} \quad (6-30)$$

The physical properties are those of the liquid phase.

Rather arbitrarily, an extension was made to second- and third-order reactions by modifying the term b ; thus

First order: $b = \sqrt{\frac{k_1}{D_v}}$

Second order: $b = \sqrt{\frac{k_2}{D_v}}$

Third order: $b = \sqrt{\frac{k_3}{D_v}}$

Typical data correlated by Eq. 6-28 include:

1. The absorption of CO_2 by sodium carbonate solutions, as a second-order reaction, with

$$k_2 = 930 \text{ m}^3/(\text{kg mole})(\text{sec}) \text{ at } 0^\circ\text{C}$$

$$k_2 = 4,000 \text{ m}^3/(\text{kg mole})(\text{sec}) \text{ at } 18^\circ\text{C}$$

2. The absorption of CO_2 by ammonia solutions likewise was correlated as a second-order reaction with $k_2 = 150$ at 18°C .

3. A reasonably good correlation was achieved for the absorption of CO_2 by diethanolamine solutions on the basis of a pseudo-third-order reaction rate, with $k_3 = 260 \text{ m}^6/(\text{kg mole})^2(\text{sec})$.

42. Second-order Kinetics

The simplest type of second-order reaction combined with absorption has the differential equation (corresponding to Eq. 6-22)

$$\frac{d^2 C_a}{dx^2} = \frac{k_c}{D_v} C_a^2 \quad (6-31)$$

subject to the conditions $C_a = C_{a0}$ when $x = 0$ and $C_a = 0$ when $x = x_L$. Upon multiplying through by

$$2 \frac{dC_a}{dx} dx = 2 dC_a$$

and integrating, Eq. 6-31 becomes

$$\left(\frac{dC_a}{dx}\right)^2 = \frac{2k_c}{3D_a} C_a^3 + I \quad (6-32)$$

where I is the constant of integration. Integration of this equation in turn does not appear to be possible in closed form, so that even this simple reaction leads to some serious mathematical difficulties.

For the general second-order reaction, $A + B \rightleftharpoons 2C$, the differential equations may be set up on the basis of the conservation law. For participant A ,

$$\text{Input rate} = -D_a \frac{\partial C_a}{\partial x} \quad (6-33)$$

$$\text{Output rate} = -D_a \left(\frac{\partial C_a}{\partial x} + \frac{\partial^2 C_a}{\partial x^2} dx \right) \quad (6-34)$$

$$\text{Accumulation rate} = \frac{\partial C_a}{\partial t} + k_1 C_a C_b - k_2 C_c^2 \quad (6-35)$$

and similarly for B and C . Accordingly,

$$\frac{\partial C_a}{\partial t} = D_a \frac{\partial^2 C_a}{\partial x^2} - k_1 C_a C_b + k_2 C_c^2 \quad (6-36)$$

$$\frac{\partial C_b}{\partial t} = D_b \frac{\partial^2 C_b}{\partial x^2} - k_1 C_a C_b + k_2 C_c^2 \quad (6-37)$$

$$\frac{\partial C_c}{\partial t} = D_c \frac{\partial^2 C_c}{\partial x^2} + (k_1 C_a C_b - k_2 C_c^2)(2) \quad (6-38)$$

This system of differential equations has been integrated numerically (Perry and Pigford, 180) with the aid of a large digital computer. Some of the results are shown in Figs. 6-8 to 6-11. For comparison, first-order kinetics and irreversible second-order are also represented. These plots

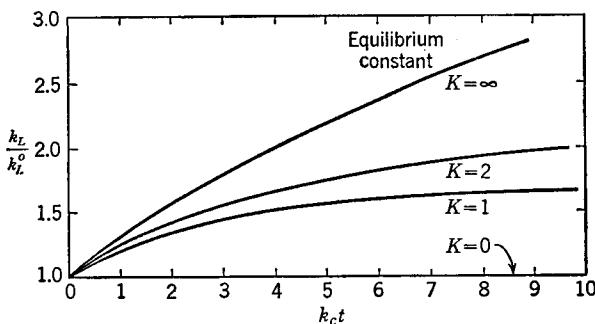


FIG. 6-8. First-order reaction. K is equilibrium constant. [Perry and Pigford (180). Courtesy *Industrial and Engineering Chemistry*.]

are in the form of a correction factor to the mass-transfer coefficient under conditions of purely physical absorption.

Ordinarily, the mass-transfer coefficient takes into account all factors influencing the process except the concentrations, according to a rate equation, rate = $k_L \Delta C$. This is still true of absorption combined with first-order reaction. However, an interesting conclusion from this work on second-order reactions is that the coefficient is a function of the driving force.

Practical absorption operations are conducted at steady state. From Figs. 6-8ff., therefore, only the limiting values are needed for such calcu-

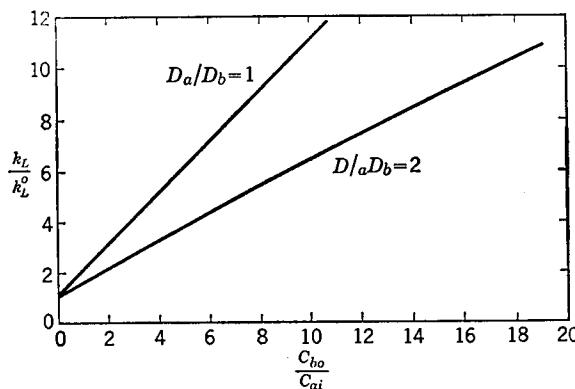


FIG. 6-9. Second-order infinitely fast irreversible reaction (diffusion-controlling). [Perry and Pigford (180). Courtesy *Industrial and Engineering Chemistry*.]

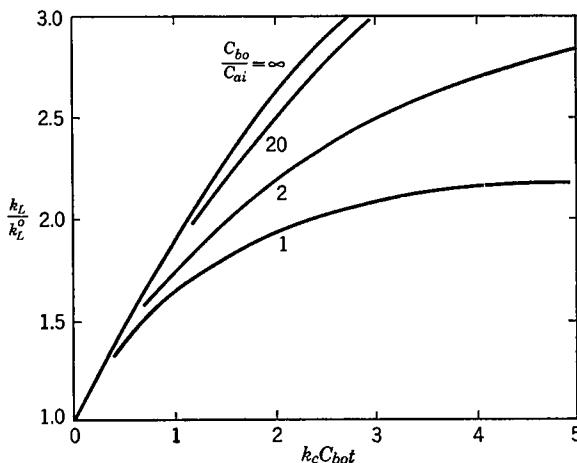


FIG. 6-10. Second-order irreversible reaction. [Perry and Pigford (180). Courtesy *Industrial and Engineering Chemistry*.]

lations. Since the driving force varies throughout the absorber, no single value of k_L is representative and its variation must be taken into account.

Illustration 6-2. A reaction for which the data of Fig. 6-11 hold is to be conducted in a packed tower at atmospheric pressure. Given the following operating data, find the required height of packed section.

$$\begin{aligned}p_{a2} &= 0.04 \text{ atm} \\C_{b1} &= 0.06 \text{ lb mole/cu ft} \\C_{b2} &= 0.01 \text{ lb mole/cu ft} \\k_L^0 &= 0.006 \text{ ft/hr} \\L_m &= 57.6 \text{ lb moles/(hr)(sq ft)} \\G_m &= 27.5 \text{ lb moles/(hr)(sq ft)} \\a &= 50 \text{ sq ft/cu ft} \\p_m &= 3.5 \text{ lb moles/cu ft} \\C_a &= 0.9p_a \text{ (equilibrium condition)}\end{aligned}$$

Solution. The operating conditions are shown in Fig. 6-12. Extrapolations of the data of Fig. 6-11 are plotted in Fig. 6-13, thus providing k_L/k_L^0 in terms of C_{b0}/C_{a1} ,

where C_{b0} is the concentration of *B* in the bulk of the liquid phase. Since both phases are lean in the reactants, the simplified material balance holds:

$$C_{b1} - C_b = \frac{G_m p_m}{L_m \pi} (p_a - p_{a1}) \quad (A)$$

$$\text{or} \quad 0.06 - C_b = \frac{(27.5)(3.5)}{(57.6)} (p_a - 0.01) = 1.67(p_a - 0.01) \quad (B)$$

Values of C_b corresponding to selected values of C_a are calculated from Eq. *B* and the equilibrium relation $C_a = 0.9p_a$ and recorded in Table 6-3.

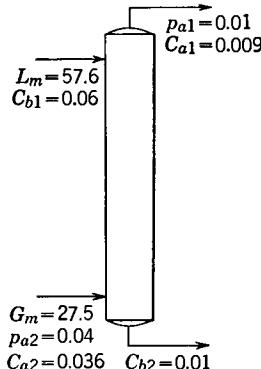


FIG. 6-12. Data for Illustration 6-2.

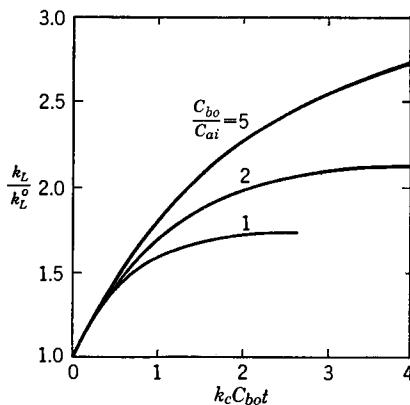


FIG. 6-11. Second-order reversible reaction with $K = 1$. [Perry and Pigford (180). Courtesy Industrial and Engineering Chemistry.]

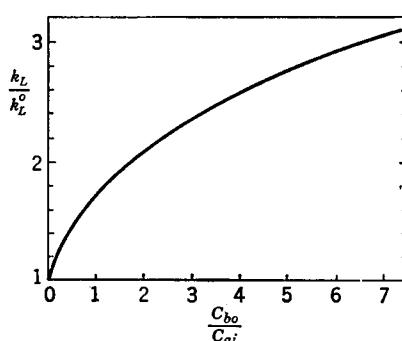


FIG. 6-13. Correction to mass-transfer coefficient in the steady state (Illustration 6-2).

In the absence of chemical reaction, the rate equation is

$$G_m \, dp_a = \frac{L_m}{\rho_m} \, dC_a = k_L^0 a (C_{a1} - C_{aL}) \, dh \quad (C)$$

Upon neglecting the resistance of the gas film, Eq. C becomes

$$\frac{L_m}{\rho_m} \, dC_a = k_L^0 a (C_a - C_{aL}) \, dh \quad (D)$$

With chemical reaction, k_L^0 is replaced by k_L and $C_{aL} = 0$, so that

$$h = \frac{L_m}{\rho_m a} \int_{0.009}^{0.036} \frac{dC_a}{k_L C_a} \quad (E)$$

Values of the integrand are shown in Table 6-3. Integrating with Simpson's rule,

$$\int_{0.009}^{0.036} \frac{dC_a}{k_L C_a} = \frac{0.0135}{3} [3,860 + 4(3,890) + 6,000] = 110 \quad (F)$$

and the height of packed section is therefore

$$h = \frac{57.6(110)}{50(3.5)} = 36.3 \text{ ft}$$

For comparison, without chemical reaction,

$$h = \frac{L_m}{\rho_m k_L^0 a} \ln \frac{C_{a2}}{C_{a1}} = \frac{57.6}{3.5(0.006)(50)} \ln \frac{0.036}{0.009} = 76.3 \text{ ft}$$

TABLE 6-3. DATA FOR ILLUSTRATION 6-2

C_a	p_a	C_b	C_b/C_a	k_L/k_L^0	k_L	$1/k_L C_a$
0.036	0.040	0.0100	0.28	1.2	0.0072	3,860
0.0225	0.025	0.0350	1.56	1.9	0.0114	3,890
0.0090	0.010	0.0600	6.7	3.1	0.0186	6,000

NOTATION

- a interfacial surface, sq ft/cu ft of vessel
- b $\sqrt{k_c/D_v}$ (Eqs. 6-23ff.)
- C_a liquid-phase concentration of A , which was originally in the gas phase
- C_b liquid-phase concentration of reactant B originally in the liquid phase
- C_{bm} concentration of nondiffusing component of the liquid phase
- C_g concentration in the liquid phase in equilibrium with partial pressure p_g in the gas phase (Eq. 6-1)
- C_L concentration in the liquid phase (Eq. 6-1)
- d vessel diameter
- D_a diffusivity of substance A
- D_b diffusivity of substance B
- D_v diffusivity, sq ft/hr
- G_m molal superficial mass flow rate of gas phase, lb moles/(hr)(sq ft of vessel cross section)
- h height of packed section
- H Henry's-law constant = p/C , (cu ft)(atm)/lb mole
- Ha Hatta number (Eqs. 6-27ff.)

H_{00}	height of a transfer unit, corresponding to partial-pressure difference across both film resistances
H_{0L}	height of a transfer unit, corresponding to concentration difference across both film resistances
j_A	diffusive mass-transfer factor (Eq. 6-4)
k	mass-transfer coefficient, lb moles/(hr)(sq ft)(unit driving force)
k_c	specific reaction rate, concentration units
k_g	mass-transfer coefficient across gas film, lb moles/(hr)(sq ft)(atm)
k_L	mass-transfer coefficient across liquid film, lb moles/(hr)(sq ft)(lb mole/cu ft)
k_L^0	mass-transfer coefficient defined by Eq. 6-27
k_{00}	mass-transfer coefficient across both films, partial-pressure difference
k_{0L}	mass-transfer coefficient across both films, concentration difference
L_m	molal superficial mass flow rate of liquid phase, lb moles/(hr)(sq ft of vessel cross section)
M	molecular weight
M_{av}	average molecular weight
N	number of transfer units (Eqs. 6-13ff.)
p_{Ag}	partial pressure of A in the gas phase
p_{bm}	partial pressure of nondiffusing component of the gas phase
p_g	partial pressure in the gas phase
p_L	partial pressure corresponding to concentration C_L in the liquid phase
p_i	partial pressure at the interface between two films
r_A	rate of mass transfer, lb moles/hr
Re	Reynolds number, $d \rho \mu / \mu$
S	interfacial area, sq ft
Sc	Schmidt number, $\mu / \rho D_v$
Sh	Sherwood number, $k d M / \rho D_v$
u	linear velocity
x	distance in the direction of diffusion
x_L	film thickness
μ	viscosity
ρ	density, lb/cu ft
ρ_m	molal density, lb moles/cu ft

PROBLEMS

6-1. Assuming the Arrhenius law to apply, estimate from Fig. 6-1 the rate of the chemical reaction between carbon and oxygen at 1200°C and compare with the measured value at the highest air flow rate shown.

6-2. A slab of calcium carbonate is coated with a decomposition layer of calcium oxide 0.25 in. thick, the surface of which is maintained at 1800°F. On the basis that reaction is virtually instantaneous at 1672°F and that the rate is limited by the rate of heat supply to the interior, find the rate of decomposition. Compare with the data of Slonim (203), who states that $dx/dt = 0.28(1 - x)$ fraction decomposed per second, at 1672°F. The heat of decomposition of CaCO_3 is 1640 Btu/lb CO_2 produced, and the thermal conductivity of CaO is 0.32 Btu/(hr)(sq ft)(°F/ft).

6-3. The rate of reaction between powders of BaCO_3 and SiO_2 at 890°C is represented by the equation

$$(1 - \sqrt[4]{1 - x})^2 = 0.00022t$$

where x = fraction converted

t = time, min

What fraction conversion is attained with powders of the particle sizes used in this experiment when they are maintained at this temperature for 1 hr (Jander, 112; Fischbeck, 69)?

6-4. The reaction of distilled solid sodium with air at 30°C has been found to conform to the equation

$$w = 0.031t^{0.5}$$

where w is grams sodium converted per square centimeter of sodium surface and t is in hours (Howland and Epstein, 104).

(a) What is the apparent order of the reaction?

(b) Explain how the assumption that the reaction is limited by the rate of diffusion through the already converted material leads to this form of equation.

6-5. The effect of oxygen partial pressure on the rate of gasification of coke was measured at 950°F with the following results (Lewis, Gilliland, and Paxton, 142):

log mean p_{O_2} , atm.....	0.05	0.09	0.17	0.23	0.52	0.66
(% gasified/min)(10 ⁴).....	2	3	4.5	7.5	17.5	20.0

A 50:50 mixture of oxygen and an inert gas is pumped through a bed of carbon at a space velocity of 0.05 lb mole gas/(min) (lb mole carbon) at 950°F and 1 atm. How long does it take to gasify 1 per cent of the carbon?

6-6. The rate of attack of hydrogen sulfide on iron at atmospheric pressure has been measured with the following (smoothed) results:

Time, min	Weight gain, g/sq cm		
	760°C	593°C	482°C
5	0.01	0.0006	
10	0.019	0.0011	
20	0.037	0.00195	0.0001
40	0.070	0.0035	0.000185
60	0.100	0.0050	0.00027
100	0.0077	0.00042
200	0.014	0.00078
500	0.030	0.00180

Find the order of the reaction and the energy of activation (Hügli, Hudgins, and Delahay, 105).

6-7. Toluene was nitrated with mixed aqueous nitric and sulfuric acids in a continuous stirred-tank reactor at 35°C with such a high degree of agitation that mass-transfer effects were absent (Barduhn and Kobe, 10). The rate equation is

$$r = fN_T(100N_n)^g \frac{g \text{ mole mononitrotoluene made}}{(\text{hr})(\text{liter of acid phase})}$$

where N_T and N_n = mole fractions of toluene in organic phase and of nitric acid in acid phase, respectively

f and g = functions of sulfuric acid concentration as follows:

Mole % H ₂ SO ₄ in nitrating acid.....	30.7	34.0	37.0
f	193	518	2,150
g	1.206	0.435	0.262

Though the rate of reaction of a two-liquid-phase system is properly the sum of the rates in the separate phases (Hougen and Watson, 103), the present investigators found that no mononitrotoluene was formed in the organic phase though there was some disappearance of nitric acid in that phase because of oxidation, and they were consequently able to develop the correlation in terms of the volume of the acid phase alone.

In a particular case, acid of the following concentration is used:

	Mole %	Wt %
H ₂ SO ₄	34.0	60.2
HNO ₃	22.6	25.7
H ₂ O.....	43.4	14.1

The specific gravity of this acid is 1.69, and that of completely spent acid is 1.65; more complete density data may be found in Hougen and Watson (103). Compare the sizes of a one-stage continuous stirred-tank reactor and a tubular reactor when the feed rates of acid and toluene are 4,000 and 10,000 lb/hr, respectively.

6-8. For a mass-transfer operation in which both gas- and liquid-film resistances were appreciable, these data were measured or calculated:

	Gas phase	Liquid phase
Re.....	500	50
Sc.....	0.74	13.9
F, lb moles/(hr)(sq ft).....	30	15
C _{bm} , lb moles/cu ft.....	1.6
p _{bm} , atm.....	0.9	

Henry's-law constant is $H = 0.1 \text{ atm}/(\text{lb mole/cu ft})$.

(a) Find k_g , k_L , and k_{bg} .

(b) Calculate the rate of mass transfer at a point where $p_{ag} = 0.1 \text{ atm}$ and $C_{ai} = 0.25 \text{ lb mole/cu ft}$.

6-9. For the system of Prob. 6-8, tests were made of the effects of gas-flow rate and temperature as follows:

°F	F, lb moles/hr	D _v , sq ft/hr	μ, centipoises	ρ, lb/cu ft	Re	Sc
100	30	0.71	0.0185	0.075	500	0.84
200	30	0.91	0.0208	0.063		
300	30	1.11	0.0230	0.055		
100	10					
100	70					

The partial pressure of the nondiffusing component is $p_{bm} = 0.9 \text{ atm}$ in all cases. Calculate the value of k_g for each test.

6-10. The reversible first-order reaction $A \rightleftharpoons C$ occurs simultaneously with absorption of substance A . Initially, substance C is absent. Show that the equation corresponding to Eq. 6-22 is

$$D_v \frac{d^2 C_a}{dx^2} = k_1 C_a - k_2 (C_{a0} - C_a)$$

and find the solution corresponding to Eq. 6-24.

6-11. Calculate the Hatta number from the correlation of Van Krevelen and Hofstijzer (Eq. 6-28) for the following data:

System	Sh	Sc	Re
CO ₂ in Na ₂ CO ₃	0.61	615	6.53
CO ₂ in KOH.....	7.7	550	1.34
CO ₂ in NH ₃	2.98	540	2.46
CO ₂ in diethanolamine.....	5.4	1,180	3.5
CO ₂ in diethanolamine.....	2.15	950	3.35

6-12. In the third case of Prob. 6-11, the value of $k_g = 5.3(10^{-5})$ kg mole/(sec) (sq m)(atm), $k_L = 3.0$ m/sec, and $H = 0.0025$ kg mole/(cu m)(atm).

(a) What is the value of k_{OL} for absorption in aqueous ammonia?

(b) What is the value of k_{OL} for absorption in water?

6-13. Calculate the Hatta number for absorption of CO₂ in aqueous NaOH solution, of concentration 2.5 kg moles/cu m, when the properties are substantially those of water at 25°C and $k = 10,000$ cu m/(kg mole)(sec).

6-14. Consider the process described by Eq. 6-36. Under steady-state conditions, show that

$$\left(\frac{dC_a}{dx}\right)^2 + aC_a^3 + bC_a^2 + cC_a + I = 0$$

where a , b , c , and I are constants involving C_{a0} , C_{b0} , C_{c0} , k_1 , k_2 , and D_a .

CHAPTER 7

FLUID-PHASE REACTIONS CATALYZED BY SOLIDS

43. Mechanism of Heterogeneous Catalysis

Most often, catalysts are employed to speed up reactions that are sluggish or will not otherwise proceed at all. Also, they may change the operating temperature level, or influence the product distribution, or more rarely, slow down a reaction. The main classes are homogeneous and heterogeneous catalysts. The former were touched on in Chap. 2. Heterogeneous catalytic processes, employing chiefly solid catalysts, are of perhaps the greatest industrial significance. Apart from any specific catalytic behavior, solids are favored because of their thermal stability and ease of separation from the reacted fluids. Examples of industrially important reactions catalyzed by solids are numerous; a random selection is shown in Table 7-1.

Mechanism of surface catalysis is very complex. Fluid-phase reactions of this type are conceived to proceed according to at least these five steps:

1. Diffusion of the reacting molecules to the surface
2. Adsorption of the reactants on the surface
3. Reaction on the surface
4. Desorption of the products
5. Diffusion of the products into the fluid

An equation for the over-all rate of reaction embodying the rates of all these steps would be quite formidable, and the rate constants would be so inextricably bound up with the variables that they would be difficult to evaluate accurately. Usually it is hoped that only one of the steps offers appreciable resistance to the reaction. In the present chapter, the factors influencing the rates of the individual steps will be developed or recalled as necessary and some attention will be devoted to ways of detecting controlling steps.

Some combinations of steps for the simpler reactions lead to fairly tractable equations. In other cases the attempt to base rate equations on a rational mechanism may have to be abandoned and instead purely empirical correlations of the operating variables may have to be resorted

TABLE 7-1. SOME INDUSTRIAL PROCESSES EMPLOYING SOLID CATALYSTS

Type of process	Product	Catalyst
Alkylation	Ethylbenzene	Silica-alumina
Cracking	Gasoline	Alumina-silica
Dehydration	Amines	Alumina
Dehydrogenation	Butadiene	Chromia-alumina
Dehydrogenation	Styrene	Promoted iron oxide
Esterification	Esters	Ion-exchange resins
Fischer-Tropsch	Gasoline	Iron oxide and cobalt thoria
Hydrogenation	Ammonia	Promoted iron oxide
Hydrogenation	Methanol	Zinc chromite
Hydrogenation	Rosin acids	Copper chromite
Hydrogenation	Vegetable oils	Nickel
Isomerization	Isopentane	Supported platinum
Oxidation	Formaldehyde	Silver or copper
Oxidation	Nitric acid	Platinum
Oxidation	Phthalic anhydride	Vanadium pentoxide
Oxidation	Sulfuric acid	Platinum or vanadium pentoxide
Polymerization	Gasoline	Phosphoric acid on kieselguhr
Re-forming	Aromatic hydrocarbons	Supported platinum
Re-forming	High-octane gasolines	Supported platinum
Water-gas reaction	CO + H ₂	Iron oxide-magnesia

to. Unfortunately, in such an event, extrapolation much beyond the experimental range is not safe.

For various reasons, solid catalysts are usually in the form of comparatively small particles, rarely over $\frac{1}{4}$ -in. diameter. In a bed of such particles, an appreciable pressure drop may occur which may have a serious effect on the reaction rate. Still another factor is the rate of heat transfer, which is sometimes quite poor in beds of particles. Consequently, where the thermal effects accompanying reaction are appreciable, the rate of heat transfer can become easily the most important operating condition. These factors, as well as mass transfer to the surface of the particles, have been the subjects of many investigations and are treated in other chapters.

44. Chemisorption and Physical Adsorption

One of the oldest theories relating to catalysis by solid surfaces was proposed by Faraday in 1825; in some respects it is held even today. This theory states that adsorption of reactants must first occur and that the reaction proceeds in the adsorbed fluid film. It was visualized that the reacting molecules are brought closer together by condensation, thus permitting more frequent collisions and consequently more rapid reaction. There is much evidence against this simple view. For instance, the more effective adsorbents are not always the more effective catalysts; and cata-

lytic action is highly specific; that is, certain reactions are influenced only by certain catalysts. Apparently more than just bringing the reacting molecules together is needed. The modern view, therefore, regards adsorption as a necessary but not sufficient condition for ensuring reaction under the influence of a solid surface.

Adsorption is due to an attraction between the molecules of the surface, called the adsorbent, and those of the fluid, called the adsorbate. Experimentally the intensity of this attraction is found to possess either of two different orders of magnitude. In some cases the attraction is mild, of the same nature as that between like molecules, and is called physical adsorption. In other cases the force of attraction is more nearly akin to the forces involved in the formation of chemical bonds, so that process is called chemical adsorption or chemisorption.

Behavior of these phenomena differs markedly in several other respects, as follows.

Thermal effects. Adsorption is an exothermic process. In physical adsorption of gases the heat effect is of the same order of magnitude as the heat of condensation, that is, a few hundred calories per gram mole. In chemisorption the heat effects are more nearly like those accompanying chemical reaction, say, 10 to 100 kcal/g mole. For instance, the heat of adsorption of oxygen on carbon is about 80 kcal/g mole, compared with a heat of combustion of carbon of 94 kcal/g mole. Here a stable compound is actually formed, for when an attempt is made to remove adsorbate by evacuation, some carbon monoxide comes off with the oxygen.

Effect of temperature. It is important to distinguish between the amount and the rate of adsorption. Since both kinds of adsorption are exothermic, increase in temperature tends to diminish the total amount of adsorption at equilibrium. Physical adsorption is rapid, and equilibrium is established rapidly even at low temperatures. Chemisorption requires energy of activation (Table 7-2); its rate is slow except at elevated temperatures, and equilibrium is established slowly. The net effect of increasing temperature on the total adsorption is typified by Fig. 7-1 and the

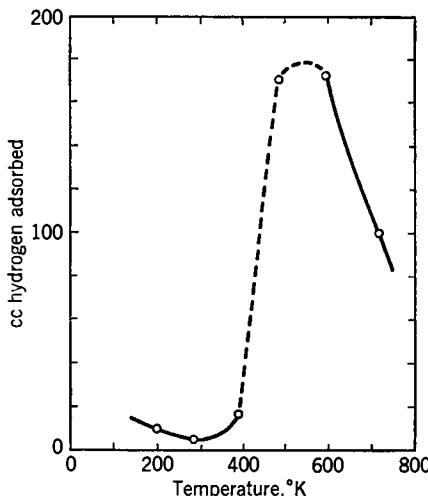


FIG. 7-1. Adsorption of hydrogen on $\text{MgO-Cr}_2\text{O}_3$ catalyst at a pressure of 165 mm Hg with 46.5 g of adsorbent. [After Taylor and Williamson (212).]

following description of the adsorption of hydrogen on a mixed magnesia-chromia catalyst (Taylor and Williamson, 212).

At -78°C the adsorption was small, rapidly attained, and reversible by evacuation at the same temperature, these being common characteristics of physical adsorption. At 0°C , a small amount of physical adsorption took place rapidly, but there was a continued amount of very slow adsorption proceeding over a period of days. Apparently chemisorption was setting in at this temperature. At 100°C , the amount of physical adsorption was believed nil, since it was already much smaller

TABLE 7-2. CHEMISORPTION HEAT AND ACTIVATION ENERGY*

System	Heat of chemisorption, kcal/g moles	Activation energy, kcal/g moles
H_2 on C (diamond)	58	14-22
H_2 on C (graphite)	45	6
CO on Cr_2O_3	9-15	0.2-0.7
N_2 on Fe (1.3% Al_2O_3 + 1.6% K_2O)	35	16
CO on Pd.	17.1-18.1	2.3-9.0
H_2 on W powder.	20-75	10-25

* Laidler (128).

at 0°C than it had been at -78°C , but the rate of chemisorption was quite measurable. Up to 300°C or so, both amount and rate of adsorption increased. At higher temperatures, apparently dissolution of the bonds between the hydrogen and the surface molecules resulted in decreased adsorption.

Effect of pressure. Equilibrium physical adsorption is markedly influenced by pressure; in fact, the process is completely reversible by evacuation. On the other hand, pressure has very little effect on the equilibrium amount of chemisorption, the unimolecular layer which is characteristic of this phenomenon being formed even at very low pressures. The rates, however, of both types of adsorption increase with increasing pressure.

Effect of surface. For physical adsorption, only the amount of surface is of concern, but chemical adsorption is highly specific. For example, hydrogen is chemisorbed by nickel but not by alumina, and oxygen by carbon but not magnesia. Such behavior is, of course, consistent with the view that the characteristics of chemisorption are those of reactions in general. The physical condition of a surface as well as its chemical composition is important to chemisorption. Heterogeneity of catalyst surfaces is evidenced by the fact, for instance, that the heat of adsorption gradually diminishes as chemisorption proceeds. Surfaces consist of atoms of varying degrees of saturation. Those at edges of crystals and at cracks or

protuberances are presumably less saturated and consequently more active. Several theories of surface activity are current. A recent view is that it is due to certain types of lattice defects. The effectiveness of certain additives in small amount, called promoters, in increasing the activity of catalysts is in some cases explained satisfactorily by observing that the promoter atoms enter the crystal lattice of the catalyst and thereby cause lattice distortions and strains. The existence of surface heterogeneity and the occurrence of chemisorption and chemical reactions preferentially at certain positions are now well established. These positions are variously called active points or active centers or active sites. Some idea of the order of magnitude is given by an estimation that the total number of sites active for the cracking of cumene is $3.6(10^{19}) \text{ g}^{-1}$, or $1.2(10^{17}) \text{ (sq m)}^{-1}$ (Mills, Boedeker, and Oblad, 157).

¹ Another distinction to emphasize is that chemisorption is restricted to the formation of a unimolecular layer, which again indicates reaction with the surface, since valence forces diminish rapidly with distance. Physical adsorption is never restricted to a unimolecular layer.

In summary, these important facts which have a bearing on reaction kinetics have been brought out:

1. Adsorption is a necessary preliminary step to reaction catalyzed by solid surfaces.
2. Chemisorption is invariably the type of adsorption involved in such a case. This has the characteristics of chemical reaction, in this instance with the molecules of the solid surface.
3. Catalytic surfaces are heterogeneous, and chemisorption takes place preferentially on "active sites" of the surface.

45. Adsorption Rates and Equilibria

Many equations for adsorption equilibria have been advanced on both experimental and theoretical grounds. One of the earliest and simplest is that of Langmuir, which has been outstandingly successful in the interpretation of adsorption behavior and surface catalysis. Certain idealized conditions are taken as a basis for this development, namely, that there is no interaction between adsorbed molecules, the surfaces are smooth and of uniform adsorptive capacity, and only a unimolecular layer of adsorbate is formed. When applied to chemical reactions, this theory is called the Langmuir-Hinshelwood mechanism (Hinshelwood, 89). Other systematic application has been made by Hougen and Watson (100, 101).

Other adsorption theories have been applied to reaction kinetics. An extension of the Langmuir theory was made by Brunauer, Emmett, and Teller (Emmett, 61), whose equation, commonly designated as the BET equation, is of great utility in the measurement of particle surfaces (Prob. 7-1). The well-known Freundlich isotherm leads to some quite

simple and often widely applicable rate equations, as shown in Sec. 49. A highly successful equation for the kinetics of ammonia synthesis has been advanced by Temkin and Pyzhev (213; see also Laidler, 129, and Frankenburg, 70). These investigators employed an adsorption equation which takes into account surface heterogeneity and derives from that of Langmuir by assuming that the heat of adsorption decreases linearly as the coverage of the surface increases. The equation is cited in Prob. 7-9.

Coming back to the Langmuir theory, most surface reactions of interest involve only gaseous reactants, so the present discussion will be restricted to gases. Apparently the process of chemisorption involves a reaction between the adsorbate, say G , and active positions on the surface, say σ . Accordingly, the process can be represented by a chemical-type reaction equation; thus



When adsorption of a polyatomic molecule is accompanied by dissociation the reaction may be written



Adsorption processes are in general reversible and reach equilibrium, as implied in these equations.

Plausibly enough, it is assumed that the rate of adsorption r_1 of a particular substance at any time is proportional to its partial pressure p and to the fraction $1 - \theta$ of surface remaining uncovered at that time. Thus

$$r_1 = k_1 p (1 - \theta) \quad (7-3)$$

On the other hand, the rate of desorption is proportional only to the fraction θ of surface covered; that is,

$$r_{-1} = k_{-1} \theta \quad (7-4)$$

At equilibrium the rates of adsorption and desorption are equal. Therefore

$$k_1 p (1 - \theta) = k_{-1} \theta \quad (7-5)$$

$$\text{or} \quad \theta = \frac{Kp}{1 + Kp} \quad (7-6)$$

where $K = k_1/k_{-1}$ is an equilibrium constant for adsorption.

When dissociation accompanies adsorption (Eq. 7-2) application of the law of mass action gives

$$r_1 = k_1 p (1 - \theta)^2 \quad (7-7)$$

$$r_{-1} = k_{-1} \theta^2 \quad (7-8)$$

These rates are again equal at equilibrium, so upon equating and rearranging,

$$\theta = \frac{K^{\frac{1}{2}} p^{\frac{1}{2}}}{1 + K^{\frac{1}{2}} p^{\frac{1}{2}}} \quad (7-9)$$

When two gases are adsorbed on the same surface, let θ_a and θ_b be the fractions of the surface covered by the individual kinds of molecules. The fraction of uncovered surface is then $(1 - \theta_a - \theta_b)$, and

$$r_{1a} = k_{1a}p_a(1 - \theta_a - \theta_b) \quad (7-10)$$

$$r_{-1a} = k_{-1a}\theta_a \quad (7-11)$$

$$r_{1b} = k_{1b}p_b(1 - \theta_a - \theta_b) \quad (7-12)$$

$$r_{-1b} = k_{-1b}\theta_b \quad (7-13)$$

When the rates of adsorption and desorption are equated for the equilibrium condition, the resulting equations are solved as follows:

$$\theta_a = \frac{K_a p_a}{1 + K_a p_a + K_b p_b} \quad (7-14)$$

$$\theta_b = \frac{K_b p_b}{1 + K_a p_a + K_b p_b} \quad (7-15)$$

Taking again the case of two gases—but when the gas *B* is diatomic and dissociates upon adsorption—the rate equations for *B* are

$$r_{1b} = k_{1b}p_b(1 - \theta_a - \theta_b)^2 \quad (7-16)$$

$$r_{-1b} = k_{-1b}\theta_b^2 \quad (7-17)$$

Upon combining these with Eqs. 7-10 and 7-11, the θ 's become

$$\theta_a = \frac{K_a p_a}{1 + K_a p_a + \sqrt{K_b p_b}} \quad (7-18)$$

$$\theta_b = \frac{\sqrt{K_b p_b}}{1 + K_a p_a + \sqrt{K_b p_b}} \quad (7-19)$$

Extension to more complex cases can be made by inspection of the results so far derived. For example, consider the reversible reaction taking place in the presence of a chemically inert material *I*, with all five substances adsorbed:



The expressions for the various θ 's are

$$\theta_a = \frac{K_a p_a}{1 + K_a p_a + K_b p_b + K_r p_r + K_s p_s + K_i p_i} \quad (7-21)$$

$$\theta_b = \frac{K_b p_b}{1 + K_a p_a + K_b p_b + K_r p_r + K_s p_s + K_i p_i} \quad (7-22)$$

and similarly for θ_r , θ_s , and θ_i . In case dissociation of substance *B*, for example, accompanies adsorption, the term $\sqrt{K_b p_b}$ is substituted for $K_b p_b$ in the preceding equations.

Some of the equations for the fraction of surface covered assume particularly simple forms at low pressure, when the surface may be only sparsely covered, or at high pressures, when the surface is practically completely

covered. When the surface is sparsely covered, $1 - \theta$ is virtually unity and Eq. 7-5 becomes $\theta = Kp$. When the surface is largely covered, θ is virtually unity and consequently $1 - \theta = 1/Kp$. Analogous equations can be written for the other cases of adsorption.

Instead of the surface area as a factor in the rate of adsorption, the concept of the concentration C of uncovered active sites on the surface is employed in some chemical engineering literature. In these terms, Eqs. 7-3 and 7-4 would be written

$$r_1 = k_1 p C \quad (7-23)$$

$$r_{-1} = k_{-1}(C_t - C) \quad (7-24)$$

where C_t is the total number of active sites present in the catalyst (generally expressed per unit mass of catalyst). No particular advantage accrues by reason of this substitution, since only indirect methods can be employed for evaluating C , and very few determinations have thus far been made. The discussion will therefore be continued in terms of θ 's.

The reason for the present concern with the fraction of surface covered by adsorbates is that the over-all rates of surface-catalyzed reactions are influenced and sometimes controlled by the adsorption rates, which are dependent on the amounts of surface available.

The rates of reactions catalyzed by solid surfaces are usually expressed per unit mass of catalyst. Typically, the rate

$$r_a = - \frac{1}{w_c} \frac{dn_a}{dt}$$

has the units pound moles of A transformed per hour per pound catalyst.

46. Surface-reaction-rate Controlling (Equilibrium Adsorption)

The factors influencing the over-all rates of surface-catalyzed reactions have been mentioned in Sec. 43 and are considered again in Sec. 48. The relations to be derived in this and in the next section are restricted to the cases where diffusion is not a factor. However, they will hold with diffusion if the partial pressures in the bulk gas p_a are replaced by those at the interface p_{ai} .

Two limiting cases exist:

1. Adsorption equilibrium is maintained at all times, and the over-all rate of reaction is governed by the rate of combination on the surface.

2. The rate of reaction on the surface is so rapid that adsorption equilibrium is not attained yet a steady state is reached in which the amount of adsorbed material remains constant at some value less than the equilibrium amount without complication by the surface reaction. Often, the rate of adsorption of one of the participants, either a reactant or a product in the case of a reversible reaction, is appreciably slower than the others and is therefore controlling.

In the following, the discussion is phrased in terms of partial pressures of gases. However, all relations derived will hold equally well when activities are substituted for partial pressures, and then they will be applicable to liquids and nonideal gases.

The rate of a reaction occurring on the surface is proportional to the amounts of the reactants on the surface and consequently to the fractions of surface covered by each. Accordingly, for the reaction $A + B \rightarrow M + N$, the rate is

$$\begin{aligned} r = -\frac{1}{w_c} \frac{dn_a}{dt} &= k_1 \theta_a \theta_b = \frac{k_1 K_a p_a K_b p_b}{(1 + K_a p_a + K_b p_b + K_m p_m + K_n p_n)^2} \\ &= \frac{k p_a p_b}{(1 + K_a p_a + K_b p_b + K_m p_m + K_n p_n)^2} \end{aligned} \quad (7-25)$$

As another example, take the reversible reaction occurring in the presence of an inert substance I which is adsorbed along with the participants of the reaction. The reaction is $A + B \rightleftharpoons M + N$, and the net rate of reaction is

$$r = k_1 \theta_a \theta_b - k_{-1} \theta_m \theta_n = k_1 \left(\theta_a \theta_b - \frac{\theta_m \theta_n}{K_r} \right) \quad (7-26)$$

where K_r is the equilibrium constant of reaction. Substituting for each θ and noting that these substitutions all have the same denominator,

$$r = \frac{k_1 (K_a K_b p_a p_b - K_m K_n p_m p_n / K_r)}{(1 + K_a p_a + K_b p_b + K_m p_m + K_n p_n + K_i p_i)^2} \quad (7-27)$$

A simplification in form is achieved by letting $K = K_a K_b K_r / K_m K_n$ and $k = k_1 K_a K_b$, with the result

$$r = \frac{k (p_a p_b - p_m p_n / K)}{(1 + K_a p_a + K_b p_b + K_m p_m + K_n p_n + K_i p_i)^2} \quad (7-28)$$

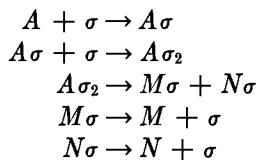
The various terms in equations of this type have been identified by Yang and Hougen (242) by comparison with the fundamental form

$$r = \frac{\text{(kinetic terms)(driving force)}}{\text{adsorption terms}} \quad (7-29)$$

Thus, in Eq. 7-28, k is the kinetic term, $p_a p_b - p_m p_n / K$ is the driving force, and the denominator is the adsorption term. This nomenclature is adopted in the summaries of Tables 7-3 and 7-4.

When the number of moles of products does not equal that of the reactants, as in the reaction $A \rightleftharpoons M + N$, a slight change in viewpoint is required, called the *dual-site* mechanism. It is assumed that the molecule A which is adsorbed on one active site reacts with an adjoining vacant site to form an intermediate compound. This dissociates into molecules

M and *N*, leaving each adsorbed on an active site of its own. In chemical-equation form, the mechanism is



The rate of formation of the intermediate compound $A\sigma_2$ is proportional to the surface θ_a occupied by *A* and to the amount of unoccupied surface θ_v . Accordingly, the net rate of reaction is

$$r = k_1\theta_a\theta_v - k_{-1}\theta_m\theta_n = \frac{k(p_a - p_m p_n / K)}{(1 + K_a p_a + K_m p_m + K_n p_n)^2} \quad (7-30)$$

Dissociation of one of the adsorbed molecules introduces another modification. Take the reaction $A_2 + B \rightleftharpoons M + N$. The rate of the forward reaction is

$$r_1 = k_1\theta_a^2\theta_b \quad (7-31)$$

since two active sites are involved for each A_2 molecule and a third one for molecule *B*. Molecules *M* and *N*, which are adsorbed on their individual sites, must react with a vacant site in order to reverse the over-all reaction. Thus the rate of the reverse reaction is

$$r_{-1} = k_{-1}\theta_m\theta_n\theta_v \quad (7-32)$$

With dissociation, θ_a is given by

$$\theta_a = \frac{\sqrt{K_a p_a}}{1 + \sqrt{K_a p_a} + K_b p_b + K_m p_m + K_n p_n} \quad (7-33)$$

The over-all rate is then

$$r = k_1\theta_a^2\theta_b - k_{-1}\theta_m\theta_n\theta_v = \frac{k(p_a p_b - p_m p_n / K)}{(1 + \sqrt{K_a p_a} + K_b p_b + K_m p_m + K_n p_n)^3} \quad (7-34)$$

As a final example, take the reaction between two substances which are adsorbed on two different kinds of active sites on the same surface, each specific for one of the substances. The substances do not interfere with each other's adsorption, so the surface terms for each have the form

$$\theta = \frac{Kp}{1 + Kp}$$

Consequently the rate of the reaction $A + B \rightarrow$ unadsorbed products is

$$r = \frac{k_1 K_a K_b p_a p_b}{(1 + K_a p_a)(1 + K_b p_b)} = \frac{k p_a p_b}{(1 + K_a p_a)(1 + K_b p_b)} \quad (7-35)$$

which is much different in form from the rate equation for the reaction taking place on a uniform surface under otherwise identical conditions.

Table 7-3 covers the more common cases of reactions whose over-all rate is controlled by the rate of surface reaction. The rate equation for each case may be developed with Eq. 7-29, using the proper entries from this table. As pointed out later, many equations like those in Tables 7-3 and 7-4 may need to be tested before the mechanism of a particular reaction can be established.

47. Rapid Surface Reaction (Adsorption-rate Controlling)

When reaction between adsorbed substances is very rapid, the over-all reaction rate is limited by the rate at which continued adsorption takes place. Normally, only one of the several participants is not in adsorptive equilibrium. Let this be substance *A* in the reaction $A + B \rightleftharpoons M + N$. For visualization, consider the processes of adsorption and surface reaction to proceed in alternate steps. Initially let equilibrium between adsorbed participants exist on the surface. Let a further amount of *A* be adsorbed, thus disturbing the equilibrium on the surface. Since the rate of surface reaction is assumed rapid, however, the reaction equilibrium is quickly reestablished. Clearly, as adsorption of *A* proceeds, this substance reacts at such a rate that adsorptive equilibrium cannot be established, but an amount is present at all times which corresponds to chemical equilibrium between the participants reacting on the surface.

Under these conditions, the fraction of surface covered by *A* is

$$\theta_a = \frac{K_a p_a^*}{1 + K_a p_a^* + K_b p_b + K_m p_m + K_n p_n} \quad (7-36)$$

where p_a^* is the partial pressure corresponding to chemical equilibrium on the surface. At equilibrium the net rate of surface reaction is zero, so that

$$r = k_1 \theta_a \theta_b - k_{-1} \theta_m \theta_n = 0 \quad (7-37)$$

$$\text{whence } \frac{\theta_m \theta_n}{\theta_a \theta_b} = \frac{k_1}{k_{-1}} = K' \quad (7-38)$$

where K' is an equilibrium constant for the surface reaction. Note, however, that the surface equilibrium is continually being disturbed by further adsorption, whereby the over-all reaction is enabled to proceed.

Upon substituting into Eq. 7-38 for the θ 's in terms of p 's and rearranging,

$$p_a^* = \frac{p_m p_n}{p_b K} \quad (7-39)$$

where $K = K' K_a K_b / K_m K_n$. This expression for p_a^* is substituted wherever p_a^* occurs in the expressions for the θ 's. For example,

$$\theta_a = \frac{K_a p_m p_n / K p_b}{1 + K_a p_m p_n / p_b K + K_b p_b + K_m p_m + K_n p_n} \quad (7-40)$$

TABLE 7-3. SURFACE-REACTION CONTROLLING (ADSORPTIVE EQUILIBRIUM MAINTAINED OF ALL PARTICIPANTS)

Reaction	Special condition	Basic rate equation	Driving force	Adsorption term
1 $A \rightarrow M + N$	General case	$r = k\theta_a$	p_a	$1 + K_a p_a + K_m p_m + K_n p_n$
1a $A \rightarrow M + N$	Sparingly covered surface	$r = k\theta_a$	p_a	1
1b $A \rightarrow M + N$	Fully covered surface	$r = k\theta_a$	1	1
2 $A \rightleftharpoons M$	$r = k\theta_a - k_{-1}\theta_m$	$p_a - \frac{p_m}{K}$	$1 + K_a p_a + K_m p_m$
3 $A \rightleftharpoons M + N$	Adsorbed A reacts with vacant site	$r = k_1\theta_a\theta_v - k_{-1}\theta_m\theta_n$	$p_a - \frac{p_m p_n}{K}$	$1 + K_a p_a + K_m p_m + K_n p_n$
4 $A_2 \rightleftharpoons M$	Dissociation of A_2 upon adsorption	$r = k_1\theta_a^2 - k_{-1}\theta_m\theta_v$	$p_a - \frac{p_m}{K}$	$(1 + \sqrt{K_a p_a + K_m p_m})^2$
5 $A + B \rightarrow M + N$	$r = k\theta_a\theta_b$	$p_a p_b$	$(1 + K_a p_a + K_b p_b + K_m p_m + K_n p_n)^2$
5a $A + B \rightarrow M + N$	Adsorbed B reacts with A in gas but not with adsorbed A	$r = k\theta_a\theta_b$	$p_a p_b$	$1 + K_a p_a + K_b p_b + K_m p_m + K_n p_n$
6 $A + B \rightleftharpoons M$	$r = k_1\theta_a\theta_b - k_{-1}\theta_m\theta_v$	$p_a p_b - \frac{p_m}{K}$	$(1 + K_a p_a + K_b p_b + K_m p_m + K_n p_n)^2$
7 $A + B \rightleftharpoons M + N$	$r = k_1\theta_a\theta_b - k_{-1}\theta_m\theta_n$	$p_a p_b - \frac{p_m p_n}{K}$	$(1 + K_a p_a + K_b p_b + K_m p_m + K_n p_n)^2$
8 $A_2 + B \rightleftharpoons M + N$	Dissociation of A_2 upon adsorption	$r = k_1\theta_a^2\theta_b - k_{-1}\theta_m\theta_b\theta_v$	$p_a p_b - \frac{p_m p_n}{K}$	$(1 + \sqrt{K_a p_a + K_b p_b + K_m p_m + K_n p_n})^3$

Notes: The rate equation is

$$r = \frac{k \text{ (driving force)}}{\text{adsorption term}}$$

When an inert substance I is adsorbed, the term $K_I p_I$ is to be added to the adsorption term.

The rate of reaction is equal to the net rate of adsorption:

$$\text{Adsorption rate: } r_1 = k_1 p_a (1 - \theta_a - \theta_b - \theta_m - \theta_n) = k_1 p_a \theta_v \quad (7-41)$$

$$\text{Desorption rate: } r_{-1} = k_{-1} \theta_a \quad (7-42)$$

$$\text{Net rate: } r = k_1 p_a \theta_v - k_{-1} \theta_a = k_1 \left(p_a \theta_v - \frac{\theta_a}{K_a} \right) \quad (7-43)$$

On substituting for θ_v and θ_a in terms of pressures,

$$r = \frac{k(p_a - p_m p_n / K p_b)}{1 + K_a p_m p_n / K p_b + K_b p_b + K_m p_m + K_n p_n} \quad (7-44)$$

as the rate for the reaction $A + B \rightleftharpoons M + N$, with adsorption of substance A as the controlling step. Similar expressions are written when the rate of adsorption of some other participant is controlling.

As another example, take a reaction in which the controlling adsorbate dissociates on adsorption, say the reaction $A_2 \rightleftharpoons M$. For chemical equilibrium on the surface,

$$p_a^* = \frac{p_m}{K} \quad (7-45)$$

From Eq. 7-9, the surface covered by substance A is

$$\theta_a = \frac{\sqrt{K_a p_m / K}}{1 + \sqrt{K_a p_m / K} + K_m p_m} \quad (7-46)$$

It follows, then, for the net rate of adsorption and consequently for the rate of reaction, that

$$r = k_1 p_a \theta_v^2 - k_{-1} \theta_a^2 = \frac{k(p_a - p_m / K)}{(1 + \sqrt{K_a p_m / K} + K_m p_m)^2} \quad (7-47)$$

Reactions may occur directly between an adsorbed molecule B and a molecule A still in the gas phase. Substance A may or may not be adsorbed, but in this type of reaction any adsorbed A molecules do not participate in the reaction but merely reduce the amount of surface available for adsorption of active participants. Let the reaction be $A + B \rightarrow M + N$. Its rate is proportional to the rate of impact of gas molecules A on adsorbed molecules B , or

$$r = k_1 p_a \theta_b = \frac{k p_a p_b}{1 + K_a p_a^* + K_b p_b + K_m p_m + K_n p_n} \quad (7-48)$$

If substance A is not adsorbed, in the denominator of this equation, $K_a p_a^* = 0$.

In Table 7-4 is a summary of the equations thus far derived, together with a few others of some common types of reactions. A comprehensive summary has been made by Yang and Hougen (242).

TABLE 7-4. ADSORPTION-RATE CONTROLLING (RAPID SURFACE REACTION)

Reaction	Special condition	Basic rate equation	Driving force	Absorption term
1 $A \rightarrow M + N$...	$r = kp_a\theta_v$	p_a	$1 + \frac{K_a p_m p_n}{K} + K_m p_m + K_n p_n$
2 $A \rightleftharpoons M$...	$r = k \left(p_a \theta_v - \frac{\theta_a}{K_a} \right)$	$p_a - \frac{p_m}{K}$	$1 + \frac{K_a p_m}{K} + K_m p_m$
3 $A \rightleftharpoons M + N$...	$r = k \left(p_a \theta_v - \frac{\theta_a}{K_a} \right)$	$p_a - \frac{p_m p_n}{K}$	$1 + \frac{K_a p_m p_n}{K} + K_m p_m + K_n p_n$
4 $A_2 \rightleftharpoons M$	Dissociation of A_2 upon adsorption	$r = k \left(p_a \theta_v^2 - \frac{\theta_a^2}{K_a} \right)$	$p_a - \frac{p_m}{K}$	$\left(1 + \sqrt{\frac{K_a p_m}{K}} + K_m p_m \right)^2$
5 $A + B \rightarrow M + N$	Unadsorbed A reacts with adsorbed B	$r = kp_a\theta_v$	p_a	$1 + \frac{K_a p_m p_n}{K p_b} + K_b p_b + K_m p_m + K_n p_n$
6 $A + B \rightleftharpoons M$...	$r = k \left(p_a \theta_v - \frac{\theta_a}{K_a} \right)$	$p_a - \frac{p_m}{K p_b}$	$1 + \frac{K_a p_m}{K p_b} + K_b p_b + K_m p_m$
7 $A + B \rightleftharpoons M + N$...	$r = k \left(p_a \theta_v - \frac{\theta_a}{K_a} \right)$	$p_a - \frac{p_m p_n}{K p_b}$	$1 + \frac{K_a p_m p_n}{K p_b} + K_b p_b + K_m p_m + K_n p_n$
8 $A_2 + B \rightleftharpoons M + N$	Dissociation of A_2 upon adsorption	$r = k \left(p_a \theta_v^2 - \frac{\theta_a^2}{K_a} \right)$	$p_a - \frac{p_m p_n}{K p_b}$	$\left(1 + \sqrt{\frac{K_a p_m p_n}{K p_b}} + K_b p_b + K_m p_m + K_n p_n \right)^2$

Notes: The rate equation is

$$r = \frac{k \text{ (driving force)}}{\text{adsorption term}}$$

Absorption rate of substance A is controlling in each case. When an inert substance I is adsorbed, the term $K_I p_I$ is to be added to the adsorption term.

48. Diffusion and Combined Mechanisms

As mentioned earlier in this chapter, five principal steps occur in the mechanism of a fluid reaction catalyzed by a solid surface. The special cases where one of the steps has a dominant influence on the rate of the reaction, such as diffusive mass transfer or adsorption of some one participant or surface reaction, have already been discussed. The general case now requires attention.

For clarity, the procedure will be described for a first-order reaction, $A \rightarrow B$, where both substances are adsorbed. The five rate equations are

$$r = k_1(p_{ag} - p_{ai}) \quad \text{diffusion of } A \text{ to the surface} \quad (7-49)$$

$$r = k_2 \left(p_{ai} \theta_v - \frac{\theta_a}{k_3} \right) \quad \text{adsorption of } A \quad (7-50)$$

$$r = k_4 \theta_a \quad \text{surface reaction} \quad (7-51)$$

$$r = k_5 \left(p_{bi} \theta_v - \frac{\theta_b}{k_6} \right) \quad \text{desorption of } B \quad (7-52)$$

$$r = k_7(p_{bi} - p_{bg}) \quad \text{diffusion of } B \text{ from the surface} \quad (7-53)$$

$$\theta_v = 1 - \theta_a - \theta_b \quad (7-54)$$

Under steady-state conditions, the rates of all five steps must be equal when they are correctly defined in terms of interfacial surface conditions as in Eqs. 7-49 to 7-53. The six equations contain five quantities which cannot be measured directly, namely, p_{ai} , p_{bi} , θ_a , θ_b , and θ_v . However, these unknowns can be eliminated by algebraic manipulation of the six equations, as follows:

$$p_{ai} = p_{ag} - \frac{r}{k_1} \quad (7-55)$$

$$p_{bi} = p_{bg} + \frac{r}{k_7} \quad (7-56)$$

$$\theta_a = \frac{r}{k_4} \quad (7-57)$$

$$\theta_b = 1 - \theta_a - \frac{1}{p_{ai}} \left(\frac{r}{k_2} + \frac{\theta_a}{k_3} \right) = 1 - \frac{r}{k_4} - \frac{k_1 r}{k_1 p_{ag} - r} \left(\frac{1}{k_2} + \frac{1}{k_3 k_4} \right) \quad (7-58)$$

$$r = \frac{k_5(k_7 p_{bg} + r)}{k_7} \left(1 - \frac{r}{k_4} \right) - k_5 \left(p_{bg} + \frac{r}{k_7} + \frac{1}{k_6} \right) \left[1 - \frac{r}{k_4} - \frac{k_1 r}{k_1 p_{ag} - r} \left(\frac{1}{k_2} + \frac{1}{k_3 k_4} \right) \right] \quad (7-59)$$

The last equation contains only constants which can be evaluated from empirical data of r as a function of p_{ag} and p_{bg} , though the practical handling of this cubic equation presents some problems.

More tractable equations arise from fewer steps. Thus, consider only diffusion and surface reaction, that is, steps 1, 3, and 5. The partial pressures in the vicinity of the surface are p_{ai} and p_{bi} , so

$$\theta_a = \frac{k_1 p_{ai}}{1 + k_1 p_{ai} + k_2 p_{bi}} \quad (7-60)$$

$$p_{ai} = p_{ag} - \frac{r}{k_3} \quad (7-61)$$

$$p_{bi} = p_{bg} + \frac{r}{k_4} \quad (7-62)$$

Consequently,

$$r = k_5 \theta_a = \frac{k_1 k_5 p_{ai}}{1 + k_1 p_{ai} + k_2 p_{bi}} = \frac{k_1 k_5 (p_{ag} - r/k_3)}{1 + k_1 (p_{ag} - r/k_3) + k_2 (p_{bg} + r/k_4)} \quad (7-63)$$

Rearranging,

$$\left(\frac{k_2}{k_4} - \frac{k_1}{k_3} \right) r^2 + \left(1 + \frac{k_1 k_5}{k_3} + k_1 p_{ag} + k_2 p_{bg} \right) r = k_1 k_5 p_{ag} \quad (7-64)$$

When the mass-transfer coefficients k_3 and k_4 are comparatively large, that is, when the rate of diffusion is high, Eq. 7-64 reduces to

$$r = \frac{k_1 k_5 p_{ag}}{1 + k_1 p_{ag} + k_2 p_{bg}} \quad (7-65)$$

This is, of course, the equation that would have been predicted for surface-reaction controlling.

Combinations of adsorption and surface-reaction steps have not been employed in developing over-all rate equations. So many alternatives are possible with either of these steps that they have been adequate individually in association with the diffusion step for establishing satisfactory rate equations. If desired, adsorption and surface-reaction steps may be combined, of course, by the methods indicated.

From these comparatively simple examples of a first-order reaction, it appears that rather formidable equations arise when more than one rate step is involved. Generally, an attempt is made to fit rate data to an equation, based on the assumption that only one of the five steps need be considered, or at the worst, one of the diffusion steps combined with either a surface reaction or an adsorption step.

The nature of the response of a reaction rate to changes in flow rate and temperature may reveal the existence of a dominant diffusion step. Rate data can be analyzed for the influence of the diffusion step with the aid of correlations on mass-transfer coefficients. Such procedures have

been treated by Yang and Hougen (242). A numerical example is worked out subsequently.

Except for direct test, there appears to be no positive way to establish the importance of diffusion in any specific case. Kayser and Hoelscher (119) observed that many industrial catalysts are so active that diffusion is often the controlling factor. As a guide, they suggest that at $D_p G/\mu$ much less than 100, diffusion may become significant. Thus they were able to establish that diffusion rate controlled the rate of hydrogenation of propylene over a palladized alumina catalyst; Hoelscher (94) devoted further study to this topic. Satterfield, Resnick, and Wentworth (192) found that diffusion controlled the decomposition of hydrogen peroxide in an empty tube whose walls were coated with catalyst, up to $dG/\mu = 10,000$, where d is the inside diameter of the tube, and in a sphere packed bed up to $D_p G/\mu = 200$, approximately.

Illustration 7-1. The surface-catalyzed reaction $2A \rightarrow B$ takes place at a pressure of 6 atm. Initially, 20 mole % of A is present, the balance being inert. Experimental rate and partial-pressure data are shown in Table 7-5. It is expected that diffusion of A to the surface and the rate of surface reaction are the only steps appreciably affecting the over-all rate. Substance B is not absorbed. Find the constants of the rate equation, given that $k_a a = 137.5$ for the test conditions.

Solution. The surface-reaction and mass-transfer equations are

$$r = \frac{k p_{ai}^2}{(1 + K_a p_{ai})^2} \quad (A)$$

$$r = k_a a (p_{ag} - p_{ai}) = 137.5 (p_{ag} - p_{ai}) \quad (B)$$

Table 7-5 shows the values of p_{ai} calculated from the second equation. Rewriting the first equation,

$$\frac{p_{ai}}{\sqrt{r}} = \frac{1}{\sqrt{k}} + \left(\frac{K_a}{\sqrt{k}} \right) p_{ai} \quad (C)$$

On Fig. 7-2 the plot of p_{ai}/\sqrt{r} against p_{ai} is a straight line, showing that the assumed mechanism is correct, with rate equation

$$r = \frac{226 p_{ai}^2}{(1 + 0.69 p_{ai})^2} \quad (D)$$

For comparison, a plot is also shown of p_{ag}/\sqrt{r} against p_{ag} , which is not straight. If desired, p_{ai} can be eliminated from Eq. D by substitution from Eq. B.

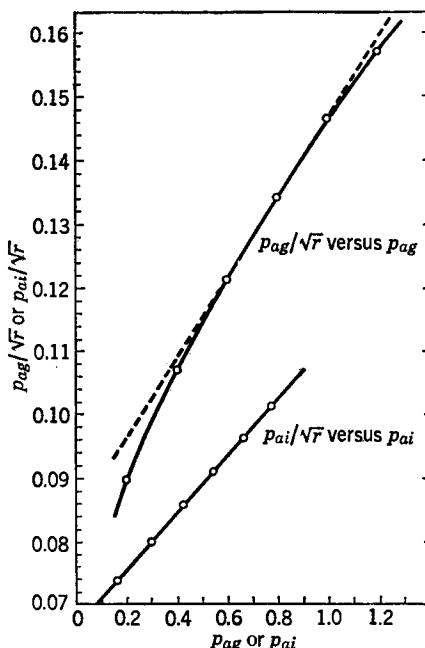


FIG. 7-2. Combined diffusional and surface-reaction resistances (Illustration 7-1).

TABLE 7-5. DATA FOR ILLUSTRATION 7-1

p_{ag}	r	p_{ai}	p_{ai}/\sqrt{r}	p_{ag}/\sqrt{r}
1.2	58.5	0.775	0.1013	0.1570
1.0	47.5	0.655	0.0961	0.1465
0.8	35.5	0.540	0.0909	0.1340
0.6	24.35	0.423	0.0857	0.1213
0.4	13.9	0.299	0.0802	0.1071
0.2	4.96	0.164	0.0735	0.0897

49. Simplified Equations

The rate equations of this chapter have all been derived on the basis of the Langmuir adsorption theory. Though this is known to have serious limitations, the resulting equations often are adequate and are assumed to give an insight into the mechanism. However, for practical purposes, with limited data particularly, simpler equations often suffice (Weller, 230; Boudart, 30).

Over limited pressure ranges the Langmuir isotherm

$$\theta = \frac{ap}{1 + bp} \quad (7-66a)$$

can be replaced to an approximation by a power term. Thus

$$\theta = kp^n \quad (7-66b)$$

where n is a fraction. Consequently rate equations for heterogeneous reactions assume the simpler power forms

$$r = k(p_a)^m(p_b)^n(p_c)^0 \quad (7-67)$$

or the difference of two such power terms. The subscripts may refer to reactants, products, or diluents. Weller (230) cites several instances where an equation of this form fits the data fully as well as a far more complicated one derived from the Langmuir theory. Thus data on the synthesis of phosgene from carbon monoxide and chlorine over charcoal were correlated by Potter and Baron (183) by the equation

$$r = \frac{kK_{CO}K_{Cl_2}p_{CO}p_{Cl_2}}{(1 + K_{Cl_2}p_{Cl_2} + K_{COCl_2}p_{CO}p_{Cl_2})^2} \quad (7-68)$$

where the controlling mechanism was a surface reaction between adsorbed CO and Cl_2 . The following simplified equation correlated fully as well over the experimental range:

$$r = kp_{CO}(p_{Cl_2})^{1/2} \quad (7-69)$$

Also, the reaction between methane and sulfur in the presence of silica gel catalyst undoubtedly has a true mechanism involving several physical

and chemical steps. Yet over the experimental range of 550 to 700°C, Nabor and Smith (165) represent the data by the second-order rate equation

$$r = k_{N_{CH_4}N_S} \quad (7-70)$$

Clearly, rate equation Eq. 7-67 is patterned directly after the law of mass action. Its constants are of course far more readily evaluated than those of equations previously derived in this chapter. In the cases tested, the exponents in Eq. 7-67 were integral and half-integral values.

50. Interpretation of Data

Determination of the mechanism of a surface-catalyzed reaction, or fitting a rate equation to data on such a system, is accomplished by trial. Ordinarily, a large number of possible controlling steps must be investigated. This may be accomplished by some procedure like the following:

1. Postulate various mechanisms, by analogy with similar systems whose mechanism is known, or on the basis of general knowledge, or by sheer inspiration.

2. Write the rate equation for each step. These equations may be of the forms discussed in Secs. 46 and 47. Several empirical constants occur in each such rate equation.

3. Apply the experimental data to evaluate the constants, which should all be either zero or positive. Negative numbers which frequently arise are meaningless, and any assumed mechanism leading to such numbers cannot be valid. [However, see Chou (42) for a criticism of this statement from a statistical point of view.] For convenience, the rate equation may be arranged in such a form that the constants occur linearly only. This permits the ready application of the method of least squares, or in simpler cases, direct plotting of the data as a straight line. For example, Eq. 5 of Table 7-3 can be written in the form

$$\left(\frac{p_a p_b}{r} \right)^{1/2} = a + b p_a + c p_b \quad (7-71)$$

where a , b , and c are constants related to the constants of the original equation.

4. When more than one of the postulated rate equations have all constants either zero or positive, a choice between them can be made on the basis of goodness of fit to the experimental points. To do this, the rate equation is integrated; then a plot is made of conversion against time and checked against the experimental data.

Proper control of the nature of the experimental data can simplify greatly the problem of equation fitting. Auxiliary experiments on adsorption characteristics may be helpful. For example, on palladium catalyst, hydrogen is not adsorbed, propane is weakly adsorbed, and

propylene is strongly adsorbed (Ryerson, 189); these data narrow considerably the choice of mechanisms to investigate for the catalytic dehydrogenation of propane.

Flow reactors are perhaps the type most widely used for experimenting with solid catalyzed reactions since the attainment of steady-state conditions makes control and analysis much easier. As mentioned in Sec. 1, flow reactors may be integral or differential. When analyzing data taken with a differential flow reactor, it may be permissible to use average values over the reactor or even the initial values of the partial pressures of the participants, thus avoiding the complications arising from changes in these quantities as reaction progresses. In case none of the products appear in the feed mixture, the differential reactor provides initial rate data.

The number of possible mechanisms may be narrowed down when initial rates are known as a function of concentrations or the total pressure of the system. Such rates can be obtained by extrapolation of data obtained over a wide range or directly from experiments in a differential reactor as mentioned. Equations for initial rates do not possess adsorption and rate terms for the products, so they are simpler in form, yet they differ sufficiently from the mechanism to be of value in establishing it.

For example, suppose that in the case of a first-order reversible reaction the surface-reaction rate is controlling but it is desired to test whether simple adsorption or adsorption accompanied by dissociation occurs. These are possibilities 2 and 4 of Table 7-3, namely, the reactions $A \rightleftharpoons M$ and $A_2 \rightleftharpoons M$, for which the initial rates are

$$r_0 = \frac{kp_a}{1 + K_a p_a} \quad (7-72)$$

$$r_0 = \frac{kp_a}{(1 + \sqrt{K_a p_a})^2} \quad (7-73)$$

In the absence of reaction products, p_a is proportional to the total pressure, so the previous equations also may be written

$$r_0 = \frac{k' \pi}{1 + K' \pi} \quad (7-74)$$

$$r_0 = \frac{k' \pi}{(1 + \sqrt{K' \pi})^2} \quad (7-75)$$

Clearly, a study of the effect of total pressure on the initial rate of this reaction will distinguish between the two mechanisms. Several experiments at different initial total pressures are required.

Since the system pressure is one of the more easily varied experimental conditions, it is a convenient and generally useful criterion for identifying mechanisms. The effect of pressure on initial rate is often particularly

illuminating. Typical curves for several first- and second-order reactions are shown in Fig. 7-3 (Hougen, 99). Comparison of actual data with these curves may be helpful in narrowing down the number of possible mecha-

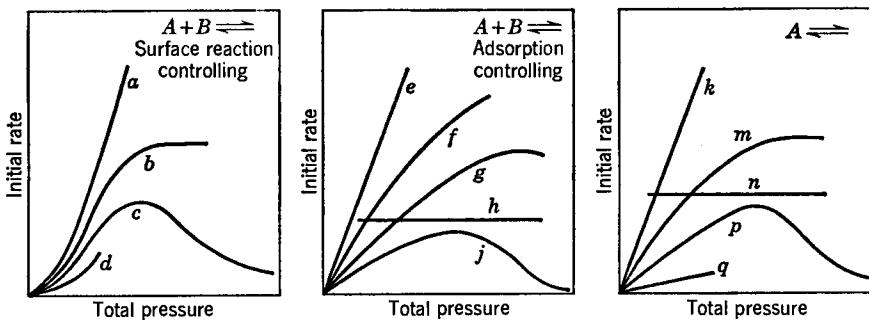


FIG. 7-3. Relation between total pressure and initial rate. (a) B not adsorbed (asymptotic); (b) both adsorbed without dissociation (asymptotic); (c) both adsorbed, A dissociated (asymptotic); (d) homogeneous reaction; (e) adsorption of A controlling, B not adsorbed; (f) adsorption of B controlling, A dissociated; (g) adsorption of A controlling, B at equilibrium adsorption (asymptotic); (h) desorption of product R controlling, irreversible reaction; (j) adsorption of A controlling with dissociation, B at equilibrium adsorption (asymptotic); (k) adsorption of A controlling; (m) surface reaction controlling, single site; (n) desorption of product controlling, irreversible reaction; (p) surface reaction controlling, dual site; (q) homogeneous reaction. [Hougen (99). Courtesy Chemical Engineering Progress.]

nisms. Since this number is often quite large, perhaps 15 or 20 or even more, every bit of assistance is desirable.

Several examples of equation fitting may be described briefly.

Illustration 7-2. Nitrous oxide decomposes under the catalytic influence of a platinum surface. Some measurements at 741°C are shown in Table 7-6 (Hinshelwood, 91). Oxygen (B) and possibly nitrous oxide (A) are adsorbed. Therefore check the two rate equations

$$r = -\frac{dp_a}{dt} = \frac{kp_a}{1 + K_a p_a + K_b p_b} \quad (A)$$

$$r = -\frac{dp_a}{dt} = \frac{kp_a}{1 + K_b p_b} \quad (B)$$

Solution. Rearrange the rate equations thus:

$$y = \frac{p_a}{r} = \frac{1 + K_a p_a + K_b p_b}{k} = A + B p_a + C p_b \quad (C)$$

$$y = \frac{p_a}{r} = \frac{1 + K_b p_b}{k} = A + B p_b \quad (D)$$

The derivatives $1/r = -dt/dp_a$ shown in Table 7-6 were evaluated by the six-point formula (Milne, 158). The constants of the rate equations will be evaluated by the method of least squares. For Eq. C,

$$\Sigma(A + B p_a + C p_b - y)^2 = \text{minimum}$$

TABLE 7-6. DATA FOR ILLUSTRATION 7-2

<i>t</i>	315	750	1,400	2,250	3,450	5,150
p_{O_2}	10	20	30	40	50	60
p_{NO_2}	85	75	65	55	45	35
1/r (calculated)....	26.7	55.9	73.1	97.7	142.8	196.0

Upon setting the three derivatives with respect to *A*, *B*, and *C* equal to zero and rearranging,

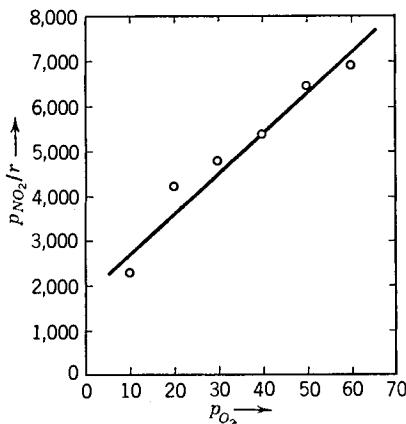


FIG. 7-4. Oxidation of nitrous oxide (Illustration 7-2).

Since negative constants are physically inadmissible, only Eq. *B* meets the requirements, and the correct rate equation is

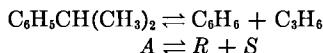
$$r = \frac{0.00056 p_a}{1 + 0.0506 p_b}$$

Figure 7-4 shows the data points and the least-squares line. Possibly the first point is an experimental inaccuracy; the other points are fairly nearly collinear.

TABLE 7-7. DATA FOR ILLUSTRATION 7-2

p_b	p_a	1/r	p_a/r	p_a^2	$p_a p_b$	p_b^2	$p_a y$	$p_b y$
10	85	26.7	2,270	7,200	850	100	193,000	22,700
20	75	55.9	4,191	5,600	1,500	400	314,000	83,800
30	65	73.1	4,752	4,230	1,950	900	309,000	143,000
40	55	97.7	5,374	3,030	2,200	1,600	296,000	215,000
50	45	142.8	6,426	2,020	2,250	2,500	289,000	321,000
60	35	190.6	6,660	1,220	2,100	3,600	240,000	412,000
210	360	29,673	23,300	10,850	9,100	1,641,000	1,197,500

Illustration 7-3. Measurements of total pressure were employed to identify the mechanism of the cracking of cumene (Corrigan, Garver, Rase, and Kirk, 49). The reaction is



Both single- and dual-site mechanisms were considered, with stoichiometric and initial rate equations as follows, for various possible controlling steps:

Single-site:

$$\begin{aligned} 1. \quad A + \sigma &\rightleftharpoons A\sigma & r_0 &= a\pi \\ 2. \quad A\sigma &\rightleftharpoons R\sigma + S & r_0 &= \frac{a\pi}{1 + b\pi} \end{aligned}$$

$$3. \quad R\sigma \rightleftharpoons R + \sigma \quad r_0 = a$$

Dual-site:

$$\begin{aligned} 4. \quad A + \sigma &\rightleftharpoons A\sigma & r_0 &= a\pi \\ 5. \quad A\sigma + \sigma &\rightleftharpoons R\sigma + S\sigma & r_0 &= \frac{a\pi}{(1 + b\pi)^2} \\ 6. \quad R\sigma &\rightleftharpoons R + \sigma & r_0 &= a \\ 7. \quad S\sigma &\rightleftharpoons S + \sigma & r_0 &= a \end{aligned}$$

Examination of the experimental data showed that mechanism 2 is the controlling one; that is, adsorbed cumene decomposes on the surface into adsorbed benzene and un-adsorbed propylene. The complete rate equation is

$$r = \frac{k(p_a - p_r p_s/K)}{1 + K_a p_a + K_r p_r}$$

Illustration 7-4. The catalytic hydrogenation of propylene and ethylene was studied in a flow reactor (Sussman and Potter, 208). The controlling step was found to be the surface reaction between adsorbed olefin and hydrogen which is adsorbed with dissociation. It was noted that hydrogen is only weakly adsorbed in comparison with the hydrocarbons, so that its contribution to the "adsorption term" is nil. Consequently the rate equation is

$$r = \frac{p_{\text{hydrogen}} p_{\text{olefin}}}{(a + bp_{\text{olefin}} + cp_{\text{saturate}})^s}$$

For propylene at 76°C, the constants were evaluated as $a = 0.842$, $b = 2.32$, and $c = 1.00$.

Data on ethylene were obtained in a differential reactor with about 2 per cent conversion of olefin, so the initial rate equation was applicable:

$$r_0 = \frac{p_{\text{hydrogen}} p_{\text{ethylene}}}{(a + bp_{\text{ethylene}})^s} \quad \frac{\text{g moles}}{(\text{hr})(\text{g mole catalyst})}$$

The constants were evaluated by plotting $(p_{\text{hydrogen}} p_{\text{ethylene}}/r_0)^{1/2}$ against p_{ethylene} . Of the 18 mechanisms investigated, four gave a negative value for either a or b and all but two of the remainder showed a poor fit of the data to a straight line. Of the two acceptable equations, the one stated above gave the better fit, with $a = 0.875$ and $b = 1.08$ at 77°C.

Illustration 7-5. The reaction

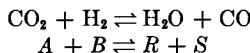


TABLE 7-8. MECHANISMS FOR CATALYZED REACTION $A + B \rightleftharpoons R + S$, ILLUSTRATION 7-5

No.	Stoichiometric equation	Process	Rate equation
I-1	$A + \sigma \rightleftharpoons A\sigma$	A adsorbed, B and S not adsorbed	$\frac{p_a - p_r p_s / K p_b}{r} = a + \frac{b p_r p_s}{p_b} + c p_r$
I-2	$A\sigma + B \rightleftharpoons R\sigma + S$	Reaction between gas molecule and an adsorbed one	$\frac{p_a p_b - p_r p_s / K}{r} = a + b p_a + c p_r$
I-3	$R\sigma \rightleftharpoons R + \sigma$	Desorption of R	$\frac{K p_a p_b / p_s - p_r}{r} = a + b p_a + \frac{c p_a p_b}{p_s}$
II-1	$A + \sigma \rightleftharpoons A\sigma$	All substances adsorbed	$\frac{p_a - p_r p_s / K p_b}{r} = a + b p_b + \frac{c p_r p_s}{p_b} + (d + e)p_s$
II-2	$B + \sigma \rightleftharpoons B\sigma$	$p_b - p_r p_s / K p_a = a + b p_a + \frac{c p_r p_s}{p_a} + (d + e)p_s$
II-3	$A\sigma + B\sigma \rightleftharpoons R\sigma + S\sigma$	Surface reaction between adsorbed molecules	$\sqrt{\frac{p_a p_b - p_r p_s / K}{r}} = a + b p_a + c p_b + (d + e)p_s$
III-1	$A + \sigma \rightleftharpoons D\sigma + S$	Intermediate complex formation	$\frac{p_a - p_r p_s / K p_b}{r} = a + \frac{b p_r}{p_b} + c p_r$
III-2	$D\sigma + B \rightleftharpoons R\sigma$	$\frac{K p_a p_b / p_s - p_r}{r} = a + \frac{b p_a}{p_s} + c p_r$
III-3	$R\sigma \rightleftharpoons R + \sigma$	$\frac{K p_a p_b / p_s - p_r}{r} = a + \frac{b p_a}{p_s} + \frac{c p_a p_b}{p_s}$
IV-1	$A + \sigma \rightleftharpoons D\sigma + S$	$\frac{p_a - p_r p_s / K p_b}{r} = a + \frac{b p_r}{p_b} + c p_b + d p_r$
IV-2	$B + \sigma \rightleftharpoons B\sigma$	$\frac{p_b - p_r p_s / K p_a}{r} = a + \frac{b p_r p_s}{p_a} + \frac{c p_a}{p_s} + d p_r$
IV-3	$B\sigma + D\sigma \rightleftharpoons R\sigma + \sigma$	$\sqrt{\frac{K p_a p_b / p_s - p_r}{r}} = a + \frac{b p_a}{p_s} + c p_b + d p_r$
IV-4	$R\sigma \rightleftharpoons R + \sigma$	$\frac{K p_a p_b / p_s - p_r}{r} = a + \frac{b p_a}{p_s} + c p_b + \frac{d p_a p_b}{p_s}$

was investigated (Barkley, Corrigan, Wainwright, and Sands, 11) at 1000°F and substantially atmospheric pressure in the presence of an Fe-Cu catalyst. The controlling step appears to be the reaction of adsorbed CO₂ with a molecule of H₂ still in the gas phase and resulting in an adsorbed CO molecule and an H₂O molecule in the gas phase. The rate equation is

$$r = \frac{k(p_a p_b - p_r p_s / K)}{1 + K_a p_a + K_s p_s} \quad \text{lb moles/(hr)(lb catalyst)}$$

with $k = 0.595$, $K = 0.267$, $K_a = 4.46$, and $K_s = 41.65$ when the pressures are in atmospheres. Before the above conclusions were drawn, all the mechanisms of Table 7-8 were examined. Evaluation of the constants is shown in Table 7-9. Both mechanisms I-2 and III-3 lead to all positive constants. However, plots of the integrated rate equations show that the first of these fits the experimental data somewhat better.

TABLE 7-9. CONSTANTS OF THE RATE EQUATIONS OF TABLE 7-8

Eq. no.	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>d + e</i>
I-1	26.1	821.8	-231.7		
I-2	1.68	7.5	70.0		
I-3	24.4	3.23	1.25		
II-1	34.3	123.6	416.2	-600.0
II-2	-63.4	34.6	1,166.0	334.0
II-3	*	*	*	*	*
III-1	44.1	113.5	-435.1		
III-2	16.4	0.9	67.06		
III-3	12.8	2.43	2.94		
IV-1	2.29	112.0	-3,500.0	-16.3	
IV-2	36.2	946.0	0.10	-383.0	
IV-3	78.9	-204.0	-0.81	-135.0	
IV-4	24.6	7.6	-1.32	0.12	

* These constants were not evaluated, but it was shown that they could not all be positive. CO₂+H₂ = H₂O+CO A+B = R+S

PROBLEMS

7-1. These data were obtained for the adsorption of nitrogen on activated alumina powder at 77.3°K:

Partial pressure, mm Hg	Gram moles nitrogen adsorbed per gram of alumina
31.7	0.000831
40.1	0.000853
56.6	0.000890
64.5	0.000903
82.7	0.000953
96.7	0.000985
112.4	0.001015
128.8	0.001045
148.6	0.001081
169.3	0.001118

At this temperature, the vapor pressure is $p_s = 759$ mm Hg. The area covered by one nitrogen molecule is $16.2(10^{-20})$ sq m. The adsorption is believed to follow the Brunauer, Emmett, and Teller equation,

$$\frac{V}{V_m} = \frac{a(p/p_s)}{(1 - p/p_s)[1 + (a - 1)(p/p_s)]}$$

where a = a constant

p = partial pressure

V = volume of gas adsorbed by unit mass of adsorbent

V_m = volume of gas adsorbed by unit mass of adsorbent as a unimolecular layer
Both volumes are measured at 0°C and 760 mm Hg. Find:

(a) The quantities a and V_m .

(b) The surface area of the alumina, sq m/g.

7-2. As interpreted by Rase and Kirk (186), the rate of pyrolysis of alkylbenzenes is controlled by the mechanism



for which the rate equation is

$$r = \frac{kK_a(p_a - p_r p_s/K)}{1 + K_a p_a + K_r p_r}$$

Show that the integrated equation for a flow reactor is (starting with pure A)

$$\frac{W}{F} = \gamma \left[\left(\frac{1}{2\delta} - \frac{1}{2\delta^3} \right) \ln \frac{1 + \delta x}{1 - \delta x} + \frac{x}{\delta^2} \right] + \beta \left[\frac{1}{2\delta^3} \ln \frac{1 + \delta x}{1 - \delta x} - \frac{1}{2\delta^2} \ln (1 - \delta^2 x^2) - \frac{x}{\delta^2} \right]$$

where $\beta = 2/kK_a\pi + K_r/kK_a$

$\gamma = 1/kK_a\pi + 1/k$

$\delta = 1/x^* = \sqrt{1 + \pi/K}$

x^* = equilibrium conversion

7-3. Check mechanisms 1 to 5 of Illustration 7-3, given the following smoothed initial rate data at 950°F:

r_0 , lb moles/(hr)(lb catalyst).....	4.3	6.5	7.1	7.5	8.1
π , atm.....	0.98	2.62	4.27	6.92	14.18

7-4. For the reaction of Illustration 7-5, these data were obtained at 1000°F when the feed contained 20 per cent CO_2 :

x , $\frac{\text{lb moles CO}_2 \text{ converted}}{\text{lb moles CO}_2 \text{ fed}}$	0.604	0.586	0.482	0.399	0.099	0.037
$\frac{W}{F}$, $\frac{\text{lb catalyst}}{\text{lb moles CO}_2 \text{ fed}/\text{hr}}$	121	70.0	30.2	19.1	5.5	2.5

Evaluate:

- The partial pressures of all participants.
- The rate $r = dx/d(W/F)$, as a function of x .
- The constants for mechanisms I-2 and III-1.

7-5. Controlling mechanism for the catalytic dehydration of butanol-1 was found

to be the surface reaction rate (Maurer and Sliepcevich, 148), with the initial rate equation

$$r_0 = \frac{kK_a f}{(1 + K_a f)^2} \quad \text{lb moles/(hr) (lb catalyst)}$$

Some of the data were:

r_0	$p, \text{ atm}$	f/p
0.27	15	1.00
0.51	465	0.88
0.76	915	0.74
0.76	3,845	0.43
0.52	7,315	0.46

where f is the fugacity of butanol-1. Find the constants k and K_a .

7-6. Data on the hydrogenation of ethylene are quoted by Sussman and Potter (208) following. The catalyst weight was 2.20 g. Average bed temperature was 41°C, and pressure was atmospheric. Check the validity of the following controlling steps and the corresponding initial rate equations:

(a) Desorption-of-product controlling,

$$r_0 = \frac{p_{\text{H}_2} p_{\text{C}_2\text{H}_4}}{a + b p_{\text{C}_2\text{H}_4}}$$

(b) Adsorption-of-hydrogen controlling,

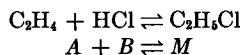
$$r_0 = \frac{p_{\text{H}_2}}{a + b p_{\text{C}_2\text{H}_4}}$$

(c) Surface-reaction controlling, with dissociation of H_2 upon adsorption,

$$r_0 = \frac{p_{\text{H}_2} p_{\text{C}_2\text{H}_4}}{(a + b p_{\text{C}_2\text{H}_4})^3}$$

Flow rate, g moles/sec	p_{H_2},atm	$p_{\text{C}_2\text{H}_4},atm$	$r,g moles/(hr)(g catalyst)$
0.000266	0.405	0.595	0.00882
0.000266	0.401	0.599	0.00900
0.000362	0.611	0.389	0.01172
0.000698	0.776	0.224	0.01444
0.000564	0.908	0.092	0.01964
0.000766	0.933	0.067	0.02021
0.000766	0.933	0.067	0.02060
0.001062	0.951	0.049	0.02008
0.001062	0.951	0.049	0.02030
0.000360	0.603	0.397	0.01253
0.000362	0.611	0.389	0.01183

7-7. The synthesis of ethyl chloride from ethylene and hydrogen chloride in the presence of methane was studied in a differential reactor (Thodos and Stutzman, 214). Zirconium oxychloride deposited on silica gel was the catalyst. The reaction is



Test data for r_a , the rate of reaction, pound moles ethylene converted per hour per pound catalyst, are shown in the table as functions of the several partial pressures, at 400 psig and an average of 350°F.

r_a	Partial pressure, atm.				
	0.000262	0.000260	0.000252	0.000216	0.000263
CH ₄	7.005	7.090	7.001	9.889	10.169
C ₂ H ₄	0.300	0.416	0.343	0.511	0.420
HCl.....	0.370	0.215	0.289	0.489	0.460
C ₂ H ₅ Cl.....	0.149	0.102	0.181	0.334	0.175

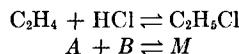
Equilibrium constant for the reaction is $K_r = p_m/p_a p_b = 35.5$. Check the mechanisms leading to these equations:

$$r_a = \frac{k(p_a p_b - p_m/K_r)}{(1 + K_a p_a + K_b p_b + K_m p_m + K_I p_I)^2}$$

$$r_a = \frac{k(p_a - p_m/K_r p_b)}{1 + K_a p_m/K_r p_b + K_b p_b + K_m p_m + K_I p_I}$$

Subscript I designates an inert component of the reacting mixture.

7-8. The rate of the catalytic reaction



in the presence of methane is given by the equation

$$r_a = \frac{k(p_a p_b - p_m/K_r)}{(1 + K_a p_a + K_b p_b + K_m p_m + K_I p_I)^2}$$

The constants are functions of temperature according to the equation

$$\log K = \frac{a}{T} + b$$

where T is in degrees Rankine and the constants are given in the table. Pressures are in atmospheres. Rates are lbmoles ethylene converted/(hr) (lb catalyst).

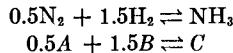
	k	K_a	K_b	K_I	K_m	K_r
a	-11,778	-7,026	-8,037	-2,829	-5,060	+5,265
b	15.211	10.108	11.456	3.833	7.809	-4.96

Given a feed at 400 psig and containing 0.8485, 0.1010, and 0.0505 mole fraction of methane, ethylene, and hydrogen chloride, respectively. Find the amount of catalyst per pound mole of feed per hour needed to achieve 40 per cent conversion of ethylene at constant temperatures of 300, 350, and 400°F (Thodos and Stutzman, 214).

7-9. The kinetics of ammonia synthesis has been considered by Temkin and Pyzhev (213). The over-all rate is controlled by the rate of adsorption of nitrogen. In the development of the rate equation, a logarithmic form of adsorption isotherm

$$\theta = k \ln p$$

has been used and has been confirmed experimentally. For the reaction



the rates of adsorption and desorption are

$$r_a = k_a p_a e^{-\theta_a}$$

$$r_{-a} = k_{-a} e^{\theta_a}$$

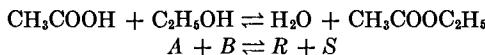
Noting that chemical equilibrium exists on the surface, show that the over-all rate of reaction is

$$r = k_1 p_a \left(\frac{K_p^2 p_b^3}{p_c^2} \right)^\alpha - k_2 \left(\frac{p_c^2}{K_p^2 p_b^3} \right)^\beta$$

where K_p is the equilibrium constant. From experimental work, $\alpha = \beta = 0.5$. At the elevated pressures of commercial operations, deviations from the ideal-gas law are appreciable, so activities must be substituted for partial pressures.

Integrate this equation for a flow reactor in which the flow rate is F lb moles/hr, the catalyst weighs W lb, ammonia is initially absent, and the fractional conversion is f .

7-10. The rate of the vapor-phase silica gel-catalyzed esterification of ethanol with acetic acid is controlled by the adsorption rate of acetic acid (Venkateswarlu, Satyanarayana, and Rao, 224; Hoerig, Hanson, and Kowalke, 95).



At 266°C and atmospheric pressure the rate equation is

$$r = \frac{dx}{d\left(\frac{W}{F}\right)} = \frac{0.0477[\phi(N_r)(N_a - N_r N_s/N_b K)]}{1 + 11.8N_s} \frac{\text{lb moles converted/lb feed}}{\text{lb catalyst/(lb feed/hr)}}$$

where $\phi(N_r) = 0.3 + 0.9N_r$ represents a correction to the activity of the acetic acid for $N_r > 0.15$; the presence of water has been found to favor the adsorption of acetic acid as expressed by this relation. The N 's are mole fractions.

A mixture of the following composition is charged at the rate of 406 lb/hr:

Mole fraction	
Acetic acid.....	0.4089
Ethanol.....	0.4496
Water.....	0.1415

The equilibrium constant is $K = 11.7$, corresponding to an equilibrium conversion of 77.1 per cent for an equimolar charge of acetic acid and ethanol. Find the amount of catalyst needed to achieve 50 per cent conversion.

7-11. For the oxidation of nitric oxide, the following rate equations are presented for 30°C (Baker, Wong, and Hougen, 8):

Homogeneous:

$$-\frac{1}{V} \frac{d(NO)}{dt} = 3.775 p_{O_2} p_{NO}^2 \quad \text{g moles NO/(liter)(hr)}$$

Catalyzed by silica gel:

$$r = \frac{p_{NO}^2 p_{O_2}}{a + b p_{NO}^2 + c p_{NO}} \quad \text{g moles NO converted/(g catalyst)(hr)}$$

$$a = 0.005834$$

$$b = 23.63$$

$$c = 0.03268$$

p = partial pressure, atm

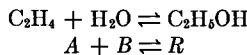
Compare the sizes of flow reactors needed for the catalyzed and the homogeneous reactions, given these additional data:

Feed composition $p_{\text{NO}} = 0.05 \text{ atm}$, $p_{\text{O}_2} = 0.95 \text{ atm}$, $\pi = 1 \text{ atm}$

Bulk specific gravity of catalyst 0.6

Required conversion 95%

7-12. Direct catalytic hydration of ethylene in the vapor phase at 2,000 psia was studied by Mace and Bonilla (146), with the conclusion that surface reaction is controlling, without adsorption of ethanol.



The rate equation is

$$r = \frac{zK_a K_b (p_a p_b - p_r/K)}{(1 + K_a p_a + K_b p_b)^2} \quad \text{g moles/(g catalyst)(hr)}$$

Test data are:

<i>T</i> , °F.....	508	520	550	580
<i>z</i>	0.0043	0.00665	0.0172	0.0233
<i>K_a</i> = <i>K_b</i>	0.0156	0.00889	0.00208	0.00114

Also, $RT \ln K = 28.6T - 9,740$, where *T* is in degrees Kelvin and *R* = 1.99.

Calculate the pounds of catalyst needed to convert 20 per cent of C_2H_4 under isothermal conditions at 520°F, when the total feed rate is 10 lb moles/hr and contains equimolar proportions of ethylene and water.

7-13. Oxidation of NO is catalyzed by active carbon according to this rate equation at 30°C:

$$r = \frac{p_{\text{NO}}^2 p_{\text{O}_2}}{a + b p_{\text{NO}}^2 + c p_{\text{NO}_2}} \quad \text{g moles NO converted/(g catalyst)(hr)}$$

$$a = 0.0001619$$

$$b = 4.842$$

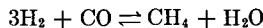
$$c = 0.001352$$

p = partial pressure, atm

Find the volume of reactor for converting 50 tons/day of NO to NO_2 , when using an air-NO mixture containing 1.5 mole % of the latter and the conversion is 90 per cent. Bulk specific gravity of the catalyst is 0.48, and the total pressure is 3 atm (Rao and Hougen, 185).

7-14. Initial rates of formation of CH_4 from CO and H_2 in the presence of nickel catalyst were correlated (Pursley, White, and Sliepcevich, 184) by the equation

$$r_0 = \frac{1.1 p_{\text{CO}} (p_{\text{H}_2})^{1/2}}{1 + 1.5 p_{\text{H}_2}} \quad \text{lb moles CH}_4/(\text{hr})(\text{lb catalyst})$$



Pressures are in atmospheres. Find the volume of reactor for converting 10 lb moles/hr of the CO present in an equimolar mixture of monoxide and hydrogen. Assume 20 per

cent conversion and that the initial rate given by the equation holds roughly up to this conversion. Catalyst density is 30 lb/cu ft. Pressure = 1 atm.

7-15. Develop the over-all rate equation for the reaction $A \rightleftharpoons B$, taking these steps into account:

(a) Adsorption rate of A

$$r = k_1 \left(p_a \theta_v - \frac{\theta_a}{k_2} \right)$$

(b) Desorption rate of B

$$r = k_3 \left(\frac{\theta_b}{k_4} - p_b \theta_v \right)$$

(c) Surface reaction rate

$$r = k_5 \left(\theta_a - \frac{\theta_b}{k_6} \right)$$

Note that $\theta_v = 1 - \theta_a - \theta_b$.

CHAPTER 8

FIXED AND FLUIDIZED BEDS OF PARTICLES

51. Transfer Processes in Granular Masses

Contacting of fluids with solid particles during chemical reaction is frequently done. The most common instances are those in which the solid is employed as a catalyst, but there are also many cases where the solid is prepared in granular form to improve its reactivity with a fluid or where it is employed to exchange heat with the reacting fluid, as in a pebble heater. Such operations are conducted mostly under flow conditions, with attendant pressure drop along the direction of flow. Moreover, heat effects occur, and sometimes limitations exist in the diffusive mass-transfer rate. Simultaneous occurrence of all these effects is not uncommon.

Mathematical description of a reacting fluid flowing through a bed of solid particles demands a system of partial differential equations, which may be derived by application of the laws of conservation of momentum, thermal energy, and mass. In Sec. 66, the various terms entering into these conservation laws are stated for a cylindrical reactor. Here will be considered, first of all, the simplest case of transfer in one (mathematical) dimension.

For evaluating pressure drop, the more familiar mechanical-energy balance may be used instead of the momentum balance. In packed beds, as in the empty tubes considered in Sec. 31, static-head and kinetic-energy terms are generally negligible, so the pressure-drop equation will be similar in form to that shown there for empty tubes, though slightly more complicated because of the necessity of taking into account the void space, particle size, particle shape, and roughness. Actual formulas are presented later in this chapter.

Analysis of the rates of heat and mass transfer is somewhat more complex since changes occur both in the direction of over-all mass flow and laterally. Applying the conservation law to heat transfer, the over-all rate of accumulation of heat is equal to the sum of the individual rates of accumulation due to:

1. Conduction of heat through the fluid
2. Conduction of heat through the solid
3. Enthalpy accompanying the flow of fluid

4. Enthalpy accompanying the flow of solid

5. Chemical reaction

Also, heat transfer between solid and fluid may occur by convection and radiation.

In the general case, temperatures of the solid and fluid will be different, so two equations may be set up (Singer and Wilhelm, 202). Confining the discussion for the moment to the case of uniform conditions throughout the cross section, the following equations are written, per unit volume. The first is the heat balance on both the solid and the fluid, and the second on the solid alone.

$$-\frac{\partial}{\partial t} [s_f \rho_f \epsilon T_f + s_s \rho_s (1-\epsilon) T_s] = \frac{\partial}{\partial L} \left(-k_{ef} \frac{\partial T_f}{\partial L} - k_{es} \frac{\partial T_s}{\partial L} \right) + \frac{\partial}{\partial L} (s_f G_f T_f + s_s G_s T_s) + r \rho_B \Delta H_r \quad (8-1)$$

$$-\frac{\partial}{\partial t} (s_s \rho_B T_s) = \frac{\partial}{\partial L} \left(-k_{es} \frac{\partial T_s}{\partial L} \right) + (h_c + h_r)_v (T_s - T_f) + \frac{\partial}{\partial L} (s_s G_s T_s) + \alpha r \rho_B \Delta H_r \quad (8-2)$$

where $(h_c + h_r)_v$ = convection and radiation coefficient per unit volume
 k_{ef} = effective thermal conductivity of fluid, which is higher than true conductivity because of convection

k_{es} = effective conductivity of solid, which is different from true conductivity because of adsorbed fluid films

ρ_B = bulk density of catalyst = $(1 - \epsilon) \rho_s$

Certain simplifications of these equations are possible. Except with metallic particles, which in any event are rarely used, the terms involving k_{es} may be neglected. Also, the mass rate of flow of solid is often small in comparison with that of the fluid, so the terms involving G_s may be dropped. Finally, except in devices such as the pebble heater or heat regenerators or recuperators, the fluid and solid temperatures are substantially equal at any one point. Accordingly, the above equations simplify to

$$-\frac{\partial}{\partial t} (s_m \rho_m T) = \frac{\partial}{\partial L} \left(-k_{ef} \frac{\partial T}{\partial L} \right) + \frac{\partial}{\partial L} (s_f G T) + r \rho_B \Delta H_r, \quad (8-3)$$

where

$$s_m \rho_m = s_f \rho_f \epsilon + s_s \rho_s (1 - \epsilon)$$

Similar equations can be written for the rate of mass transfer of each participant. In a packed bed, both molecular and eddy diffusion are

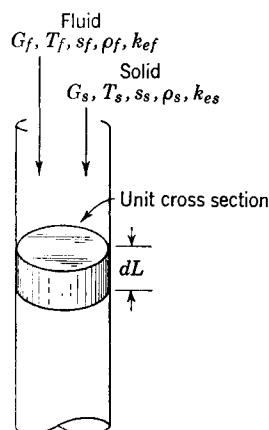


FIG. 8-1. Energy balance on flow reaction in packed bed (Eqs. 8-1 to 8-3).

factors. An effective diffusivity which takes both factors into account may be defined by a modified Fick's law,

$$r_d = - \frac{D_e}{G/\rho_f} \frac{\partial(GC/\rho_f)}{\partial L} \quad (8-4)$$

Measurements and correlations of the effective diffusivity D_e have been made by Bernard and Wilhelm (20) and Fahien and Smith (66) which may be represented approximately by

$$(Pe)_d = \frac{D_p G}{\rho_f D_e} = 9 + 175 \left(\frac{D_p}{D_t} \right)^2 \quad 30 < \frac{D_p G}{\mu} < 700 \quad (8-5)$$

where $(Pe)_d$ is the Peclet number for mass transfer.

For each participant in the reaction, the material balance is expressed by an equation like the following, where the assumption is made that $D_e/(G/\rho_f)$ does not vary with position:

$$-\frac{\partial C}{\partial t} = -\frac{D_e}{G/\rho_f} \frac{\partial}{\partial L} \left[\frac{\partial(GC/\rho_f)}{\partial L} \right] + \frac{\partial}{\partial L} \left(\frac{GC}{\rho_f} \right) + r\rho_B \quad (8-6)$$

Verbally, this equation states that the over-all accumulation of mass is equal to the sum of the individual accumulations due to diffusion, bulk mass flow, and chemical reaction. Whenever the mass transfer of some one participant is controlling, only one equation like Eq. 8-6 is involved.

The three-dimensional case is expressed most compactly in vector notation thus:

$$-\frac{\partial}{\partial t} (s_m \rho_m T) = \text{div} (-k_e \text{grad } T) + \text{div} (s_f GT) + r\rho_B \Delta H_r \quad (8-7)$$

$$-\frac{\partial C}{\partial t} = \text{div} \left(-\frac{D_e}{G/\rho_f} \text{grad} \frac{GC}{\rho_f} \right) + \text{div} \frac{GC}{\rho_f} + r\rho_B \quad (8-8)$$

Physically, the term *grad* (short for gradient) is a mathematical operator which forms the derivative with respect to position. The term *div* (short for divergence) is a mathematical operator which expresses the rate of accumulation at a point in space. Mathematical forms assumed by these operators depend on the coordinate system and the number of dimensions. For example, Eqs. 8-3 and 8-6 are written for one-dimensional cartesian coordinates. In terms of cylindrical coordinates R and L , with axial symmetry, Eqs. 8-7 and 8-8 become [assuming k_e and $D_e/(G/\rho_f)$ constant]:

$$\begin{aligned} \frac{\partial}{\partial t} (s_m \rho_m T) &= k_e \left(\frac{1}{R} \frac{\partial T}{\partial R} + \frac{\partial^2 T}{\partial R^2} + \frac{\partial^2 T}{\partial L^2} \right) \\ &\quad - \left[\frac{1}{R} \frac{\partial}{\partial R} (R s_f GT) + \frac{\partial (s_f GT)}{\partial L} \right] - r\rho_B \Delta H_r \quad (8-9) \end{aligned}$$

$$\frac{\partial C}{\partial t} = \frac{D_e}{G/\rho_f} \left[\frac{1}{R} \frac{\partial(GC/\rho_f)}{\partial R} + \frac{\partial^2(GC/\rho_f)}{\partial R^2} + \frac{\partial^2(GC/\rho_f)}{\partial L^2} \right] - \left[\frac{1}{R} \frac{\partial(RGC/\rho_f)}{\partial R} + \frac{\partial(GC/\rho_f)}{\partial L} \right] - r\rho_B \quad (8-10)$$

In the direction of mass flow, transfer of heat by conduction and of mass by diffusion is usually negligible, also bulk flow in the R direction. For this important special case, the previous equations become

$$\frac{\partial}{\partial t} (s_m \rho_m T) = k_e \left(\frac{1}{R} \frac{\partial T}{\partial R} + \frac{\partial^2 T}{\partial R^2} \right) - \frac{\partial}{\partial L} (s_f GT) - r\rho_B \Delta H_r \quad (8-11)$$

$$\frac{\partial C}{\partial t} = \frac{D_e}{G/\rho_f} \left[\frac{1}{R} \frac{\partial(GC/\rho_f)}{\partial R} + \frac{\partial^2(GC/\rho_f)}{\partial R^2} \right] - \frac{\partial(GC/\rho_f)}{\partial L} - r\rho_B \quad (8-12)$$

Fractional conversion f of the limiting participant may be substituted for the concentration. Thus, substituting

$$\frac{GC}{\rho_f} = \left(\frac{GC}{\rho_f} \right)_0 (1 - f) \quad (8-13)$$

into Eq. 8-12,

$$-\frac{\partial}{\partial t} \left(\frac{1-f}{G/\rho_f} \right) = \frac{D_e}{G/\rho_f} \left(\frac{1}{R} \frac{\partial f}{\partial R} + \frac{\partial^2 f}{\partial R^2} \right) - \frac{\partial f}{\partial L} + r\rho_B \left(\frac{\rho_f}{GC} \right)_0 \quad (8-14)$$

Reactors are most commonly cylindrical in shape, so Eqs. 8-11, 8-12, and 8-14 are of the greatest utility.

Complete formulation of a reactor problem requires knowledge of initial and boundary conditions, such as the nature of heat transfer at the reactor wall or control of the wall temperature. To achieve numerical solutions, experimental data are needed for the friction factor, effective conductivity, and effective diffusivity, or the coefficients of heat and mass transfer. These data are reviewed subsequently for fixed and fluidized beds.

The phenomena of heat, mass, and momentum transfer are well known to be interrelated. Correlations have been achieved in some cases between the usual dimensionless groups and certain factors for mass transfer j_d and heat transfer j_h , which are defined as follows:

$$j_d = \frac{k_e \rho_{bm} M}{G_0} \left(\frac{\mu}{\rho D_v} \right)^{2/3} \quad (8-15)$$

$$j_h = \frac{h}{C_p G_0} \left(\frac{C_p \mu}{k} \right)^{2/3} \quad (8-16)$$

In the absence of direct data for packed beds on one or the other of these factors, advantage can be taken of the fact that in the turbulent range $j_d = j_h$, within about 25 per cent.

52. Solutions of Equations

Formal mathematical solutions of the partial differential equations representing transfer processes in granular masses are quite difficult to achieve and are complex even when simplifying assumptions are made. Brief reference may be made to some of the few solutions that have been published. All these are for the steady state in cylindrical reactors.

Singer and Wilhelm (202) solved the equations corresponding to Eqs. 8-1 and 8-2, but for cylindrical coordinates. They assumed no conduction of heat in the direction of flow and constant physical properties; also that the rate of heat evolution due to chemical reaction was a function of temperature alone and specifically independent of concentration. These equations were

$$G_0 s_f \int_0^R R \frac{\partial T_f}{\partial L} dR - \int_0^R (a + bT_s)R dR - k_{ef} R \frac{\partial T_f}{\partial R} - k_{es} R \frac{\partial T_s}{\partial R} = 0 \quad (8-17)$$

$$h_v \int_0^R (T_s - T_f)R dR - k_{es} R \frac{\partial T_s}{\partial R} - \int_0^R (a + bT_s)R dR = 0 \quad (8-18)$$

Baron (12) developed a graphical method of solution for the case of no axial conduction, no convection, and identical fluid and solid temperatures. These equations were

$$\frac{\partial T}{\partial L} = \frac{1}{Pe} \left(\frac{\partial^2 T}{\partial R^2} + \frac{1}{R} \frac{\partial T}{\partial R} \right) + \frac{r \rho_B D_p \Delta H_r}{s G_0} \quad (8-19)$$

$$\frac{\partial f}{\partial L} = \frac{1}{Pe} \left(\frac{\partial^2 f}{\partial R^2} + \frac{1}{R} \frac{\partial f}{\partial R} \right) + \frac{r \rho_B M_{av} D_p}{G_0 y_0} \quad (8-20)$$

where $Pe = \text{Peclet number} = D_p G_0 s / k_B$

f = fractional conversion of limiting reactant

y_0 = mole fraction of limiting reactant at inlet

D_p = particle diameter

A problem widely treated is that of flow through an empty tube on whose catalytic surface a first-order reaction takes place isothermally. This equation is

$$D_v \left[\frac{1}{R} \frac{\partial}{\partial R} \left(R \frac{\partial C}{\partial R} \right) + \frac{\partial^2 C}{\partial L^2} \right] - \frac{G}{\rho_f} \frac{\partial C}{\partial L} = 0 \quad (8-21)$$

with the condition at the surface

$$-D_v \frac{\partial C}{\partial R} = kC \quad (8-22)$$

Damköhler (51) first solved these equations. Baron, Manning, and Johnstone (13) also presented the solution and developed one for a reversible reaction of the first order in both directions. These solutions were applied to experiments on the oxidation of sulfur dioxide. Hoelscher (93) developed the solution in the form of a number of curves relating the geometry of the system, the diffusivity, and the specific reaction rate. Johnstone, Houavouras, and Schowalter (114) applied the equation to data on the catalytic oxidation of ammonia. Weger and Hoelscher (228) reviewed the hydrogenation of olefins by palladium black deposited on the wall of a carbon tube.

In some instances, the solution of a partial differential equation may be reducible to that of ordinary differential equations. An equation in cartesian coordinates leads to second-order linear ordinary differential equations with constant coefficients whose solutions are expressed in terms of exponentials or trigonometric functions. Cylindrical coordinates lead to ordinary differential equations whose solution is expressed in terms of infinite series called Bessel functions. The method of solving a partial differential equation may be explained by an example in cartesian coordinates, because the properties of trigonometric functions are perhaps better known than those of Bessel functions. Both analytical and numerical solutions will be shown.

Illustration 8-1. A liquid is flowing at a linear velocity G between two wide parallel plates coated with a catalyst. Inlet concentration is C_0 . A first-order reaction takes place isothermally on the surface. Derive the steady-state equation, assuming no lateral flow and negligible diffusion in the direction of bulk flow. Also, given the following numerical data, find at a distance $x = 10$ from the inlet both the concentration at the wall and the average over the cross section.

$$a = \text{half width} = 0.05$$

$$C_0 = 1.5$$

$$D_v = 3.5(10^{-5})$$

$$G = 0.35$$

$$k = 7.0(10^{-4})$$

Solution. Since there is symmetry about the mid-plane, the solution will be carried out only between the middle and the upper wall (Fig. 8-1a). Applying the conservation law to a differential volume of dimensions dx , dy , and unit width, in the x direction,

$$\text{Accumulation} = \text{input} - \text{output}$$

$$= GC dy - \left(GC + \frac{\partial GC}{\partial x} dx \right) dy = -G \frac{\partial C}{\partial x} dx dy$$

In the y direction,

$$\text{Accumulation} = -D_v \frac{\partial C}{\partial y} dx - \left[-D_v \left(\frac{\partial C}{\partial y} + \frac{\partial^2 C}{\partial y^2} dy \right) \right] dx = D_v \frac{\partial^2 C}{\partial y^2} dx dy$$

Since the net accumulation is zero,

$$\frac{\partial C}{\partial x} = \frac{D_v}{G} \frac{\partial^2 C}{\partial y^2} = \alpha \frac{\partial^2 C}{\partial y^2} \quad (A)$$

At the wall, in the steady state, the rate of diffusion equals the rate of reaction; that is,

$$-D_v \frac{\partial C}{\partial y} = kC \quad y = a \quad (B)$$

At the inlet, except near the wall where equilibrium is established instantaneously and Eq. B holds,

$$C(0, y) = C_0 \quad (C)$$

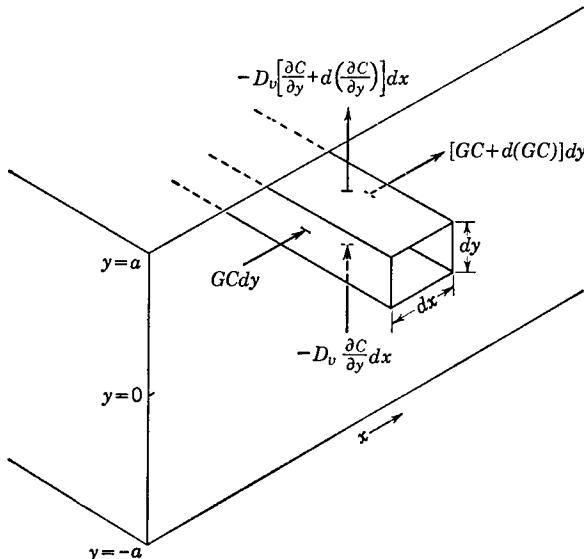


FIG. 8-1a. Flow between parallel catalyst-coated plates (Illustration 8-1).

A general method of solving linear partial differential equations is by separation of variables after substitution. Try a solution of the form

$$C(x, y) = f(x)g(y)$$

and substituting into Eq. A,

$$g \frac{\partial f}{\partial x} = \alpha f \frac{\partial^2 g}{\partial y^2}$$

$$\text{or} \quad \frac{1}{\alpha f} \frac{\partial f}{\partial x} = \frac{1}{g} \frac{\partial^2 g}{\partial y^2} = -\lambda^2$$

In the last equation, two functions of independent variables are equal, which can be true only if both functions are constant. Subsequently it will appear that this constant must be negative, so it is written above as $-\lambda^2$. Solving the resulting ordinary differential equations,

$$\frac{1}{\alpha f} \frac{\partial f}{\partial x} = -\lambda^2$$

$$f = e^{-\alpha \lambda^2 x}$$

$$\frac{1}{g} \frac{\partial^2 g}{\partial y^2} = -\lambda^2$$

$$g = A \sin \lambda y + B \cos \lambda y$$

Therefore

$$C = e^{-\alpha \lambda^2 x} (A \sin \lambda y + B \cos \lambda y) \quad (D)$$

Clearly, the exponent must be negative as shown; otherwise the concentration would become infinite instead of zero as x increases. Since C is symmetrical about the mid-plane and since $\sin \lambda y \neq \sin -\lambda y$, A must be zero and

$$C = Be^{-\alpha \lambda^2 x} \cos \lambda y \quad (E)$$

Applying the condition of Eq. B ,

$$D_v B \lambda e^{-\alpha \lambda^2 a} \sin \lambda a = k B e^{-\alpha \lambda^2 a} \cos \lambda a \quad (F)$$

or

$$\lambda \tan \lambda a = \frac{k}{D_v} \quad (G)$$

Equation G has an infinite number of roots, say λ_n , to each of which corresponds a solution of the original partial differential equation. Since a linear combination of solutions of a linear partial differential equation is likewise a solution,

$$C = \sum_1^{\infty} B_n e^{-\alpha \lambda_n^2 x} \cos \lambda_n y \quad (H)$$

Applying the condition of Eq. C ,

$$C_0 = \sum_1^{\infty} B_n \cos \lambda_n a \quad (I)$$

Evaluation of the coefficients B_n is accomplished with the aid of the following trigonometric relations, which hold when λ_m and λ_n are roots of Eq. G :

$$\int_0^a \cos \lambda_m x \cos \lambda_n x dx = \begin{cases} 0 & \text{when } \lambda_m \neq \lambda_n \\ \frac{a}{2} + \frac{\sin 2\lambda_n a}{4\lambda_n} & \text{when } \lambda_m = \lambda_n \end{cases} \quad (J)$$

Accordingly, upon multiplying Eq. I by $\cos \lambda_m y$ and integrating between 0 and a , all but one of the terms on the right disappear, so that

$$B_n = \frac{\int_0^a C_0 \cos \lambda_n y dy}{\int_0^a \cos^2 \lambda_n y dy} = \frac{4C_0 \sin \lambda_n a}{2\lambda_n a + \sin 2\lambda_n a} \quad (K)$$

Certain particular values of the concentration are of interest. At the wall,

$$\begin{aligned} C(x, a) &= \sum B_n e^{-\alpha \lambda_n^2 x} \cos \lambda_n a \\ &= \sum e^{-\alpha \lambda_n^2 x} \frac{2C_0 \sin 2\lambda_n a}{2\lambda_n a + \sin 2\lambda_n a} \end{aligned} \quad (L)$$

The average value at a particular cross section is

$$\begin{aligned} C_m &= \frac{1}{a} \int_0^a C dy = \frac{1}{a} \sum e^{-\alpha \lambda_n^2 x} \frac{B_n}{\lambda_n} \sin \lambda_n a \\ &= \sum e^{-\alpha \lambda_n^2 x} \frac{4C_0 \sin^2 \lambda_n a}{\lambda_n a (2\lambda_n a + \sin 2\lambda_n a)} \end{aligned} \quad (M)$$

Table 8-1 shows the evaluation of Eqs. L and M for $x = 10$. Values of λ_n are obtained by numerical solution of Eq. G .

TABLE 8-1. DATA FOR ILLUSTRATION 8-1

n	λ_n	$\lambda_n a$	$\sin \lambda_n a$	$\sin 2\bar{\lambda}_n a$	$e^{-0.001\lambda_n^2}$	C	
						At wall	Average
1	17.2	0.86	0.758	0.989	0.743	0.815	1.093
2	68.5	3.425	-0.281	0.540	0.0092	0.002	0.00002
3	128.7	6.435	0.153	0.305	2(10 ⁻⁷)	0.000	0.000
4	190.5	9.525	0.000	0.000
						0.817	1.093

Illustration 8-2. The preceding illustration will be solved by the numerical method for partial differential equations described in Sec. 78. In terms of finite differences, Eq. A becomes

$$\frac{C_{m+1,n} - C_{m,n}}{h_x} = \alpha \frac{C_{m,n+1} - 2C_{m,n} + C_{m,n-1}}{h_y^2} \quad (N)$$

Letting $M = h_y^2/\alpha h_x$, this becomes

$$C_{m+1,n} = \frac{C_{m,n+1} + (M-2)C_{m,n} + C_{m,n-1}}{M} \quad (O)$$

Setting $M = 2$,

$$C_{m+1,n} = \frac{C_{m,n+1} + C_{m,n-1}}{2} \quad (P)$$

At the wall and at the inlet, from Eq. B,

$$-D_v \frac{C_{0,a} - C_{0,a-1}}{h_y} = kC_{0,a} \quad (Q)$$

or

$$C_{0,a} = \frac{C_{0,a-1}}{1 + kh_y/D_v} \quad (R)$$

Taking $h_y = 0.01$,

$$h_x = \frac{h_y^2 G}{MD_v} = \frac{(0.01)^2 (0.35)}{2(3.5)(10^{-5})} = 0.5 \quad (S)$$

Accordingly,

$$C_{0,a} = \frac{C_{0,a-1}}{1 + 7(10^{-4})(0.01)/3.5(10^{-5})} = \frac{C_{0,a-1}}{1.2} \quad (T)$$

At the inlet cross section, the concentration is different from $C_0 = 1.5$ only near the wall. Therefore it is legitimate to assume that $C_{0,a-1} = 1.5$, and consequently that $C_{0,a} = 1.5/1.2 = 1.25$. All the values in col. 1 of Table 8-2 are now known, and the remaining values of that table are obtained by repeated applications of Eqs. P and R. Because of symmetry, only half the increments of y need be computed. As an example, the calculation of col. 10 is

$$C_{10,1} = 0.5(0.918 + 1.248) = 1.083$$

$$C_{10,0} = \frac{1.083}{1.2} = 0.902$$

$$C_{10,2} = 0.5(1.102 + 1.349) = 1.226$$

$$C_{10,3} = 0.5(1.248 + 1.418) = 1.333$$

and so forth. For $x = 10$, col. 20 shows that the concentration at the wall is 0.775, compared with 0.817 by the analytical method of Illustration 8-1. The average value obtained by integration of col. 20 is 1.086, which compares favorably with 1.093 obtained by the analytical method. The accuracy of the numerical method could have been improved by taking smaller increments of y .

An important advantage of the numerical method over the analytical is that application to higher-than-first-order reactions is not much more difficult numerically, whereas analytical solutions become virtually impossible for complex reactions.

TABLE 8-2. DATA FOR ILLUSTRATION 8-2

$n \backslash m$	0	1	2	3	4	5	6	7	8	9	10
0	1.25	1.145	1.102	1.058	1.029	1.000	0.977	0.955	0.936	0.918	0.902
1	1.50	1.375	1.323	1.270	1.235	1.200	1.173	1.146	1.124	1.102	1.083
2	1.50	1.5	1.438	1.412	1.370	1.346	1.314	1.293	1.267	1.248	1.226
3	1.50	1.5	1.5	1.469	1.456	1.428	1.412	1.387	1.372	1.349	1.333
4	1.50	1.5	1.5	1.5	1.485	1.478	1.460	1.450	1.431	1.418	1.398
5	1.50	1.5	1.5	1.5	1.5	1.493	1.489	1.475	1.463	1.447	1.432
$n \backslash m$	0	11	12	13	14	15	16	17	18	19	20
0	0.886	0.872	0.858	0.845	0.832	0.821	0.809	0.797	0.786	0.775
1	1.064	1.047	1.030	1.015	0.999	0.985	0.971	0.957	0.943	0.930
2	1.208	1.188	1.172	1.153	1.138	1.120	1.105	1.089	1.074	1.059
3	1.312	1.296	1.276	1.260	1.241	1.225	1.207	1.191	1.175	1.159
4	1.383	1.364	1.348	1.329	1.312	1.294	1.277	1.260	1.243	1.226
5	1.415	1.399	1.382	1.365	1.347	1.329	1.312	1.294	1.277	1.260

53. Fluidization

A modern development of great importance is the technology of the fluidization of beds of particles by flowing gases. Properties of mobility and hydrostatic pressure, without loss of observable free surface, may be conferred on a mass of more or less finely divided solid particles by the lifting action or drag of a fluid flowing in a vertical direction. Several stages can be recognized in this process, as illustrated by Fig. 8-2:

1. At low fluid velocities, the particles remain static and the pressure drop increases with velocity in the normal way.

2. With increasing velocity, a critical point is reached where the pressure drop corresponds to the buoyed weight of the bed, the particles are lifted out of contact with each other, and the bed as a whole begins to expand.

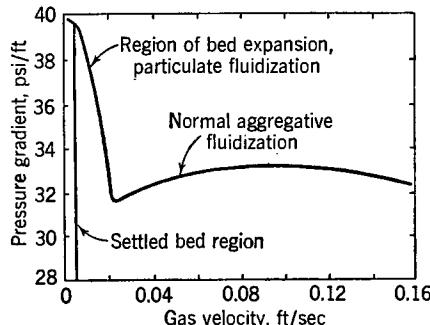


FIG. 8-2. Fluidization of cracking catalyst. [Gohr (80). Courtesy Reinhold Publishing Corporation, New York.]

3. Upon further velocity increase, the pressure drop remains substantially constant but bed expansion continues. If the fluid is gaseous, bubbles form and rise through the bed and the behavior is much like that of a boiling liquid.

4. At high velocities, the free surface disappears and particles are continuously transported from the vessel and the pressure drop keeps increasing with the velocity. This stage of fluidization corresponds to the gaseous state. It is often called *dilute-phase* fluidization, to contrast with *dense-phase* that exists when an observable free surface exists.

Figure 8-2 presents measurements of the fluidization of a petroleum-cracking catalyst. The hump at the critical point corresponds to the loosening of interlocked particles.

Velocities at which fluidization occurs are much lower than the free-falling velocities of individual particles predicted, for example, by Stokes' law. Order of magnitude of this difference is indicated by the data of Table 8-3. Experiments with small glass spheres (Lewis, Gilliland, and

TABLE 8-3. COMPARISON OF FREE-FALLING AND FLUIDIZATION VELOCITIES*

Material	Size		Velocity, fps		
			Fluidizing	Free-falling	
	U.S. sieve	Microns		Small particles	Large particles
Carborundum.....		150	0.10		3.6
Coke.....	70-325	200-43	0.10	0.66	3.88
Coke.....	40-140	350-100	0.44	1.4	

* After Parent, Yagol, and Steiner (177).

Bauer, 140) have shown that the bed porosity ϵ is the main factor influencing the spread between the fluidizing and the free-fall velocities. Their data are represented by

$$\frac{u_{\text{fluidizing}}}{u_{\text{free fall}}} = \epsilon^{2.82}$$

For example, at a porosity of 40 per cent the fluidizing velocity is only 7.6 per cent that of the free-fall velocity. Possible explanation of this behavior hinges on the fact that fluidizable beds always contain some smaller particles that have individual free-fall velocities much less than the over-all fluidization velocity. These may be lifted by the gas and made to confer their kinetic energies to the larger ones, then again lifted, and so forth, until the entire mass is eventually set in motion.

Especially with liquids, particles may remain separate and the bed

homogeneous; this is called *particulate fluidization*. With gases usually, the particles form clumps and gas forms bubbles instead of remaining uniformly distributed; this is called *aggregative fluidization*. When a stable bed exists and an observable free surface is maintained, the process is called *batch*, or *dense-phase, fluidization*. When the velocity is high enough to remove the solid particles from the vessel as quickly as they are being supplied to the vessel, the process is called *continuous*, or *dilute-phase, fluidization*.

Channeling exists when particles cohere so strongly that the gas virtually bypasses groups of them and goes through the bed in unbroken streams. In this event the pressure drop is much less than the buoyed weight of the bed. Such behavior occurs when the particles are very small or do not contain a sufficient proportion of coarser material. A large height-to-diameter ratio is conducive to channeling, particularly along the wall of the vessel, whereas increasing gas velocity alleviates it.

Slugging, or surging, exists when the gas bubbles grow so large that they may occupy the entire cross section of a small vessel. Alternate pockets of gas and slugs of particles then rise through the vessel. In large vessels, clumps of particles are lifted, then dropped as the pockets of gas below them collapse. This action is similar to the bumping of boiling liquids. Pressure drop is erratic and usually much greater than under smooth conditions. Such behavior occurs when the particles are too coarse or do not contain a sufficient proportion of finer material. Slugging is aggravated by a large height-to-diameter ratio, but alleviated by reducing the gas velocity.

Both channeling and slugging are undesirable, not only because of the surges in pressure that they cause, but because they reduce the extent of contacting between the solid and gas phases. To ensure smooth fluidization, a distribution of particle sizes appears necessary. Selection of size distribution is done entirely empirically at present. Table 8-4 presents some data on size distributions that are being successfully fluidized. Fine particles fluidize more readily than coarse ones, but sizes under 30 to 40 μ cohere and lead to channeling.

Maintenance of proper size distribution is necessary during operation. Fluidized catalysts remain in service a long time, so their size distribution changes gradually as a result of attrition or agglomeration. Finer particles are entrained by the effluent gas, usually to an amount less than about 0.05 lb/cu ft, but they are recovered in multistage cyclones or electrostatic collectors and returned as necessary to maintain the correct proportion of fines. Also, bleeding off continuously a portion of the bed and replacing it with fresh material maintains a satisfactory condition. When too large a proportion of coarse material develops, some material can be bled off the lower section of the vessel where the larger sizes concentrate. Some-

TABLE 8-4. TYPICAL PARTICLE SIZES IN FLUIDIZATION PROCESSES*

Type of process	Size		Wt %	
	U.S. sieve	Microns	Range	Average
Catalytic cracking (with electrostatic precipitators)	0-20	15-35	25
		20-40	20-40	30
		40-80	20-50	35
		80+	5-15	10
		0	0
Catalytic cracking (with two-stage cyclones)	0-20	5-15	10
		20-40	50-70	60
		40-80	20-40	30
		80+	0-2	0
Hydroforming.....	20-40	5-15	10
		40-80	40-60	50
		80+	30-50	40
	
Fluid coking.....	+20	1-4
		20-48	24-46
		48-60	20-30
		60-100	20-45
		100-200	0-10
		-200	0
	
Phthalic anhydride by oxidation of naphthalene (with porous filters)	+20	0-8	4.0
		20-80	20-45	32.5
		80-200	15-25	20.0
		74-40	3-10	6.5
		40-20	5-15	10.0
		20-5	5-30	17.5
		5-	2-17	9.5
Coal carbonization and gasification (with two-stage cyclones)	+20	0-10	5.0
		20-40	22-55	38.5
		40-100	20-50	35.0
		100-200	8-25	16.5
		-200	0-10	5.0
Shale retorting.....	+8	2-5
		8-200	65-85
		-200	10-30

* Braca and Field (32).

times high-velocity steam jets are employed to break up the coarse material.

Because of the high convection rate, a fluidized bed is substantially isothermal, even in vessels of 40- to 50-ft diameter. The conditions under which concentration gradients exist in the solid and gas phases are discussed in Sec. 59. Heat and mass transfer, pressure drop, and quantitative characterization of fluidization are also considered in later pages.

54. Pressure Drop in Fixed and Moving Beds

Flow of fluids through beds of particles and through porous solids has been investigated widely. The earliest work regarded flow through packed beds as analogous to that through pipes and employed a Fanning type of pressure-drop equation with a friction factor dependent on a Reynolds number which employs either the particle diameter or the reciprocal of the specific surface of the bed as the linear dimension. One such correlation is that of Chilton and Colburn (41). Improved correlations take into account also the proportion of free space in the bed, that is, the voidage or porosity. The most successful is based on the recognition that both kinetic and viscous energy losses must be considered in developing a pressure-drop equation. Work in this field is summarized in two recent publications (Carman, 39; Leva, Weintraub, Grummer, Pollchik, and Storch, 138).

Accurate representation of the effect of porosity was first obtained by Kozeny, for laminar flow. In contrast with some earlier hypotheses that a granular bed is equivalent to a system of parallel capillaries, for the purpose of mathematical treatment he regarded it as a single large passage with a hydraulic diameter defined by the volume and surface of the void space in the bed. Subsequently, Carman assembled many data, correlated them with Kozeny's equation, and extended it empirically to turbulent conditions. For laminar flow, the result is

$$\frac{\Delta P}{L} = \frac{5G^2a}{g\rho\epsilon^3} \left(\frac{G}{a\mu} \right)^{-1} \quad (8-23)$$

and for turbulent flow, above $G/a\mu = 100$,

$$\frac{\Delta P}{L} = \frac{0.4G^2a}{g\rho\epsilon^3} \left(\frac{G}{a\mu} \right)^{-0.1} \quad (8-24)$$

where a = specific surface of the bed, sq ft/cu ft

ϵ = fraction of free space or porosity

Further work by Leva and coworkers extended this type of correlation to higher Reynolds numbers in fixed beds. Their equation is

$$\frac{\Delta P}{L} = \frac{2fG^2}{g\rho D_p \lambda^{3-n}} \frac{(1-\epsilon)^{3-n}}{\epsilon^3} \quad (8-25)$$

where λ is the particle-shape factor defined as the surface of a sphere having the same volume as the particle, divided by the surface of the particle, and the terms f and n are shown in Fig. 8-3. The exponent n identifies the kind of flow that exists: in laminar flow, $n = 1$; in turbulent flow, $n = 2$, with values in between for intermediate conditions. Additional important variables are the porosity and the surface roughness, as distinct from shape

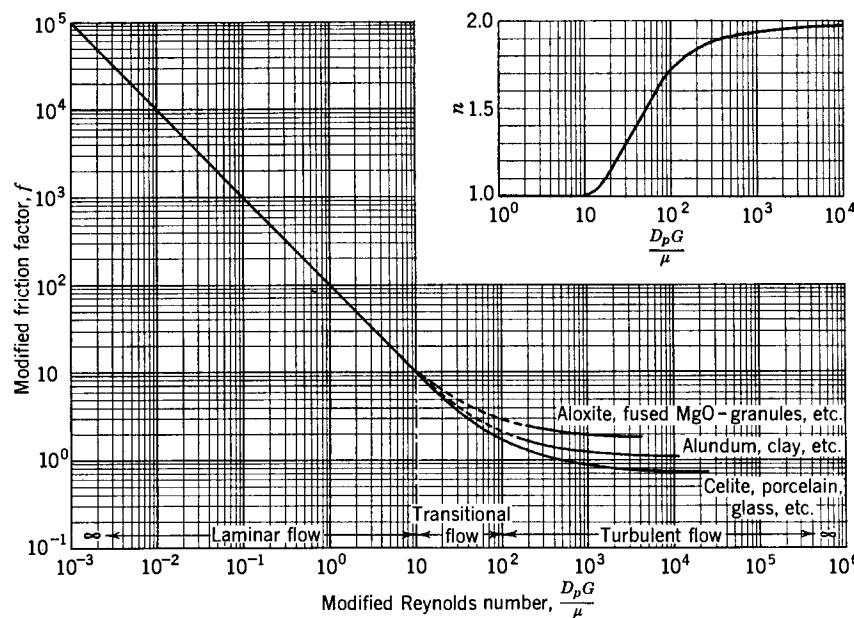


FIG. 8-3. Pressure drop in fixed beds (Eq. 8-25). [Leva, Weintraub, Grummer, Pollchik, and Storch (138).]

factor. Porosity may be estimated from Fig. 8-6 when the bed is formed by a simple process of dumping. It has not been possible to achieve a correlation in terms of roughness factor analogous to that available for pipe flow, but Fig. 8-3 covers the range from smooth glass to rough aloxite particles. It is necessary to estimate just where between these limits any particular material falls. Pressure drop for clay is roughly 1.5 times, and for aloxite it is about 2.3 times that for smooth particles.

As previously mentioned, consideration should be given to kinetic-energy losses as well as friction, a view that dates back to Reynolds. Ergun (62) has developed the following successful equation:

$$\frac{\Delta P}{L} = 150 \frac{(1 - \epsilon)^2}{\epsilon^3} \frac{\mu u}{D_p^2} + 1.75 \frac{1 - \epsilon}{\epsilon^3} \frac{Gu}{D_p} \quad (8-26)$$

where the first part represents friction and the second part the kinetic-energy losses. This equation may be more conveniently written

$$\frac{\Delta P}{L} = \frac{G}{\rho g D_p} \frac{1 - \epsilon}{\epsilon^3} \left[\frac{150(1 - \epsilon) \mu}{D_p} + 1.75G \right] \quad (8-27)$$

Moving beds. One comprehensive study has been made of moving beds, including some commercial-scale data, which shows that fixed-bed corre-

lations underestimate the pressure drop for such cases. Happel (85) developed the equation

$$\frac{\Delta P}{L} = \frac{2fG^2(1 - \epsilon)^3}{g\rho D_p} \quad (8-28)$$

where the friction factor f is shown in Fig. 8-4. Happel suggested several possibilities why the behavior of pressure drop in fixed and moving beds is different.

Illustration 8-3. Calculate the pressure drop for air flowing through a bed of spherical particles, given the following data:

$$\begin{aligned} D_p &= 0.01 \text{ ft} \\ G &= 5,000 \text{ lb/(hr)(sq ft)} \\ \mu &= 0.0435 \text{ lb/(ft)(hr)} \\ \rho &= 0.074 \text{ lb/cu ft} \\ \epsilon &= 0.45 \end{aligned}$$

Solution. Comparison will be made of several equations, both fixed- and moving-bed. With Eq. 8-24,

$$a = \frac{6(1 - \epsilon)}{D_p} = \frac{6(0.55)}{0.01} = 330 \text{ sq ft/cu ft}$$

$$\frac{D_p G}{6\mu(1 - \epsilon)} = \frac{0.01(5,000)}{6(0.0435)(0.55)} = 348$$

$$\frac{\Delta P}{L} = \frac{0.4(5,000)^2(330)}{4.18(10^6)(0.45)^3(0.074)(348)^{0.1}} = 652 \text{ psf/ft}$$

With Eq. 8-25,

$$\frac{D_p G}{\mu} = \frac{0.01(5,000)}{0.0435} = 1,150$$

$$n = 1.95 \quad (\text{from Fig. 8-3})$$

$$f = 0.8 \quad (\text{from Fig. 8-3})$$

$$\frac{\Delta P}{L} = \frac{2(0.8)(5,000)^2(0.55)^{1.05}}{4.18(10^6)(0.074)(0.01)(0.45)^3} = 760 \text{ psf/ft}$$

With Eq. 8-27,

$$\begin{aligned} \frac{\Delta P}{L} &= \frac{5,000(0.55)}{0.074[4.18(10^6)(0.01)(0.45)^3]} \left[\frac{150(0.55)(0.0435)}{0.01} + 1.75(5,000) \right] \\ &= 890 \text{ psf/ft} \end{aligned}$$

With Eq. 8-28 (moving bed),

$$\frac{D_p G(1 - \epsilon)}{\mu} = \frac{0.01(5,000)(0.55)}{0.0435} = 632$$

$$\frac{\Delta P}{L} = \frac{2(50)(5,000)^2(0.55)^3}{4.18(10^6)(0.074)(0.01)} = 1,340 \text{ psf/ft}$$

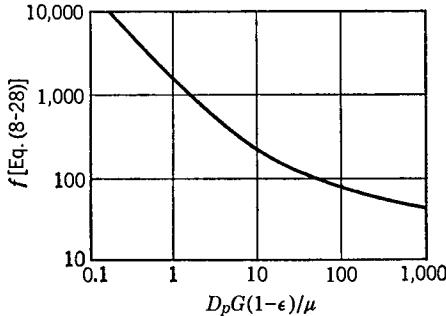


FIG. 8-4. Pressure drop in moving beds (Eq. 8-28). [Happel (85).]

It is not easy to say which of the fixed-bed equations, Eq. 8-25 or 8-27, is the better one to use since they do not agree closely, though possibly they do agree within the scatter of experimental data. Probably, the more conservative result calculated from either equation is the one to use. Note that the moving-bed equation (Eq. 8-28) gives considerably higher pressure losses.

55. Pressure Drop in Fluidized Beds

When a fluid is passed upward through a bed of fine particles, its pressure drop is calculable from the equations already presented, until a rate is reached at which the individual particles are lifted out of contact with each other and the bed begins to expand. At this time the pressure drop is equivalent to the buoyed weight of the bed; that is,

$$\Delta P = (\rho_p - \rho)(1 - \epsilon) L \quad (8-29)$$

Subsequently the pressure drop generally remains substantially constant at this value. Above bed-expansion ratios of about 20 per cent, the pressure drop has been found to continue increasing, with greater deviations in vessels of smaller diameters and in beds of large depth/diameter ratio (Lewis, Gilliland, and Bauer, 140). When bridging or electrostatic effects are present, deviations of 20 per cent or more above Eq. 8-29 have been found. When channeling occurs the actual values are less than the calculated ones (Miller and Logwinuk, 156).

Historically, study of pressure drop has been the basis for quantitative characterization of fluidized behavior. The items needed from a design point of view include the following:

1. Fluid velocity needed to initiate fluidization
2. Magnitude of velocities above the minimum fluidizing velocity that are permissible or desirable
3. Amount of bed expansion upon satisfactory fluidization
4. Energy requirements

As in any new field, there still remains much uncertainty and disagreement, and much work, both theoretical and experimental, is needed. The most concerted effort by any one group of investigators has been that of Leva and coworkers whose earlier results have been summarized (Leva, Weintraub, Grummer, Pollchik, and Storch, 138) and extended and summarized several times since (Leva, 136).

As mentioned, up to the point of initial expansion, fixed-bed relations like Eq. 8-25 apply. In fluidized systems, laminar flow occurs most commonly, in which event Eq. 8-25 becomes

$$\frac{\Delta P}{L} = \frac{200G\mu(1 - \epsilon_f)^2}{g\rho D_p^2 \lambda^2 \epsilon_f^3} = \frac{200G\mu}{g\rho D_p^2 \lambda^2} \phi_f \quad (8-30)$$

where the subscript *f* denotes the fluidized state and

$$\phi_f = \frac{(1 - \epsilon_f)^2}{\epsilon_f^3} \quad (8-31)$$

A better fit to test data is obtained by a modification as follows, where some rearrangement also has been made:

$$GN_f = 0.005 \frac{gpD_p^2 \lambda^2}{\mu} \frac{\Delta P}{L} \left[\frac{(1 - \epsilon_f)^2}{\epsilon_f^3} \right]^m \quad (8-32)$$

where N_f is the expansion ratio of the bed,

$$N_f = \frac{L_f}{L} = \frac{1 - \epsilon}{1 - \epsilon_f} \quad (8-33)$$

For fixed beds, $m = -1$; but for expanded and fluidized beds, m has been found to depend on the particle size, as discussed later. Equation 8-32 can be modified by substitution from Eqs. 8-29 and 8-33:

$$G_f = \frac{0.005gp(\rho_p - \rho)D_p^2(1 - \epsilon_f)\lambda^2}{\mu} \left[\frac{(1 - \epsilon_f)^2}{\epsilon_f^3} \right]^m \quad (8-34)$$

A comparison of pressure drops in fixed and fluidized beds is shown in Fig. 8-5. At small Reynolds numbers, the lower pressure drops in fluidized beds may be attributable to agglomeration of particles; a two- or three-fold increase in particle size is all that is required to bring the widest deviations in line, which is quite within reason. At higher Reynolds numbers the agglomerates are probably broken up by the increased turbulence; but increasing amounts of energy are absorbed in the increasing motions of the fluidized particles, which may account for the higher pressure drop of fluidized beds in this range.

The minimum fluidizing flow rate G_{mf} is obtained by equating Eqs. 8-29 and 8-30, with the result

$$G_{mf} = \frac{0.005gp(\rho_p - \rho)D_p^2\lambda^2}{\mu} \frac{\epsilon_{mf}^3}{1 - \epsilon_{mf}} \quad (8-35)$$

An empirical modification of Eq. 8-35 also has been achieved (Leva):

$$G_{mf} = 138,000 D_p^{1.82} \frac{[\rho(\rho_p - \rho)]^{0.94}}{\mu^{0.88}} \quad (8-36)$$

A trial value of G_{mf} from this equation must be corrected for Reynolds numbers above 5 by means of Fig. 8-10.

The voidage at minimum fluidization ϵ_{mf} may be obtained simply by pouring carefully a weighed amount of particles from one vessel to another so that a very loose bed is obtained. A correlation in terms of particle

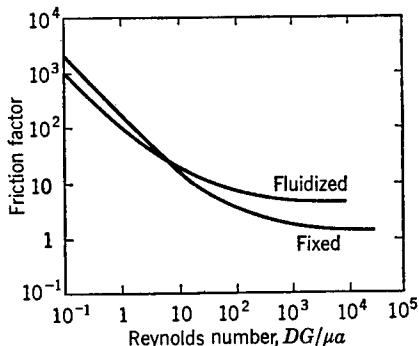


FIG. 8-5. Comparison of friction factors in fixed and fluidized beds. [Morse (163).]

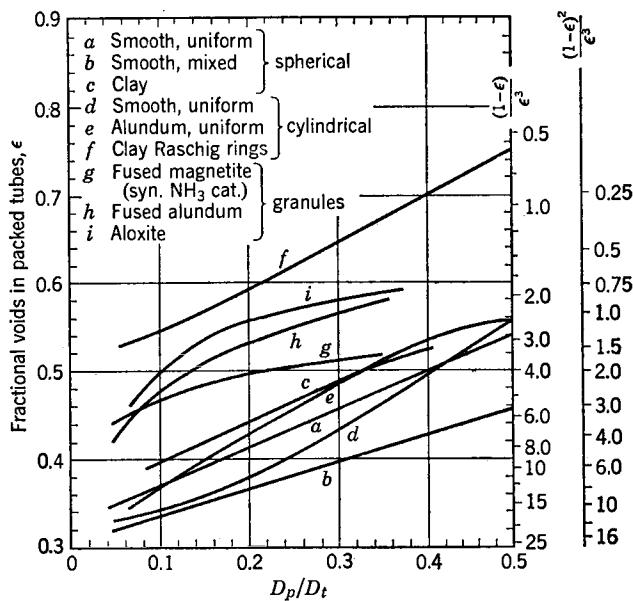


FIG. 8-6. Voidage in packed tubes. [Leva, Weintraub, Grummer, Pollchik, and Storch (138).]

diameters has been achieved for several materials of differing roughnesses, as shown in Fig. 8-7.

Several other equations for estimating the minimum fluidizing velocity have been advanced from time to time. A particularly simple one to use is that of Miller and Logwinuk (156), namely,

$$G_{mf} = \frac{5.23(10^6)\rho^{1.1}(\rho_p - \rho)^{0.9}D_p^2}{\mu} \quad (8-37)$$

Characteristics of the fluidized state. As the flow rate increases beyond that for minimum fluidization, the bed continues expanding but the pressure drop remains substantially constant. Accordingly, a plot of $\log G_f N_f$ against $\log \phi_f$ is a straight line with slope m that has been correlated with the particle diameter as shown, for example, in Fig. 8-8.

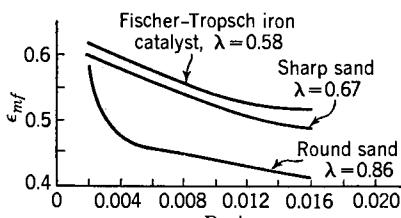


FIG. 8-7. Voidage at minimum fluidization conditions. [Leva (134, 135). Courtesy Chemical Engineering.]

the upper line with slope m represents the fluidized state, whereas the lower one with slope of -1 represents an extrapolation of the fixed-bed

bed. Comparison of the pressure-drop equations for fixed and fluidized beds enables some quantitative appraisal of the fluidized state. In Fig. 8-9

the upper line with slope m represents the fluidized state, whereas the lower one with slope of -1 represents an extrapolation of the fixed-bed

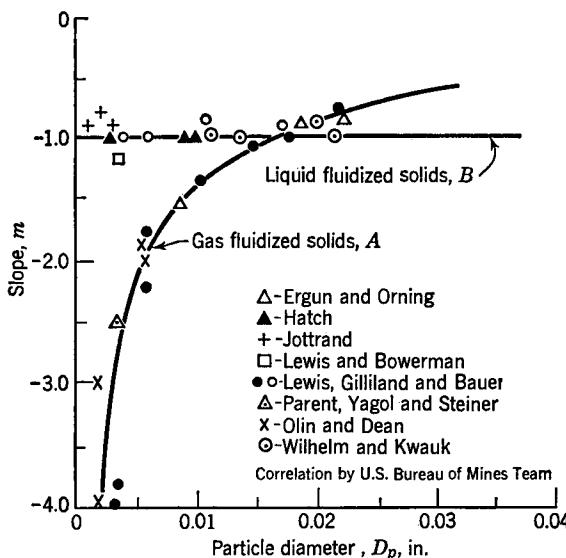


FIG. 8-8. Fluidization exponent m (Eq. 8-32). [Leva (135).]

relationship beyond the condition of minimum fluidization. Clearly, these lines intersect at the point of minimum fluidization (G_{mf}, ϵ_{mf}). The mass rate of flow, say G_e , given by this extrapolation is a hypothetical quantity only. However, it may be regarded as a rate sufficient to expand the bed to the fluidized density yet not sufficient to impart also enough energy to agitate the particles.

The spread between the ordinates of the two lines of Fig. 8-9 can be taken as a measure of fluidization, but a superior relationship can be developed. Since the pressure drop is constant beyond minimum fluidization, both G_e and G_f are proportional to the energy inputs for their respective conditions. Thus

$$W = \text{energy input} = \frac{GA \Delta P}{\rho}$$

In these terms, Leva defined a fluidization effectiveness, or "efficiency," η . This is the ratio of the energy imparted to the fluidized bed in excess of that required to achieve mere expansion to the total energy being imparted to the bed. Accordingly,

$$\eta = \frac{W_f - W_e}{W_f} = \frac{G_f - G_e}{G_f} = 1 - \phi_f^{-(m+1)} \quad (8-38)$$

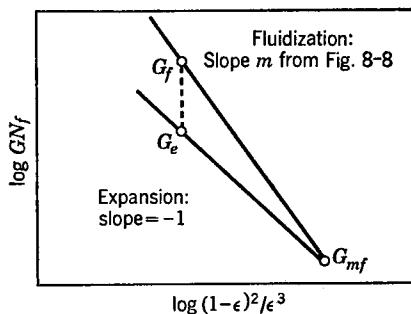


FIG. 8-9. Development of fluidization efficiency.

From the various relations between G_e , G_f , and G_{mf} and the relations of m , ϵ , ϵ_f , and ϵ_{mf} to the particle diameter typified by Figs. 8-6 to 8-8, Figs. 8-11 and 8-12 have been developed for practical calculation of η and N_f with a minimum of data for any particular system.

These correlations bear out the common observations that small particles are fluidized most readily and that such beds expand most upon fluidization. Fluidization can be regarded as more effective when a greater fraction of the energy input is absorbed by the random motion of the particles, since it is to their mobility that the fluidized state owes its useful features.

How much increase in velocity is desirable beyond that for minimum fluidization has not been developed in general terms. Bed expansions of 20 to 30 per cent are not uncommon. With increasing velocity the amount of turbulence goes up and with it comes improved heat transfer, for example. On the other hand, high velocities necessitate larger equipment because of the greater bed volume and also increase the entrainment of the finer particles. This last factor is often the controlling one in selecting the operating flow rate.

Continuous fluidization. When the solid and gas are transported continuously together through the equipment or pipelines, the process is called dilute phase or continuous fluidization.

Normally, flow equations of the sort developed in connection with pneumatic conveying of solids are applicable, though some adjustments are needed when small particles are involved. The slip velocity is the relative velocity of the fluid and the particle. Figure 8-13 compares some experimental

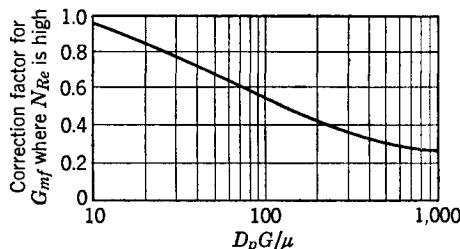


FIG. 8-10. Correction for G_{mf} from Eq. 8-36 at high Reynolds numbers. [Leva (135). Courtesy Chemical Engineering.]

slip velocities with those calculated from Stokes' law. Above particle diameters of 0.01 in. on this chart, free-fall equations hold. The mechanics of vertically moving fluidized systems has been investigated recently by Lapidus (131).

Illustration 8-4. A loose 12-in. depth of particles is to be fluidized with air at 75°F and 15 psia. Particle average diameter is 0.001 ft, the shape is that of "uniform sharp sand," and the true density is 108 lb/cu ft. Find the voidage and flow rate at minimum fluidization and the bed expansion and fluidization efficiency at a flow rate four times G_{mf} .

Solution. From Fig. 8-7, when $D_p = 0.012$ in., $\epsilon_{mf} = 0.51$. Applying Eq. 8-37,

$$G_{mf} = \frac{5.23(10^6)(0.074)^{1.1}(108 - 0.074)^{0.9}(0.001)^2}{0.0435} \\ = 46.4 \text{ lb/(hr)(sq ft)}$$

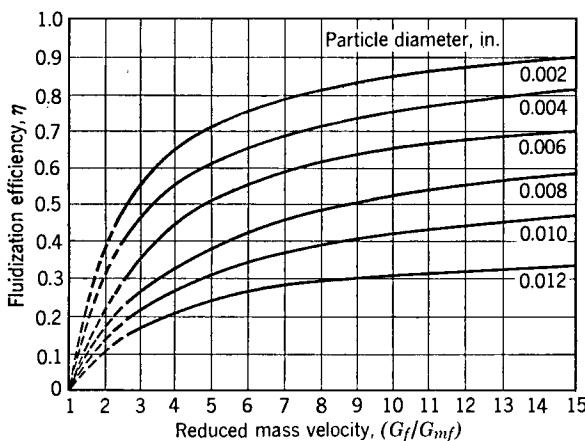


FIG. 8-11. Fluidization efficiency. [Wen and Fan (231), Wen and Leva (232). Courtesy Chemical Engineering.]

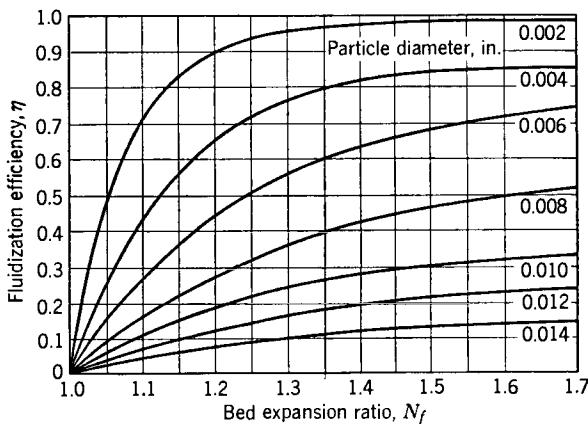


FIG. 8-12. Fluidized-bed expansion ratio. [Wen and Fan (231), Wen and Leva (232). Courtesy Chemical Engineering.]

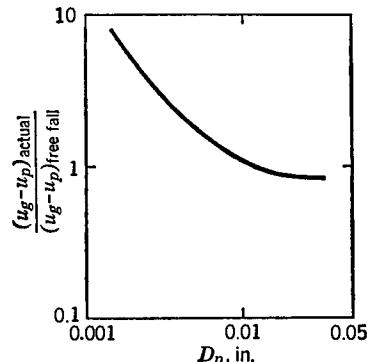


FIG. 8-13. Slip velocity in continuous fluidization. [Lewis, Gilliland, and Bauer (140).]

For comparison, use also Eq. 8-36:

$$G_{mf} = \frac{138,000(0.001)^{1.82}[0.074(108 - 0.074)]^{0.94}}{(0.0435)^{0.88}} \\ = 53.6 \text{ lb/(hr)(sq ft)}$$

This is a trial value which must be corrected by Fig. 8-10. Thus

$$\frac{G_{mf} D_p}{\mu} = \frac{53.6(0.001)}{(0.0435)} = 1.23$$

From Fig. 8-10, the correction is nil, so G_{mf} remains 53.6. This value will be used rather than that calculated from Eq. 8-37 since the remaining charts are consistent with Eq. 8-36. When $G_f/G_{mf} = 4$, from Figs. 8-11 and 8-12,

$$\eta = 21\%$$

$$N_f = 1.47$$

and accordingly,

$$\epsilon_f = 1 - \frac{1 - \epsilon_{mf}}{N_f} = 1 - \frac{0.49}{1.47} = 0.67$$

For comparison, the following equation for bed expansion (Lewis, 140) will be used:

$$N_f = 1 + \frac{0.0188}{3,600\rho\sqrt{D_p}} (G - G_{mf}) \\ = 1 + \frac{0.0188}{3,600(0.074)\sqrt{0.001}} (214.4 - 53.6) = 1.35$$

which is only a fair check. The previous method seems to be based on more data.

56. Heat Transfer

Mechanism of heat transfer through a bed of particles in which a fluid is also present may involve these steps:

1. Conduction through the particles
 2. Conduction through the fluid
 3. Convection through a fluid film at the vessel wall
 4. Convection through a film at the surface of the particle
- The first of these steps is usually of limited importance because of the small area of contact between individual particles.

The over-all process can be represented by these rate equations:

$$\frac{q}{A} = k_e \text{ grad } T \quad \text{in general} \quad (8-39)$$

$$\frac{q}{A} = \frac{k_e \Delta T}{\Delta L} \quad \text{in one dimension} \quad (8-40)$$

$$\frac{q}{A} = h \Delta T \quad \text{in terms of a convection coefficient} \quad (8-41)$$

where k_e is an apparent or effective thermal conductivity of the bed with the fluid flowing through it, and similarly h is an apparent heat-transfer coefficient. Most investigations have been confined to the over-all transfer equations, particularly Eq. 8-41, rather than attempts to fit their data to the four-step mechanism.

Effective thermal conductivity has been correlated with the properties of the fluid and the solid and with the structure of the bed (Singer and Wilhelm, 202). One comprehensive experimental investigation (Felix and Neill, 68) developed these relations for spherical particles:

$$\frac{k_e}{k_g} = \frac{1}{D_t} \left(\frac{k_p}{k_g} \right)^{0.12} \left(3.40 + \frac{0.00584 D_p G}{\epsilon \mu} \right) \quad (8-42)$$

and for cylindrical particles,

$$\frac{k_e}{k_g} = \frac{1}{D_t} \left(\frac{k_p}{k_g} \right)^{0.12} \left(3.65 + \frac{0.0106 D_p G}{\epsilon \mu} \right) \quad (8-43)$$

Calderbank and Pogorski (38) correlated the conductivity in beds of celite and alundum by the simpler equation for air flow:

$$k_e = 0.2 + 0.0092 \frac{\sqrt{A_p} G}{\mu} \quad (8-43a)$$

Presence of solid particles in a gas markedly improves the rate of heat transfer. For a gas flowing through a fixed bed, the rate may be 5 to 10 times that for a gas alone, and in fluidized systems the improvement may be twenty- or thirtyfold. There is a sharp increase in rate of heat transfer when fluidization begins—in fact so much so that this behavior has been suggested as a means of identifying the onset of fluidization.

In industrial operations, significant amounts of heat transfer between the particle surfaces and the fluid occur in regenerators and pebble heaters and in such operations as the burning of deposited carbon off the surface of catalyst particles. Transfer of heat between vessel wall and the fluid-particle composite is practiced to maintain proper temperature control of such heterogeneous reactions. These two types of heat transfer differ quite markedly with respect to the variables controlling them. Some recent experimental results will be quoted here. The literature on fixed beds is covered by Jakob (108) and McAdams (151) and that on fluidized beds by McAdams (151) and Chu (43).

Fixed beds, wall coefficient. An early correlation by Colburn (46a) has been generalized by Jakob (109) as follows:

$$\frac{h D_t}{k_g} = f D_t^{0.17} \left(\frac{D_p G}{\mu} \right)^{0.83} \frac{C_p \mu}{k} \quad (8-44)$$

where the coefficient f is given by Fig. 8-14 and D_t is in feet. Other equations have been developed by Leva (137):

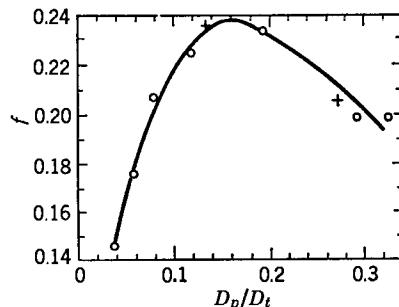


FIG. 8-14. Coefficient f in Eq. 8-44. [Jakob (109).]

$$h = 0.813 \frac{k_g}{D_t} e^{-6D_p/D_t} \left(\frac{D_p G}{\mu} \right)^{0.90} \quad \frac{D_p}{D_t} < 0.35 \quad (8-45)$$

$$h = 0.125 \frac{k_g}{D_t} \left(\frac{D_p G}{\mu} \right)^{0.75} \quad 0.35 < \frac{D_p}{D_t} < 0.60 \quad (8-46)$$

The equation

$$\frac{h D_p}{k} = 3.6 \left(\frac{D_p G}{\mu \epsilon} \right)^{0.365} \quad (8-47)$$

was advanced by Calderbank and Pogorski (38).

Fixed beds, particle-surface coefficient. Steady-state experimental methods have been devised recently for the direct measurement of the coefficient of heat transfer between the particle surfaces and the fluid flowing by. Glaser and Thodos (79) employed solid metallic spheres, cubes, and cylinders; an electric current passing through the packing generated heat that was removed continuously by gases flowing through the bed. Baumeister and Bennett (17) generated heat in a bed packed with steel balls by means of a high-frequency induction coil surrounding the test section. Both groups of investigators found an appreciable effect of the ratio of the particle and vessel diameters. However, Glaser was able to extrapolate the results and to achieve a correlation of value to commercial-size operations. This equation is

$$\frac{h}{C_p G} \left(\frac{C_p \mu}{k} \right)^{2/3} = \frac{0.535}{(\phi \text{Re})^{0.30} - 1.6} \quad 100 < \phi \text{Re} < 9,200 \quad (8-48)$$

where these special symbols are used:

$$\text{Re} = \sqrt{A_p} G / \mu(1 - \epsilon)$$

A_p = surface of a single particle

ϕ = particle sphericity, i.e., ratio of surface of sphere having same diameter as particle to surface of particle

Fluidized beds, wall coefficient. An appreciable difference has been found between the coefficient at an external surface such as the retaining wall of a vessel and at an internal surface such as a tube surrounded by fluidized material. This effect may be ascribed to the tendency for gas bubbles to move up the center of the bed rather than along the walls where the drag is greater. The external and internal coefficients are differentiated by subscripts, as h_e and h_i .

Most of the data then available were correlated by Wen and Leva (232) in terms of fluidized-bed parameters such as bed-expansion ratio, minimum fluidization velocity, and fluidization efficiency. That correlation was modified slightly by Wen and Fan (231), and charts were prepared to simplify the calculations. For external walls, the modified equation is

$$h_e = 11.6 k_g^{0.6} (C_s \rho_p)^{0.4} \left(\frac{G \eta}{\mu N_f} \right)^{0.36} \quad (8-49)$$

For internal surfaces the coefficient is related to h_e by

$$h_i = 9h_e G^{-0.37} \quad (8-50)$$

Fluidization efficiency η and the bed-expansion ratio N_f are given by Figs. 8-11 and 8-12.

Because of the lack of an entirely satisfactory mechanism of the transfer of heat between fluidized bed and vessel surface, Wender and Cooper (233) approached the problem of correlation from a largely empirical position. Some commercial hydroformer data were included in this survey. At internal surfaces,

$$\frac{h_i D_p / k_g}{1 - \epsilon} \left(\frac{k_g}{C_g \rho_g} \right)^{0.43} = 0.033 C_R \left(\frac{D_p G}{\mu} \right)^{0.23} \left(\frac{C_s}{C_g} \right)^{0.80} \left(\frac{\rho_p}{\rho_g} \right)^{0.66} \quad (8-51)$$

where C_R is a correction for the displacement of the immersed tube from the axis of the vessel, given in ref. 233. The group $k_g/C_g \rho_g$ has the dimensions square feet per hour; all other groups in this and the following equation are dimensionless. At external surfaces,

$$\frac{h D_p}{k_g (1 - \epsilon) (C_s \rho_p / C_g \rho_g)} = f (1 + 7.5 e^{-0.44 L_H C_s / D_p C_g}) \quad (8-52)$$

where f is given by Fig. 8-15. An important feature of this equation is

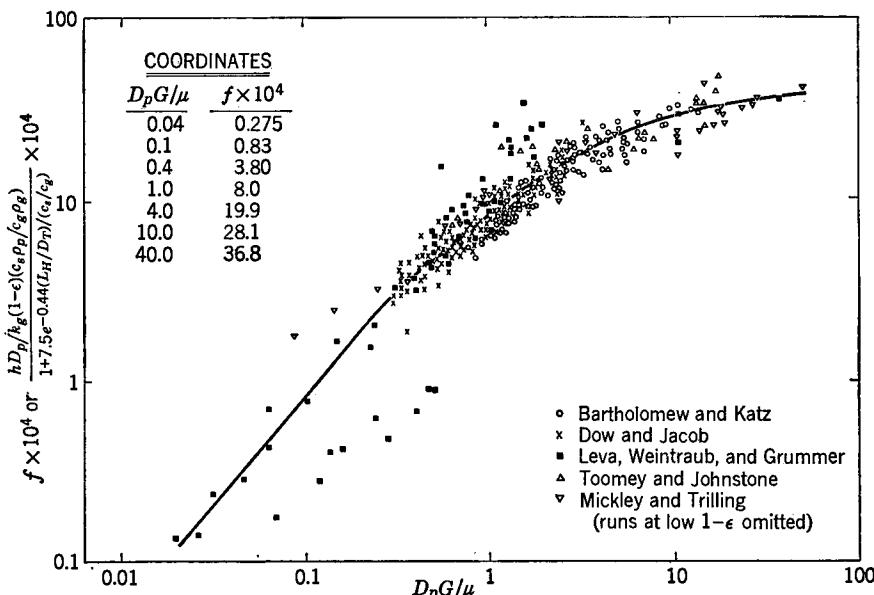


FIG. 8-15. Heat transfer at external walls of fluidized beds. [Wender and Cooper (233). Courtesy AICHE Journal.]

inclusion of the ratio of bed depth to vessel diameter, L_H/D_t .

Fluidized beds, particle-surface coefficient. Because of the difficulty of measuring the temperatures of small, mobile individual particles, little success has been achieved with measurements of heat transfer between fluidized particles and the fluid. None of the direct measurements that

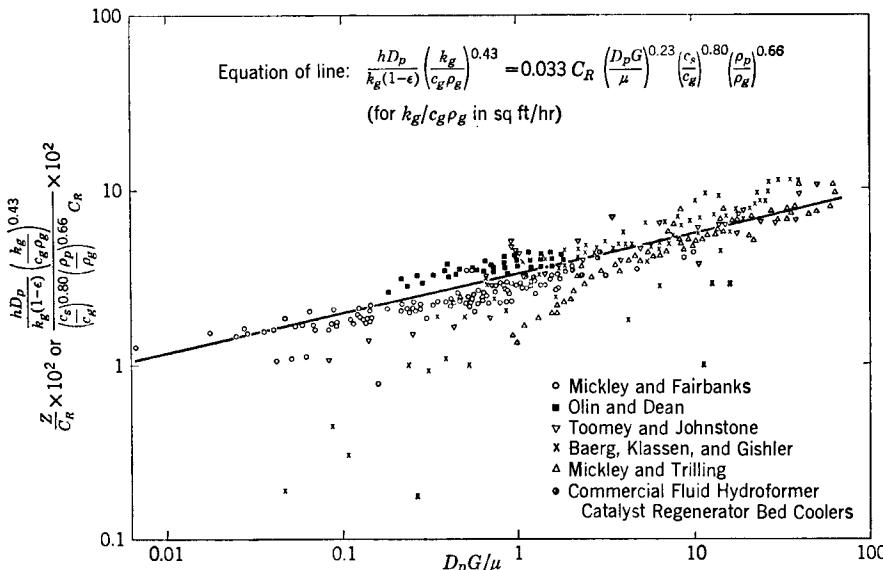


FIG. 8-16. Heat transfer at internal walls of fluidized beds. [Wender and Cooper (233). Courtesy AIChE Journal.]

have been made have been correlated with all the pertinent variables. Some confusion exists in the field: several investigations have found the coefficient to increase with particle size, and others to decrease; some have found maximum coefficients of about 0.9, and others as high as 70.

In view of this unsatisfactory situation, Gamson (73) and Chu (43) propose utilization of the equality of the mass and heat-transfer factors $j_d = j_h$. Accordingly, Chu presents the equations

$$\frac{h}{C_p G} \left(\frac{C_p \mu}{k} \right)^{2/3} = 5.7 \left[\frac{D_p G}{\mu(1-\epsilon)} \right]^{-0.78} \quad \frac{D_p G}{\mu(1-\epsilon)} < 30 \quad (8-53)$$

$$\frac{h}{C_p G} \left(\frac{C_p \mu}{k} \right)^{2/3} = 1.77 \left[\frac{D_p G}{\mu(1-\epsilon)} \right]^{-0.44} \quad \frac{D_p G}{\mu(1-\epsilon)} > 30 \quad (8-54)$$

Illustration 8-5. Alumina powder is poured into a cylinder 5.5 in. ID by 22 in. high to a depth of 10 in. The settled bed density is 64 lb/cu ft. The bed is fluidized with air, heated with an electrical heater along the axis of the tube, and cooled at the wall with a water jacket. The temperature of the bed is 75°F, and the pressure is 15 psia. Calcu-

late the coefficients of heat transfer at the wall, at the heater surface, and at the particle surface. Additional data are:

$$C_g = 0.25 \text{ Btu}/(\text{lb})(^{\circ}\text{F})$$

$$C_s = 0.19 \text{ Btu}/(\text{lb})(^{\circ}\text{F})$$

$$D_p = 0.00462 \text{ in.} = 0.000385 \text{ ft}$$

$$G = 158 \text{ lb}/(\text{hr})(\text{sq ft})$$

$$k_g = 0.0152 \text{ Btu}/(\text{hr})(\text{sq ft})(^{\circ}\text{F}/\text{ft})$$

$$\rho_g = 0.074 \text{ lb}/\text{cu ft}$$

$$\rho_p = 167 \text{ lb}/\text{cu ft}$$

$$\mu = 0.018 \text{ centipoise} = 0.0435 \text{ lb}/(\text{ft})(\text{hr})$$

Solution. Substituting into Eq. 8-36,

$$G_{mf} = \frac{138,000(0.000385)^{1.82}[0.074(167 - 0.074)]^{0.94}}{(0.0435)^{0.88}} = 15 \text{ lb}/(\text{hr})(\text{sq ft})$$

$$\text{Also, } \frac{G_{mf}D_p}{\mu} = \frac{0.000385(15)}{0.0435} = 0.13$$

From Fig. 8-10, $f = 1.0$, so that the correct value remains $G_{mf} = 15$. At the ratio $G/G_{mf} = 158/15 = 10.5$, from Figs. 8-11 and 8-12,

$$\begin{aligned} \eta &= 0.73 \\ N_f &= 1.33 \end{aligned}$$

Then Eq. 8-49 becomes

$$\begin{aligned} h_e &= 11.6(0.0152)^{0.6}[0.19(167)]^{0.4} \left[\frac{158(0.73)}{0.0435(1.33)} \right]^{0.36} \\ &= 58.0 \text{ Btu}/(\text{hr})(\text{sq ft})(^{\circ}\text{F}) \end{aligned}$$

The internal coefficient from Eq. 8-50 is

$$h_i = 9(58.0)(158)^{-0.37} = 80.3 \text{ Btu}/(\text{hr})(\text{sq ft})(^{\circ}\text{F})$$

The calculations will be made also with Eqs. 8-51 and 8-52. The data are not sufficient to evaluate precisely the extra-particle voidage, so the data of Fig. 8-6 will be used, assuming the present material to have the characteristics of "uniform sharp sand." Reading this chart, $\epsilon_{mf} = 0.57$. For the expanded bed,

$$\epsilon_f = 1 - \frac{1 - \epsilon_{mf}}{N_f} = 1 - \frac{0.43}{1.33} = 0.677$$

$$\frac{D_p G}{\mu} = \frac{0.000385(158)}{0.0435} = 1.40$$

On Fig. 8-15, the ordinate is $9.9(10^{-4})$, so that Eq. 8-52 becomes

$$\begin{aligned} h_e &= \frac{9.9(10^{-4})}{0.000385} (1 + 7.5e^{-0.44(13.3)(0.19)/(5.5)(0.25)}) \frac{(0.0152)(0.323)(0.19)(167)}{0.25(0.074)} \\ &= 94.0 \text{ Btu}/(\text{hr})(\text{sq ft})(^{\circ}\text{F}) \end{aligned}$$

For the internal coefficient, Eq. 8-51 becomes

$$\begin{aligned} h_i &= \frac{0.033(0.323)(0.0152)}{0.000385} \left[\frac{0.25(0.074)}{0.0152} \right]^{0.43} \left[\frac{0.000385(158)}{0.0435} \right]^{0.23} \left(\frac{0.19}{0.25} \right)^{0.8} \left(\frac{167}{0.074} \right)^{0.66} \\ &= 65.3 \text{ Btu}/(\text{hr})(\text{sq ft})(^{\circ}\text{F}) \end{aligned}$$

For the conditions of this illustration, Wen and Fan (231) cite the experimental value $h_i = 73.2$, with which both of the present calculations compare only moderately well

Part of the disagreement may be due to incorrect estimate of the voidage. Proceeding to the particle-surface coefficient,

$$\frac{D_p G}{\mu(1 - \epsilon)} = \frac{0.000385(158)}{(0.0435)(0.323)} = 4.33$$

Equation 8-53 becomes

$$h = 5.7(0.25)(158)(4.33)^{-0.78} \left[\frac{0.25(0.0435)}{0.0152} \right]^{-0.67} = 90.5 \text{ Btu}/(\text{hr})(\text{sq ft})(^{\circ}\text{F})$$

Illustration 8-6. Suppose that in Illustration 8-5, air flow is downward, so that the bed remains fixed. Calculate the wall coefficient.

Solution. Substituting into Eq. 8-45,

$$h = \frac{0.813(0.0152)}{0.458} \left[\frac{0.000385(158)}{0.0435} \right]^{0.9} e^{-6(0.000385)/0.458} = 0.036 \text{ Btu}/(\text{hr})(\text{sq ft})(^{\circ}\text{F})$$

Try also Eq. 8-44:

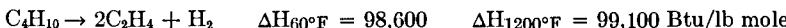
$$\frac{D_p}{D_t} = \frac{0.000385}{0.458} = 0.0008$$

$f = 0.09$ (upon extrapolation from Fig. 8-14)

$$h = 0.09(0.0152)(0.458)^{-0.83} \left[\frac{0.000385(158)}{0.0435} \right]^{0.83} \frac{0.25(0.0435)}{0.0152} = 0.0024 \text{ Btu}/(\text{hr})(\text{sq ft})(^{\circ}\text{F})$$

The agreement is poor. It should be observed, however, that both equations are based on data for much larger particles than the ones of this illustration, which are much smaller than would ordinarily be used in fixed-bed applications. Comparison with the magnitude of fluidized-bed coefficients is nevertheless interesting.

Illustration 8-7. Cracking of hydrocarbons has been conducted on a commercial scale in a pebble heater (Kilpatrick, Dean, Hall, and Seed, 120). In the present illustration, some of the operating conditions will be worked out for the cracking of butane according to the simplified reaction



The reaction is first-order with

$$\log k = \frac{-22,100}{T} + 12.4500$$

where T is in degrees Rankine and k in reciprocal seconds.

The pebbles are alumina spheres $\frac{5}{16}$ in. in diameter, heat capacity 25 Btu/(cu ft)($^{\circ}$ F), surface 126 sq ft/cu ft; and percentage voids 45. Heat capacity of hydrogen is 6.9 Btu/(lb mole)($^{\circ}$ F). Physical data for the hydrocarbons may be found in Maxwell (149).

Pebbles are preheated to 2000°F by direct contact with combustion gases and flow downward through the reactor in parallel current to butane which enters at 500°F and 20 psig. A conversion of 90 per cent is required, and the peak temperature is to be limited to 1600°F . Find the needed pebble-circulation rate, the outlet pressure of the gas, and the volume of the reactor.

Solution. For the moment, assume that the peak of 1600°F is reached at the outlet and that the pebbles cool to 1650°F . These assumptions are not binding in any way,

but merely help in selecting a suitable mass flow rate. Accordingly, the over-all heat balance is

$$Q = 0.1(1403 - 295)(58) + 1.8(1270 - 300)(28) + 0.9(1600 - 60)(6.9) - (525 - 295)(58) + 0.9(98,600) = 140,300 \text{ Btu/(hr)(lb mole feed)}$$

$$\text{Pebble circulation} = \frac{140,300}{(25)(2,000 - 1,650)} = 16 \text{ cu ft/(hr)(lb mole feed/hr)}$$

The mass flow of butane will be set on the basis of a pressure drop of 1.0 psi/ft. For spherical particles, Eq. 8-27 has been modified by Glaser and Thodos (79) as follows:

$$\frac{\Delta\pi}{L} \frac{g_c \rho \sqrt{A_p \epsilon^3}}{G^2(1 - \epsilon)} = \frac{2.89}{Re^{0.05} - 0.81} \quad (A)$$

$$\text{where } Re = \frac{\sqrt{A_p} G}{\mu(1 - \epsilon)} = \frac{0.0462 G}{0.0533(1 - 0.45)} = 1.58 G \quad (B)$$

Here A_p is the surface of a single particle. For the density calculation, assume average conditions of 45 per cent conversion, 30 psia, and 1100°F.

$$\begin{aligned} \rho &= \frac{58}{(1 + 2x)(379)(T/520)(14.7/\pi)} = \frac{5.4\pi}{(1 + 2x)T} \\ &= \frac{5.4(30)}{1,560(1.9)} = 0.0546 \text{ lb/cu ft} \end{aligned} \quad (C)$$

for the average conditions. Let $\Delta\pi/L = 1 \text{ psi/ft} = 144 \text{ psf/ft}$. Therefore

$$\frac{4.18(10^8)(144)(0.0462)(0.0546)(0.45)^3}{0.55G^2} = \frac{2.89}{(1.58G)^{0.05} - 0.81}$$

$$\text{or } G^2 = 8.61(10^6)[(1.58G)^{0.05} - 0.81]$$

Solving by trial, $G = 2,470 \text{ lb/(hr)(sq ft)} = 42.6 \text{ lb moles butane/(hr)(sq ft)}$.

For heat transfer, the correlation for spheres (Eq. 8-48) is

$$\begin{aligned} ha &= C_p G a \left(\frac{C_p \mu}{k} \right)^{-2/3} \frac{0.535}{Re^{0.3} - 1.6} \\ &= 0.81(2,470)(126) \left[\frac{0.81(0.0533)}{0.04} \right]^{-2/3} \frac{0.535}{[1.58(2,470)]^{0.3} - 1.6} \\ &= 12,300 \text{ Btu/(hr)(cu ft)(°F)} \end{aligned}$$

The rate equation is

$$r = \frac{k(n_{a0} - x)}{V} = \frac{k\pi(1 - x)}{RT(1 + 2x)} \quad (D)$$

Take as a basis unit cross section of reactor. The differential pressure drop is

$$\begin{aligned} d\pi &= \frac{1 - \epsilon}{144\epsilon^3} \frac{G^2}{g_c \rho \sqrt{A_p}} \frac{2.89}{(1.58G)^{0.05} - 0.81} dL \\ &= \frac{0.55(2,470)^2(2.89)}{144(0.45)^3(4.18)(10^8)(0.0462)\{(1.58)(2,470)]^{0.05} - 0.81\} \rho} dL \\ \text{or } d\pi &= \frac{0.0545}{\rho} dL = 0.01(1 + 2x) \frac{T}{\pi} dV_r = 0.01G_m \frac{RT^2(1 + 2x)^2}{\pi^2(1 - x)} dx \end{aligned} \quad (E)$$

since for unit cross section $dL = dV_r = G_m dx/r$, upon substituting Eq. C. Below 1200°F, the reaction rate is small and will be neglected. The heat balance is

$$\int_{500}^{1200} C_p G dT = \int_0^{V_r} ha(\Delta T)_m dV_r = C_c V_c \left(\frac{G}{58} \right) (T_{c1} - T_{c2})$$

where $(\Delta T)_m$ is the mean temperature difference and the subscript c refers to the pebbles. Substituting,

$$0.8(2470)(1200 - 500) = 12,300(\Delta T)_m \Delta V_r = 25(16) \left(\frac{2470}{58} \right) (2000 - T_{c2})$$

whence $T_{c2} = 1919^{\circ}\text{F}$

$$(\Delta T)_m = [(2000 - 500), (1919 - 1200)] = 1063$$

$$\Delta V_r = \frac{0.8(2,470)(1,200 - 500)}{12,300(1,063)} = 0.105 \text{ cu ft/sq ft}$$

$$\Delta \pi = 0.01 \left(\frac{T}{\pi} \right)_m \Delta V_r = \frac{0.01(1,310)(0.105)}{30} = 0.046 \text{ psi}$$

Above 1200°F , use the following average heat capacities:

$$\text{Btu/(lb mole)}(^{\circ}\text{F})$$

Butane..... 49.3

Ethylene..... 21.0

Hydrogen..... 6.9

Following Sec. 33, the heat balance per pound mole of feed is

$$\begin{aligned} \int \frac{ha(\Delta T)_m}{G_m} dV_r &= \int \frac{ha(\Delta T)_m}{r} dx = \int ha(\Delta T)_m \left(\frac{RT}{\pi k} \right) \left(\frac{1+2x}{1-x} \right) dx \\ &= 12,300(10.73) \int \frac{T(\Delta T)_m}{\pi k} \left(\frac{1+2x}{1-x} \right) dx = 132,000 \int \frac{T(\Delta T)_m}{\pi k} \left(\frac{1+2x}{1-x} \right) dx \\ &= [49.3(1-x) + 21.0(2x) + 6.9x](T - 1200) + 99,100x \\ &= 16(25)(1919 - T_{c2}) \\ \text{or } 132,000 \int \frac{T(\Delta T)_m}{\pi k} \left(\frac{1+2x}{1-x} \right) dx &= 49.3(T - 1200) + [99,100 - 0.4(T - 1200)]x \\ &= 400(1919 - T_{c2}) \end{aligned} \quad (F)$$

Upon substituting $G_m = 42.6$, Eq. E becomes

$$\Delta \pi = 4.58 \int \frac{T^2(1+2x)^2}{\pi^2 k(1-x)} dx \quad (G)$$

This procedure will be followed in solving Eqs. F and G simultaneously:

1. Choose an increment of x .
2. Estimate the temperature at the end of the increment.
3. Calculate T_{c2} from Eq. F.
4. Estimate the pressure at the end of the interval. Since the pressure drop is quite small and the solution of Eq. F is relatively insensitive to the pressure, a retrial is not usually necessary.
5. Calculate the integrand of Eq. F at the beginning and end of the interval.
6. Evaluate Eq. F by the trapezoidal rule. If the equation is satisfied, the correct value of T was chosen for the end of this interval.
7. Once this value of T has been established, Eq. G is also integrated by the trapezoidal rule.
8. The complete procedure is repeated for other small increments of x .

As examples, the solutions for $x_2 = 0.001$ and for $x_7 = 0.10$ will be shown. Results for all points are summarized in Table 8-5.

$$x_1 = 0$$

$$x_2 = 0.001$$

Try $T_2 = 1300$

$$T_{c2} = 1919 - \frac{49.3(1300 - 1200) + [99,100 - 0.4(1300 - 1200)](0.001)}{400}$$

$$= 1919 - \frac{5029}{400} = 1907$$

$$I_1 = \frac{1,660(1,919 - 1,200)}{34.96(517)} = 65.8$$

$$I_2 = \frac{1,760(1,907 - 1,300)(1.002)}{34.96(2,860)(0.999)} = 10.7$$

$$I_{av} = 38.3$$

$$\int_0^{0.001} = 132,000(38.3)(0.001) = 5060 \simeq 5029 \quad (\text{from solution for } T_{c2})$$

which is a close enough check.

$$\Delta\pi_2 = 0$$

For the next point illustrated,

$$x_6 = 0.05$$

$$x_7 = 0.10$$

Try $T_7 = 1465$

$$T_{c7} = 1919 - \frac{49.3(1465 - 1200) + [99,100 - 0.4(1465 - 1200)](0.10)}{400}$$

$$= 1919 - \frac{22,980}{400} = 1862$$

$$I_6 = 0.811 \quad (\text{from Table 8-5})$$

$$I_7 = \frac{(1,465 + 460)(1,862 - 1,465)}{34.8(32,500)} \left(\frac{1.2}{0.9} \right) = 0.895$$

$$I_{av} = 0.853$$

$$\int_{0.05}^{0.10} = 132,000(0.853)(0.10 - 0.05) = 5630$$

$$\int_0^{0.10} = 5630 + 17,950 = 23,580 \neq 22,980 \quad (\text{from solution for } T_{c7})$$

Try $T_7 = 1473$

$$T_{c7} = 1919 - \frac{23,350}{400} = 1861$$

$$I_7 = \frac{(1933)(388)(1.2)}{34.8(36,000)(0.9)} = 0.794$$

$$I_{av} = 0.5(0.811 + 0.794) = 0.803$$

$$\int_0^{0.10} = 17,950 + \int_{0.05}^{0.10} = 17,950 + 132,000(0.803)(0.05) = 23,250 \simeq 23,350$$

from solution for T_{ct} , which is a close enough check. For the pressure drop,

$$I = \frac{T^2(1+2x)^2}{\pi^2 k(1-x)}$$

$$I_6 = \frac{(1,924)^2(1.1)^2}{(34.8)^2(32,200)(0.95)} = 0.12$$

$$I_7 = \frac{(1,933)^2(1.2)^2}{(34.8)^2(36,000)(0.9)} = 0.135$$

and $\pi_7 = 34.82 - 4.58(0.5)(0.12 + 0.135)(0.10 - 0.05) = 34.79 \text{ psi}$

The reactor volume is obtained from the following equation:

$$V_r = G_m \int \frac{dx}{r} = G_m \int \frac{RT}{k\pi} \frac{1+2x}{1-x} dx = 458 \int \frac{T}{k\pi} \frac{1+2x}{1-x} dx \quad (H)$$

All calculations are summarized in Table 8-5. Integrands and integrals are shown for Eq. F, which is a check on the estimated temperature; Eq. G, which determines the pressure drop; and Eq. H, which determines the reactor volume. The exit pressure is 32.6 psia, and the reactor volume is 1.99 cu ft/(lb mole butane feed/hr).

If the charge rate is sufficient to require a vessel diameter of several feet, the calculated bed depth is perhaps too shallow for good operation since poor gas distribution may result. Conditions could be improved by operating at a lower pressure, say 10 psig, and at a lower mass flow rate. A final design must also take account of the actual occurrence of several side reactions, which will respond in different ways to reduction in pressure or to increase in contact time.

TABLE 8-5. CRACKING OF *n*-BUTANE (ILLUSTRATION 8-7)

x	T	T _c	k	Eq. F		Eq. G		Eq. H	
				I	\int_0^x	I	π	I	V_r
0	500	2000	0	35.00	0
0	1200	1919	517	65.8	0	4.36	34.95	3.21	0.105
0.001	1300	1907	2,860	10.7	5,029				
0.003	1340	1901	5,300	5.45	7,195	0.344	0.175
0.006	1374	1897	9,200	3.08	8,870				
0.015	1408	1889	14,500	1.85	11,735	0.211	34.80	0.135	0.212
0.05	1464	1874	32,200	0.811	17,950	0.120	34.77	0.069	0.259
0.10	1473	1861	36,000	0.794	23,250	0.135	34.74	0.072	0.305
0.30	1496	1809	49,000	0.815	44,300	0.236	34.57	0.091	0.520
0.50	1520	1756	70,000	0.772	65,250	0.375	34.29	0.115	0.792
0.70	1541	1703	91,000	0.795	86,200	0.651	33.82	0.182	1.179
0.90	1575	1650	142,000	0.886	107,600	1.98	32.61	0.430	1.988

57. Mass Transfer

Transfer of material between a fluid and the surface of a solid is often the rate-controlling step in the mechanism of a heterogeneous reaction, particularly in industrial operations where economic limitations on pressure drop often bring the flow rate into a region where neither the

rate of adsorption nor the rate of surface reaction is controlling. In fluidized systems, the flow rate is limited to minimize carry-over of solid particles.

Rate of mass transfer in fixed beds has been widely investigated, originally in the fields of absorption, adsorption, distillation, and extraction. In reacting systems, the solid particles are usually much smaller than those used in the physical operations mentioned, but similar correlations seem to apply. Fluidized beds are used for some physical operations such as drying of gases or fractionating adsorption of hydrocarbons, but their principal use is in catalytic reactions.

Though the rate of a reaction may not be controlled by the mass-transfer step, design of the reactor on the basis of mass transfer may be of value because a minimum size will be established by this means, a result of some importance in economic studies.

Mass transfer in fixed beds. For thorough coverage of the field as applied primarily to the physical operations, reference may be made elsewhere (Sherwood and Pigford, 199; Perry, 179; and Treybal, 216). Illustrative of the correlations in this field is the following equation of Hobson and Thodos (92):

$$\log j_d = 0.7683 - 0.9175 \log Re + 0.0817 (\log Re)^2 \quad (8-55)$$

where $j_d = \frac{k_g p_{bm}}{G_m} \left(\frac{\mu}{\rho D} \right)^{\frac{1}{2}}$ or $\frac{k_L C_{bm}}{L_m} \left(\frac{\mu}{\rho D} \right)^{\frac{1}{2}}$

$$Re = \frac{D_p G}{\mu}$$

This applies to mass transfer between the surface of a solid and either a gas or a liquid phase when j_d is suitably defined. Many other correlations could be quoted, some more recent ones, but this will suffice for present needs. A method for evaluating diffusivities in multicomponent systems has been developed by Wilke (236). Effective diffusivities are discussed in Sec. 58.

Mass transfer in fluidized beds. Mass-transfer coefficients have been measured in such fluidized systems as the vaporization of naphthalene particles into air, the drying of air with alumina or silica gel, and adsorption of carbon tetrachloride from air by activated carbon, as well as several systems where liquid water was the fluidizing medium. The efforts of Chu, Kalil, and Wetteroth (44), embodied in Fig. 8-17, appear to be the best correlation available that takes account of most of the pertinent variables. The data are also represented by these equations:

$$\frac{k_g p_{bm}}{G_m} \left(\frac{\mu}{\rho D} \right)^{\frac{1}{2}} = 5.7 \left[\frac{D_p G}{\mu(1 - \epsilon)} \right]^{-0.78} \quad \frac{D_p G}{\mu(1 - \epsilon)} < 30 \quad (8-56)$$

$$\frac{k_g p_{bm}}{G_m} \left(\frac{\mu}{\rho D} \right)^{\frac{1}{2}} = 1.77 \left[\frac{D_p G}{\mu(1 - \epsilon)} \right]^{-0.44} \quad \frac{D_p G}{\mu(1 - \epsilon)} > 30 \quad (8-57)$$

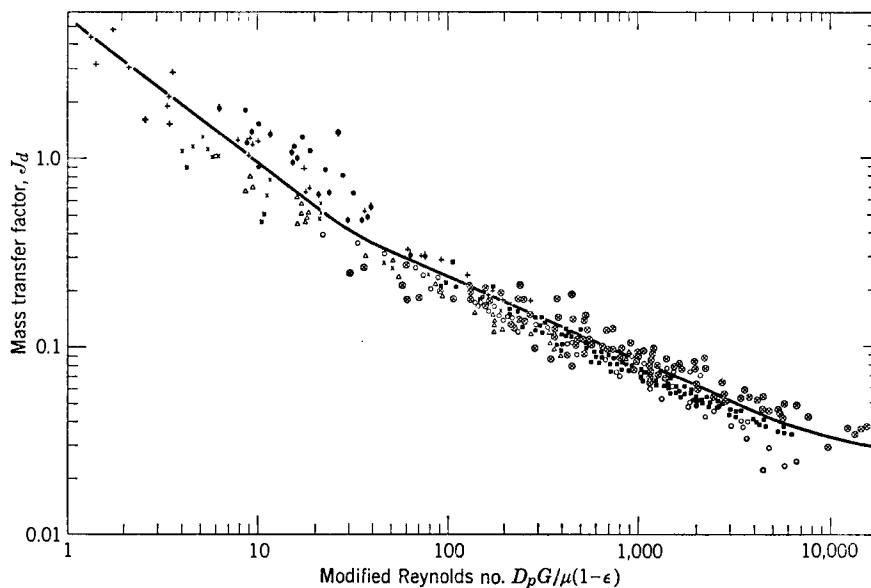


FIG. 8-17. Mass transfer in fluidized beds. [Chu, Kalil, and Wetteroth (44). Courtesy Chemical Engineering Progress.]

Reference may be made to a review of the literature on mass transfer in fluidized systems (Chu, 43).

Illustration 8-8. Activated alumina of average particle diameter 0.00462 in. is used to adsorb 99.9 per cent of the water from air containing 0.01 lb water/lb dry air, at 75°F, 15 psia, and a rate of 158 lb/(hr)(sq ft). The alumina is fed continuously to the bottom of the vessel, overflows through a standpipe, and proceeds to a regenerator. Capacity of the alumina without appreciable back pressure of water vapor is 4 per cent its weight in water. Diffusivity of water in air is 0.99 sq ft/hr. Other properties of the system are as in Illustration 8-5. Find the depth of bed.

Solution. From Illustration 8-5, $\epsilon = 0.677$. Assuming the particles to be spherical,

$$a = \frac{6(1 - \epsilon)}{D_p} = \frac{6(0.323)}{0.000385} = 5,040 \text{ sq ft/cu ft of bed}$$

Equation 8-56 becomes

$$k_a = \frac{5.7(158)(14.7)}{29(15)} \left[\frac{0.0435}{0.074(0.99)} \right]^{-\frac{1}{3}} \left[\frac{0.000385(158)}{0.0435(0.323)} \right]^{-0.78} \\ = 13.6 \text{ lb moles/(hr)(sq ft)(atm)}$$

The material balance on a differential height of reactor is

$$-G dw = k_a a (p_a - p_s) dh = k_a a p_a dh$$

since the back pressure is $p_s = 0$; w is in pounds of water per pound of dry air and is related to the partial pressure by

$$p_a = \frac{w/18}{w/18 + 1/29} \left(\frac{15}{14.7} \right) = \frac{1.64w}{1.61w + 1}$$

Consequently,

$$h = -\frac{G}{k_g a} \int \frac{dw}{p_g} = -\frac{G}{k_g a} \int_{0.01}^{0.00001} \frac{1.61w + 1}{1.64w} dw$$

$$= \frac{158}{13.6(5,040)} [0.98(0.01 - 0.00001) + 0.61 \ln 1,000] = 0.01 \text{ ft}$$

Several assumptions in the method of calculation contribute to the unrealistic bed depth obtained, namely, plug flow exists, there is no back pressure, and the rate of mass transfer to the external surface is controlling. As pointed out in Sec. 59, complete mixing of both phases probably exists. Experimental work on air drying with a fluidized bed of silica gel has been reported by Cox (50), in which the back pressure of water was quite appreciable and the mass-transfer coefficients were much lower than calculated from Eq. 8-56 (see Prob. 8-8). In tests on the adsorption of light hydrocarbons by active carbon, Kapfer, Malow, Happel, and Marsel (118) found that internal pore diffusion is the controlling step. Thus the heights of transfer units calculated from the external surface were about 0.1 to 1.0 in., whereas experimental values ranged from 6.5 to 36.9 in. For the over-all height of a transfer unit, Kapfer proposed the equation

$$H_{0g} = 6 \frac{G}{L}$$

where G = gas rate, std cu ft/hr
 L = carbon rate, lb/hr

The coefficient will vary with the particular type of carbon.

58. Fixed-bed-reactor Design

Design of a reactor containing a granular mass is in principle the same as that of empty tubular reactors. Perhaps the greatest difference is that in a granular bed, temperature and concentration gradients occur laterally as well as longitudinally (Fig. 8-18) whereas lateral gradients are uncommon in unpacked reactors (Sec. 32). The calculation procedure for a cylindrical packed reactor will be developed now.

The differential equations of a cylindrical reactor (Eqs. 8-11 and 8-14) may be solved numerically in difference form. Under steady-state conditions, letting subscript m identify increments of R and n the increments of L ,

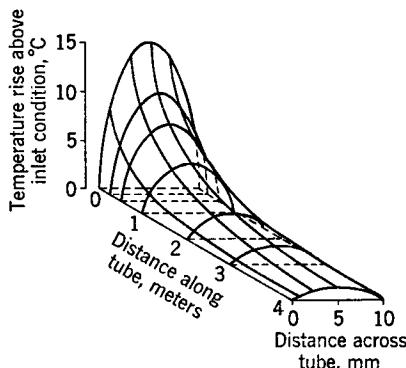


FIG. 8-18. Radial and longitudinal gradients in a packed tube in a Fischer-Tropsch reactor at 200°C. [Winnacker and Weingaertner (240). Courtesy Carl Hanser Verlag, Munich.]

$$\frac{T_{m,n+1} - T_{m,n}}{\Delta L} - \frac{k_e}{G s_f} \left[\frac{1}{R} \frac{T_{m+1,n} - T_{m,n}}{\Delta R} + \frac{T_{m+1,n} - 2T_{m,n} + T_{m-1,n}}{(\Delta R)^2} \right] + \rho_B \frac{\Delta H_r}{G s_f} \frac{r_{m,n+1} + r_{m,n}}{2} = 0 \quad (8-58)$$

$$\frac{f_{m,n+1} - f_{m,n}}{\Delta L} - \frac{D_e \rho_f}{G} \left[\frac{1}{R} \frac{f_{m+1,n} - f_{m,n}}{\Delta R} + \frac{f_{m+1,n} - 2f_{m,n} + f_{m-1,n}}{(\Delta R)^2} \right] + \rho_B \left(\frac{\rho_f}{G C} \right)_0 \frac{r_{m,n+1} + r_{m,n}}{2} = 0 \quad (8-59)$$

Here the arithmetic average value has been substituted for the rate r . Observing that $R(\Delta R) = m(\Delta R)^2$, where m is the number of increments into which R is divided, and rearranging,

$$T_{m,n+1} = T_{m,n} + \frac{\Delta L k_e}{(\Delta R)^2 G s_f} \left[\left(1 + \frac{1}{m} \right) T_{m+1,n} - \left(2 + \frac{1}{m} \right) T_{m,n} + T_{m-1,n} \right] - \rho_B \frac{\Delta L \Delta H_r}{G s_f} \frac{r_{m,n+1} + r_{m,n}}{2} \quad (8-60)$$

$$f_{m,n+1} = f_{m,n} + \frac{\Delta L D_e \rho_f}{(\Delta R)^2 G} \left[\left(1 + \frac{1}{m} \right) f_{m+1,n} - \left(2 + \frac{1}{m} \right) f_{m,n} + f_{m-1,n} \right] + \Delta L \rho_B \left(\frac{\rho_f}{G C} \right)_0 \frac{r_{m,n+1} + r_{m,n}}{2} \quad (8-61)$$

At the center of the cylinder, the terms $(1/R)(\partial T/\partial R)$ and $(1/R)(\partial f/\partial R)$ become indeterminate. Since, however,

$$\lim_{R \rightarrow 0} \left(\frac{1}{R} \frac{\partial T}{\partial R} \right) = \left(\frac{\partial^2 T}{\partial R^2} \right)_0 \quad (8-62)$$

the differential equation becomes

$$\frac{\partial T}{\partial L} - \frac{k_e}{G s_f} \left(2 \frac{\partial^2 T}{\partial R^2} \right)_0 + \frac{\rho_B \Delta H_r}{G s_f} r = 0 \quad (8-63)$$

and the corresponding difference equation is

$$T_{0,n+1} = T_{0,n} + \frac{4 \Delta L k_e}{(\Delta R)^2 G s_f} (T_{1,n} - T_{0,n}) - \rho_B \frac{\Delta L \Delta H_r}{G s_f} \frac{r_{0,n+1} + r_{0,n}}{2} \quad (8-64)$$

Similarly,

$$f_{0,n+1} = f_{0,n} + \frac{4 \Delta L D_e \rho_f}{(\Delta R)^2 G} (f_{1,n} - f_{0,n}) + \Delta L \rho_B \left(\frac{\rho_f}{G C} \right)_0 \frac{r_{0,n+1} + r_{0,n}}{2} \quad (8-65)$$

The wall condition may be a specified temperature or heat-transfer coefficient or heat flux. Letting w designate conditions at the wall, the boundary conditions may comprise specification of the following:

1. Temperature as a function of distance along the reactor; that is,

$$T_{w,n} = \phi(L_n) \quad (8-66)$$

2. Heat-transfer coefficient U_n and heat-transfer medium temperature T'_n :

$$UA \Delta T = k_e A \frac{\partial T}{\partial R} \quad (8-67)$$

or $U_n(T'_n - T_{w,n}) = k_e \frac{T_{w,n} - T_{w-1,n}}{\Delta R} \quad (8-68)$

or $T_{w,n} = \frac{T'_n + k_e T_{w-1,n} / (U_n \Delta R)}{1 + k_e / (U_n \Delta R)} \quad (8-69)$

When calculating conditions at the wall, the term $f_{w+1,n}$ occurs, which is the conversion at the first increment beyond the wall, a physical impossibility of course. However, since the concentration gradient is zero at the wall, the curve can be regarded as symmetrical about the wall and this substitution can be made:

$$f_{w+1,n} = f_{w-1,n} \quad (8-70)$$

Several numerical solutions of equations like those developed here have been reported, for instance:

1. Oxidation of sulfur dioxide, by Baron (12), a graphical method
2. Synthesis of ammonia, by Van Heerden (221) and Adams and Comings (1), a graphical method

A case involving a variable wall temperature will be worked out now.

Illustration 8-9. In a cylindrical packed reactor, a first-order reaction occurs with a rate equation

$$r = (10^4)e^{-15,000/T}(1 - f) \quad (A)$$

Inlet temperature is 600°F, inlet conversion is $f = 0$, the wall is kept in contact with a heat-transfer medium at $T' = 500°F$, and the heat transfer is such that Eq. 8-69 becomes

$$T_{w,n} = \frac{500 + 1.2T_{w-1,n}}{2.2} \quad (B)$$

Other operating conditions and physical properties are such that the pertinent difference equations become

$$T_{0,n+1} = T_{0,n} + 0.8(T_{1,n} - T_{0,n}) + 1000(r_{0,n+1} + r_{0,n}) \quad (C)$$

$$f_{0,n+1} = f_{0,n} + 2(f_{1,n} - f_{0,n}) + 8(r_{0,n+1} + r_{0,n}) \quad (D)$$

$$T_{m,n+1} = T_{m,n} + 0.2 \left[\left(1 + \frac{1}{m}\right) T_{m+1,n} - \left(2 + \frac{1}{m}\right) T_{m,n} + T_{m-1,n} \right] + 1000(r_{0,n+1} + r_{0,n}) \quad (E)$$

$$f_{m,n+1} = f_{m,n} + 0.5 \left[\left(1 + \frac{1}{m}\right) f_{m+1,n} - \left(2 + \frac{1}{m}\right) f_{m,n} + f_{m-1,n} \right] + 8(r_{0,n+1} + r_{0,n}) \quad (F)$$

Four radial increments will be used to find the distribution of conversion and temperature throughout the bed and also the mean value of the conversion at each cross section along the bed.

At the inlet the temperature is assumed 600°F except at the wall, where it is calculated from

$$T_{w,0} = 500 + \frac{1.2(600)}{2.2} = 555$$

The inlet temperatures, conversions, and reaction rates are recorded in the summary, Table 8-6. Proceeding with the solution:

$m = 0, n = 0$:

$$\begin{aligned} T_{01} &= 600 + 0.8(0) + 1000(r_{01} + 0.0071) = 600 + 1000(r_{01} + 0.0071) \\ f_{01} &= 8(r_{01} + 0.0071) \end{aligned}$$

By trial, solve these equations together with the rate equation A.

Try $r_{01} = 0.0073$

$$T_{01} = 600 + 1000(0.0073 + 0.0071) = 614.4$$

$$f_{01} = 8(0.0073 + 0.0071) = 0.115$$

$$r_{01} = (10^4)e^{-15,000/(614.4+460)}(1 - 0.115) = 0.0076 \quad \text{No check}$$

Try $r_{01} = 0.0076$

$$T_{01} = 614.7$$

$$f_{01} = 0.118$$

$$r_{01} = 0.0086(1 - 0.118) = 0.0076 \quad \text{Check}$$

$m = 1, n = 0$:

$$\begin{aligned} T_{11} &= 600 + 0.2(0) + 1000(r_{11} + 0.0071) = 600 + 1000(r_{11} + 0.0071) \\ f_{11} &= 8(r_{11} + 0.0071) \end{aligned}$$

These equations, and also the ones for point (2,0), are the same as for point (0,0), so the solutions are the same.

$m = 3, n = 0$:

$$\begin{aligned} T_{31} &= 600 + 0.2[(1 + \frac{1}{3})(555) - (2 + \frac{1}{3})(600) + 600] + 1000(r_{31} + 0.0071) \\ &= 588 + 1000(r_{31} + 0.0071) \end{aligned}$$

$$f_{31} = 8(r_{31} + 0.0071)$$

Try $r_{31} = 0.0064$

$$T_{31} = 588 + 1000(0.0064 + 0.0071) = 601.5$$

$$f_{31} = 8(0.0064 + 0.0071) = 0.108$$

$$r_{31} = 0.0071(1 - 0.108) = 0.00633 \quad \text{Check}$$

$m = 4, n = 0$:

$$T_{41} = \frac{500 + 1.2(601.5)}{2.2} = 556$$

$$r_{41} = (10^4)e^{-15,000/(556+460)}(1 - f) = 0.0038(1 - f)$$

$$f_{41} = 8(r_{41} + 0.00375) = 8[0.0038(1 - f_{41}) + 0.00375] = 0.0341$$

$$r_{41} = 0.0038(1 - f_{41}) = 0.0038(1 - 0.0341) = 0.00367$$

$m = 0, n = 1$:

$$\begin{aligned} T_{02} &= 614.7 + 0.8(614.7 - 614.7) + 1000(r_{02} + 0.0076) \\ &= 614.7 + 1000(r_{02} + 0.0076) \end{aligned}$$

$$f_{02} = 0.118 + 2(0) + 8(r_{02} + 0.0076) = 0.118 + 8(r_{02} + 0.0076)$$

Try $r_{02} = 0.0079$

$$T_{02} = 630.2$$

$$f_{02} = 0.242$$

$$r_{02} = 0.0104(1 - 0.242) = 0.0079 \quad \text{Check}$$

$m = 2, n = 1$:

$$\begin{aligned} T_{22} &= 614.7 + 0.2[1.5(601.5) - 2.5(614.7) + 614.7] + 1000(r_{22} + 0.0076) \\ &= 610.7 + 1000(r_{22} + 0.0076) \\ f_{22} &= 0.118 + 0.5[1.5(0.108) - 2.5(0.118) + 0.118] + 8(r_{22} + 0.0076) \\ &= 0.110 + 8(r_{22} + 0.0076) \end{aligned}$$

Try $r_{22} = 0.0080$

$$T_{22} = 630.3$$

$$f_{22} = 0.2345$$

$$r_{22} = 0.0104(1 - 0.2345) = 0.0080 \quad \text{Check}$$

$m = 4, n = 1$:

$$T_{42} = \frac{500 + 1.2(618.6)}{2.2} = 565$$

$$r_{42} = 0.0043(1 - f_{42})$$

$$\begin{aligned} f_{42} &= 0.0341 + 0.5[1.25(0.108) - 2.25(0.0341) + 0.108] + 8(r_{42} + 0.00367) \\ &= 0.080 + 8[0.0043(1 - f_{42}) + 0.00367] = 0.114 \end{aligned}$$

$$r_{42} = 0.0043(1 - 0.114) = 0.0038$$

Note that the substitution $f_{61} = f_{31} = 0.108$ has been made in accordance with the suggestion made earlier in this section.

The solution is continued in this manner through $n = 5$, with the results shown in Table 8-6 and Fig. 8-19. The average value of the conversion at each cross section is obtained by graphical integration of

$$(f_n)_{\text{av}} = \frac{1}{\pi r^2} \int 2\pi r f dr$$

Beyond $n = 5$, the present calculations yield irregular results, particularly near the center where the value of $f_{0,n} - f_{1,n}$ is large. This is due at least in part to the limiting

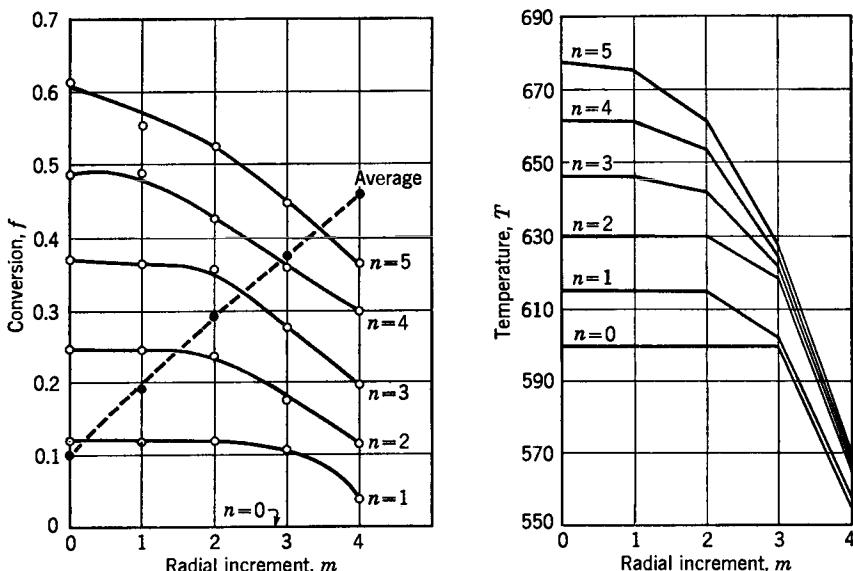


FIG. 8-19. Conversion and temperature gradients in a packed reactor (Illustration 8-9). Average is plotted against $n - 1$.

equality, Eq. 8-62. Improved results will be obtained when smaller increments are used near the center.

This illustration brings out the considerable effect that the presence of particles can have on a reaction, apart from any catalytic effect they may possess. When side reactions occur, severe temperature gradients may result in loss of main product. If the catalyst is sensitive to temperature, development of locally high temperatures can result in damage. When temperature gradients can be harmful, the reactor may be constructed of a number of small-diameter tubes, all within a shell and in contact with a heat-transfer medium—an expensive construction, of course, but there is no easy way out.

TABLE 8-6. RESULTS FOR ILLUSTRATION 8-9

n	m					Average over cross section
	0	1	2	3	4	
Temperature T						
0	600	600	600	600	555	
1	614.7	614.7	614.7	601.5	556	
2	630.1	630.2	630.3	619.0	565	
3	646.1	646.2	642.7	621.9	567	
4	662.2	662.4	653.8	623.5	567	
5	677.5	674.8	661.5	626.9	570	
Conversion f						
0	0	0	0	0	0	0
1	0.118	0.118	0.118	0.108	0.034	0.097
2	0.242	0.242	0.234	0.174	0.114	0.191
3	0.369	0.362	0.355	0.277	0.197	0.292
4	0.483	0.487	0.427	0.359	0.300	0.374
5	0.611	0.552	0.527	0.448	0.364	0.459
Reaction rate r						
0	0.0071	0.0071	0.0071	0.0071	0.0038	
1	0.0076	0.0076	0.0076	0.0064	0.0037	
2	0.0079	0.0079	0.0080	0.0074	0.0038	
3	0.0080	0.0081	0.0079	0.0068	0.0035	
4	0.0080	0.0079	0.0080	0.0062	0.0031	
5	0.0071	0.0080	0.0073	0.0055	0.0029	

59. Fluidized-bed-reactor Design

The nature of the fluidized bed implies a high degree of mixing and thus the elimination of various gradients. However, in practice the entire range from complete mixing to true plug flow can exist, depending prima-

rily on the dimensions of the bed. Besides lending the fluidized reactor some undesirable characteristics, these possibilities make the transition from pilot to commercial scale quite uncertain. Some of the pertinent work will be discussed.

Solids mixing. In small-diameter beds the solids can be observed to follow a circulatory path, and in large beds this circulation is even more pronounced. The existence of rapid circulation can be ascertained readily by starting with two layers of different-colored solids, which quickly result in a uniform mixture upon fluidization. Bart (14) injected tracer solid consisting of solid impregnated with sodium chloride halfway up a fluidized bed and analyzed samples from top to bottom. Stemmerding (205) determined the rate of mixing by applying heat at the top of a fluidized bed. Solids mixing depends on the vessel diameter and gas velocity, varying directly with the velocity and with the square of the diameter. Quite complete mixing has been observed in tubes as small as 1 in. in diameter. Solids-mixing patterns were investigated with radioisotope tracers in several commercial catalytic cracking reactors and regenerators (Singer, Todd, and Guinn, 201) with the conclusion that nearly complete mixing exists on this scale.

Gas mixing. Backmixing of gas was found to be very low in tubes 1 and 3 in. in diameter and bed depths of 3.3 to 6 ft (Gilliland and Mason, 76). Data of Stemmerding (205) show that the degree of mixing increases rapidly with tube diameter. Thus the eddy diffusivity of the gas, which is a measure of the rate of mixing, in 6-in. tubes is 10 times that in 3-in. tubes and 20 times that in 1-in. tubes. Several reports have been made on the performance of large commercial catalytic-cracking regenerators 40 ft in diameter and 15 ft or more in bed depth. Askins, Hinds, and Kunreuther (7) analyzed gas compositions sampled throughout and above the bed and observed that the gas was completely mixed. Later investigators injected helium tracer gas below the bed. Danckwerts, Jenkins, and Place (54) analyzed only the effluent gas. Handlos, Kunstman, and Schissler (84) analyzed samples from various portions of the bed and concluded that in the dense fluidized phase, where the reaction takes place, complete mixing was obtained. This paper also showed that the opposite conclusion of Danckwerts could be reinterpreted to signify complete mixing in the dense phase.

Temperature gradients. In most pilot plants and all commercial units, substantially uniform temperatures have been found. Calculations by Reman (187) have been made of the time needed for complete spreading throughout the bed of heat suddenly released at one end of a fluidized bed 1 m high, with the results shown in Table 8-7.

Effect of mixing on chemical reactions. The effect of gas mixing on the conversion or the residence time for a required conversion has been investigated mathematically by Gilliland and Mason (76) and Danckwerts

(53). Experimental results on the gasification of carbon by carbon dioxide in a laboratory reactor have been interpreted satisfactorily on the assumption of no backmixing (Lewis, Gilliland, and McBride, 141). The effect of the degree of backmixing on the kinetics of the oxidation of nitric oxide has been observed (Gilliland, Mason, and Oliver, 77). Figure 8-20 compares the residence times for complete conversion in nonmixed and

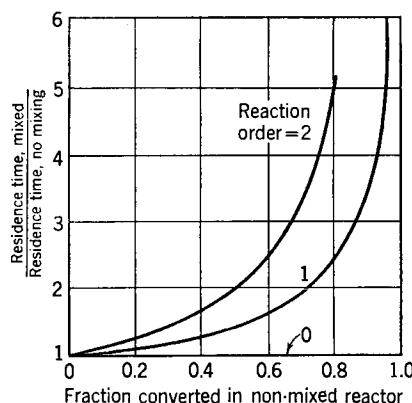


FIG. 8-20. Effect of backmixing of gas on reaction rates in a fluidized reactor. [Reman (187). Courtesy *Chemistry and Industry*.]

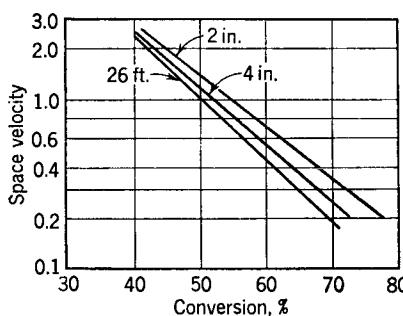


FIG. 8-21. Effect of backmixing on conversion in catalytic crackers of various diameters. [Reman (187). Courtesy *Chemistry and Industry*.]

completely mixed fluidized reactors. Figure 8-21 compares the conversions in reactors of different diameters. Clearly, the deleterious effect of gas mixing can be serious. Where a concentration gradient is desirable, a multitubular reactor can be used, which is made up of tubes 3 or 4 in. in diameter, each supplied with fluidizing gas and with the bed level above the tops of the tubes for convenience of overflow. Multistage reactors may also be employed. For example, calcination of limestone is conducted in a five-stage reactor (Fig. 11-26), of which one is a reaction stage and the others are for heat recovery.

TABLE 8-7. TIME, SEC, FOR COMPLETE SPREADING OF HEAT SUDDENLY APPLIED TO ONE END OF A FLUIDIZED BED 1 M DEEP*

Gas velocity, m/sec	Tube diameter, in.		
	1.25	4	6
0.1	270	22	10
0.3	95	7	3
0.6	50	3	1.5

* Reman (187).

Other factors. Internal diffusional resistance is probably not appreciable because of the smallness of the particles (but see the discussion following Illustration 8-8). Also, the high degree of solids movement suggests that diffusion to the external surface of the particles may not be a factor. Thus the reaction of methane with copper oxide was not appreciably affected by gaseous diffusion (Lewis, Gilliland, and Reed, 143). On the other hand, data on the regeneration of cracking catalysts in laboratory units have been correlated in terms of both diffusion and surface-reaction mechanisms (Pansing, 176). This work is discussed in Illustration 8-10.

Design basis. From the admittedly incomplete data now available, the following may be regarded as the characteristics of a fluidized-bed reactor:

1. Uniform temperature
2. Uniform solids composition
3. In the gas phase, little backmixing in small-diameter beds, but virtually complete mixing in large-diameter beds
4. Internal diffusional resistance generally negligible
5. Usually negligible resistance to diffusion to the external surface

Besides the kinetic aspects, the design of a fluidized-bed reactor must be concerned with the dynamics of fluidization. Particle sizes, residence times, and fluidization velocities are very intimately interconnected. An example of such a design may be presented now.

Illustration 8-10. A catalyst on which carbon has been deposited during a hydrocarbon cracking operation is regenerated by burning with air. The over-all regeneration rate is determined by the rates of the surface reaction and of diffusion of oxygen to the particle surface (Pansing, 176). Thus

$$r = k_r C_r p_i = k_d (p - p_i) \quad \text{lb moles/(hr)(lb catalyst)(atm)}$$

where C_r = weight fraction of carbon on regenerated catalyst

p = partial pressure, atm, of oxygen in gas

p_i = partial pressure of oxygen at interface

Experimental results for the coefficients are

$$k_d = \frac{G^2}{146 D_p^{1.5}}$$

$$\log k_r = 10.3000 - \frac{14,280}{T}$$

where D_p is the particle size in microns and T is in degrees Rankine. The equation for k_r applies only to a catalyst with average particle size $D_p = 44.5 \mu$. Observe that C_r is *not* the instantaneous carbon concentration but the terminal value, the implication being that complete mixing of the particles occurs.

As a numerical example, spent catalyst with 1.6 per cent carbon is to be regenerated to a carbon content of 0.2 wt %. Catalyst enters at 900°F and may not be heated above 1050°F. Regenerating gas enters at 100°F and 45 psig. The specific heats of solid and gas are 0.25; heat of combustion of carbon is 14,000 Btu/lb. Properties of the gas may be assumed the same as those of air.

Appropriate relations are desired between oxygen contents of inlet and outlet gases, flow rates, and the depth of the fluidized bed.

Solution. To ensure suitable regeneration, assume that 20 per cent excess air will be used. *Basis:* 100 lb/hr of regenerated catalyst.

$$\rho = 0.103 \text{ lb/cu ft at 60 psia and } 1050^\circ\text{F}$$

$$\mu = 0.106 \text{ lb/(ft)(hr)}$$

$$D_p = 44.5\mu = 0.000146 \text{ ft}$$

$$\text{Carbon burned} = 99.8 \left(\frac{0.016}{0.984} \right) - 0.2 = 1.42 \text{ lb/hr, or } 0.118 \text{ lb mole/hr}$$

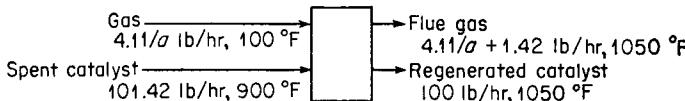
$$\text{Oxygen supplied} = 1.2(0.118) = 0.142 \text{ lb mole/hr}$$

$$\text{Heat of reaction} = 1.42(14,000) = 19,900 \text{ Btu/hr}$$

Let a = mole fraction of oxygen in the inlet gas. The total inlet gas is

$$\frac{0.142(29)}{a} = \frac{4.11}{a} \text{ lb/hr}$$

Summarizing the various streams on the sketch,



The heat balance is

$$101.42(900 - 100)(0.25) + 19,900 = \left(\frac{4.11}{a} + 1.42 \right) (1050 - 100)(0.25) + 100(1050 - 100)(0.25)$$

whence $a = 0.0417$.

$$\text{Total inlet gas} = \frac{4.11}{0.0417} = 98.5 \text{ lb/hr}$$

From Eq. 8-36,

$$G_{mf} = \frac{138,000(0.000146)^{1.82} [0.103(160 - 0.103)]^{0.94}}{(0.106)^{0.88}}$$

$$= 1.96 \text{ lb/(hr)(sq ft)}$$

Let $G = 10G_{mf} = 19.6 \text{ lb/(hr)(sq ft)}$. From Fig. 8-12, the bed-expansion ratio is $N_f = 1.17$, and from Fig. 8-7 the porosity is $\epsilon_{mf} = 0.58$. Accordingly,

$$\epsilon = 1 - \frac{1 - \epsilon_{mf}}{N_f} = 1 - \frac{0.42}{1.17} = 0.64$$

$$\rho_B = (1 - 0.64)(160) = 58 \text{ lb/cu ft}$$

$$k_d = \frac{(19.6)^2}{146(44.5)^{1.5}} = 0.0086$$

$$k_r = \log^{-1} \left(10.3000 - \frac{14,280}{1,510} \right) = 7.1$$

Let $F = \text{lb/hr of inlet gas} = 98.5 \text{ lb/hr}$

w = catalyst holdup in reactor, lb

n = lb moles oxygen/lb inlet gas = $n_{ao}p/\pi$

Upon elimination of p_i from the two rate equations,

$$r = \frac{p}{1/k_d + 1/k_r C_r} = \frac{\pi n}{n_{ao}(1/k_d + 1/k_r C_r)}$$

Accordingly,

$$\begin{aligned} \frac{w}{F} &= - \int \frac{dn}{r} = - \frac{n_{10}}{\pi} \left(\frac{1}{k_d} + \frac{1}{k_r C_r} \right) \int \frac{dn}{n} = \frac{n_{10}}{\pi} \left(\frac{1}{k_d} + \frac{1}{k_r C_r} \right) \ln \frac{n_0}{n} \\ &= \frac{1}{29(4)} \left[\frac{1}{0.0086} + \frac{1}{7.1(0.002)} \right] \ln 6 = 2.9 \\ w &= 2.9F = 2.9(98.5) = 286 \text{ lb} \end{aligned}$$

$$\text{Reactor cross section } A = \frac{F}{G} = \frac{98.5}{19.6} = 5.0 \text{ sq ft}$$

$$\text{Bed depth} = \frac{w}{\rho_B A} = \frac{286}{58(5.0)} = 0.99 \text{ ft}$$

Commercial bed depths range up to 15 ft or so. Pansing (176) states that his data do not apply accurately to commercial reactors, possibly because of nonuniform distribution of the gas and because of the complete mixing of the gas in large equipment.

PROBLEMS

8-1. It is desired to carry out a certain reaction with a magnetite catalyst at a space velocity of 125 cu ft gas/(cu ft catalyst)(hr). Sphericity of the particles is 0.58, and the density is 275 lb/cu ft. The reactor is 6 in. in diameter and 12 in. high. Consideration of the kinetics of the reaction shows that the smallest possible particle is desirable, but pressure drop must be limited to 1 psi. Gas viscosity is 0.0435 lb/(ft)(hr), and no change need be considered in the density of the gas as it flows through the bed. Find the smallest allowable particle size (Leva, 138).

8-2. Air is blown at the rate of 1,000 lb/hr through a reactor consisting of ten 2.5-in.-diameter by 10-ft-long pipes in parallel. The pipes are packed with moderately smooth cylinders 0.74 in. in diameter by 0.74 in. long. A 2-ft length of 2.5-in. pipe is just filled with 191 of these cylinders. Average air temperature is 197°F, and the inlet pressure is 5 psig. What is the pressure drop (Leva, 138)?

8-3. Will fluidization occur when air flows at the rate of 35.2 lb/(hr)(sq ft) through a bed of sandy material in a vessel 4 in. in diameter?

Sand:

Density 166 lb/cu ft
 Size 100-150 mesh, or 0.0004-ft-diameter average
 Sphericity 0.77

Air:

Temperature 70°F
 Outlet pressure 14.7 psia

8-4. Water is passed upward through a column of glass spheres. Find the velocity needed to expand the column, given these conditions:

$$\begin{aligned} D_p &= 0.205 \text{ in.} \\ \rho_p &= 146.5 \text{ lb/cu ft} \\ \rho &= 62.4 \text{ lb/cu ft} \\ \mu &= 2.42 \text{ lb/(ft)(hr)} \\ \epsilon &= 0.382 \end{aligned}$$

Observe that the flow may be turbulent.

8-5. Design conditions for a fluidized-bed operation with particles of Fischer-Tropsch catalyst are as follows:

Vessel diameter.....	2 ft
Amount of solids (at rest).....	3.33 cu ft
Flow rate.....	1,438 lb/(hr)(sq ft)
Particle density.....	312 lb/cu ft
Particle sphericity.....	0.58
Gas viscosity.....	0.062 lb/(hr)(ft)
Gas density, inlet.....	0.902 lb/cu ft
Gas density, outlet.....	1.031 lb/cu ft

Determine the following:

(a) The largest particle size that may be present for a condition of minimum fluidization.

(b) Assuming that the average particle diameter is 0.6 times the maximum found in part a, find the expansion ratio of the bed and the fluidization efficiency (Leva, 138).

8-6. Steam was superheated in a pebble heater (Batchelder and Ingols, 16). The vessel diameter was 33 in. (Fig. 11-20). In one test, saturated steam at 5 psig entered the heating zone at 1,785 lb/hr and left at 1815°F. Pebbles entered countercurrently at 3,570 lb/hr and 1980°F and left at 455°F.

The pebbles were alumina spheres, 0.375 in. in diameter, bulk density 127 lb/cu ft, true density 226.5 lb/cu ft, and a voids percentage of 46.0. Calculate the coefficient of heat transfer between steam and pebble surface, and compare with that calculated from Eq. 8-47.

8-7. Lime has been calcined in a three-compartment fluidized reactor (Lenhart and Rockwood, 133). The design rate was 8.5 tons/24 hr of limestone that has been ground to -6, +80 mesh, or a mean particle diameter of 0.02 in. A sketch of the equipment with some of the operating conditions indicated is in Fig. 8-22.

Reaction-zone temperature is maintained at 1700°F and 18 psia, using methane fuel as the source of heat. Combustion air cools the finished lime in the bottom compartment; the top compartment serves to preheat the entering limestone.

Because of the great particle surface and the high rate of heat transfer, temperatures may be assumed uniform in each compartment and equal for the solid and gas exit streams. Measurements of reaction rates have been made (Slonim, 203) under conditions such that the reverse reaction was negligible, with the discovery that the reaction is first-order:

$$r = \frac{df}{dt} = k(1 - f)$$

where f is the fractional conversion. Over the range from fine powder to 5-mm grains,

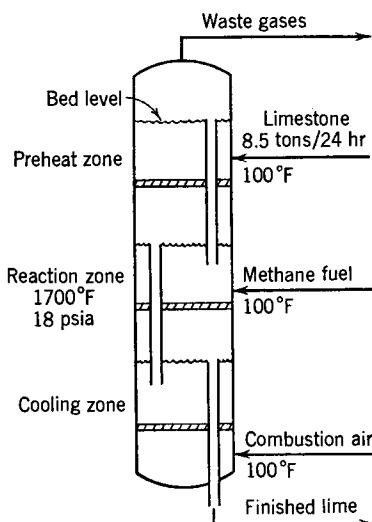


FIG. 8-22. Fluidized-bed calcination of limestone (Prob. 8-7).

the rate was independent of particle size. Specific reaction rates and equilibrium pressures are:

T , °F.....	1700	1600	1500	1400	1300	1200
k , sec ⁻¹	0.38	0.16	0.06	0.02	0.006	0.0017
p , atm.....	1.55	0.68	0.27	0.095	0.031	0.0095

Conversion of 99 per cent is desired. Establish the basic features of the design, such as the residence time of the limestone in the middle compartment, amount of fuel, amount of excess air, and the exit temperatures. For simplicity, neglect heat losses to the surroundings.

If practical, assume the fluidizing rate in the reaction zone to result in approximately 25 per cent bed expansion. A solution by successive approximation will be required. For instance, the exit temperatures can be assumed, then the heat balance made, the amount of fuel calculated, and the minimum fluidizing rate established to a first approximation. The assumed temperatures will then need to be checked.

8-8. Drying of air by a fluidized bed of silica gel was studied in a column 4 ft square (Cox, 50). The particles had an average size of 0.145 in., corresponding to an external surface of 280 sq ft/cu ft. The mass-transfer coefficient depended on the depth of bed, but in the range of depths from 0.5 to 1.0 ft its value was

$$k_g a = 7.5 \text{ lb}/(\text{sec})(\text{cu ft})(\text{lb water/cu ft of air})$$

The vapor pressure p_b of adsorbed water was related to the vapor pressure p^* of pure water by

$$p_b = 1.635 w p^*$$

where w is the moisture content, pounds per pound, of the gel. In shallow fluidized beds, the compositions of the gas and solid phases are substantially uniform.

In a particular case, air at 80°F and atmospheric pressure and 90 per cent humidity is to be dried in a three-stage fluidized-bed unit, each bed depth being 1 ft. Air velocity is 8 fps, sufficient for proper fluidization. Initially the silica gel is completely free of water. Calculate the countercurrent circulation ratio of dry silica gel to dry air needed for removal of 95 per cent of the water from the air. The bed temperature may be taken as 100°F, the rise being due to heat of adsorption.

8-9. Solve Illustration 8-10 with the same gas flow rate, oxygen concentration, and temperature, but:

- (a) Take $G = 5G_{mf}$.
- (b) Take $G = 10G_{mf}$ and carbon content of regenerated catalyst = 0.02 wt %.
- (c) Assume that the flows of catalyst and gas are parallel-current and that both phases are in pistonlike flow, that is, with no backmixing. Accordingly, C_R is a variable in the rate equation.

CHAPTER 9

HETEROGENEOUS CATALYSIS

60. Solid Catalysis

Catalysis of fluid-phase reactions by solids, called heterogeneous, or contact, catalysis, has been touched on in Chap. 7. The purpose of the present chapter is to discuss in more detail the terminology of this field, the properties and preparation of catalysts, and the relations between the natures of catalysts and the reactions they influence.

Several effects may be produced by a catalyst:

1. Increase in the rate of a reaction
2. Directing the reaction toward a particular product
3. Elimination of undesired side reactions
4. Initiation of a new reaction

Examples of some of these effects are illustrated by the data of this chapter.

The chemical nature of a substance determines whether or not it is potentially a catalyst; its physical properties govern its effectiveness and serviceability. These properties include the surface area, porosity, pore diameter, particle diameter, structural strength, heat capacity, thermal conductivity, and stability under reaction conditions.

Given proper chemical nature, high rate of reaction accompanies large specific surface, which may be due to small particle diameter or high porosity or both. The pore size controls the accessibility of the internal surface through its effect on diffusion rate. Only infrequently are industrial catalysts pure substances. The principal component is mixed with other substances of varying catalytic activity to improve its effectiveness or serviceability. Mixing may result in some of these improvements:

1. Increase of available surface
2. Stabilization against crystal growth and sintering
3. Creation of a favorable orientation of surface molecules
4. Improvement of mechanical strength

Thus Table 9-1 shows the increase in surface resulting from small amounts of additives and also an increase in activity without increase in surface. Figure 9-1 shows the effects of several additives on the catalytic activity of iron for ammonia synthesis. Figure 9-2 illustrates selectivity.

An additive which has no catalytic properties of its own but which enhances the activity of a catalyst is called a promoter. Other substances

in small amount which reduce the activity are called poisons; usually these are not added deliberately to the catalyst but are unavoidably deposited on it during the reaction process. Accelerators are substances which can be added to a reacting system to maintain the activity of the catalyst by nullifying poisoning or other means. Substances added during

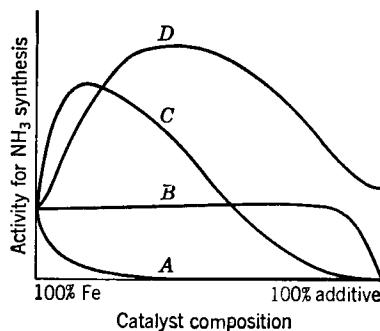


FIG. 9-1. Effect of additives on catalytic activity of iron for ammonia synthesis. (A) $\text{Fe} + \text{S}$ (poisoning); (B) $\text{Fe} + \text{quartz}$ (support); (C) $\text{Fe} + \text{Al}_2\text{O}_3$ (promotion); (D) $\text{Fe} + \text{Mo}$ (superadditivity of catalyst activities). [Mittasch (160).]

manufacture to reduce the activity are called inhibitors; they may be of value where the chief property of the catalyst is selectivity rather than improvement of the rate.

Promoters are the goal of much current research in catalysis. These additives, in amounts of usually a few per cent only, may act in several ways:

TABLE 9-1. SURFACE AREAS AND ACTIVITIES OF IRON CATALYSTS FOR AMMONIA SYNTHESIS*

Composition	Surface, sq m/g	Activity, % NH_3 , at 842°F, 100 atm, SV = 5,000
Fe_3O_4 unreduced.....	0.02	
Fe (0.15% Al_2O_3 impurity).....	0.55	3.3
Fe + 1.07% K_2O	0.56	
Fe + 1.03% Al_2O_3	9.44	
Fe + 10.2% Al_2O_3	11.03	8.2
Fe + 1.3% Al_2O_3 + 1.59% K_2O	4.04	12.3

* Frankenburg (70).

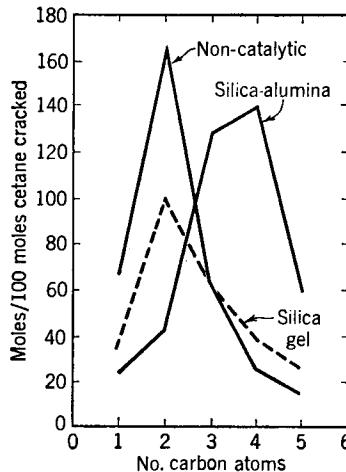


FIG. 9-2. Product distribution from cracking of cetane. [Gladrow, Krebs, and Kimberlin (78).]

1. Loss of surface during usage may be inhibited by increase of thermal stability. For example, the promoter may form a solid solution with the catalyst and raise the melting point, thus obviating sintering.
2. When a reaction consists of two steps and the catalyst accelerates only one of them, the promoter may accelerate the slow step and thus improve the over-all kinetics.
3. On one theory active centers on the surface are believed to be associated with defects in the crystal lattice. If their molecules are slightly different in size from those of the catalyst, promoters may substitute into the lattice and cause distortion. A very small amount of such an additive can have a very large effect on the number of lattice defects and consequently on the catalyst activity. Much direct evidence exists for this view.
4. An additive may act by increasing the amount of boundary surface between crystals. When this interstitial material has an improved catalytic effect over that of the bulk, promotion is achieved.
5. When more than one reaction is possible, the promoter may be able to poison the part of the surface which favors the undesirable reaction.

Accelerators may be diluents which shift the equilibrium composition in a favorable direction or afford better temperature control, or they may counteract coking or poisoning, or they may improve selectivity by poisoning undesired side reactions.

Poisons act most frequently by adsorbing on the catalyst surface and thus masking off the active centers. Simple deposition of inert material on the catalyst surface may occur, blocking off the pores and making the inner surface inaccessible. Some poisons cause sintering of the surface. Other poisons counteract the selectivity of the catalyst, presumably by adsorbing preferentially on the portion of the surface which catalyzes the desired reaction.

Carriers serve principally as a framework on which the catalyst is deposited, usually substances of adequate mechanical strength but with no catalytic effects of their own in a particular application. Apart from their main function, however, carriers may possess other virtues, such as:

1. They may be highly porous, thus increasing the effective catalyst surface by spreading out the catalyst in a thin film.
2. They may improve stability by keeping the catalyst crystals sufficiently far apart to prevent their fusing together.
3. Actual chemical interaction with the catalyst may result in an improved catalyst.
4. The increase in active surface may reduce sensitivity to poisons.
5. Heat capacity of the carrier is often sufficient to dissipate heat and prevent local overheating, which might cause sintering.

Substances used as carriers may be classified as follows:

1. Low area; nonporous; large particle size, 0 to 1 sq m/g. Examples are alundum, ground glass, Fiberglas, mullite, and silicon carbide. They are used only with highly active catalysts.
2. Low area; porous; large particle size; large pores. Porosity 20 to 65 per cent, 4 to 8 mesh and larger, 0.1 sq m/g. Examples are alumina, carborundum, pumice, periclase, and porous and sintered metals. Used when small surface is adequate and mechanical strength is required.
3. High area; nonporous; small particle size, 0.1 to 10 μ , 2 to 20 sq m/g. Examples are asbestos and pigments such as carbon black, kaolin, iron oxide, titania, and zinc oxide.
4. High area; porous; small particle size; small pores. Porosity 20 to 65 per cent, 5 to 50 μ , 50 to 1,000 sq m/g. Examples are activated carbons, dry gels, bentonite, bauxite, skeletal alumina, and magnesia. This class is used to obtain the highest activity for the catalyst.

61. Some Physical Properties of Solid Catalysts

Both the kinetics and the hydrodynamics of reactions are influenced by the physical properties of individual catalyst particles, chiefly the diameter, specific surface, porosity, and pore diameter. These properties are correlatable with the catalytic activity, and elaborate methods have been devised for their measurement. Table 9-2 shows some of these properties of typical catalysts.

Catalyst activity for a particular reaction is measured by comparing the product yield with that obtained by a reference catalyst under standardized conditions or by comparing the space velocities needed to achieve the same conversion with both. As an example, the activity of a cracking catalyst is measured by the American Cyanamid Company (2) under these standardized conditions:

Volume of catalyst.....	25 ml
Temperature of activity furnace.....	938-941°F
Space velocity.....	4 vol/(hr)(vol catalyst)
Process time.....	2 hr

A mid-continent-blend gas oil is used as the cracking stock. The conversion is taken as the weight of gas plus the gasoline with 400°F end point on the ASTM distillation. The activity is defined as the ratio of the reciprocals of the space velocities needed to obtain the same conversion with the test catalyst and with the standard.

Particle size and size distribution above 74 μ or 200 mesh are measured by screening and below this size by elutriation or sedimentation. The surface average diameter corresponding to the average of the reciprocals of the diameters is generally meant when speaking of the average. Fluidized-

bed processes employ particles in the range 20 to 300 μ . Both fixed- and moving-bed operations are restricted by pressure-drop limitations to much larger sizes; 4 to 8 mesh is common, but the range may be $\frac{1}{16}$ to $\frac{3}{4}$ in. Slurry processes often employ powders of 200 mesh or so, the limitation being the filterability of the slurry after the reaction is complete. Many catalysts are preformed, as cylinders, rings, spheres, and granules, as well as irregular shapes.

Particle surface. Specific surfaces of practical catalysts cover a wide range, from less than 1 to as much as 1,000 sq m/g (500 to 500,000 sq ft/lb). Great specific surface is achieved by small diameter or high porosity. Most of the surface is internal; thus, for comparison with the data of Table 9-2 where the average diameters are probably well over 100 μ , the

TABLE 9-2. PROPERTIES OF SOME CATALYSTS*

Catalyst	Surface, sq m/g	Pore volume, ml/g	Pore radius, A
Activated carbon.....	500-1500	0.6-0.8	10-20
Silica gel.....	200-600	0.4	15-100
$\text{SiO}_2\text{-Al}_2\text{O}_3$ cracking catalyst.....	200-500	0.2-0.7	33-150
Activated clays.....	150-225	0.4-0.52	100
Activated alumina.....	175	0.39	45
Kieselguhr.....	4.2	1.14	11,000
Fe for ammonia synthesis.....	4-11	0.12	200-1,000
Porous plate (Coors 760).....	1.6	0.17	2,150
Pumice.....	0.38	0	
Fused-copper catalyst.....	0.23	0	
Solid spheres, 5- μ diameter.....	1.0	0	

* Wheeler (235).

external surface of 5- μ spheres is about 1 sq m/g. Fine particles are difficult to handle, requiring low flow rates for reasons of pressure drop or entrainment. On the other hand, the great internal surface is not always available because of the low rate of diffusion in small-diameter pores. Consequently, the amount of surface is not a measure of catalyst activity unless other properties do not change as the surface is changed (Table 9-1).

Amount of catalyst surface is measured by physical adsorption. Usually the adsorbate is nitrogen near its atmospheric boiling point (-195.8°C). The techniques and equations developed by Brunauer, Emmett, and Teller [for example, see Emmett (61)] are most widely employed for this purpose. The amount of adsorption is obtained as a function of partial pressure up to 600 or 800 mm Hg. The method detects the amount required to form a unimolecular layer; an independent

equation provides the surface covered by a single molecule. The BET equation is cited in Prob. 7-1.

Internal porosity is most accurately measured by the helium-mercury method. Total dead space in a bed of particles is measured by the amount of helium that can be pumped into an evacuated space of known volume containing a known mass of particles. After the helium is pumped out, mercury is pumped in. Since mercury will not penetrate the pores at atmospheric pressure, the internal porosity can be calculated. The total porosity of a bed of catalyst particles may be 75 per cent or more and that of the particles themselves, 50 per cent.

Pore sizes of common catalysts range from 10 to 200 Å in diameter. Accessibility of the internal surface depends on the pore diameter and the operating conditions. The over-all rate of reaction on the catalyst surface is determined by the net rate of diffusion into the pores and the chemical-reaction rate. For a porous sphere under steady-state conditions, when the rate equation is $r_c = kC^n$ per unit of surface, a material balance on a differential spherical shell of radius r follows:

$$\text{Input by diffusion} = -4\pi r^2 D \frac{dC}{dr} \quad (9-1)$$

$$\text{Output by diffusion} = - \left[4\pi r^2 D \frac{dC}{dr} + d \left(4\pi r^2 D \frac{dC}{dr} \right) \right] \quad (9-2)$$

$$\text{Output by reaction} = r_c dS = kC^n (4\pi r^2 \rho_p S_p dr) \quad (9-3)$$

Equating and simplifying,

$$\frac{d}{dr} \left(r^2 \frac{dC}{dr} \right) = \frac{\rho_p S_p r^2 k}{D} C^n \quad (9-4)$$

$$\text{or} \quad \frac{d^2C}{dr^2} + \frac{2}{r} \frac{dC}{dr} = \frac{\rho_p S_p k}{D} C^n \quad (9-5)$$

where S_p = specific surface of particle

D = diffusivity

r_c = over-all rate of reaction expressed per unit of surface

For a first-order reaction, the solution of Eq. 9-5 is presented by Wheeler (235). Figure 9-3 illustrates the availability of internal surface for several first-order reactions as a function of the rate of diffusion and the over-all rate of reaction. The form of the abscissa derives from the solution of the differential equation. The ordinate is often called the effectiveness factor, being the ratio of the effective catalyst surface to the surface that would be available if there were no diffusional resistance. As another example, an investigation of silica-alumina cracking catalyst, 4 to 5 mesh, was able to achieve effectiveness factors ranging from 0.55 to 0.98 by varying the pore diameter (Johnson, Kreger, and Erickson, 113).

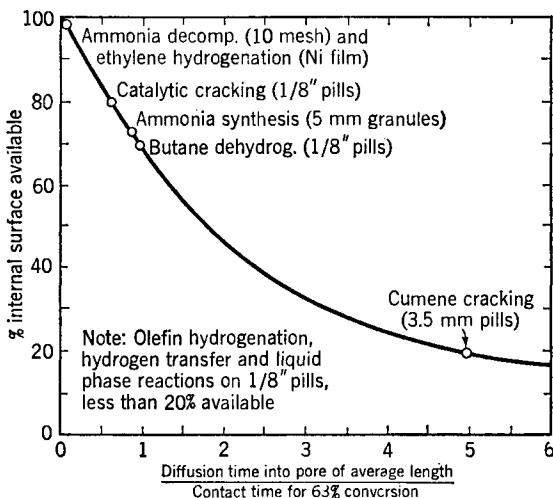


FIG. 9-3. Dependence of fraction of internal surface available on diffusion and reaction rates. [Wheeler (235).]

Pore size is controlled during the manufacturing process. Thus, in the preparation of silica gel, use of 1 *N* HCl treating solution results in pores 10 Å in diameter, whereas 1 per cent NH₄Cl results in pores three times that size.

Two principal methods are employed for accurate measurement of the pore size:

1. Measurement of the total amount of adsorption, as in the BET method, and taking into account the fact that the vapor pressure over a concave meniscus in a capillary is less than that of the bulk liquid and is a function of the pore diameter.

2. The mercury-porosimeter method, in which mercury is forced into the pores at high pressures. The pressure required to force mercury into a pore is inversely proportional to the radius, a pore of 100 Å requiring a pressure of 10,000 psi. These measurements and the whole subject of pore size are treated comprehensively by Wheeler (235).

62. Principles of Selection of Catalysts

The ultimate goal of research in catalysis is to develop a rational method of selecting the best catalyst for a specific reaction. It appears certain that the catalyst always participates in the reaction, forming more or less stable intermediates which react further in some way or decompose directly into the end products. Accordingly, the search for a new catalyst may begin with substances that reasonably can be expected to interact with the reactants, but it should not end with such substances because the

study of catalysis is full of surprises and the interaction may be subtle and transitory.

To a certain extent, it is known what general chemical class of catalyst is needed for a particular case. However, catalyst members of the same class are strongly individualistic and may differ greatly in activity, selectivity, resistance to degradation, and cost. (Consult the figures and tables in this chapter.) Even small differences in these properties can mean great sums of money on the commercial scale. To achieve the goal completely, knowledge is required of the exact nature of the chemical interaction with the catalyst and of the properties of the intermediate. Both inductive and deductive methods will have to be employed. A start has been made by classifying the many thousands of observations in the literature: (1) by types of chemical reactions, with their catalysts, and (2) by catalysts, with the reactions they influence (Berkman, Morrell, and Egloff, 19; Innes, 107; Oblad, 171). A brief rundown according to these classifications will be given now.

Types of catalysts. *Strong acids* are able to donate protons to a reactant and to take them back. In this class fall the common acids, aluminum halides, and boron trifluoride. Also acid in nature are silica-alumina, gamma-alumina, silica-magnesia, silica-zirconia, and related compounds, though how this acidity arises is controversial. These reactions involve a carbonium-ion complex formed by the donation of a proton by the catalyst to a free-electron pair in the organic reactant. Depending on the operating conditions, the carbonium complex can react to accomplish alkylation, cracking, cyclization, hydrogen transfer, isomerization, polymerization, or otherwise.

Base catalysis involves the transfer of a proton to the catalyst from the reactant. An example is the polymerization of butadiene by sodium and sodamide. Little work has been done with this class of catalysts.

Metal oxides, sulfides, and hydrides form a transition between acid-base catalysts and metals; thus they catalyze hydrogenation-dehydrogenation as well as many of the reactions catalyzed by acids, such as cracking and isomerization. The oxidation activity of the oxides is related to the presence of two valence states which allow oxygen to be released and reabsorbed alternately. Because of the great variety of reactions catalyzed by this group, little progress has been made in classification or in establishing mechanisms.

Metals. The principal industrial metallic catalysts are found in periodic group VIII and are thus transition elements having almost full or completed 3d, 4d, and 5d electron orbits. According to one theory, electrons from adsorbed molecules can fill the vacancies in the incomplete shells and thus make a chemical bond. What happens subsequently will depend on the operating conditions. The detailed chemical mechanisms of

metal-catalyzed reactions such as ammonia synthesis and hydrogen reductions are still speculative.

Types of reactions. *Halogenation and dehalogenation.* Effective catalysts exist in more than one valence state and are able to accept and donate halogens freely. Gas-phase-reaction catalysts of this type are silver and copper halides deposited on carriers such as silica gel; liquid-phase-reaction catalysts include ferric chloride as the most common one.

Hydration and dehydration. All catalysts of this class have a strong affinity for water. Alumina is the principal one. Also used are phosphoric acid or its acid salts on carriers, silica-alumina gel, and silica gel with tantala, zirconia, or hafnia.

Dehydration and dehydrogenation combined. Catalysts most suitable are primarily dehydration agents combined with mild dehydrogenation agents. Included in this class are phosphoric acid, silica-magnesia, silica-alumina, alumina derived from aluminum chloride, and various metal oxides.

Hydrogenation and dehydrogenation. These catalysts form unstable surface hydrides. Transition-group and bordering metals such as Ni, Fe, Co, and Pt are suitable, as well as transition-group oxides or sulfides. This is an extremely important group of reactions, including ammonia and methanol syntheses, the Fischer-Tropsch, oxo and synthol processes, and the production of alcohols, aldehydes, ketones, amines, and edible oils.

Isotope exchange between compounds is of importance in studying reaction mechanisms. For hydrogen-isotope transfer, Ni, Fe, Pt, and various oxides are effective, including ZnO , $SiO_2-Al_2O_3$, and Cr_2O_3 . Some of these are also catalysts for oxygen- and nitrogen-isotope exchange.

Oxidation catalysts are able to give and take back oxygen, by reason of being able to exist in several oxidation states. These metals and their oxides are effective: Va, Pt, Ag, Cu, Ni, and Mn.

Unclassified. This group contains some reactions whose mechanisms are not well understood. Innes (107) has summarized the most important ones in a four-page table, according to the principal reaction products.

63. Preparation of Catalysts

The manufacture of some catalysts is conducted on a large scale commercially by companies specializing in such work. It is a process requiring special techniques and much care because of the dangers of poisoning by small amounts of impurities. Many catalysts are made to the special formulation and order of the user, and some may be obtained only through licensors of certain processes, but many are available on the open market,

particularly for the well-established and widely practiced processes. Some of the catalysts thus available are listed in Table 9-3.

TABLE 9-3. SOME COMMERCIALLY AVAILABLE CATALYSTS

American Cyanamid Company:

NR-2. For gas re-forming by methane steam process; 20% NiO, 0.15% Na₂O, 0.5% SO₃ on carrier; 18 sq m/g; cylinders, $\frac{1}{2}$ by $\frac{1}{2}$ in.; life, 4-5 years; typical VHSV = 200, 1540°F, 1 atm

HI-3. For water-gas shift reaction; 95% Fe₂O₃, 4% Cr₂O₃, 0.2% SO₃; cylinders, 0.27 in. in diameter, 0.5 in. long; life, 7 years; typical VHSV = 600, 850°F

FM-1. For ammonia synthesis; 64.6% Fe₂O₃, 31.0% FeO, 1.4% K₂O, 2.5% Al₂O₃, 0.5% SiO₂; irregular granules from fusion process, 96% through 10-mm, 4% through 4-mm openings; life, 7 years

MS-1. Fluid hydroforming; 10% MoO₃; surface, 250 sq m/g; pore volume, 0.28 cu cm/g; 98% through 100 mesh, 60% through 200 mesh; 12% attrition in 40 hr; typical WHSV = 1.0 lb/(hr)(lb catalyst) at 950°F, 250 psig

Baker Platinum Division, Engelhard Industries, Inc.:

Platinum-group metals for oxidation, hydrogenation, dehydrogenation, and dehalogenation:

1. 5% Pt, Pd, Ru, or Rd on powdered charcoal, activated alumina, or calcium carbonate

2. Granular and pelleted: 0.3% Pt on $\frac{1}{8}$ -in. activated alumina; 1.0% Pt on 4-8-mesh coconut charcoal; 0.3% Pt on silica gel

3. Others: colloidal, 0.5 g Pd/liter; 90-10% Pt-Rh gauze; platinum black

Davison Chemical Company:

Code 902. For oxidation of naphthalene; 10% V₂O₅, 33% K₂SO₄, 55% silica; powder, 85% through 100 mesh and 45% through 200 mesh, also pellets $\frac{1}{8}$ by $\frac{1}{8}$ in.; typical VHSV = 1,400, 850°F, for naphthalene oxidation

Code 904. For making vinyl chloride from acetylene and HCl; 4-10-mesh activated carbon (91%) impregnated with mercuric chloride (9%)

The Girdler Company:

G-15. Hydrogenation; Ni electrolytically precipitated on kieselguhr; 27% Ni, 9% kieselguhr, 64% hardened soya flakes; granules 100% through 6 mesh

G-8. Desulfurization, for conversion of alkyl mercaptans to H₂S in presence of hydrocarbons; copper- and chromium-promoted iron; $\frac{1}{8}$ -in. tablets; typical VHSV = 400-1,000 at 550-800°F

Preparation of the active chemical agent, conferring on it a suitable structural form, and activation—these are the usual steps in the manufacture of a catalyst. Individual pure chemicals are comparatively rarely employed as solid catalysts. Some substances like activated alumina and silica gel have suitable combinations of activity, surface, structural strength, and cost per pound, and a few like the platinum metals or silver are so active in particular applications that they are adequate in small amount without admixture. However, many active substances are either too expensive to be employed in bulk or cannot be prepared as a porous

structure of suitable strength and extended surface, so they are mixed with carriers or supports. In such an instance the active material is distributed over the entire surface of the carrier as a thin film, only a comparatively small amount of active material being required. For example, platinum deposited to the extent of 0.5 wt % on alumina or silica or carbon can have an exposed surface in excess of 100 sq m/g of carrier plus catalyst.

Shapes in which catalysts are prepared include powders, granules, pellets, cylinders, rings, and spheres. In some instances carrier and catalyst are mixed as powders and then formed into these shapes, and in other instances the carriers are preformed and the active material is subsequently deposited on the carrier surface, according to one of the following methods:

1. Impregnation involves soaking the carrier with a solution of some salt of the catalyst, then drying it and converting it into the active form. This simple method has one disadvantage in that migration of the salt to the external surface takes place during the drying, thus leaving some of the internal surface uncovered.

2. Precipitation also involves soaking the carrier with a solution but employs a chemical agent to deposit the catalyst on the surface.

3. Coprecipitation of both carrier and catalyst from solution may be used, followed by shaping and drying.

4. Wet mixing of the two components in a slurry may be followed by shaping and drying.

5. Spraying or sprinkling onto the external surface is satisfactory when a nonporous carrier is used.

6. Electroplating, vapor or liquid adsorption, and deposition of catalyst on the carrier surface by decomposition of some substance are other techniques sometimes employed.

Occasionally rather specialized procedures are necessary. For example, Raney nickel is prepared by leaching the aluminum out of a 50-50 Al-Ni alloy with 20 per cent caustic. Some clay catalysts are made by leaching the natural product with sulfuric acid, which takes out some of the alumina and other materials. Some metal catalysts are evaporated onto a glass support. Very active metal catalysts can be utilized in the form of foil or wire mesh.

Activation of catalyst surfaces is a necessary step in the original manufacturing process as well as periodically during use. This operation may remove adsorbed or otherwise deposited foreign materials, or it may change the physical or chemical nature in some way. Surface irregularities, projections, and strains in the crystals are all conducive to increased activity; so their formation is encouraged.

The activation procedure varies from case to case. Sometimes moder-

ate heating is sufficient to drive off adsorbed poisons. Calcination is frequently necessary, at temperatures somewhat above those to be used in process, but with care exercised to avoid sintering. The surface may be treated with chemicals to dissolve off undesirable substances or to change the chemical nature. Metal catalysts are often prepared in reducing atmospheres, in the presence of hydrogen, which thus serves as the activating agent. Other catalysts must be treated with oxygen or hydrogen sulfide or carbon monoxide or chlorinated hydrocarbons. Thus cobalt molybdate catalyst is reactivated by burning deposited coke off the surface and then reducing in a hydrogen-rich atmosphere. Some platinum catalysts for naphtha re-forming are subjected to successive oxidizing and reducing atmospheres and are treated with chlorine compounds. Heating followed by rapid chilling may sometimes induce strains that will improve the activity. Reactivation of a catalyst rendered inactive because of deposits on the surface sometimes may be accomplished by attrition in a tumbling barrel.

When a catalyst is subject to poisoning during use, a major factor in its serviceability is reactivation, preferably during process but if need be periodically in place or in separate equipment. If possible, of course, it is preferable to avoid poisoning by some change in operation. A fine example of this is the naphtha-re-forming process for making high-octane gasoline. As in all hydrocarbon processes at elevated temperatures, carbon deposition tends to occur; however, this is prevented by employing a large recycle of hydrogen, from 3 to 10 moles of hydrogen per mole of naphtha. Though hydrogen is unfavorable to the chemical equilibrium, the process on the whole is extremely successful and has virtually crowded out regenerative-type fluidized-bed and moving-bed processes with its simple fixed-bed units. Some re-forming processes reactivate at intervals of several days or weeks (Table 9-4).

Several descriptions may now be given of catalyst-making procedures, both industrial and laboratory types. Comparatively few industrial processes are described in the literature. A symposium on the preparation of catalysts in the laboratory has been published (209). Reference may also be made to Ciapetta and Plank (45) and Komarewsky, Riesz, and Morritz (122).

Fischer-Tropsch catalyst for the original process was in the proportions 100Co:5ThO₂:10MgO. The manufacture is described by Storch, Golumbic, and Anderson (206) and is depicted in Fig. 9-4. A solution of nitrates (4 per cent Co) in the proper proportions is mixed with an equal volume of 10 per cent sodium carbonate at 100°C and with kieselguhr (twice the weight of Co present). The slurry is filtered and washed, then reslurried with fine powder from the screening plant, and refiltered. The filter cake

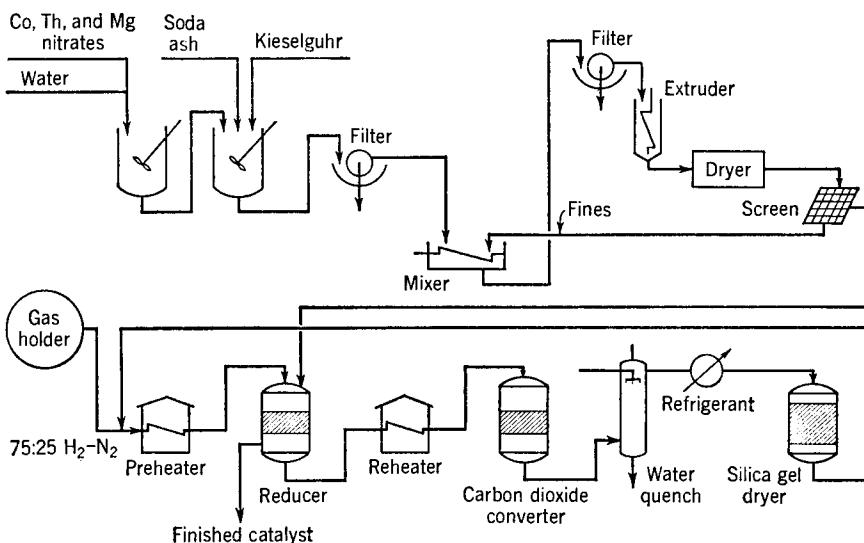


FIG. 9-4. Commercial production of Fischer-Tropsch catalyst in German plants.

is extruded through holes 3 mm in diameter, dried for 2 hr, and screened. Granules 1 to 3 mm in diameter are placed in the reducer and subjected to a stream of 75:25 hydrogen-nitrogen at a space velocity of 10,000 vol/(hr) (vol) and a bed temperature of about 400°C for 50 min. Carbon dioxide

TABLE 9-4. OPERATING AND REGENERATION CYCLE OF NAPHTHA-RE-FORMING PROCESS USING PLATINUM CATALYST IN A FIXED BED

Operation	Time required, min
1. Reaction.....	4,800
2. Hydrogen-rich recycle gas purge.....	25
3. Depressur.....	10
4. Low-pressure inert-gas purge.....	45
5. Repressur with inert gas.....	20
6. Regeneration, first phase.....	600
7. Reheat.....	90
8. Regeneration, second phase.....	260
9. High-pressure inert-gas purge and cool.....	40
10. Depressur.....	10
11. Repressur with inert gas.....	20
12. Depressur.....	10
13. Low-pressure inert-gas purge.....	45
14. Hydrogen-rich purge and repressur.....	25
Total.....	6,000

present in the effluent gas is converted to methane by passage through "shift" catalyst in the converter; the gas is then dried and recirculated through the preheater. The reduced catalyst is cooled by purging with nitrogen and with carbon dioxide, then discharged into a special container for transport to the synthesis plant.

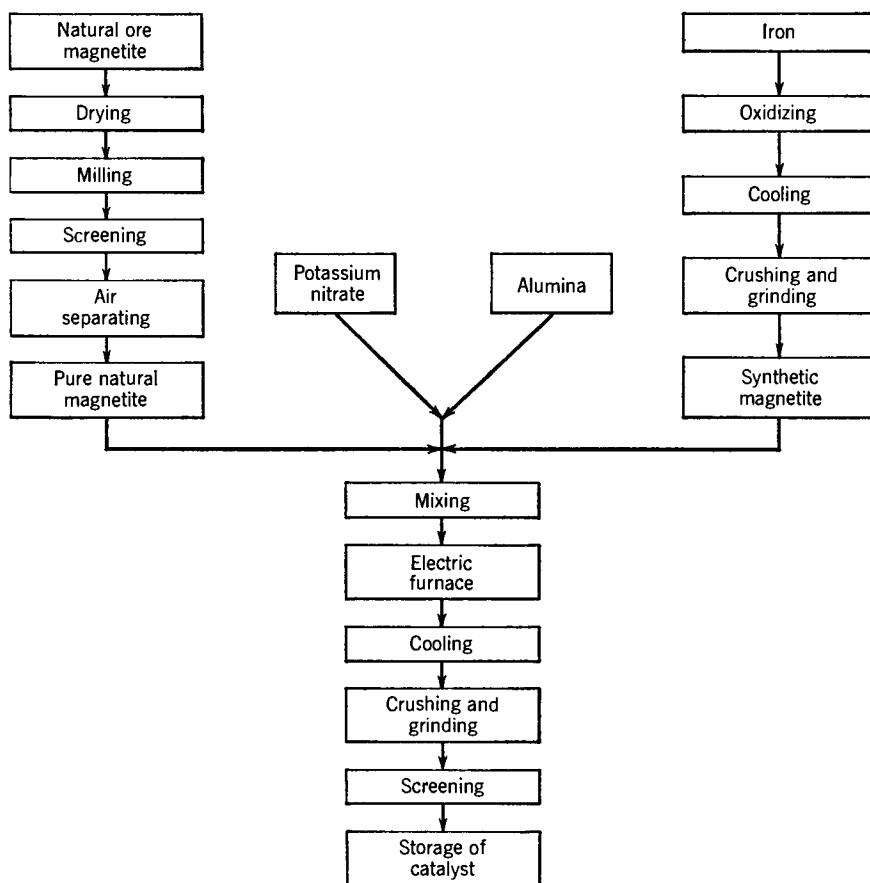


FIG. 9-5. Ammonia-synthesis-catalyst manufacture by the TVA process.

Ammonia synthesis catalyst of iron promoted by potassium and aluminum oxides is described by Bridger, Pole, Beinlich, and Thompson (34). Block flow sketch (Fig. 9-5) shows the manufacturing process. Synthetic magnetite is made by burning high-purity iron in oxygen. With some natural magnetite this is fused with ingot iron, potassium nitrate, alu-

minum oxide, and recycled catalyst fines, in an electric furnace. The fused product is crushed and screened to 3 to 6 mesh. The reference article has a detailed description of the process and plant.

Water-gas conversion catalyst manufacture is described by Bridger, Gernes, and Thompson (33) and is depicted by block flow sketch (Fig. 9-6).

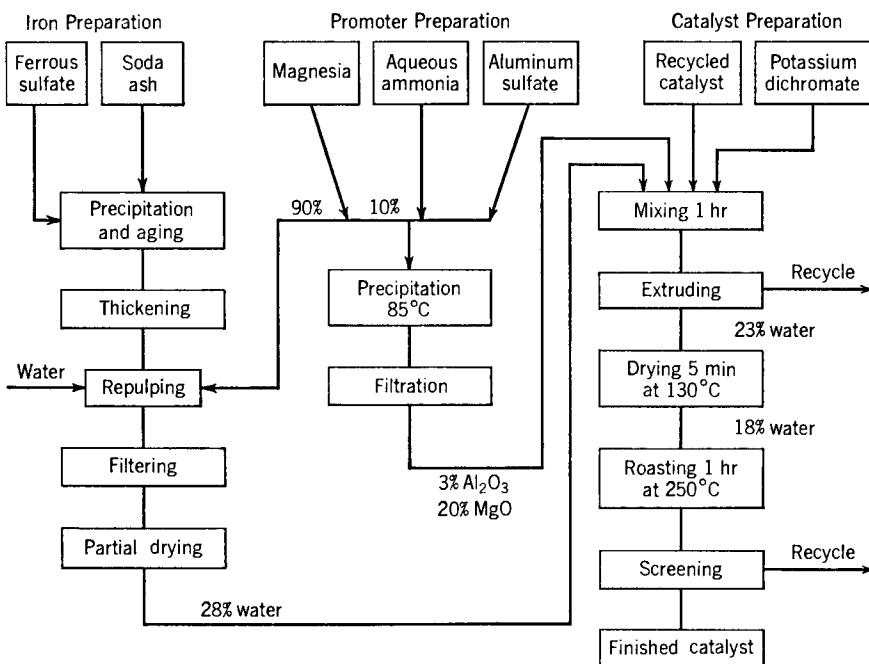


FIG. 9-6. Manufacture of water-gas conversion catalyst by the TVA method.

This is an iron-base catalyst for promoting the reaction $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$. These steps are involved:

1. Precipitation of ferrous carbonate by addition of soda ash solution to ferrous sulfate solution
2. Washing the precipitate by multiple decantation and repulping
3. Addition of magnesium oxide to the thickened precipitate just before filtration
4. Mixing the partially dried filter cake with potassium dichromate and freshly precipitated aluminum hydroxide containing some magnesium hydroxide as filter aid
5. Extruding the mixture into $\frac{5}{16}$ -in. rods and cutting them to $\frac{1}{2}$ -in. lengths
6. Drying the pellets, then roasting them for 0.5 to 1 hr at 250°C . The

reference article, a product of TVA, contains a detailed flowsheet, plant layout, and detailed descriptions.

Synthetic-bead cracking catalyst for gasoline production is described in *Chemical & Metallurgical Engineering* (4). Solutions of sodium silicate and aluminum sulfate are mixed and sprayed into a layer of oil where they form beads. These beads are treated with hot water to set the structure, base-exchanged to replace the sodium with aluminum, washed to remove soluble salts, then dried. Subsequently they are maintained for a time at high temperature to relieve the stresses caused by the drying operation. Figure 9-7 is a simplified flow sketch.

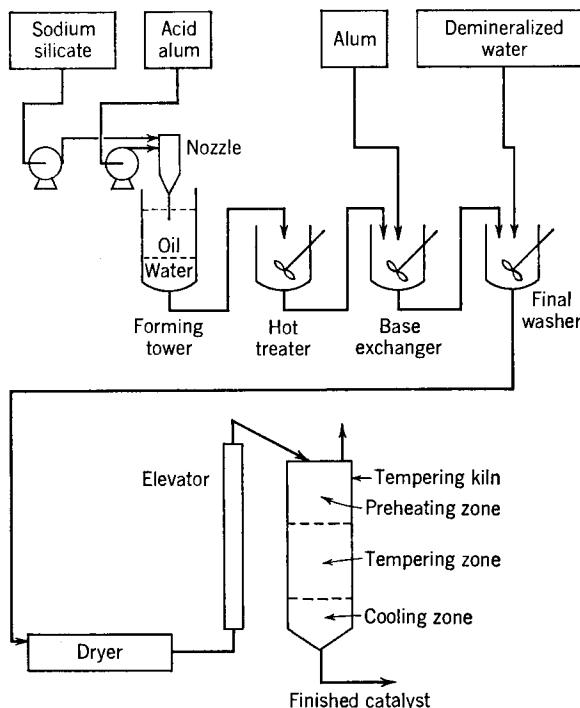


FIG. 9-7. Manufacture of synthetic-bead cracking catalyst.

Microspheroidal cracking catalyst manufacture is described in *Chemical Engineering* (5). Figure 9-8 is a simplified flow sketch. A hydrogel is made by mixing dilute solutions of sodium silicate and sulfuric acid. After impregnation with aluminum sulfate solution, alumina is precipitated in the gel by addition of aqueous ammonia. The slurry is thickened by filtering, then pumped at 5,000 psi through spray nozzles into a spray tower 50 ft high, where the droplets are dried countercurrently to hot

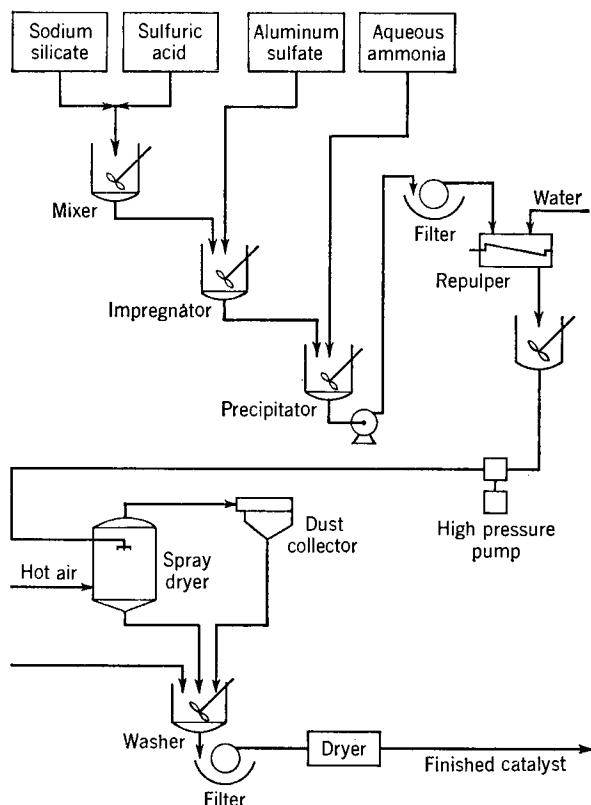


FIG. 9-8. Manufacture of microspheroidal cracking catalyst.

gases. The dried material is washed to remove soluble salts, filtered, and finally dried in rotary equipment.

64. Industrial Catalytic Processes

The search for catalysts or improved catalysts seems to be a never-ending one, since even small reductions in operating temperature or pressure or small differences in yields or product distribution can have great economic importance on the commercial scale. The general properties of catalysts have already been discussed, as well as some of the principles that have been established thus far as a guide for the selection of catalysts for specific chemical reactions. However, the successful catalyst is still a work of art—though the guidance by scientific principles is of increasing value—and much of the inspiration must come from an examination of what has been done practically.

In the succeeding pages, many industrially important catalytic processes are described. Catalyst compositions, operating temperatures and

pressures, and kinetic equations, or contact times or space velocities, are given when available. Though space velocities can vary greatly with the age and small variations in the composition of the catalyst and with the desired over-all yields and conversions per pass, the data cited do provide an estimate of the order of magnitude of reactor sizes for certain processes. The space velocities given are volumetric hourly space velocities (VHSV), that is, gas volumes measured at standard temperature and pressure per hour per volume of catalyst bed, or weight hourly space velocities (WHSV), pounds of charge per hour per pound of catalyst.

Further details about many of the processes mentioned in this chapter may be found in general works of reference such as Ullmann (220), Kirk and Othmer (121), Groggins (82), and Winnacker-Weingaertner (237). Valuable brief summaries with flowsheets appear in *Petroleum Refiner* (6).

Only a comparatively few inorganic processes deliberately employ catalysts, though these few are extremely important, as the examples will show. On the other hand, the opportunities for catalysts in the organic field are so vast as to delight the most enterprising or to dismay the timid. For comparison with the examples of catalytic processes that will be described shortly, some of the major organics that are *not* made catalytically may be listed: acetic and other acids by oxidation of hydrocarbons; acetylene, ethylene, and other olefins by thermal cracking; chloroparaffins, ethanolamines, nitroparaffins; ethylene and propylene oxides by the chlorohydrin process; phenol by sulfonation and monochlorobenzene-caustic processes; and urea.

Special mention is made of processes for the manufacture and upgrading of motor gasoline. This industry is by far the largest user of catalysts and has been the inspiration for much of the progress in the development of catalysts and the techniques of their manufacture and use.

Inorganic chemicals. *Ammonia from nitrogen and hydrogen.* Haber developed the physical chemistry, Mittasch discovered the catalyst, and Bosch built the equipment, all in the early 1900s. Mittasch tested 20,000 mixtures for their catalytic value, finally some Swedish magnetite that was essentially the same composition as the catalysts used today—iron promoted with small amounts of alumina and potassia. The history and technology of ammonia synthesis are well documented (Bokhoven et al., 27; Comings, 47; Frankenburg, 70; Hein, 86; Nielsen, 169; Shearon and Thompson, 198a; Thompson, Guillameron, and Updegraff, 215).

The original process, largely practiced today, operates at 200 to 250 atm, 1020°F, VHSV 35,000 to 45,000, catalyst life of 2 to 5 years. A Haber-Bosch reactor containing 2 tons of catalyst has an output of 18 tons ammonia/24 hr, with a contact time of about 20 sec. The Claude reactor operates at 1,000 atm, yield of 144 lb ammonia/(24 hr) (lb catalyst), contact time of about 40 sec. A catalyst made from the de-

composition of aluminum ferrocyanide permits operation at 100 atm and 750 to 800°F (Mont-Cenis process).

Data relating to catalysts for ammonia synthesis are shown in Figs. 9-1 and 9-9 and in Table 9-1. Preparation of a suitable catalyst is described in Sec. 63 (Fig. 9-5). In addition to the principal reaction, ammonia synthesis requires a catalyst for the removal of CO from the synthesis gas. This is accomplished by the so-called "shift reaction," $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$, under the influence of an iron oxide catalyst whose manufacture is described in Sec. 63 (Fig. 9-6).

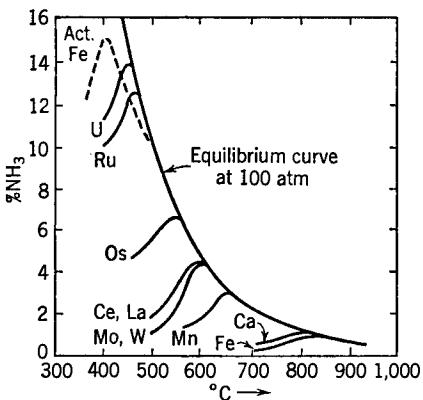


FIG. 9-9. Activity of ammonia-synthesis catalysts at 100 atm and equal space velocities. [Kröger (125). Courtesy Vandenhoeck and Ruprecht, Göttingen, Germany.]

rate equation has been mentioned in Sec. 45 and Prob. 7-9.

Chlorine by oxidation of HCl. In the old Deacon process, the catalyst was 1 per cent copper chloride deposited on clay carriers. Fixed-bed reactors at 900°F have been employed, but some interest has been expressed recently in a fluidized-bed operation. A molten potassium and iron chloride catalyst at 850°F has been employed recently at the I.G. Oppau plant.

Hydrogen. Nickel activated by alumina or Ni-ThO₂ mixtures deposited on activated carbon catalyze the formation of hydrogen and carbon monoxide from methane and water at 1600°F in fixed-bed units. Iron oxide promoted with chromium oxide catalyzes the formation of more hydrogen from the carbon monoxide and water.

Hydrogen cyanide is made by the oxidation of a mixture of ammonia and methane, catalyzed by a platinum-rhodium gauze at 1800°F, at atmospheric pressure, with a linear gas velocity through the gauze of 3 fps. A more recent process employs a platinum-ruthenium catalyst and uses no air but supplies the needed heat for this highly endothermic reaction by external heating; the temperature is about 2000°F.

Hydrogen sulfide oxidation yields elemental sulfur. Catalysts are moist iron hydroxide or activated carbon which are effective at room temperature; without a catalyst, temperatures above 750°F are needed. Some new plants use an activated bauxite with high iron content, VHSV 1,000

to 2,000, and 500 to 750°F (Sawyer, Hader, Herndon, and Morningstar, 193).

Nitric acid is made principally by the oxidation of ammonia under the catalytic influence of 90 to 10 platinum-rhodium, in the form of about 20 layers of 80-mesh screen made of wires 0.003 in. thick. This screen has a metal surface of 1.5 sq ft/sq ft. A mixture of iron and bismuth oxides in a granular bed is also employed as a catalyst. A platinum converter operated at 100 psig needs 105 oz of alloy for a daily production of 55 tons of 100 per cent HNO_3 . After initial ignition, the reaction is adiabatic and is maintained at 1620 to 1670°F by suitable preheat of the charge. Under these conditions the reaction time is about 0.0001 sec, but at atmospheric pressure 0.01 to 0.02 sec is needed. Oxygen is adsorbed on the surface of the catalyst and reacts with ammonia that subsequently diffuses to the surface. The diffusion rate of ammonia controls the over-all rate (Oele, 173).

Sulfuric acid. Oxides of nitrogen catalyze the oxidation of sulfur dioxide in the chamber process. The mechanism involves the formation of nitrososulfuric acid, which reacts with water to form sulfuric acid and to regenerate nitrogen oxides. The bulk of the reaction takes place in the chambers, of which there are many kinds, providing varying degrees of cooling and gas mixing, both of which make for improved performance. Several types of reactors are compared in Table 9-5 and Fig. 11-17.

The contact process employs solid catalysts, either platinum (5 to 10 wt %) deposited on asbestos or preferably vanadium pentoxide promoted by an alkali and deposited on a carrier of pumice or kieselguhr. These catalysts are compared with an iron catalyst in Fig. 9-10. Oxidation is

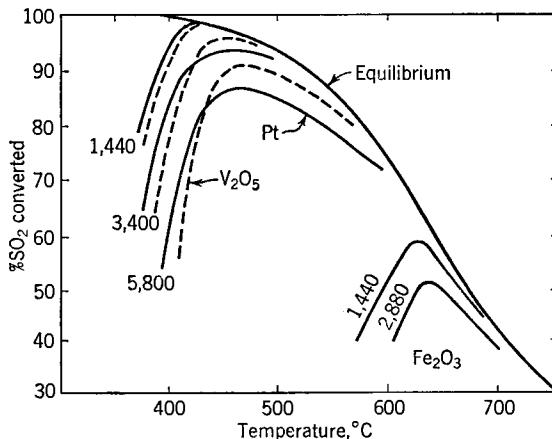


FIG. 9-10. Effectiveness of catalysts for oxidation of SO_2 . Inlet gas composition 7 per cent SO_2 , 10 per cent O_2 , 83 per cent N_2 . Space velocity in units volume per hour per volume. [Ost-Rassow (175). Courtesy Johann Ambrosius Barth, Munich.]

generally carried out in two or more stages, of successively lower temperatures, to take advantage of high reaction rate at high temperatures and high equilibrium conversion at lower temperatures. Platinum is effective at 780 to 790°F, whereas the vanadium pentoxide requires 70 to 90°F more. A Chemical Construction Company plant making 17 tons/day of 100 per cent acid has about 3,000 lb, or 100 cu ft, of vanadium pentoxide catalyst. Contact time is less than 2 sec. The catalyst may be on perforated trays or packed in tubes.

TABLE 9-5. COMPARISON OF REACTORS FOR SULFURIC ACID BY THE CHAMBER PROCESS

Type of reactor	Production of 60°Be acid, lb/(cu ft)(24 hr)
Original lead chamber.....	0.2-0.3
Gaillard-Parrish chamber.....	1.2-1.6
Mills-Packard chamber.....	1.1-1.4
Petersen (packed) tower.....	3.8-8.2

Kinetics on vanadium pentoxide catalyst has been abundantly investigated. Eklund (58) carried out extensive experimental work and proposed the rate equation

$$r = k \sqrt{\frac{p_{SO_2}}{p_{SO_3}}} \left[p_{O_2} - \left(\frac{p_{SO_3}}{K p_{SO_2}} \right)^2 \right]$$

The equilibrium constant and the specific reaction rates for three catalysts of different particle sizes are shown in Fig. 9-11. The fact that the specific

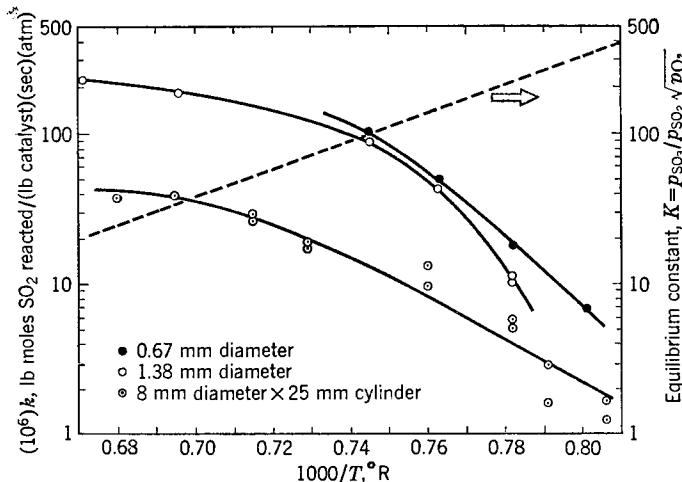


FIG. 9-11. Specific reaction rates for sulfur dioxide oxidation with vanadium oxide catalyst. [Data of Eklund (58).]

reaction rate does not increase as rapidly with temperature as predicted by the Arrhenius equation indicates that diffusion rate influences the overall rate of reaction. This equation cannot be extrapolated to 0 per cent SO_3 , where in any event diffusion would undoubtedly limit the rate; Eklund suggests that the rate below 5 per cent conversion of SO_2 be taken constant at the rate for 5 per cent conversion.

Some general classes of organic reactions. *Esterification* is the process of substituting an alkyl or aryl group for the ionizable H of an organic acid. The process is catalyzed by hydrogen ion. Strong acids and salts of strong acids with weak bases are used. Zinc chloride enhances the catalytic effect of acids. Other catalysts include boron and silicon fluorides; aluminum, ferric, and magnesium chlorides; and metals in the finely divided state, especially popular because readily separable from the product.

Fermentation is the carrying out of chemical transformations under the catalytic influence of enzymes which are nitrogenous organic materials produced by living organisms (bacteria, molds, and yeasts). They are of colloidal nature, molecular weights up to 300,000. Their catalytic action is highly specific, strongly influenced by the pH and the temperature, and sensitive to promotion or inhibition by many substances. The optimum temperatures for most enzymes lie between 65 and 100°F. Enzymes are named according to their functions, the ending *-ase* being applied to denote the function. Thus hydrolytic catalysts are termed hydrolases, and oxidation-reduction enzymes are oxydases.

Halogenation. Catalytic agents most frequently employed for chlorinations are metallic iron, cupric oxide, bromine, sulfur, iodine; the halides of iron, antimony, tin, arsenic, phosphorus, aluminum, and copper; vegetable and animal carbons and activated bauxite and other clays. Most of these catalysts are halogen carriers. Thus Fe, Sb, and P are able to exist in two-valence states as halogen compounds; in the presence of free chlorine they alternately accept and surrender the chlorine in an activated form. Similarly, iodine, bromine, and sulfur form unstable compounds with chlorine. Bromination catalysts are analogous to those for chlorination. For iodination, phosphorus is the principal accelerator. Fluorination needs no catalyst. Oxygen is an inhibitor for halogenation.

Hydrogenation catalysts are for the most part metal oxides and metals such as Fe, Ni, Co, and others. These substances have the property of adsorbing gaseous hydrogen and releasing it in nascent form. Mixtures of a catalyst and a promoter are used, typically Ni-alumina, Cu-ZnO, Cu-Cr₂O₃, and ZnO-Cr₂O₃. Very active catalysts may take the hydrogenation of oxygen compounds to the hydrocarbon stage; examples are Ni, Co, Fe, Mo, and W and their oxides and sulfides. A catalyst of the mild type may, for example, take an aldehyde only to the alcohol stage; Cu, ZnO, Cr₂O₃, Pt, Pd, V₂O₅, and manganese promoted with rare-earth

oxides are of this type. Mixtures of the mild type with alkaline materials effect condensations along with hydrogenation. The vigorous types in combination with catalysts such as alumina and thoria combine hydrogenation with splitting out of water. Metal-sulfide catalysts are so selective that they permit hydrogenation of certain polyolefins to olefins without affecting the latter or aromatics.

Nitration of aromatics with nitric acid is catalyzed by the HSO_4^- ion supplied by sulfuric acid. Silica gel catalyzes the vapor-phase nitration of benzene with NO_2 . The lower oxides of nitrogen catalyze nitration of benzene derivatives with nitrogen tetroxide. Nitration of paraffins does not require catalysis.

Oxidation catalysts alternately adsorb oxygen and release it in activated form. Primary oxides of metals serve as acceptors, not only in oxidations with elemental oxygen, but also with such oxidants as chromic, permanganic, and hypochloric acids as well as hydrogen peroxide. Some specific examples of catalysts are silver oxide for ethylene oxide from ethylene; silver or copper for formaldehyde from methanol; compounds of alkali metals, manganese, or aluminum for the oxidation of liquid hydrocarbons; vanadium and molybdenum oxides for phthalic anhydride from naphthalene; dissolved manganese naphthenate for fatty acids from high-molecular-weight hydrocarbons. Most oxidations occur at elevated temperatures.

Oxo process is the reaction between an olefin, hydrogen, and carbon monoxide to produce oxygenated compounds, largely aldehydes, which may be hydrogenated subsequently to alcohols. Temperatures are 300 to 400°F, pressures 150 to 300 atm, cobalt catalysts. The original process employed solid Fischer-Tropsch catalyst. The active agent is dicobalt octacarbonyl, $[\text{Co}(\text{Co})_4]_2$. In a fixed-bed unit with solid catalyst, liquid heptene may be charged at the liquid hourly space velocity of 0.4. A slurry process pumps liquid through the reactor at a space velocity of 1.3 to 3 and the gas at 250. The catalyst is 2.5 per cent cobalt naphthenate on a carrier. Order of magnitude of the liquid-phase specific reaction rate is $k = 0.02$ to 0.07 min^{-1} at 230°F and about 200 atm. Reviews of the oxo process have appeared recently (Wender, Sternberg, and Orchin, 234; Schroeder, Benson, and Field, 195).

Polymerization catalysts are classified as the radical type and the ionic type. A radical type dissociates into free radicals under the reaction conditions. Inorganic and organic peroxides are like this; benzoyl peroxide is perhaps the most widely used. Boron trifluoride and aluminum chloride are examples of the highly polar molecules which act as ionic catalysts. These strong dipoles are thought to disturb the electrical symmetry of the double bond of the monomer, causing chain formation. Inhibitors are employed to stop polymerization at any desired point. Examples are

sulfur and substances which contain quinoid, nitro, amino, or phenolic hydroxy groups. The kinetics of polymerization has been intensively studied (Hohenstein, 96; Küchler, 126). Fractional orders of reaction often occur.

Some organic chemicals. *Acetaldehyde* is made by the hydration of acetylene with water at 185°F and 0 psig, with a catalyst of aqueous mercuric sulfate containing sulfuric acid and ferric sulfate. The catalyst is regenerated with nitric acid and air. *Acetaldehyde* is also made by the air oxidation of ethanol at 1000°F, 5 to 10 psig, silver gauze catalyst.

Acrylonitrile is made from acetylene and hydrogen cyanide at 0 psig with a catalyst of aqueous cuprous chloride containing some hydrogen chloride and alkali chlorides and 36 wt % water. Yields are 1 to 1.5 lb/(hr)(cu ft of solution).

Aniline is made by the hydrogen reduction of nitrobenzene catalyzed by nickel sulfide supported on alumina, at 570°F. The catalyst is regenerated with air and reactivated with hydrogen.

Butadiene by the dehydrogenation of butane employs activated alumina impregnated with 18 to 20 per cent chromic oxide, 1125°F, 5 in. Hg absolute, VHSV 1 to 3. On-stream time is 8 to 10 min. Regeneration is with air.

Carbon bisulfide requires a silica gel catalyst for its formation from methane and sulfur, 1050 to 1150°F, 20 to 30 psig, VHSV 400 to 600.

Cumene is made from benzene and propylene at 335 to 435°F, 600 to 800 psig, liquid hourly space velocity 4 to 15, phosphoric acid on a carrier as catalyst.

Ethanol from ethylene and water employs phosphoric acid on diatomaceous earth, 570°F, 1,000 psig, VHSV 1,800.

Ethyl chloride formation from ethylene and hydrogen chloride at 100°F, 40 psig, uses aluminum chloride mixed with liquid organic chlorides as catalyst.

Ethylene oxide by the air oxidation of ethylene employs silver catalyst, 400 to 600°F, 100 to 300 psig, in either fixed or fluidized beds.

Formaldehyde is prepared by the oxidation of methanol. In the German I.G. process the catalyst is silver crystals ranging in diameter from 0.15 to 1.25 mm. The vapors flow over a bed of catalyst about 10 mm thick at 1110°F and 5 to 10 psig. Other processes use silver catalyst in the form of a gauze. Copper gauze was once used commercially. An iron-promoted molybdenum oxide catalyst permits operation at much lower temperatures, 660 to 840°F.

Glycerol is made from propylene and oxygen with acetone as a by-product. Several steps are involved. Propylene is oxidized to acrolein at 570 to 750°F, 1 to 10 atm, catalyst cuprous oxide supported on SiC. Isopropanol is made by the hydration of propylene with the aid of sulfuric

acid. The acrolein and isopropanol form allyl alcohol under the catalytic influence of uncalcined MgO mixed with some ZnO, at 750°F. Finally, glycerol is made by the reaction of water and allyl alcohol, catalyzed by 0.2 per cent pertungstic acid in 2 M aqueous hydrogen peroxide, at 140 to 160°F, 2 hr contact time.

Methanol is made from carbon dioxide and hydrogen at about 600°F and 200 atm, in equipment similar to that used for ammonia synthesis. Commercial catalysts are ZnO or CuO in admixture with a difficultly reducible oxide such as Cr₂O₃. The most active mixture of ZnO-Cr₂O₃ is in the proportion 70:30, but smaller concentrations of Cr₂O₃ provide greater selectivity. Space velocity VHSV is 10,000 to 25,000. The kinetics appears to be controlled by the trimolecular surface reaction, with rate equation

$$r = \frac{a_{\text{CO}}a_{\text{H}_2}^2 - a_{\text{CH}_3\text{OH}}/K}{(A + Ba_{\text{CO}} + Ca_{\text{H}_2} + Da_{\text{CH}_3\text{OH}})^3} \quad \text{lb moles/(hr)(lb catalyst)}$$

At 662°F, for example, the constants are $A = 94$, $B = 25$, $C = 0.4$, $D = 9.8$, and $K = 4.8(10^{-5})$. The activities are expressed in atmospheres (Natta, 166).

Methylamine from methanol and ammonia employs silica-alumina, 840 to 860°F, 200 to 250 psig.

Methyl mercaptan from methanol and hydrogen sulfide employs 5 to 12 per cent thoria in alumina, or cobalt thoria, 600 to 875°F, 125 to 225 psig.

Phenol production from cumene and air requires oxidation of the cumene emulsified in an alkaline aqueous solution, pH 8.5 to 10.5, 265°F, followed by decomposition of the resulting benzene peroxide in the presence of dilute sulfuric acid.

Phthalic anhydride is made by air oxidation of ortho-xylene or naphthalene. In the former case, vanadium pentoxide catalyst is used at 900 to 1150°F, 0.1 to 0.15 sec contact time. Newer catalysts for the oxidation of naphthalene contain 10 per cent V₂O₅, 20 to 30 per cent K₂SO₄, and the balance silica. A typical fixed-bed unit operates at 645 to 705°F, 7.5 psig, 4.2 sec contact time, and a space velocity of 0.07 lb/(hr)(lb catalyst). A fluidized-bed unit operates at 700°F, 15 psig, contact time of 19 sec, space velocity of 0.03 lb/(hr)(lb catalyst).

Polyethylene is made by several methods. Mass polymerization is conducted at 375°F, 1,500 atm, 100 to 200 ppm oxygen as catalyst. In another process, ethylene is dissolved in a hydrocarbon and slurried with a catalyst of Cr₂O₃ on a silica-alumina support, 200 to 300°F, 100 to 500 psig. The slurry contains about 5 per cent ethylene and 0.5 per cent catalyst. In the last method, ethylene is dissolved in a hydrocarbon along with a catalyst of aluminum triethyl plus titanium tetrachloride, 140 to 170°F, 100 psig.

Styrene by the dehydrogenation of ethylbenzene employs zinc oxide promoted by alumina or chromates, 2.6 lb steam/lb ethylbenzene to reduce the partial pressure, 1050 to 1170°F, 0 psig, catalyst life 9 months.

Trichloroethylene from acetylene and chlorine. The raw materials combine to tetrachloroethane by solution in a recycle stream of this material containing 0.1 wt % antimony trichloride or ferric chloride, 160 to 195°F, 0.5 psig. The tetrachloroethane is converted to trichloroethylene by the action of 10 per cent lime slurry at 160 to 215°F.

Vinyl acetate from acetylene and glacial acetic acid forms in the vapor phase, 350 to 400°F, 2 to 3 psig, VHSV 300 to 400, catalyst of activated carbon impregnated with 20 to 30 per cent zinc acetate.

Vinyl chloride from acetylene and hydrogen chloride is catalyzed by activated carbon impregnated with mercuric chloride, in a multitubular reactor, 200°F, 2 to 5 psig.

Gasoline manufacture and upgrading. *Alkylation* involves the reaction of isoparaffins, chiefly isobutane, with propylene, butene, and pentenes to make high-octane gasoline. The reaction is liquid-phase, catalyzed by either hydrogen fluoride or sulfuric acid. HF alkylation is conducted at 85 to 100°F; acid to hydrocarbon ratio 0.2:1; isobutane to olefin ratio of 7, maintained by recycle; acid concentration 85 to 95 per cent; and acid loss of 0.5 to 0.8 lb/bbl alkylate. Sulfuric acid alkylation takes place at 40 to 50°F, 40 psig, isobutane-to-olefin ratio of 10, acid concentration 90 to 100 per cent but preferably above 98 per cent, acid-phase volume of 60 to 70 per cent of the reaction mixture. Acid consumption is about 0.5 lb/gal alkylate, but depends markedly on the type of charge stock and the presence of small amounts of diolefins.

Cracking converts high-molecular-weight gas oils into gasoline. To a degree this can be accomplished without the aid of a catalyst, but the catalytic processes are superior. Commercial catalysts include natural clays, synthetic silica-alumina, and silica-magnesia. Promoters are usually incorporated. Operating conditions, nature of the feedstock, and the catalyst influence the yield and octane number of the gasoline and the by-product distribution.

In a fluidized bed, normal cracking conditions are in the range 880 to 980°F, 10 to 16 psig, WHSV 1 to 3 lb/(hr)(lb catalyst), and catalyst-circulation to oil-rate weight ratio of 8 to 12. The last figure is a measure of how long the catalyst is used before it needs regeneration. Regeneration conditions are 1050 to 1100°F and 8 to 10 psig and residence times of 20 to 40 sec. In a moving-bed unit operating conditions are about 840 to 920°F, 10 to 15 psig, space velocity 1 to 2.5 vol/(hr)(vol) and catalyst-to-oil ratio of 2 to 5. The kinetics of catalytic cracking is approximately first-order, like that of thermal cracking, particularly of the lighter fractions

(Fig. 9-12). In the gas-oil range when cracking to gasoline, the initial rate is first-order, but as the conversion increases the rate approaches second-order (Blanding, 25). Under commercial conditions, diffusion does not appear to affect the rate. Fine reviews of the subject have been prepared (Greensfelder, 81; Oblad, Milliken, and Mills, 172; Shankland, 198).

Fischer-Tropsch process synthesizes aliphatic hydrocarbons in the gasoline range and some oxygenated compounds from mixtures of hydrogen and carbon monoxide. Nickel, cobalt, and iron catalysts are used. Preparation of the standard German catalyst of several years ago is described in Sec. 63; it is used at 1 to 10 atm, 350 to 390°F, and VHSV 150. Iron catalysts made by hydrogen reduction of magnetite or mill scale and promoted with potassium oxide are effective in the range 400 to 500°F; at 500°F and 400 psig, a VHSV of 600 can be used. Allowable space velocities are almost directly proportional to the pressure. Iron catalysts were used in the dense-phase fluidized-bed operations at Brownsville, Texas, and are now used in the dilute-phase fluidized reactor in the South African plant. Fluid-bed operations employ temperatures of about 600°F, pressures of 20 to 30 atm, linear velocities of 1 fps in dense-phase units and 5 to 10 fps in dilute phase. Literature is fairly plentiful (Storch, Columbic, and Anderson, 206; Winnacker and Weingaertner, 240; Schroeder, Benson, and Field, 195).

TABLE 9-6. PERFORMANCE OF CRACKING CATALYSTS*

Components.....	Silica-alumina	Silica-magnesia	Silica-alumina-fluoride
Composition.....	90-10	73-27	88-10-1.8
BET surface, sq m/g.....	437	449	139
Pore volume, ml/g.....	0.421	0.592	0.384
Average pore diameter, Å.....	39	53	110
Activity, sec required to achieve 45% conversion of methyl-cyclohexane.....	1.0	5.6	24.5
Selectivity, mole % of various hydrocarbons in conversion product formed at 47-49.4% conversion of MCH:			
C ₁	7.9	35.3	1.0
C ₂	6.9	12.1	2.8
C ₃	25.0	17.1	19.0
C ₄	32.1	11.7	30.1
C ₅	8.5	4.1	13.5
C ₆	10.1	6.8	9.1

* Plank, Sibbett, and Smith (181).

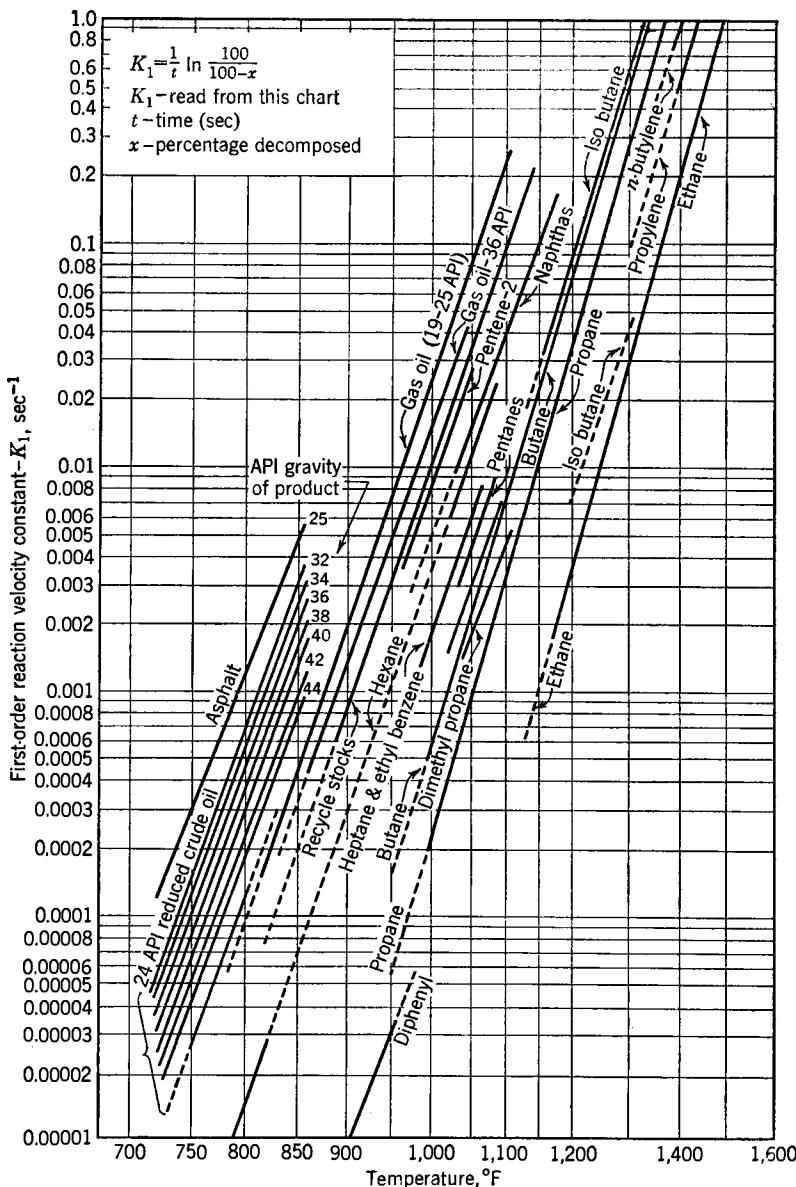


FIG. 9-12. Specific reaction rates for the decomposition of hydrocarbons. Definition of conversion: heptane and lighter, volume per cent of hydrocarbon destroyed; naphthas and gas oils, volume per cent of gasoline produced; others, volume per cent of product indicated. [Nelson (167). Courtesy McGraw-Hill Book Company, Inc., New York.]

Isomerization of normal pentane and hexane to the isoparaffins results in a considerable octane improvement. The process is similar to catalytic re-forming of naphthas and employs a platinum or related metal catalyst on a porous carrier. Operating conditions are in the range 700 to 900°F and 300 to 700 psig. Butane is converted to isobutane as a charge stock for alkylation or conversion to butene. Nonregenerable aluminum chloride dissolved in antimony trichloride is employed as a catalyst, at about 200°F, 300 psig, catalyst-to-butane ratio of 1, contact time 10 to 40 min in the liquid phase.

Polymerization converts propylene and butylene and to some extent the higher olefins into dimers and trimers which are in the gasoline range. The commercial catalyst is phosphoric acid, either deposited as a liquid film on sand granules or impregnated in a solid carrier. In the solid process, conditions are 350 to 450°F, 500 to 900 psig, 1.2 to 3.6 lb/(hr) (lb catalyst). The liquid process operates at 300 to 400°F, 400 to 500 psig; rate data are quoted in Probs. 5-14 and 5-15 and Fig. 5-3.

Re-forming prepares high-octane gasoline from low-octane naphthas by converting most of the naphthene and some of the paraffin content into aromatics, as well as eliminating some of the paraffins by gasifying them. As catalysts, molybdenum oxide deposited on alumina is used in continuously regenerated fluidized units, chromia and alumina in moving-bed units, and platinum on alumina or alumina-silica carriers in fixed-bed units. Some fixed-bed units can operate for several years at a slightly reduced activity without regeneration; others are regenerated at intervals of a few months or a few days. The fixed-bed units are by far the most popular. They operate at 850 to 950°F, 200 to 700 psig, space velocities of 1 to 5 lb/(hr)(lb catalyst) and recycle 3 to 10 moles of hydrogen per mole of charge naphtha in order to prevent carbon deposition on the catalyst. The operating cycle for one type of fixed-bed process is shown in Table 9-4.

Desulfurization of gasolines or naphthas is accomplished by converting the sulfur content to hydrogen sulfide, which is then removed by stripping. Cobalt molybdate on alumina carrier is used at about 750°F, 450 psig, space velocity 1.5 vol/(hr)(vol), hydrogen content of total charge with recycle 80 to 90 mole %. Regeneration is accomplished at 1200°F with air and steam or flue gas. Kinetic data have been published (Hoog, 97; Taylor, 211).

CHAPTER 10

SCALINGUP TEST RESULTS

65. Methods of Scale-up

Design of commercial-sized equipment and plant is based on experience, test work, fundamental principles, and correlations of data. When available, experience is fine; test work properly done is invaluable, though expensive; fundamental principles and data correlations are highly desirable and of course inexpensive, if already existing. In such fields of chemical engineering interest as fluid flow or heat and mass transfer, many correlations of the pertinent variables have been achieved, permitting the design of large-scale equipment with a limited amount of direct data. Though much interest exists and much effort has been expended in developing similar generalizations of data for the design of chemical reactors, rather less success has been achieved because of the greater complexity of this field. Consequently, greater dependence must usually be placed on direct experimental work. Since the smaller the test scale the less expensive the work, the question arises, how far upward is it possible to extrapolate reliably small-scale laboratory or pilot-plant results? No really firm answer exists, but it seems to be fairly commonly agreed that scale-up may be done satisfactorily by stages in which the test equipment is successively five to ten times the previous size, the degree of satisfaction depending, of course, on the thoroughness of the test work and its correlations.

Much of the earlier portions of this text has been devoted to principles and methods which are of assistance in the design of reactors and the translation of small-scale to commercial-scale operation. In the present chapter a number of topics will be touched on that have not been considered previously, yet are of interest and importance to scale-up. Several techniques may be employed for scale-up, either singly or jointly as the particular case demands. These may be described briefly as follows:

1. A direct experimental approach may be used, by which the effects of all pertinent variables are tested over the full range of interest, for example, initial concentrations, diluents, temperature, pressure, heating rate, agitation, space velocity, and catalyst properties. From plots and cross plots of such data combined with correlations for the purely physical

processes affecting the operation, a choice of conditions for the commercial plant can be made. The planning and building of laboratory and pilot-plant equipment cannot be treated here. Reference may be made, however, to the literature, notably the series of articles devoted to actual pilot plants that has been appearing since 1947 in the periodical *Industrial and Engineering Chemistry*. Also, recently a number of books have been published which are devoted to principles and practice of experimental work (98, 115, 116a, and 229).

2. Differential equations can be formulated for the combined and simultaneous processes of chemical reaction, diffusion, heat transfer, and pressure drop. Data such as specific reaction rate, diffusivity, heat-transfer coefficients, and friction factors can be obtained from available correlations or by test work. Upon substitution of such data into the differential equations, the latter may then be solved. In many instances, particularly in heterogeneous catalytic systems, the equations are difficult to solve without the aid of large electronic computers. Fortunately, there is an ever-increasing development and utilization of such mathematical machines. Indeed, in the very near future the electronic computer may well become the most serious competitor of the pilot plant.

3. By reason of its successes in other fields of chemical engineering, the method of dimensional similitude has been applied also to chemical reactions. Similitude can be of varying degrees of completeness, depending on the variables comprising the dimensionless groups. Thus *geometrical* similitude takes into account geometrical magnitudes only; *kinematic*, velocities also; *dynamic*, forces; *thermodynamic*, heat transfer; and *chemical*, the reaction velocity. The variables can be cumulative in the order listed.

4. The concept of the *reactor unit*, analogous to the mass-transfer unit widely employed in chemical engineering, appears to have some utility in reaction kinetics.

The last two topics will be developed in the following pages.

66. Chemical Similitude

Application of chemical similitude to reactions leads to a number of interesting conclusions which may be stated now in advance of deduction later. It appears that for all types of reactions, temperatures or the temperature-time profile must be the same in the large and small plants. In homogeneous systems the reaction times and the initial concentrations must be the same; in heterogeneous ones, the product of the reaction time and the interfacial area per unit volume of the reactor must be the same for both. Both dynamic and chemical similarity ordinarily cannot be achieved simultaneously; for example, if reaction times are preserved, the Reynolds numbers, which also involve linear or mass velocities, cannot also be preserved. In heterogeneous catalytic processes, complete simili-

tude can be achieved if both the catalyst particle size and activity can be varied; when heat transfer is by conduction or convection, particle size must be proportional to the vessel diameter and the catalyst activity must vary inversely with the square of the reactor diameter—both of these are very severe and usually impractical limitations on the catalyst. Frequently, only some of the factors influencing the reaction are of major importance, so that equality of only the dimensionless groups they involve is sufficient. For example, when diffusion rate is the controlling factor in a heterogeneous reactor, dynamic similitude alone suffices for scale-up.

Dimensional analysis of chemical reactors was initiated by Damköhler (51, 52), then continued and extended by a few other investigators. The summary given here follows largely the treatment by Bosworth (29).

The laws of conservation of mass, momentum, and energy may be applied to a chemically reacting system, thereby giving rise to a number of equations between variables which can be arranged into several dimensionless groups. Without sacrificing the spirit of the investigation and for the sake of simplified notation, consider only a gas-phase reaction of the first order, say $A \rightarrow 2B$. The various elements comprising the three conservation laws will be analyzed, taking as a reference the behavior in unit volume of a circular cylindrical reactor of length L and radius R . The steady state will be assumed, so there will be no accumulation of the three physical quantities involved. Let accumulations refer to the participant A whose concentration is C . Linear velocity is u .

Conservation of mass

$-r$ = rate of accumulation as a result of chemical reaction (10-1)

$$\frac{\partial}{\partial L} (uC) = u \frac{\partial C}{\partial L} + C \frac{\partial u}{\partial L} = u \frac{\partial C}{\partial L} + rC \Delta V \quad (10-2)$$

= rate of accumulation due to bulk flow

where ΔV is volume change per unit disappearance of A .

$$\frac{\partial}{\partial L} \left(D \frac{\partial C}{\partial L} \right) = \text{rate of accumulation due to diffusion} \quad (10-3)$$

Conservation of momentum

$$-\rho u \frac{\partial u}{\partial L} = \text{force as a result of momentum transferred by bulk flow} \quad (10-4)$$

$$-\frac{\partial P}{\partial L} = \text{force as a result of external pressure (relatively nil)} \quad (10-5)$$

$$\rho u r \Delta V = \text{force as a result of volume change due to reaction} \quad (10-6)$$

$$\frac{\mu}{\rho} \frac{\partial^2 u}{\partial R^2} = \text{force as a result of shear viscosity} \quad (10-7)$$

Conservation of thermal energy

$$-\frac{\partial}{\partial L} (C_p \rho u \Delta T) = \text{accumulation of heat accompanying flow of fluid} \quad (10-8)$$

where ΔT is the temperature in excess of the wall temperature.

$$rQ = \text{heat generated by reaction} \quad (10-9)$$

$$u \frac{\partial P}{\partial L} = \text{heat generated by friction (relatively negligible)} \quad (10-10)$$

$$k \frac{\partial^2 \Delta T}{\partial} \frac{\Delta T}{R^2} = \text{heat transferred by conduction from direction of reactor wall} \quad (10-11)$$

$$4\alpha\epsilon\sigma T^3 \Delta T \simeq 4\alpha\epsilon\sigma [(T + \Delta T)^4 - T^4] = \text{heat transferred by radiant exchange with walls} \quad (10-12)$$

where α is the wall surface per unit volume.

Neglecting Eqs. 10-5 and 10-10, these terms lead to seven dimensionless groups which must be equal for both model and prototype in order for complete similitude to exist. These groups are shown as items *a* to *g* in Table 10-1.

As an application, the behavior of a reaction may be compared in two vessels whose radii are in the ratio λ . For simplicity, the conditions in the two reactors will be taken so nearly similar that all important physical properties such as viscosity and density are substantially the same in both. Accordingly, comparison of the dimensionless groups yields these relations, where the primes ('') designate the prototype:

TABLE 10-1. DIMENSIONLESS GROUPS IN CHEMICAL REACTION

Homogeneous reaction	Heterogeneous reaction*	Name of group
(a) $\frac{rL}{uC}$	(h) $\frac{r}{SC}$	Damköhler
(b) $\frac{rR^2}{DC}$	(i) $\frac{rD_p}{DC}$	
(c) $\frac{u}{rL \Delta V}$	(j) $\frac{S}{r \Delta V}$	
(d) $\frac{R_u \rho}{\mu}$	(k) $\frac{D_p S L \rho}{\mu}$	Reynolds
(e) $\frac{C_p u R^2 \rho}{k L}$	(l) $\frac{C_p S \rho R^2}{k + \frac{1}{3} D_p \rho \sigma T^3}$	Peclet
(f) $\frac{Q r R^2}{k \Delta T}$	(m) $\frac{Q r R^2}{(k + \frac{1}{3} D_p \rho \sigma T^3) \Delta T}$	
(g) $\frac{Q r}{\Delta T (4\alpha\epsilon\sigma T^3 - C_p \rho r \Delta V)}$	(n) $\frac{Q r}{C_p \rho r \Delta V \Delta T}$	

* r is defined per unit volume. See Prob. 10-6.

$$R' = \lambda R \quad (10-13)$$

$$L' = \lambda L \quad (10-14)$$

$$u' = \lambda^{-1} u \quad (10-15)$$

$$T' = \lambda^{-\frac{2}{3}} T \quad (10-16)$$

$$r' = \lambda^{-2} r \quad (10-17)$$

$$e^{-b/T'} = \lambda^{-2} e^{-b/T} \quad (10-18)$$

The last of these follows from Eq. 10-17 and the Arrhenius equation. When radiant heat transfer is not a factor, Eq. 10-16 is ignored. From these equations it appears, for example, that greater flow rates and faster reaction rates are needed in the smaller reactor when complete similitude is to hold (Eqs. 10-15 and 10-17). Other applications will be cited later.

Similar relations hold for heterogeneous systems. As a linear dimension, the particle diameter is used instead of the radius of the reactor, and the space velocity S instead of the linear velocity u . Seven dimensionless groups for heterogeneous reactions are also listed in Table 10-1, items h to n , though only six of these are independent. The term $\frac{4}{3}D_p\sigma T^3$ is the contribution of thermal radiation to the thermal conductivity.*

Comparing two heterogeneous reactors whose radii are in the ratio λ and making the same assumptions regarding physical properties that were made in the derivation of Eqs. 10-13ff., two corresponding sets of relations are obtained, depending on the dominant mode of heat transfer. When conductive heat flow is dominant,

$$R' = \lambda R \quad (10-19)$$

$$L' = \lambda L \quad (10-20)$$

$$D'_p = \lambda D_p \quad (10-21)$$

$$S' = \lambda^{-2} S \quad (10-22)$$

$$r' = \lambda^{-2} r \quad (10-23)$$

$$\Delta T' = \Delta T \quad (10-24)$$

When radiative heat flow dominates and the temperatures are equal,

$$R' = \lambda R \quad (10-19a)$$

$$L' = \lambda^{\frac{2}{3}} L \quad (10-20a)$$

$$D'_p = \lambda^{\frac{2}{3}} D_p \quad (10-21a)$$

$$S' = \lambda^{-\frac{4}{3}} S \quad (10-22a)$$

$$r' = \lambda^{-\frac{4}{3}} r \quad (10-23a)$$

$$\Delta T' = \lambda^{\frac{2}{3}} \Delta T \quad (10-24a)$$

The conditions of similitude in heterogeneous catalytic reactors require, for example, that the prototype be relatively shorter and that the particle diameter increase more slowly than the vessel diameter. Also, the catalyst activity must be different in the two sizes of reactors.

Bosworth (29) interestingly observes—from the fact that small-scale reactions should occur at faster rates than large ones for similitude to

* See Bosworth, "Heat Transfer Phenomena," John Wiley & Sons, Inc., New York, 1952.

hold—that it may be desirable to conduct laboratory experiments with a chemical system kinetically similar to but faster than the one of interest on the commercial scale. For instance, if commercial production of ethyl derivatives is desired, test work might well be performed on the corresponding methyl derivatives, whose rates would be greater under otherwise similar conditions.

On the whole, the requirements for complete dimensional similitude are impractical. Whether chemical or dynamic or thermodynamic or geometric similitude individually or in partial combination is adequate depends on the characteristics of each reaction mixture and the operating conditions. Table 10-2 lists the dimensionless groups that may be ignored in certain special cases. Changes in operating conditions, notably temperature, may alter the relative importance of the dimensionless groups.

TABLE 10-2. SPECIAL CASES REQUIRING LIMITED SIMILITUDE

Condition	Dimensionless groups of Table 10-1 that may be ignored	
	Homogeneous	Heterogeneous
Batch, or low flow rate.....	<i>a, c, d, e</i>	<i>h, j, k, l</i>
Small diffusional resistance.....	<i>b</i>	<i>i</i>
Constant volume.....	<i>c, g</i>	<i>j, n</i>
Small radiation heat transfer.....	<i>g</i>	<i>n</i>
Adiabatic, with small heat of reaction.....	<i>f, g</i>	<i>m, n</i>

Thus increasing the temperature has a much greater effect on the chemical reaction rate r than on the diffusivity or the viscosity; accordingly, the effects of groups b, d, i , and k of Table 10-2 are minimized by increasing temperature. It should be noted that some physical properties are themselves functions of some dimensionless groups. Thus effective thermal conductivities and effective diffusivities in packed beds depend on the Reynolds number. The effect of a condition like a large pressure drop is brought out in Illustration 10-2.

When the controlling condition is either heat transfer or diffusive mass transfer, dynamical similitude is required, since the coefficients of both processes depend on the Reynolds number. Chemical similitude alone is required when the chemical reaction rate controls the operation; equality of the Damköhler group, rL/uC , is then sufficient. In this group, the term L/u is the reaction time. Thus chemical similitude is achieved when the reaction rates, the reaction times, and the initial concentrations are the same in both model and prototype. Utilizing the law of mass action, for

an n th-order reaction, $r_a = k_n(C_a)^n$, the Damköhler group becomes

$$\frac{r_a t}{C_a} = k_n t (C_a)^{n-1}$$

where the units of k_n depend on the order of the reaction.

When chemical similitude is preserved, the geometry and the heat-transfer behavior are also fixed, but not necessarily as required by dynamical similitude. Table 10-3 shows the geometrical relations for homogeneous reactions and for heterogeneous ones with two different particle-size to reactor-volume relationships. Similarly, Table 10-4 shows the behavior of heat transfer through the walls of the vessels of model and prototype whose volumes are in the ratio $1/\lambda^3$. Diffusive mass transfer is neglected in both tables.

Illustration 10-1. For complete similitude, deduce the relation between space velocities of prototype and model when the radii are in the ratio λ and the reaction is homogeneous.

Solution. The two flow-reactor equations are

$$\frac{1}{S} = \frac{V_r}{F} = \int \frac{dx}{r} \quad \frac{1}{S'} = \frac{V'_r}{F'} = \int \frac{dx}{r'}$$

From Eqs. 10-13ff.,

$$V'_r = \lambda^3 V_r$$

$$F' = u' A' \rho = \frac{u \lambda^2 A \rho}{\lambda} = u A \rho \lambda = \lambda F$$

$$\text{Then} \quad \frac{1}{S'} = \frac{V'_r}{F'} = \frac{\lambda^3 V_r}{\lambda F} = \int \frac{dx}{r'} = \lambda^2 \int \frac{dx}{r} = \lambda^2 \left(\frac{1}{S} \right)$$

Thus, for complete similitude, space velocities are not preserved.

Illustration 10-2. Consider a gas-phase reaction occurring with large pressure drop in a tubular-flow reactor. Find the relations between the dimensions of prototype and model for chemical similitude, when the charge rates are in the ratio λ . Also, compare the heat transfer through the vessel wall.

TABLE 10-3. GEOMETRICAL RELATIONS IN CHEMICAL SIMILITUDE

Item	Ratio of prototype to model		
	Homogeneous	Heterogeneous	
Particle diameter.....	..	λ	1
Reactor volume.....	λ^3	λ^3	λ^3
Catalyst surface/volume.....	..	λ	1
Volumetric rate of flow.....	λ^3	λ^2	λ^3
Reactor volume/volumetric rate of flow.....	λ^2	λ	1

TABLE 10-4. HEAT-TRANSFER RELATIONS IN CHEMICAL SIMILITUDE

Item	Ratio of prototype to model	
	Homogeneous	Heterogeneous
Particle diameter.....	...	λ
Heat-transfer surface.....	λ^2	λ^2
Volumetric flow rate.....	λ^3	λ^2
Heat transfer per unit of surface.....	1	λ^2
Heat transfer per unit of throughput.....	λ^{-1}	1

Solution. Since chemical similitude requires equal residence times, necessarily equal pressure drops must obtain. Let the charge rates be in the ratio $W'/W = \lambda$. Applying the pressure-drop relationship (Eq. 5-16),

$$\frac{W^{1.8}L}{R^{4.8}} = \frac{(W')^{1.8}L'}{(R')^{4.8}}$$

or
$$\frac{L'}{L} = \lambda^{-1.8} \left(\frac{R'}{R} \right)^{4.8} \quad (A)$$

For equal residence times,

$$\frac{R^2L}{W} = \frac{(R')^2L'}{W'}$$

or
$$\frac{L'}{L} = \lambda \left(\frac{R'}{R} \right)^{-2} \quad (B)$$

Accordingly,
$$\frac{R'}{R} = \lambda^{2.8/6.8} = \lambda^{0.41} \quad (C)$$

$$\frac{L'}{L} = \lambda(\lambda^{0.41})^{-2} = \lambda^{0.18} \quad (D)$$

As a numerical example, suppose that $\lambda = 100$, and the tubes of the prototype are 4 in. ID and 1,000 ft long. Then

$$R = \frac{4}{(100)^{0.41}} = 0.605 \text{ in.}$$

$$L = \frac{1,000}{(100)^{0.18}} = 436 \text{ ft}$$

At constant heat flux, the total heat transfer through the walls will be in the ratio

$$\frac{Q'}{Q} = \frac{R'L'}{RL} = \lambda^{0.69} = (100)^{0.69} = 15.1 \quad (E)$$

Also at constant heat flux, the heat transfer per unit of mass flow rate is

$$\frac{Q'W}{QW'} = \frac{R'L'W}{RLW'} = \lambda^{-0.41} = (100)^{-0.41} = 0.164 \quad (F)$$

In order to maintain equal time-temperature relationships and thus equal reaction rates, the heat transfer per unit of mass must be the same in both reactors. This means that the heat transfer per unit of surface must be $1/0.164 = 6.6$ times as great in the prototype as in the model. This is not, of course, in agreement with Table 10-4, since pressure drop was not taken into account there.

67. The Reactor-unit Concept

A similarity in form exists between the equation for the rate of mass transfer by diffusion and that for a first-order reaction:

$$\frac{dx}{dt} = k(1 - x) \quad (10-25)$$

Consequently, the number of reactor units N_R for a specified degree of conversion has been defined by Hurt (106) analogously to the mass-transfer unit as

$$N_R = \int \frac{dx}{1 - x} = \ln \frac{1 - x_0}{1 - x} = kt \quad (10-26)$$

and the height of a reactor unit HRU by

$$\text{HRU} = \frac{Z}{N_R} \quad (10-27)$$

where Z is the height of a flow reactor.

These definitions have been extended (24, 37) to constant-volume reactions of the n th order whose rate equation is

$$-\frac{dC}{dt} = kC^n \quad (10-28)$$

with the result

$$N_R = C_0^{1-n} \frac{(1 - f)^{1-n} - 1}{n - 1} = kt \quad (10-29)$$

where $f = (C_0 - C)/(C_0 - C_e)$ is the fraction of equilibrium conversion. For heterogeneous reactions whose rate is defined by the equation

$$\frac{dN}{dt} = k(N - N_e)^n \quad (10-30)$$

where N_e is the mole fraction at equilibrium, the number of reactor units is

$$N_R = \frac{(N_0 - N_e)^{1-n} - (N - N_e)^{1-n}}{1 - n} = kt \quad (10-31)$$

The value of the reactor-unit concept depends, of course, on the success with which it can be used to correlate data. Many mass-transfer data have been correlated to express the height of a transfer unit as a function of the physical properties and operating conditions. The height of vessel needed to carry out a particular operation is then obtained by multiplying the HTU by N_R . Another possible application could be to heterogeneous systems in which diffusion is a factor, since the heights of units for diffusive mass transfer and chemical resistance could possibly be compounded in some way into an over-all unit. Thus far, however, no correlations have

been developed for the height of a reactor unit, so the concept is interesting only because of the analogy.

N_R is of some interest in comparing the sizes of reactors needed to effect various degrees of conversion under conditions for which the HRUs could reasonably be expected to remain constant, though the same result can be achieved by direct integration of the rate equation. To simplify such comparisons, Caddell and Hurt (37) have prepared general plots of N_R against the fractional conversion f , on which Table 10-5 is based.

TABLE 10-5

f	N_R		
	$n = 0$	$n = 1$	$n = 2$
0.5	0.5	0.7	1.5
0.9	0.9	2.3	9
0.95	0.95	3.0	19
0.99	0.99	4.6	100

PROBLEMS

10-1. The radii of two reactors are related by $R' = \lambda R$. Also, $T' = 800$ and the constant in the Arrhenius equation is $b = 4,000$. Find the values of T and λ for chemical similarity to hold, assuming that the difference in temperatures does not affect the pertinent physical properties significantly.

10-2. Consider a homogeneous reaction proceeding to the same degree of completion in two reactors whose radii are in the ratio λ . Compare the outputs of the reactors, that is, the volumes of products made in unit time, under conditions of chemical similitude. Compare also the outputs per unit volume of reactor.

10-3. Suppose that in the case of a heterogeneous reaction, the performance of a reactor is to be compared with a laboratory unit of one-fifth its diameter. For complete similarity, compare the reactor lengths, the catalyst-particle diameters, and the catalyst activities.

10-4. Repeat the solution of Illustration 10-2 when the flow is laminar rather than turbulent, as assumed in Eq. 5-16.

10-5. A flow reaction in a catalyst packed bed is controlled by the rate of diffusive mass transfer. When the feed rates are in the ratio λ , find the relations between the dimensions of prototype and model and also the heat-transfer relationships. Note that Reynolds numbers are the same for both reactors.

10-6. (a) Rewrite the dimensionless groups of heterogeneous reaction (Table 10-1) when the rate is expressed per unit of surface rather than per unit of volume. (b) When radiant heat transfer is not a factor and the physical properties remain substantially constant, show that the following terms will be constant for complete similitude: $r/D_p S$, $D_p r$, $D_p S L$, $R^2 S$, and $rR^2/(D_p \Delta T)$. (c) For the conditions of part b, under conditions of complete similitude what must be the relative volume of reactor needed to accomplish 100 times the hourly production of a pilot unit? (d) Answer part c when diffusion is not a factor.

CHAPTER 11

INDUSTRIAL REACTORS

Industrial reactors are of many types, as might be expected of a field that has developed over a period of many years, even if it were not the tremendously complex one of chemical reaction. Sometimes the choice of equipment was due to expediency and was jelled by tradition; or it may have been an inventor's individual preference, uninhibited by much knowledge of scientific principles. Also, before alloys of high thermal and chemical resistance were developed, both design and operation were controlled by the limited properties of materials of construction, and the effects of these influences sometimes remain. Though they are perhaps not extreme examples, the different reactors used at one time or another for oxidation of sulfur dioxide, synthesis of ammonia, and oxidation of ammonia afford an interesting comparison of several ways of doing the same thing (Figs. 11-16 to 11-18).

In the majority of cases, a chemical reactor does three things: it provides residence time, transfers heat, and agitates or mixes phases. The principal factors bearing on the design of reactors are:

1. The phases involved
2. Temperature range
3. Operating pressure
4. Residence time or space velocity
5. Corrosiveness
6. Heat transfer
7. Temperature control
8. Agitation for uniformity or temperature control
9. Batch or continuous operation
10. Production rate

Particularly at high pressures and high or very low temperatures, economy of construction and operation is a controlling factor.

The major classes of vessels that are, or have been, or may be employed for chemical reactions are described briefly in this chapter. For orientation purposes, an attempt has been made to present some quantitative data, such as space velocities and dimensions and operating conditions whenever a reactor for a specific operation is discussed or illustrated.

Data on space velocities must be understood to be only approximate since they are greatly influenced by relatively small changes in operating conditions, feedstock characteristics, product specifications, and by the quality of the reactor design itself. Reactors used primarily for metallurgical purposes and with only slight potential for chemical applications are not covered here. Electrolytic and photochemical reactors are also among the types missing here, since they are highly specialized and, particularly in the former case, not amenable to the methods of reactor calculation discussed in this text.

No one type of construction is employed exclusively. For very high pressures, forged and laminated and wound and welded construction are all used. At elevated temperatures, insulating liners are often required, to keep down metal-shell temperatures and thus permit use of thinner walls. Walls may also be kept cool by circulating cold charge gas through an annular space at the wall, as in ammonia reactors, or by external cooling. Cooling may be necessary to minimize corrosion. Thus in the high-temperature preparation of metallic chlorides, the reactors are lined with considerable thicknesses of ceramic materials, but since there is always the possibility of leakage, the steel walls are also cooled by external air streams to below about 600°F; otherwise the steel would burn freely in the chlorine.

68. Stirred-tank Reactors

Stirred tanks (autoclaves) are the most prevalent type of reactor, being adaptable to batch or continuous operation, for small to medium production rates, over a wide range of pressures and temperatures. Agitation is obtained with stirrer blades of various shapes, chiefly turbines or propellers, or by forced circulation with an external or a built-in pump. Small reactors can be agitated by rocking, shaking, or tumbling of the entire vessel. Process design of the agitation system includes the number, size, type, and location of impellers and baffles. To a degree, this kind of design is still an art. As a rough guide, the effectiveness of agitation may be expressed in terms of power input per unit volume of reactants, thus:

Severity of agitation	Moderate	Vigorous	Intense
Input, hp/1,000 gal	0.5-1.0	2.5	5+

From a reactor-efficiency standpoint, "vigorous" agitation in a continuous stirred-tank reactor will provide over 90 per cent of the conversion attainable with perfect mixing. The Stratco reactor (Fig. 11-4) is an example of one that provides intense stirring: in the 500-gal reactor for making grease, the circulation rate is 4,000 gpm and the power input 30 hp; in the 9,000-gal alkylation reactor, circulation is 50,000 gpm and the input is 250 hp.

Kinds of heat-transfer provisions include jacketed walls, internal coils, and external heat exchangers (Fig. 11-1). Heating also may be accomplished by direct firing or electrically. If the reaction occurs with evolution of vapors, a reflux condenser can be used for cooling. Choice of method depends on how readily the surface fouls and requires cleaning, the amount

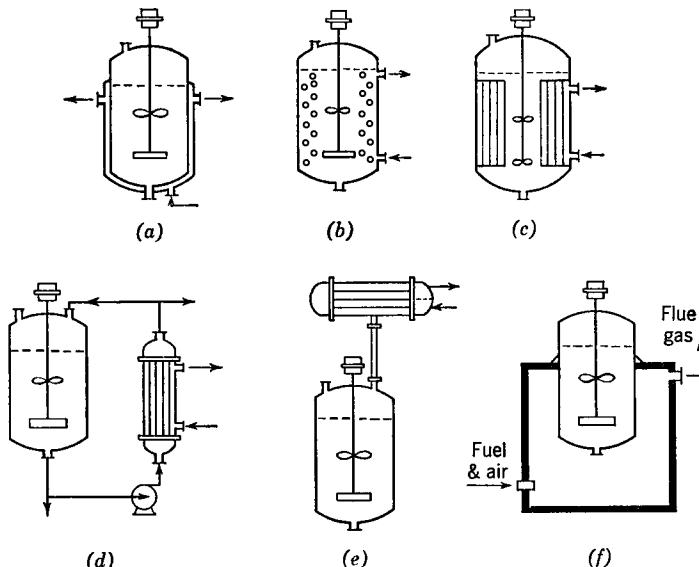


FIG. 11-1. Heat transfer to stirred-tank reactors. (a) Jacket; (b) internal coils; (c) internal tubes; (d) external heat exchanger; (e) external reflux condenser; (f) fired heater.

of surface needed, the possibility of damage through leakage of the heat-transfer medium, and the temperature and pressure of the heat-transfer medium. The jacket is preferred when a limited amount of surface is adequate and the pressure of the heat-transfer medium is not high enough to require expensive strengthening of the vessel wall. To improve heat transfer, the jacket may be so fitted that the heat-transfer medium follows a spiral path and flows at a high velocity. Some vessels have been cast with a heat-transfer coil within the wall and are thus suitable with high-pressure heat-transfer media.

Cylindrical vessels are most common and are predominantly vertical (Fig. 11-2). Horizontal reactors (Figs. 11-4 to 11-6) may be preferred for the processing of slurries or where greater liquid surface is desired for evaporation or gas absorption, or where the boiling-point rise due to hydrostatic head is harmful, or because of headroom limitations or when handling viscous materials (Fig. 11-6). In a stirred vertical reactor, the depth of liquid is roughly equal to the diameter of the vessel; if greater depth is

desired, pump circulation or several impellers and special baffling may be needed.

Multistage continuous stirred-tank reactors are shown in Fig. 4-1. Single- and multiple-shell units are both common. The multiple-vessel unit is more expensive, but it is more readily adaptable to changes in

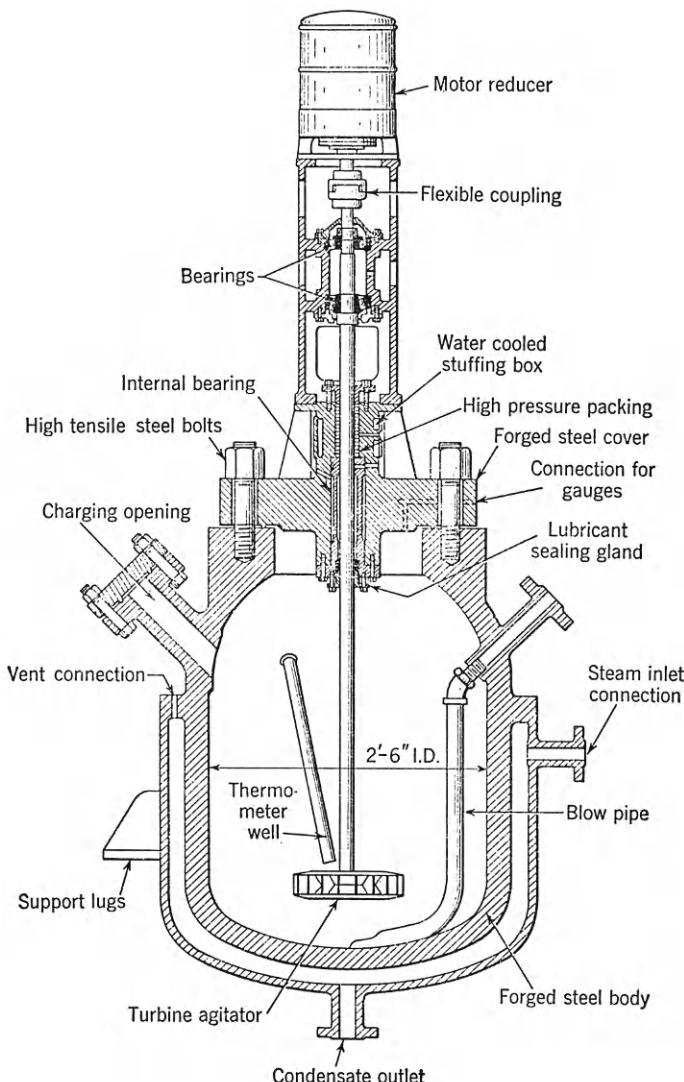


FIG. 11-2. Steam-jacketed autoclave, 120 gal, 200 psig, 300°F. (Courtesy Blaw-Knox Company.)

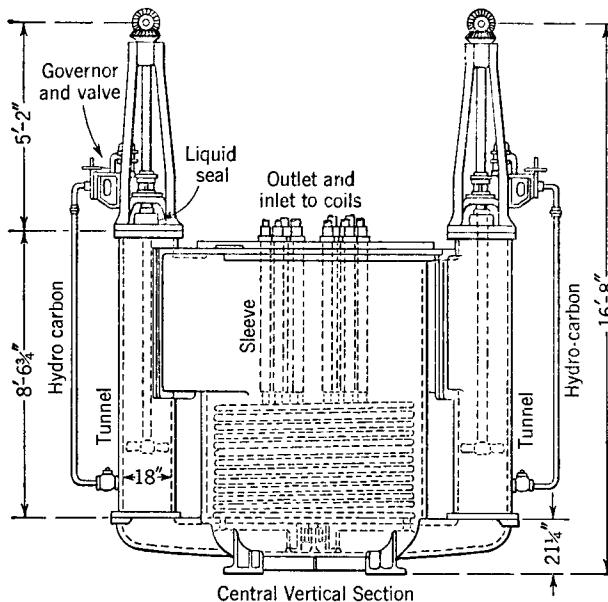


FIG. 11-3. Hough nitrator, cast iron, with external tunnels. [Groggins (82). Courtesy McGraw-Hill Book Company, Inc., New York.]

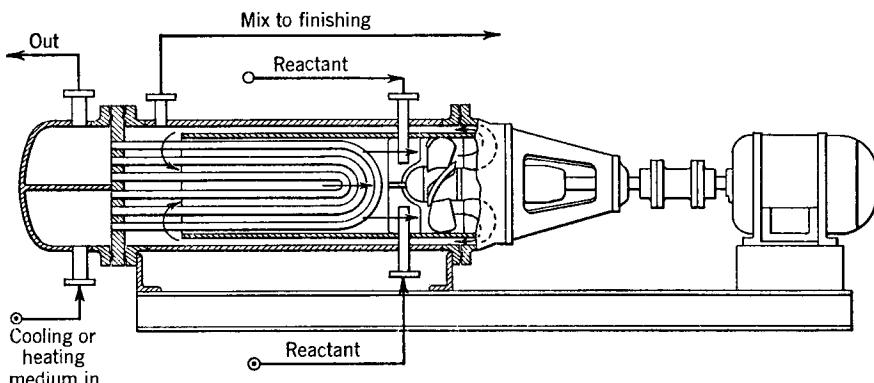


FIG. 11-4. Horizontal heat-exchange reactor. (Courtesy Stratford Engineering Corporation, patents issued and pending.)

requirements such as the number of stages, removing intermediate streams, paralleling stages for increased throughput, and the amount of heat transfer. Wherever possible, flow between stages is by gravity, since pump maintenance is always a serious problem. The single-shell types are more compact, cheaper, and easier to operate and maintain.

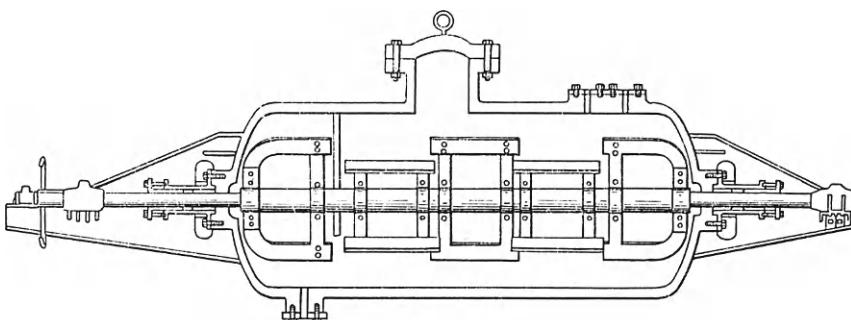


FIG. 11-5. Horizontal autoclave, 650 gal, 100 psig. (Courtesy Blaw-Knox Company.)

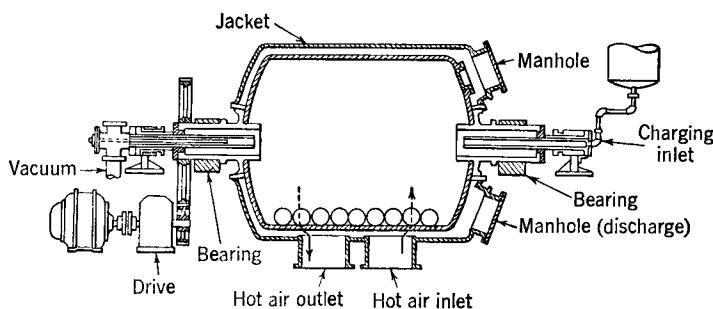


FIG. 11-6. Ball-mill sulfonator. [Groggins (82). Courtesy McGraw-Hill Book Company, Inc., New York.]

69. Tubular Reactors

Tubular reactors are of three main types: (1) single-jacketed tube, (2) shell-and-tube heat exchanger, and (3) tube furnace, in which the tubes are exposed to radiation and convection from combustion gases. The furnace type is primarily for endothermic processes, whereas the others are suitable for either endo- or exothermic. The single tube requires no particular comment.

Shell-and-tube. The reaction may take place either in the tubes or in the shell. The reaction zone may contain solid packing for phase mixing or increased turbulence, or it may contain solid catalyst in granular or lump form, or the walls may be coated with catalyst, or it may be empty. Heat-transfer media may be of any nature, from refrigerants to water, steam, Dowtherm, and molten salts. Figure 11-7 illustrates a frequently adopted principle of using the reaction mixture to do its own heating or cooling within the reactor itself. In this reactor, the reactant air is pre-heated by the reaction products and in turn cools them rapidly. Equilibrium conversion of air to NO is favorable only at temperatures above

4000°F or so, but rapid cooling to below about 2200°F assures acceptable retention of conversion.

Packed towers of the type employed for purely physical mass-transfer operations are also employed for conducting heterogeneous reactions. For example, a multitubular packed reactor for continuous chlorination of benzene consists of a number of 4-in. tubes, each about 25 ft long, packed with ceramic Raschig rings, in a 4-ft-diameter shell, capable of chlorinating about 35 tons of benzene per 24 hr. To minimize polychlor formation, the temperature is maintained below 110°F by circulating cooling water on the shell side.

At elevated temperatures and pressures, very elaborate provisions are necessary to achieve economy. A good example in the shell-and-tube field is the ammonia-synthesis reactor. Some description of the process is given in Sec. 64. Pressures are in the range 250 to 1,000 atm, and temperatures up to 1000°F. Several types of reactors are shown in Fig. 11-16 (see also Table 11-3). They have in common the feature incorporated by Bosch in the first reactor he built, of running cold charge gas through an annular space at the wall to keep it cool and thus permit thinner construction. Construction economy is achieved also by incorporating desirable heat transfer between charge stock and product within the reactor shell. Ammonia formation is exothermic; the rate of reaction of course increases rapidly with temperature, but equilibrium is favorable at low temperatures. Figure 11-15 shows the attainable conversion under adiabatic and isothermal conditions. By reason of the built-in provisions for heat transfer, commercial ammonia reactors achieve an ammonia concentration in the effluent of 13 to 15 per cent at 300 atm, which is appreciably better than adiabatic operation provides even at equilibrium. Oxidation of sulfur dioxide exhibits similar behavior (Fig. 11-15); temperature control in this process is obtained by internal or external heat exchange (Fig. 11-17). Yet another method of achieving temperature control is to inject a cold stream into the reaction mixture at several points along the reaction path; this may be an inert material or some of the charge stock (Prob. 5-15). Further consideration of temperature control will be found under fixed-bed reactors (Sec. 71).

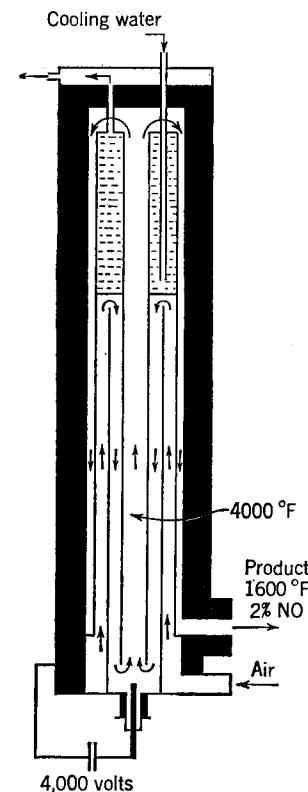


FIG. 11-7. Schoenherr furnace for NO from air.

Tubular furnaces are widely applied for the cracking of hydrocarbons to make olefins or gasoline and for other purposes where fairly high temperatures are needed. As a nonhydrocarbon example, phenol has been made in this type of reactor from monochlorobenzene and aqueous sodium hydroxide at about 700°F and 4,000 psia.

A furnace consists of a combustion chamber lined with refractory and tubes mounted on the walls and ceiling and sometimes on the floor. In the radiant section, the tubes are in direct view of the flames. There is also a convection section, either in the main chamber but separated by a bridge wall or in the passage leading to the stack. Convection tubes serve to preheat the charge or to maintain a reaction temperature attained in the radiant section or to recover heat by preheating combustion air or generating steam. Many different arrangements of tubes and firing and oil-flow patterns are used, and all have merit in some applications. Some are shown in Fig. 11-8. Adequate thermal efficiency and a proper oil-temperature gradient are basic requirements. For improved control, the radiant section may be slit in two by a wall. Oil flow is usually through a single tube or through at most two tubes in parallel. Tube diameters are from 3 to 6 in. ID, and there may be a hundred or more 20- to 40-ft tubes in series.

In the radiant section, heat-transfer rates may be in the range of 5000 to 25,000 Btu/(hr)(sq ft of tube surface), with a rate of 8000 to 15,000 as a good range. Convection section rates are 2000 to 5000 Btu/(hr)(sq ft). Furnace volumes are about 4 cu ft/sq ft of tube surface, corresponding to a heat release of 20,000 to 30,000 Btu/(hr)(cu ft). A method for designing the radiant section has been published by Lobo and Evans (145). A more recent, simplified treatment is by McCarthy (152). Residence times of cracking operations are calculated from rate-of-cracking data like those of Fig. 9-12 (see Illustration 5-5). Since cracking rate is not appreciable below 800°F, space velocities are generally based on the reactor volume above this temperature. From a design angle, the furnace thus consists of preheat and reaction sections. Some order-of-magnitude space velocities are given in Table 11-1.

TABLE 11-1. ORDER-OF-MAGNITUDE SPACE VELOCITIES IN TUBULAR FURNACES

Process	Pressure, psig	Temperature, °F	Lb/(hr)(cu ft above 800°F)
Olefin production:			
From ethane-propane mixtures.....	80	1400-1550	80-110
From naphthas and gas oils.....	20	1200-1350	100-125
Heavy-oil cracking:			
For gasoline (50% gasoline).....	200-600	1000	400-1,000
For viscosity reduction (10% gasoline).....	200-600	900	500-1,000

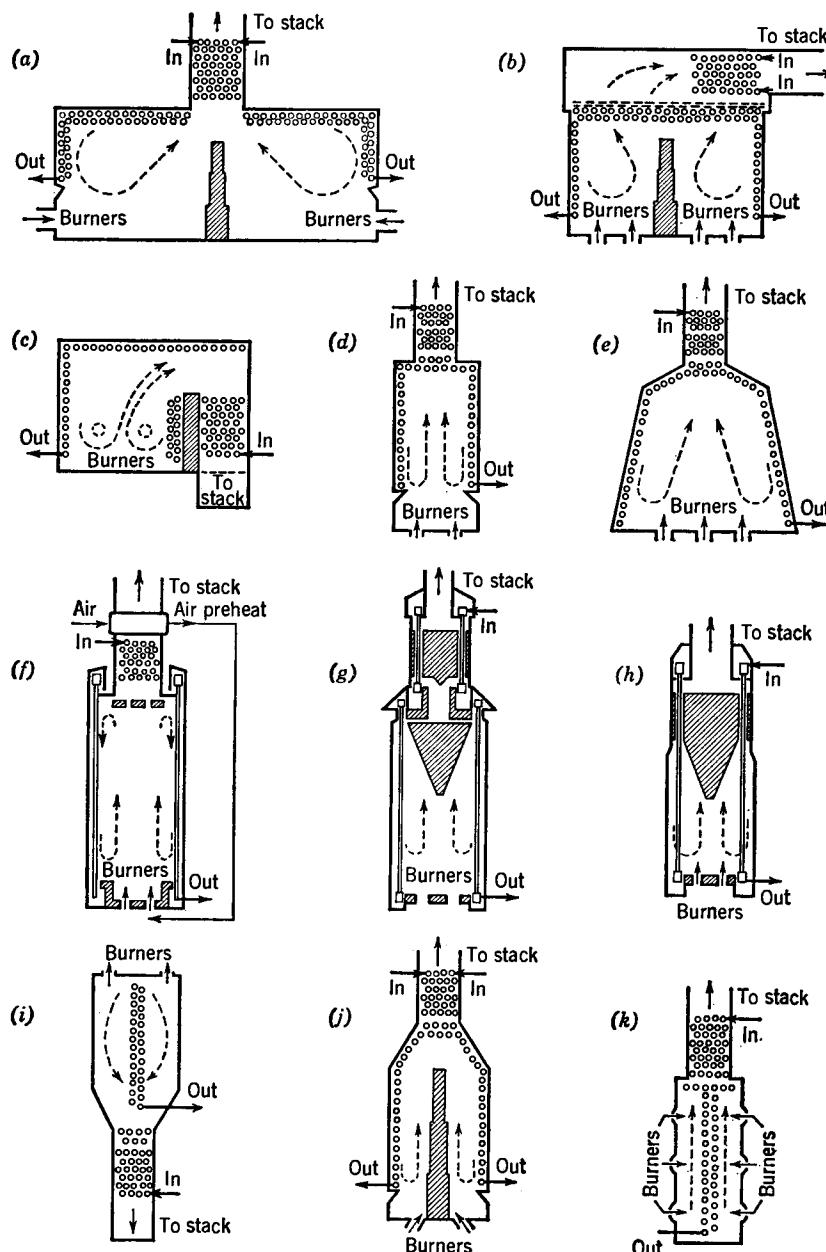


FIG. 11-8. Basic types of tubular furnaces. [Nelson (167). Courtesy McGraw-Hill Book Company, Inc., New York.]

70. Kilns and Hearth Furnaces

Kilns and hearth furnaces are primarily for high-temperature service, the former up to 2500°F and the others up to 4000°F. Construction material is generally a steel shell lined with ceramics, sometimes up to several feet in thickness.

Vertical kilns are used in operations where no fusion or softening takes place, as in the burning of limestone or dolomite, though rotary kilns are also used for these particular operations. The vertical kiln is the antecedent of modern moving-bed equipment, such as the pebble heater and catalytic reactors of this type. A cross section of a continuous lime kiln is shown in Fig. 11-9. These vessels range in size from 8 to 15 ft in di-

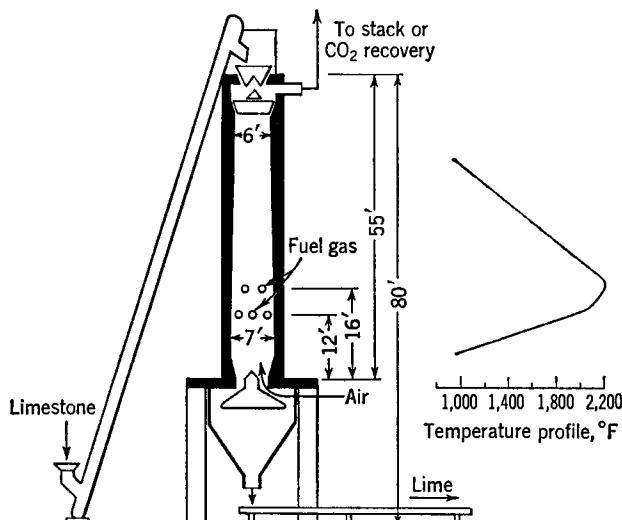


FIG. 11-9. Continuous lime kiln for capacity of approximately 55 tons/24 hr.

ameter and 50 to 80 ft high. In lime calcination peak temperatures are about 2200°F, though decomposition proceeds freely at 1850°F. Fuel supply may be coke mixed and fed with the limestone, if the finished lime can tolerate the additional ash, or producer gas, or other gas or fuel oil. Space velocity is 0.8 to 1.5 lb CaO/(hr)(cu ft of kiln), or 45 to 100 lb CaO/(hr)(sq ft of kiln cross section), depending on the size and modernity of the kiln, the method of firing, and the lump size, which is in the range of 4 to 10 in.

Rotary kilns are somewhat more diversely applied, for the decomposition of solids, for reactions between finely divided solids, and for reactions of solids with gases. Also, there is an industrial example of a reaction of a

solid with a liquid, namely, sodium chloride with sulfuric acid in a Laury kiln.

The kiln is a long narrow cylinder, with a length-to-diameter ratio in the range of 10 to 20. General-purpose kilns are 100 to 125 ft long, but cement kilns may be much larger, one being 12 ft in diameter by 475 ft long. An inclination to the horizontal of 2 to 5° is sufficient to move the solid along. Speed of rotation is 0.25 to 2 rpm. Generally only small particles are handled, fine powders or lumps up to an inch or so. Heating is usually by direct contact of the stock with combustion gases, though jacketed kilns may be used for some low-temperature applications. Figure 11-10 shows the temperature profile of the stock and the gas in a cement

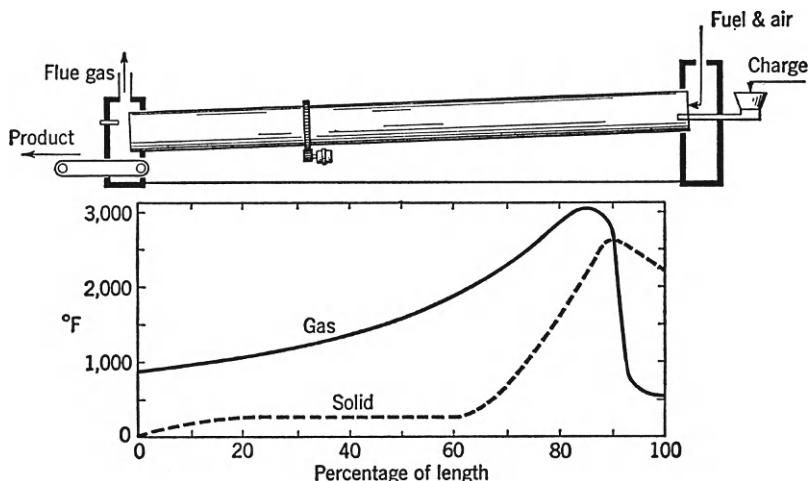


FIG. 11-10. Temperature profiles in a rotary cement kiln.

kiln. Approximate space velocities are shown in Table 11-2. Some of the factors influencing this are lump size, moisture content of the stock, heating value of the fuel, and preheat of combustion air or charge stock.

Hearth furnaces consist of one or more flat or concave pans, either moving or stationary, usually equipped with scraper-stirrers. Though this equipment is mostly used for ore-treating and metallurgical purposes, a few inorganic chemicals are made this way, for example, Leblanc soda ash, sodium sulfide from sodium sulfate and coal, and sodium sulfate and hydrogen chloride from salt and sulfuric acid. A modern type of salt-cake furnace is shown in Fig. 11-11. Salt and sulfuric acid are charged continuously to the center of the pan, and the rotating scrapers gradually work the reacting mass toward the periphery, where the sodium sulfate is discharged over the edge of the pan. Hydrogen chloride leaves through a vent pipe and is recovered by absorption in water. Both products leave

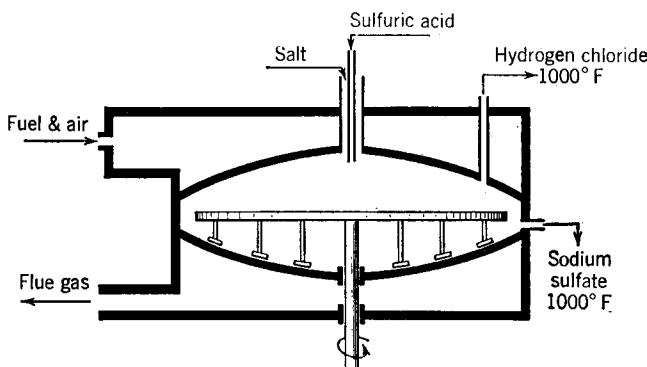


FIG. 11-11. Mechanical salt-cake furnace.

TABLE 11-2. SPACE VELOCITIES IN ROTARY KILNS

Process	$Lb/(hr)(cu\ ft\ of\ kiln)$
Cement, dry process.....	1.1-2.6
Cement, wet process, 44% water.....	0.7-1.7
Limestone calcination.....	1.1-2.1
Dolomite calcination.....	1.0-1.4
Alumina preparation.....	1.2-1.7
Barium sulfide preparation.....	0.9-2.0
Ignition of inorganic pigments.....	0.4-4.6
Iron pyrite roasting.....	0.7-0.9

at about 1000°F. Pans are from 11 to 18 ft in diameter and can handle 6 to 10 tons of salt/24 hr. For comparison, a Laury horizontal rotating cylindrical kiln, 5 by 22 ft, has a capacity of 1 ton/hr of salt cake.

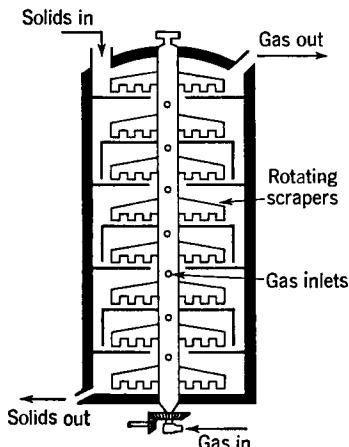


FIG. 11-12. Multiple-hearth reactor.

Reactions in which a limited amount of fusion or sintering occurs can be handled continuously in multiple-hearth furnaces, of which one type appears in Fig. 11-12. In some cases the plates rotate, in others the scraper arms rotate, and in still others the arms oscillate and discharge the plates with each stroke. Material is charged at the top, moves along as rotation proceeds, and drops onto successively lower plates while combustion gases or gaseous reactants flow upward. Applications of this type of equipment include roasting of ores, calcination, burning of calcium sulfate or bauxite, and reactivation of spent adsorbent clays in the petroleum industry. A reactor with nine trays, 16 ft in diameter and 35 ft high, can roast about 1,250 lb/hr

of iron pyrite. The residence time is 4 to 5 hr, and the corresponding sulfur-burning rate is about 60 lb/(hr)(sq ft of hearth surface).

For comparison, in another type of roaster the charge is ground so that 95 per cent is finer than 0.003 in., then blown with combustion air into an open chamber. Capacity of this equipment for pyrite roasting is about three times that of the multiple-hearth unit, expressed per cubic foot of reactor, and the contact time is only a few seconds compared with several hours.

Very-high-temperature operations like those for production of steel or other metals or glass utilize single-hearth furnaces, often with heat regenerators for fuel economy. These regenerators may consist of two sets of chambers filled with open brickwork, used alternately for absorbing heat from flue gases and for preheating combustion air and fuel gas. Figure 11-13 is a schematic of a Siemens-Martin furnace. Such a unit

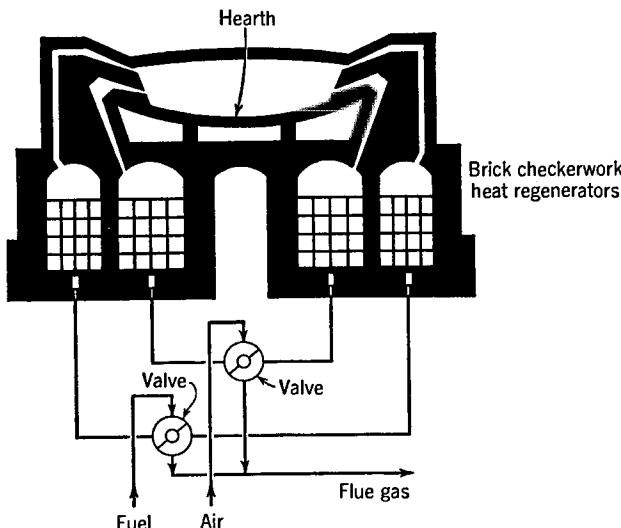


FIG. 11-13. Schematic diagram of Siemens-Martin furnace and heat regenerators.

with a hearth 13 ft wide and 40 ft long has a production of 10 tons/hr of steel with a residence time of 10 hr. The hearth volume is about 5,000 cu ft, and the total regenerator volume is about 25,000 cu ft.

71. Fixed-bed Reactors

A fixed-bed reactor contains a mass of small particles, 0.1 to 0.2 in. in diameter usually, through which the reaction mixture is passed. Non-catalytic packing is sometimes used to moderate temperature changes. Thus ethylene has been produced at 1500°F by partial oxidation of ethane

in a reactor packed with porcelain particles, at a space velocity of 800 std cu ft/(hr)(cu ft), a rate roughly comparable to catalytic reactions. The effectiveness of this kind of unit has been attributed to good heat distribution by reradiation from the solid. For the most part, however, fixed-bed units contain catalyst particles. This classification does not include reactors where the primary purpose of the packing is to improve contact between phases.

The packing may be arranged in several ways:

1. A single large bed
2. Several horizontal beds supported on trays
3. Several parallel packed tubes in a single shell
4. Several beds, each in its own shell

Variations from the single large bed are primarily because of the need for control of temperature by means of heat exchange, but occasionally for improvement of gas distribution or by reason of pressure drop. There are few fixed-bed units that do not have some provision for heat transfer. Some of the many possibilities are shown in Fig. 11-14. Autothermic processes, in which there is heat transfer between charge stock and product, are widely employed. Combinations of these several types of

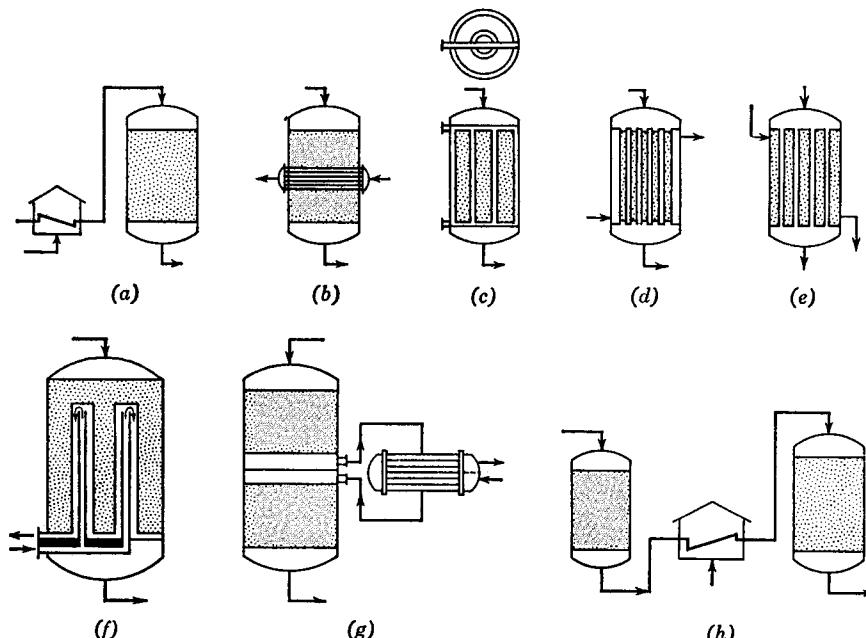


FIG. 11-14. Heat transfer in fixed-bed reactors. (a) Adequate preheat; (b) internal heat exchanger; (c) annular cooling spaces; (d) packed tubes; (e) packed shell; (f) tube and thimble; (g) external heat exchanger; (h) multiple shell, with external heat transfer.

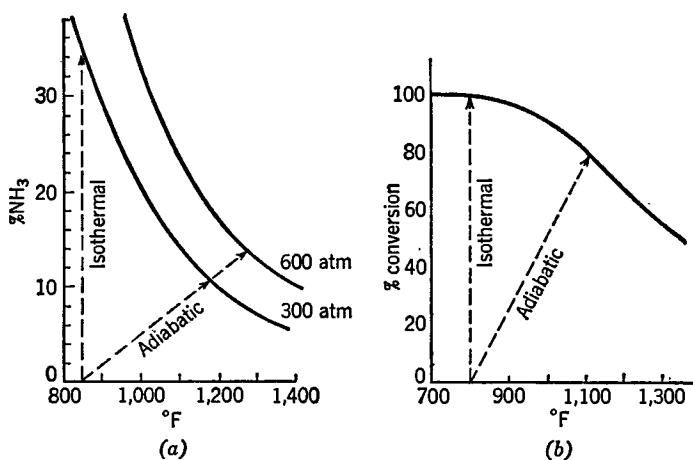


FIG. 11-15. Equilibrium conversions under isothermal and adiabatic conditions. (a) Ammonia synthesis; (b) oxidation of sulfur dioxide. [Heinzel (88).]

heat exchange may be applied in a single unit, as exemplified by the ammonia reactors (Fig. 11-16).

When the heat of reaction is not particularly great, it may be possible to regulate the inlet temperature so that adiabatic operation will be satisfactory. The original Houdry catalytic cracking unit was of this type; though there were several reactors, they were used alternately on 10-min cycles for reaction and regeneration. Butane dehydrogenation to

TABLE 11-3. DATA ON REACTORS FOR AMMONIA SYNTHESIS (FIG. 11-16)

Item	Haber-Bosch	Uhde	Claude	Casale	Fauser	N.E.C.*
Capacity, tons NH_3 /day.....	93	39	55	44	55	50
Pressure, atm.....	325	100-150	800-1,000	600	250	300
Height, m.....	12	8	5	10	14	11
Inside diameter, mm.....	800	1,170	500	600	850	700
Wall thickness, mm.....	160	160	300	250	160	175
Ammonia content						
of effluent, %.....	13-15	8-9	25	20	12-16	15-16
Ratio, recycle to fresh gas.....	6-7	10	2.5	4-5	4.5-5	5-6
Reactor volume, cu m.....	2					
Catalyst weight, tons.....	6					
Space velocity, vol/(hr)(vol).....	31,500					
Effluent temperature, $^{\circ}\text{C}$	550		650			

* Nitrogen Engineering Corporation (now Chemical Construction Corporation, New York).

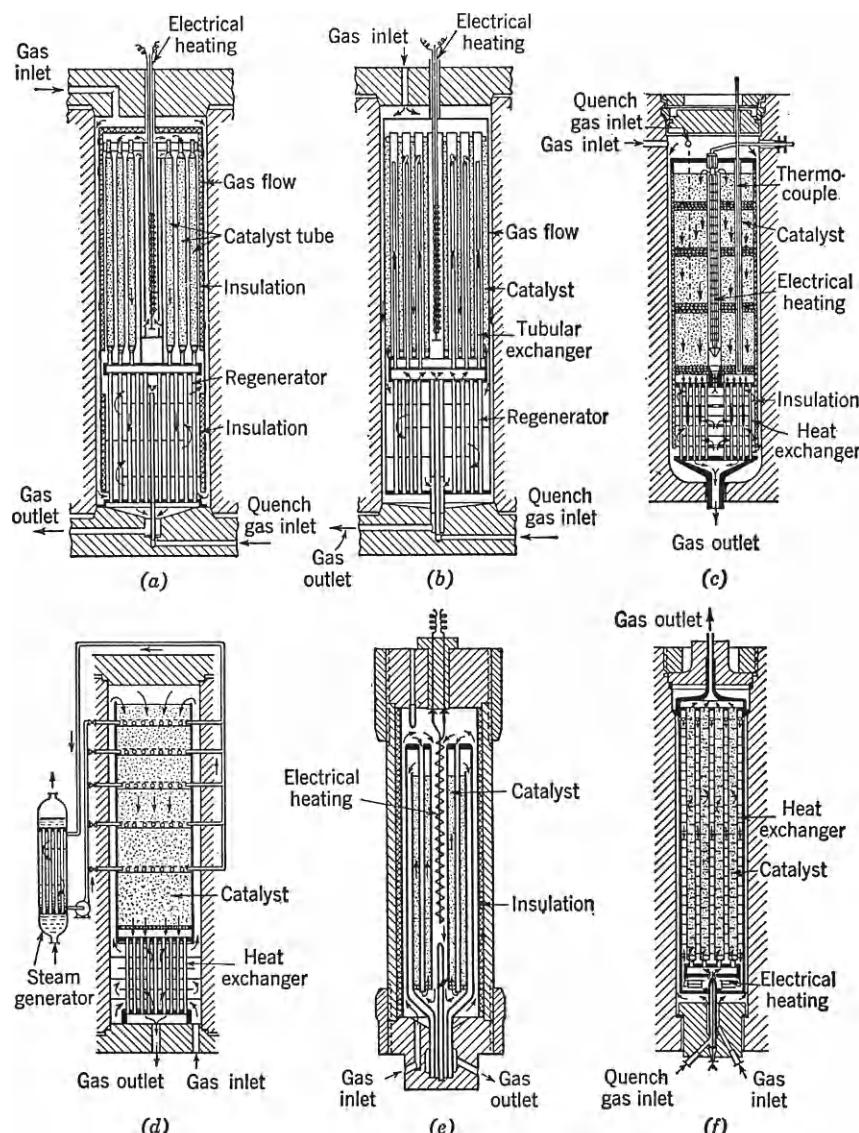


FIG. 11-16. Reactors for ammonia synthesis. See Table 11-3 for data on these reactors. (a) Haber-Bosch; (b) Chemical Construction Corporation; (c) Uhde; (d) Fauser; (e) Casale; (f) Claude. [Winnacker and Weingaertner (238). Courtesy Carl Hanser Verlag, Munich.]

butene and butadiene is now being accomplished by the same scheme. Catalytic units for re-forming naphthas to high-octane gasolines or aromatics are without heat exchange in the reactors themselves, but do employ several reactors in series with furnaces in between to maintain temperatures (Fig. 11-19).

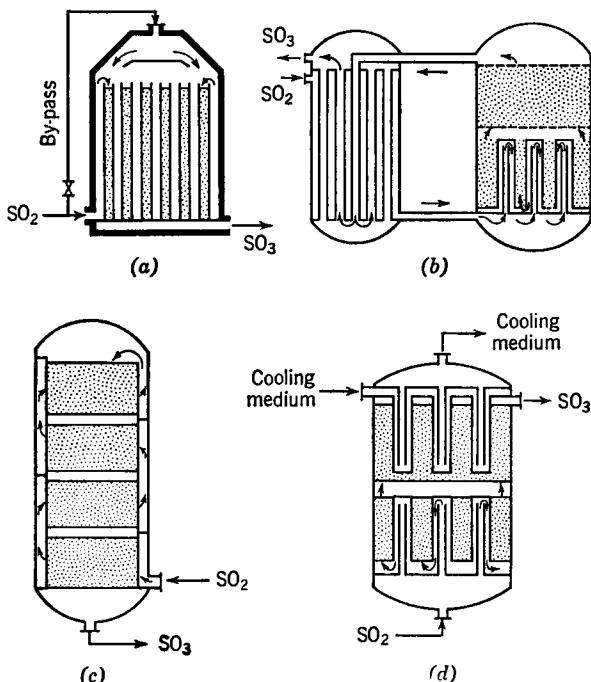


FIG. 11-17. Types of reactors for catalytic oxidation of sulfur dioxide. (a) Feed against product heat exchange; (b) external heat exchanger and internal tube and thimble; (c) multibed reactor, cooling with charge gas in spiral jacket; (d) tube and thimble for feed against product and for heat-transfer medium.

Flow of reactants is downward through the bed so as not to cause movement of the particles which could result in attrition or even entrainment. Though a few spherical reactors have been built and a few of rectangular or oval cross section (Fig. 11-23), most packed reactors are vertical circular cylinders with convex heads. The structure of the bed consists of a metal or ceramic grid on which are several layers of successively smaller-diameter packings, often spherical in shape, and finally the catalyst particles. The over-all depth of the bed is roughly equal to the diameter. To minimize pressure drop, the feed may enter through a central pipe or from a peripheral annulus (Fig. 11-19).

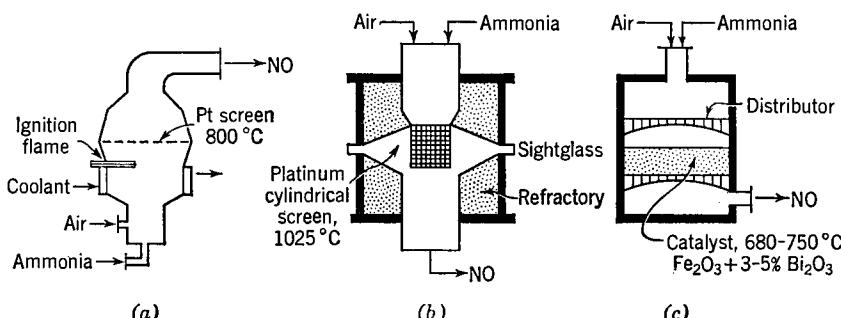


FIG. 11-18. Reactors for oxidation of ammonia. (a) Frank-Caro; (b) Parsons: outside dimensions, 80 cm high, 61 cm diameter; converts 100 kg ammonia/hr; (c) I.G.: 6 m high, 5.4 m diameter, catalyst bed depth 10 to 15 cm; converts 500 to 600 kg ammonia/(sq m)(hr). [Kröger (124). Courtesy Vandenhoek & Ruprecht, Göttingen, Germany.]

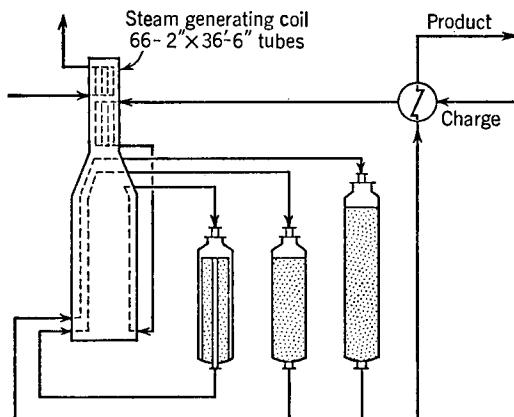


FIG. 11-19. Platinum-catalyst fixed-bed re-former system for 5,000-bpsd charge rate. Reactors 1 and 2, 5 ft 6 in. diameter by 9 ft 6 in. high; reactor 3, 6 ft 6 in. by 12 ft 0 in.

72. Moving Beds

The term moving bed is applied to equipment in which solid particles move vertically downward as a mass. The particles may be reelevated to the top of the reactor in external equipment by pneumatic or mechanical means in a continuous fashion, unless they are a product, as in the case of limestone calcination, in which case they are discharged from the bottom of the reactor. Besides the case where the solid is the reactant, there are two principal applications of the moving bed:

1. Heat transfer, which is of the order of 500 to 5000 Btu/(hr)(cu ft) (°F)

2. Catalytic reactions, where the solid catalyst becomes fouled readily but can be regenerated continuously

A unit of this type consists of two zones, one for preheating or regenerating and the other for heating or reacting. Both units may be in the same shell (Figs. 11-20 and 11-21), or two sections may be used alternately for

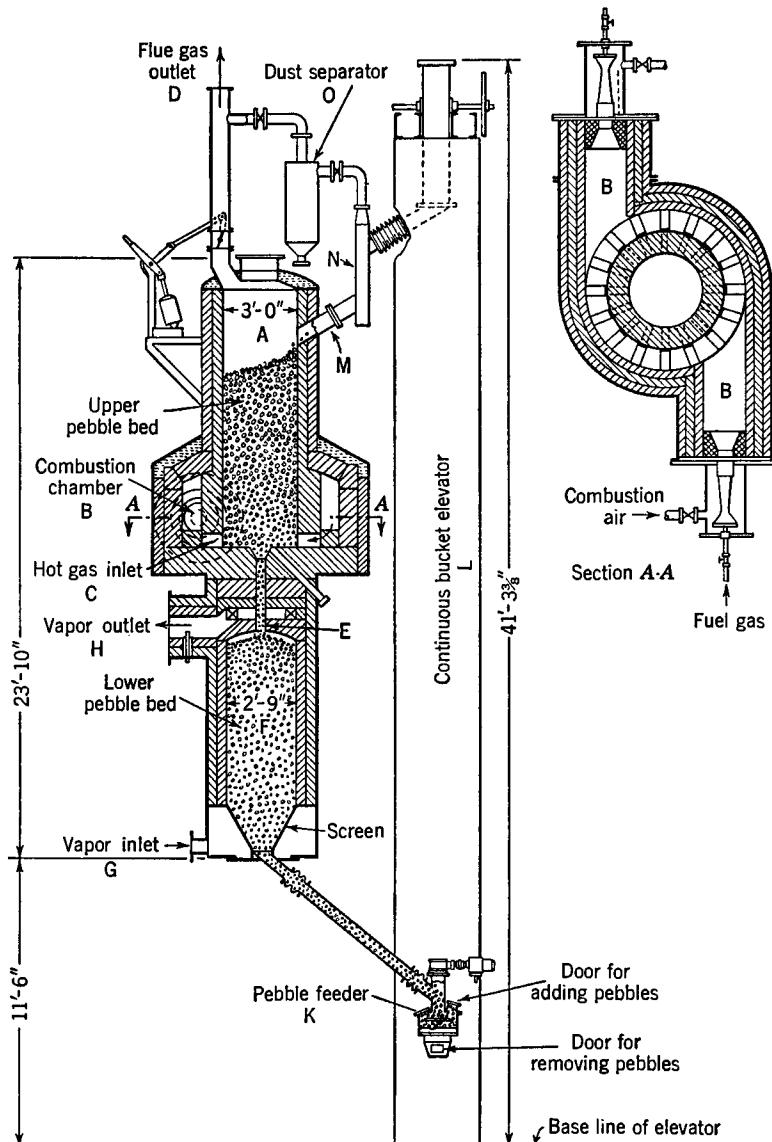


FIG. 11-20. Pebble heater. [Batchelder and Ingols (16).]

each purpose (Fig. 11-22), or the regenerator may be a separate unit (Fig. 11-23). Bucket elevators are frequently used, though in the petroleum industry they have been largely replaced by gas lifts. Star feeders, sliding plates, and slide valves are among the many devices for regulating

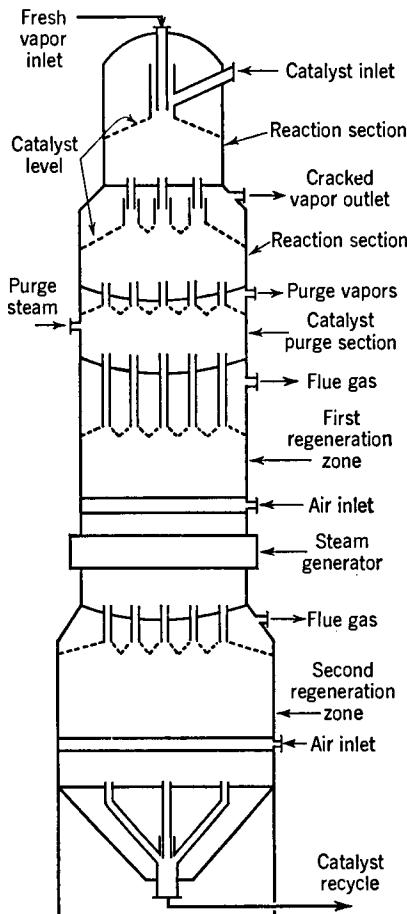


FIG. 11-21. Moving-bed combined catalytic cracker and regenerator.

solids flow through a unit. Various mechanical and control features of moving beds are described by Berg (18).

Certain aspects of the operation of moving-bed catalytic cracking are presented by Bourguet and Wantuck (31). The reactor for a typical 20,000-bpsd unit is 16 ft in diameter. The catalyst passes through the reaction zone as a slowly gravitating compact bed 12 to 16 ft deep. Lift pipes for different-sized units vary from 14 in. by 180 ft to 32 in. by 260 ft.

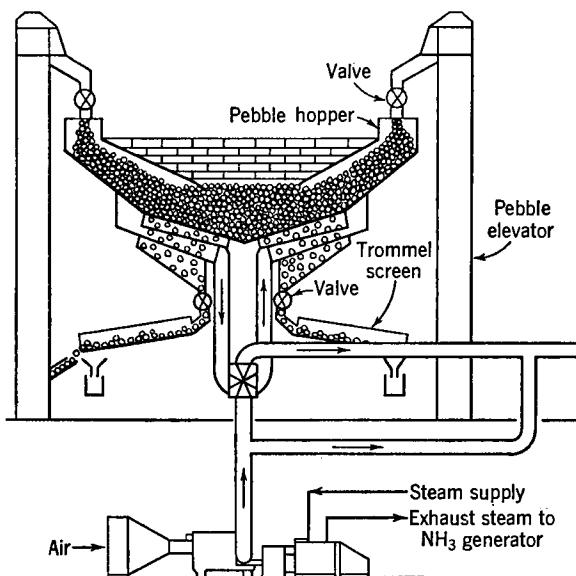


FIG. 11-22. Pebble reactor for direct oxidation of atmospheric nitrogen, operating at 4000°F. [Ermenc (63). Courtesy *Chemical Engineering Progress*.]

Pressure drop across the lift pipe is about 2 psi. Attrition of bead silica-alumina cracking catalyst is 0.1 to 0.5 lb/ton circulated. The circulation of catalyst is two to seven times the charge rate of the oil, pound per pound, and the space velocity is 1 to 4 lb oil/(hr)(lb catalyst in the reactor). Heat-exchange rate between catalyst and reactant vapors is of the order of 25,000 Btu/(hr)(cu ft)

73. Fluidized Beds

Fluidized-bed reactors are used primarily for contacting gases with solids. Virtually all applications are of the dense-phase bed type, where a fairly definite bed level is maintained and the solids overflow through a standpipe. The dilute-phase type, in which the solid is entrained continuously out of the reactor, is applicable where there is difficulty in maintaining proper size distribution for a stable dense phase.

Catalytic fluidization processes require a minimum of two vessels or two compartments in a single shell, one for reaction and the other for regeneration (Figs. 11-24 and 11-25). As pointed out in Sec. 59, large reactors behave as a more or less completely mixed single stage, so for some applications a multicompartiment reactor is needed. Figure 11-26 shows a five-stage unit in a single shell for the calcination of lime, though in this instance the additional stages are for heat recovery. A proposed unit for the recovery of low concentrations of uranium from

ores containing lime and silica is shown in Fig. 11-27. One of the stages is for the recovery of HCl from the substantial quantity of calcium chloride formed in the process, by reacting it with steam at elevated temperature.

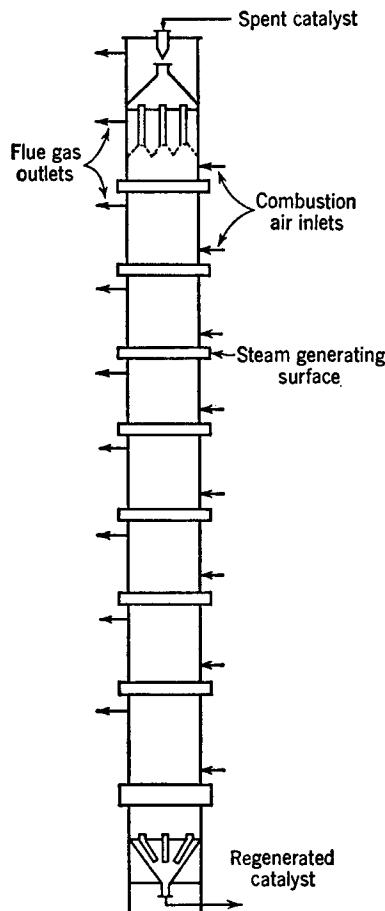


FIG. 11-23. Moving-bed regenerator for 15,000-bpsd catalytic cracking unit 70 ft high by 8 ft square. Catalyst circulation, 50 tons/hr; air rate, 10,000 std cfm; burning rate, 2,000 lb carbon/hr; steam generation, 20,000 lb/hr.

Transfer of solids between stages and out of the vessels takes place very much like liquid flow in a plate column. Since it is expensive to elevate vessels needlessly, the transfer of solids between vessels requires careful hydraulic analysis (Daniels, 55).

A major operating problem is that of entrainment. This is minimized with cyclone separators, from one to three stages, frequently mounted

within the reactor itself, supplemented sometimes by electrostatic precipitators. Particle-recovery efficiencies may need to be 99.9 per cent or more for economical operation with catalysts. Other auxiliary equipment may be necessary. Thus in hydrocarbon systems where reactivation is by burning off carbon, adsorbed hydrocarbons are stripped off with steam

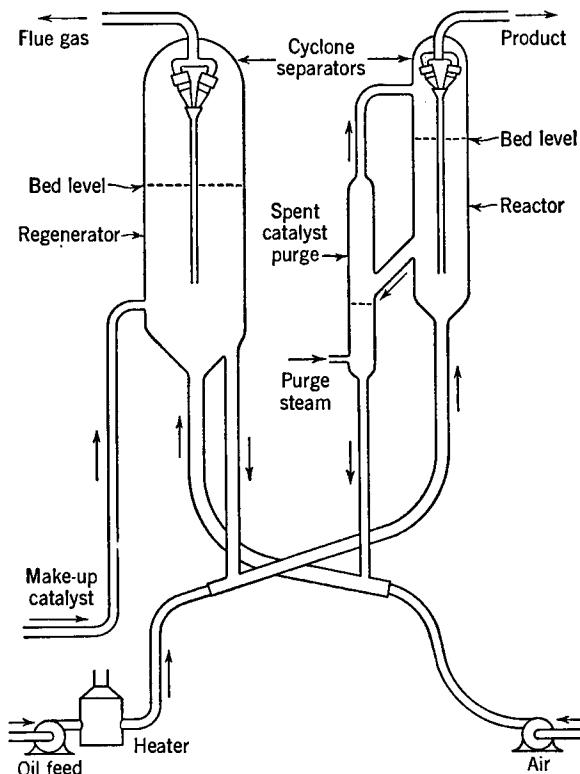


FIG. 11-24. Fluidized-bed catalytic cracking and catalyst regenerating unit.

before the catalyst is burned. Still other problems are posed by erosion of lines, hydrogen attack, control of solids flow, and heat transfer.

Certain operating data of a 15,000-bpsd fluidized catalytic cracking unit are shown in Table 11-4. Presumably, this reactor operates at about 20 psia and 850°F and the regenerator at about 1100°F. In this system there is no well-defined solids level and the amount of entrained material entering the cyclones is quite high, equivalent to complete circulation of the catalyst inventory every 36 min. Recovery of solids entering the cyclones is 99.98 per cent.

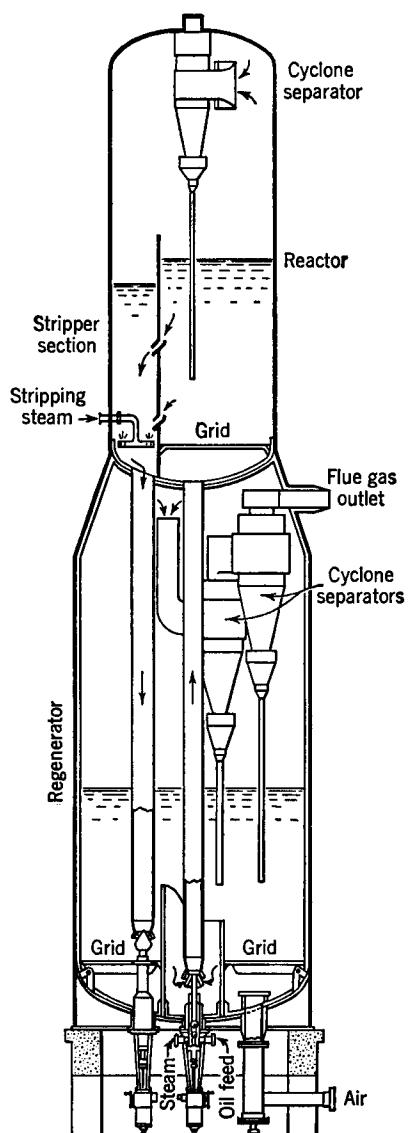


FIG. 11-25. Fluidized catalytic cracker and regenerator in a single shell. [Ziegenhain (243). Courtesy *Petroleum Engineer*.]

TABLE 11-4. DESIGN AND OPERATING DATA FOR A FLUID CATALYTIC CRACKING UNIT*

Item	Quantity
Unit charge, nominal.....	15,000 bpsd
Catalyst inventory, total.....	250 tons
Catalyst inventory, regenerator bed.....	100 tons
Superficial velocity, regenerator.....	2.5 fps
Bed density, regenerator.....	28.0 lb/cu ft
Flue gas plus solids density, cyclone inlet.....	0.5 lb/cu ft
Catalyst circulation rate, unit.....	24.0 tons/min
Catalyst circulation rate, to cyclones.....	7.0 tons/min
Catalyst loss rate, design expectation.....	2.0 tons/day

* Kraft, Ullrich, and O'Connor (123).

74. Special Types of Reactors

Equipment designed primarily for interphase contacting as in absorption, distillation, or extraction is often used for reactions. Many

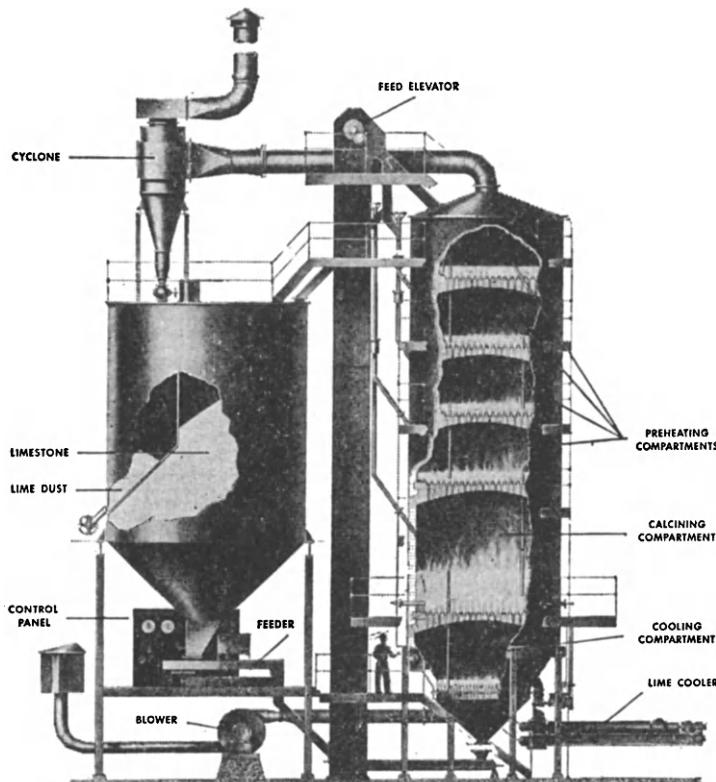


FIG. 11-26. Five-compartment fluidized limestone calciner, 13 ft in diameter, 45 ft high, charge 100 tons limestone/day. [Courtesy Dorr-Oliver Incorporated.]

heterogeneous fluid reactions are conducted in packed columns. The Solvay soda ash process employs a type of bubble-cap tray.

Electrochemical operations such as oxidation, reduction, and electrolysis require special equipment whose description lies outside the scope

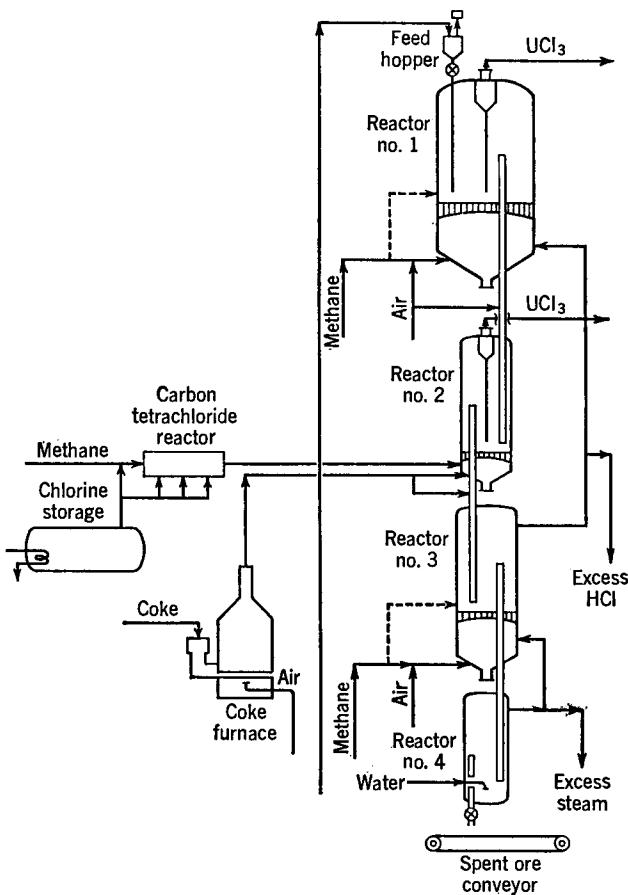


FIG. 11-27. Proposed unit for chlorination of uranium ores and recovery of chlorine reacting with the lime present. (Courtesy The C. W. Nafisinger Company.)

of this chapter. Electric-arc and photochemical processes are also left to specialized literature.

A plate-and-frame filter press serves as a polymerization reactor (Fig. 11-28) and could be used wherever the heated or cooled frames might be an advantage.

A ball-mill sulfonator is shown in Fig. 11-6, suitable when viscosity is high.

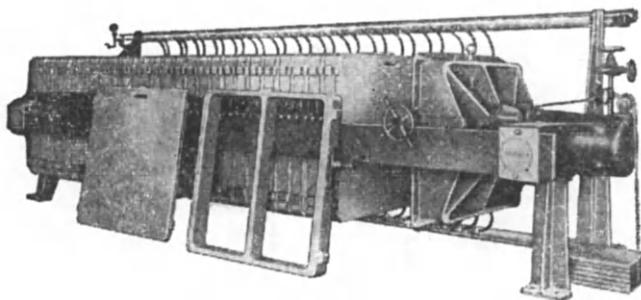


FIG. 11-28. Filter-press polymerization reactor: 30 chambers, each producing two 24-by 52-in. slabs, 5 in. thick. (Courtesy *T. Shriver & Company, Inc.*)

Flame reactors. Some reactions between gases are conducted noncatalytically at high temperatures by mixing the reactants in a burner or nozzle and discharging a flaming mixture into an open chamber. Cooling may be provided at the nozzle or in the chamber or by rapid quenching at the discharge from the chamber. Some reactions of this type include the formation of HCl from its elements and several partial oxidations, such as ethylene from ethane, acetylene from methane, and Fischer-Tropsch synthesis gas from methane; in these last reactions, just enough oxidation is permitted to achieve the necessary high temperatures.

Peak temperatures are attained very quickly in flames. If followed by rapid quenching by injection of a cold stream, excellent control of by-products can be maintained. The subject of flames has been widely investigated because of the importance of combustion processes (Lewis and von Elbe, 139; Gaydon and Wolfhard, 75). Stable flames exist only within relatively narrow limits of reaction velocity and gas flow rate. Roughly, gas velocities must be at least 0.8 fps, and peak temperatures at least 2200°F (Bartholomé, 15). If the reaction velocity is greater than the flow rate, the reaction moves back into the mixing nozzle; if the flow rate is too high, the flame is carried out of the reactor.

Space velocities of flame reactions range widely, depending on the reaction and also upon whether the reactants are premixed in a burner or enter the chamber unmixed. Some examples are in Table 11-5. Reactors are of relatively simple design, consisting merely of mixing nozzles or a burner, an open chamber, and suitable cooling provisions. A reactor for the production of acetylene and ethylene from hydrocarbon liquids is

shown in Fig. 11-29. Descriptions of the process are given by Barry, Braconier, Fox, Grover, and Leroux (13a) and by Patton, Grubb, and Stephenson (177a).

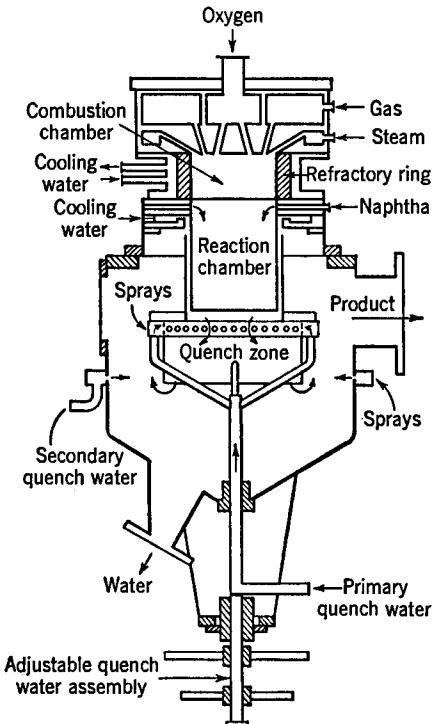


FIG. 11-29. Flame reactor for conversion of liquid hydrocarbons to acetylene and ethylene. [Patton, Grubb, and Stephenson (177a). Courtesy Petroleum Refiner.]

TABLE 11-5. SPACE VELOCITIES IN FLAME REACTORS

Process	Feed	Std cu ft/(hr)(cu ft)
$\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$	Not premixed	600
$\text{CH}_4 + \text{O}_2 \rightarrow$ Fischer-Tropsch synthesis gas.....	Not premixed	16,000
$\text{CH}_4 + \text{O}_2 \rightarrow \text{C}_2\text{H}_2$	Premixed	150,000

CHAPTER 12

MATHEMATICS FOR REVIEW

75. Introduction

Many physical laws are expressed as rate processes, for example, the rate of heat transfer (Fourier's law), the rate of diffusion (Fick's law), the rate of fluid flow, and the rate of chemical reaction. In terms of derivatives, some of these laws assume quite simple mathematical forms. Two aspects of this matter are of concern in a particular situation:

1. How to formulate or derive the differential equation
2. How to solve the resulting equation, that is, achieve a relation between the variables from which derivatives are absent

With regard to formulation, in simpler cases a rewriting of the physical law in mathematical form is all that is required. For instance, Newton's law of cooling of a body in contact with the atmosphere, which states that the rate is proportional to the excess of the body temperature over that of the atmosphere, can be written directly as $-dT/dt = k(T - T_s)$. Only a few rules can be given for the formulation of differential equations in general, namely:

1. Visualize a mechanism for the physical process. In mass transfer, for instance, the resistance may be regarded as confined to a thin stagnant film to which Fick's law may be applied.
2. Recall the applicable principles and laws and their mathematical forms.
3. Choose a differential element of time dt or of space, for instance, dV , and write down what happens to each of the other variables during dt or in dV .
4. Relate the differential changes of the various quantities by one of the conservation laws, that is, input = output + accumulation.

In any field, adeptness comes with practice. Inspection of many examples, the case method, is perhaps the best way to learn how to formulate differential equations. Many examples are scattered throughout this book, for instance, in Secs. 26, 30 to 32, 34, and 41.

A great deal more can be said about the solution of differential equations. Rules for the more common ones are collected in Sec. 76. A comprehensive catalogue of specific equations and their solutions has been

compiled by Kamke (117). Many differential equations cannot be solved formally, so approximation methods must be resorted to, of which a great many are available; generally, the more accurate, the more complex and laborious. For many practical purposes, the simpler methods adopted in this book are adequate. When better methods are needed for some professional work, books like those of Milne (159) and Salvadori (191) and many others can be consulted.

Partial differential equations arise when the simultaneous variation of more than two variables occurs. The same general principles hold for them as for ordinary differential equations. Besides the differential equation itself, other statements are needed for a complete mathematical description of a physical problem, such as the initial conditions sufficient to evaluate the constants arising from the integration of ordinary equations and specification of the initial and boundary-value conditions sufficient to evaluate the parameters that arise in the formal solution of partial differential equations.

The procedures for solving partial differential equations cannot be presented entirely satisfactorily in digest form. For a good digest, reference may be made to Eshbach (64), and for complete treatments, to Miller (155) and Mickley, Sherwood, and Reed (154). An example of the formal solution of a partial differential equation is shown in Sec. 52. Formal solutions of such equations are often difficult to obtain, so numerical methods must often be used. A great wealth of such methods for partial differential equations exists, of which one of the simpler ones is adopted in this book for illustrative purposes.

Problems in reaction kinetics frequently require use of numerical and graphical techniques for differentiation as well as for the solution of other than differential equations. Such methods are described in this chapter.

76. Ordinary Differential Equations

An ordinary differential equation (ODE) is a relation between several variables and the derivatives with respect to only one of them. A partial differential equation (PDE) contains derivatives with respect to more than one variable. The *order* of a DE is the order of the highest derivative present. The *degree* is the degree of the highest derivative present after rationalization and clearing of fractions. A *solution* of a DE has been considered achieved when the variables have been separated, even though the indicated integrations cannot be performed analytically. The *general solution* of an n th-order DE contains n arbitrary constants. A *particular solution* is obtained for fixed values of these arbitrary constants. A *linear* DE is of the first degree in the derivatives and the dependent variable. Any linear combination of particular solutions of a linear DE is likewise a solution.

For reference purposes, the chief DEs occurring in reaction kinetics are listed here with their solutions. Derivations may be found in all textbooks on the subject.

Variables separable

$$\frac{dx}{dt} = f(x)g(t) \quad (12-1)$$

Solution: $\int \frac{dx}{f(x)} = \int g(t) dt + C$

First-order linear

$$\frac{dx}{dt} + f(t)x = g(t) \quad (12-2)$$

Solution: $x = e^{-z} \left[\int g(t)e^z dt + C \right]$

where $z = \int f(t) dt$

Bernoulli

$$\frac{dx}{dt} + f(t)x = g(t)x^n \quad (12-3)$$

Solution: Convert to linear form by substituting

$$z = x^{1-n}$$

Second-order (special cases)

$$\frac{d^2x}{dt^2} = f(t) \quad (12-4)$$

Solution: $x = t \int f(t) dt - \int tf(t) dt + C_1 t + C_2$

$$\frac{d^2x}{dt^2} = f(x) \quad (12-5)$$

Solution: $x = \int \frac{dx}{C_1 + 2 \int f(x) dx} + C_2$

$$\frac{d^2x}{dt^2} = f\left(\frac{dx}{dt}\right) \quad (12-6)$$

Solve by eliminating the parameter $p = dx/dt$ from

$$t = \int \frac{dp}{f(p)} + C_1 \quad \text{and} \quad x = \int \frac{p dp}{f(p)} + C_2$$

$$\frac{d^2x}{dt^2} = f\left(\frac{dx}{dt}, t\right) \quad (12-7)$$

Eliminate the variable x with the substitution $p = dx/dt$. The resulting first-order equation in p and t may be solvable.

$$\frac{d^2x}{dt^2} = f\left(\frac{dx}{dt}, x\right) \quad (12-8)$$

Eliminate the variable t by substituting $p = dx/dt$. The resulting first-order equation in p and x may be solvable.

Second-order linear with constant coefficients, homogeneous

$$\frac{d^2x}{dt^2} + a \frac{dx}{dt} + bx = 0 \quad (12-9)$$

When the roots of the auxiliary equation $m^2 + am + b = 0$ are m_1 and m_2 ,

$$x = C_1 e^{m_1 t} + C_2 e^{m_2 t} \quad \text{when } m_1 \neq m_2 \quad (12-10)$$

$$x = e^{m_1 t}(C_1 + C_2 t) \quad \text{when } m_1 = m_2 \quad (12-11)$$

$$x = e^{pt}(C_1 \sin qt + C_2 \cos qt) \quad \text{when } m_1 = p + q\sqrt{-1}, m_2 = p - q\sqrt{-1} \quad (12-12)$$

Second-order linear with constant coefficients, nonhomogeneous

$$\frac{d^2x}{dt^2} + a \frac{dx}{dt} + bx = f(t) \quad (12-13)$$

The complete solution is the sum of the solution of the corresponding homogeneous equation [with $f(t) = 0$] and a particular solution. The latter is obtained by forming a linear combination of the different terms which occur in $f(t)$ and their distinct first and second derivatives, then substituting into the complete DE and evaluating the coefficients by inspection. Thus, if $f(t) = te^t + t^2$, the particular solution is $x_p = Ate^t + Be^t + Ct^2 + Dt + E$, in which the coefficients are to be determined as stated.

Simultaneous equations. No general rule can be given except to eliminate one variable at a time if possible. Solutions are shown in Secs. 17 and 29.

Bessel equation

$$t^2 \frac{d^2x}{dt^2} + t \frac{dx}{dt} + (t^2 - n^2)x = 0$$

$$\text{Solution: } x = C_1 J_n(t) + C_2 J_{-n}(t) \quad \text{when } n \text{ is not an integer} \quad (12-14)$$

$$x = C_1 J_n(t) + C_2 Y_n(t) \quad \text{when } n = 0 \text{ or an integer} \quad (12-15)$$

$J_n(t)$ and $Y_n(t)$ are known as the Bessel functions of the first and second kinds, respectively. They are defined by infinite series. When plotted they appear like trigonometric functions of diminishing amplitude and period. Numerical values are tabulated by Jahnke and Emde (110), who

use the symbol N_p instead of the more common Y_n . The solutions of many equations of the first and second orders can also be expressed in terms of Bessel functions. For a list, see Jahnke and Emde (111).

77. Numerical and Graphical Calculations

Taylor's theorem is the basis of many numerical methods. It defines the function $x = f(t)$ at a point $t = a + h$, in terms of values of the function and its derivatives at the point $t = a$.

$$f(a + h) = f(a) + hf'(a) + \frac{h^2f''(a)}{2!} + \frac{h^3f'''(a)}{3!} + \frac{h^4f^{(4)}(a)}{4!} + \dots \quad (12-16)$$

Similar equations are defined for functions of more than one variable.

Equation in one variable, $f(x) = 0$. If $x = a_0$ is approximately a root, then an improved value is

$$a_1 = a_0 - \frac{f(a_0)}{f'(a_0)} \quad (12-17)$$

This value in turn can be improved. For example, in the equation $x \ln x - 2 = 0$, an approximate root is $x = 2.4$ and an improved value is

$$x = 2.4 - \frac{2.4 \ln 2.4 - 2}{1 + \ln 2.4} = 2.344$$

Simultaneous equations

$$F(x,y) = 0 \quad \text{and} \quad G(x,y) = 0$$

Approximate values of the roots $x = a_0$ and $y = b_0$ can be estimated or obtained by plotting the curves and noting their intersections. Improved values are

$$a_1 = a_0 + \frac{F_y G - FG_y}{F_x G_y - F_y G_x} \quad (12-18)$$

$$b_1 = b_0 + \frac{-F_x G + FG_x}{F_x G_y - F_y G_x} \quad (12-19)$$

where $F_x = \partial F / \partial x$, etc. The functions and their derivatives are evaluated at the point (a_0, b_0) . For example, the equations

$$\begin{aligned} F(x,y) &= x^2 + y - 1 = 0 \\ G(x,y) &= 0.2x - y^3 + 0.3 = 0 \end{aligned}$$

have the approximate roots $x = 0.5$ and $y = 0.7$. Accordingly,

$$F = (0.5)^2 + 0.7 - 1 = -0.05$$

$$G = 0.2(0.5) - (0.7)^3 + 0.3 = 0.057$$

$$F_x = 2(0.5) = 1$$

$$F_y = 1$$

$$G_x = 0.2$$

$$G_y = 3(0.7)^2 = 1.47$$

$$x = 0.5 + \frac{(1)(0.057) - (-0.05)(1.47)}{(1)(1.47) - (1)(0.2)} = 0.603$$

$$y = 0.7 + \frac{-(1)(0.057) + (-0.05)(0.2)}{(1)(1.47) - (1)(0.2)} = 0.647$$

Differentiation with mirrors. The data are plotted, and a smooth curve is drawn. A front-surface mirror is held across the curve at the point where the slope is desired and adjusted until the image of the curve appears to be an unbroken continuation of the curve in front of the mirror (Fig. 12-1). This establishes the normal and enables accurate construction of the tangent. Alternatively, the slope of the tangent may be computed directly from that of the normal by the formula

$$\text{Tangent slope} = - \frac{1}{\text{normal slope}} \left(\frac{L_y}{L_x} \right)^2 \quad (12-20)$$

where L_x and L_y are the scale factors along the ordinate and the abscissa, that is, the number of units per inch or other linear dimension.

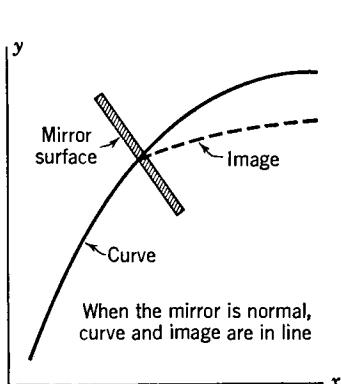


FIG. 12-1. Differentiation by the mirror method.

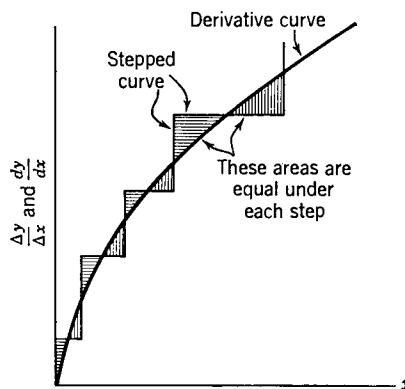


FIG. 12-2. Construction of derivative curve.

Differentiation by the derived-curve method. From the tabular data, values of $\Delta y/\Delta x$ are calculated and plotted as a stepped curve. The smooth derivative curve is drawn so that for each step the area under the curve is as nearly as possible equal to that under the step (Fig. 12-2).

Differentiation by three-point formulas. The slopes at each of three points equally spaced at interval h are given in terms of the ordinates. Thus

$$y'_0 = \frac{-3y_0 + 4y_1 - y_2}{2h} \quad (12-21)$$

$$y'_1 = \frac{-y_0 + y_2}{2h} \quad (12-22)$$

$$y'_2 = \frac{y_0 - 4y_1 + 3y_2}{2h} \quad (12-23)$$

This may be repeated for as many groups of three equally spaced points as desired.

Differentiation by five-point formulas

$$y'_0 = \frac{-25y_0 + 48y_1 - 36y_2 + 16y_3 - 3y_4}{12h} \quad (12-24)$$

$$y'_1 = \frac{-3y_0 - 10y_1 + 18y_2 - 6y_3 + y_4}{12h} \quad (12-25)$$

$$y'_2 = \frac{y_0 - 8y_1 + 8y_3 - y_4}{12h} \quad (12-26)$$

$$y'_3 = \frac{-y_0 + 6y_1 - 18y_2 + 10y_3 + 3y_4}{12h} \quad (12-27)$$

$$y'_4 = \frac{3y_0 - 16y_1 + 36y_2 - 48y_3 + 25y_4}{12h} \quad (12-28)$$

Formulas for as many as seven points are presented by Milne (158).

Integration graphically. The tabular data are plotted, and a smooth curve is drawn, then a stepped curve such that the area under each step is as nearly as possible equal to that under the smooth curve. The integral between two ordinates is the sum of the areas of the rectangles under the stepped curve between these ordinates (Fig. 12-4).

Integration by the trapezoidal rule. The smooth curve is replaced by a series of straight lines connecting successive points. Between two points,

$$\int_{t_0}^{t_1} = \frac{h}{2} (x_0 + x_1) \quad (12-29)$$

Between n equally spaced points,

$$\int_{t_0}^{t_n} = h \left(\frac{x_0 + x_n}{2} + x_1 + x_2 + \cdots + x_{n-1} \right) \quad (12-30)$$

Integration by Simpson's rule. This method replaces the curve by a series of parabolas passed through three uniformly spaced points at a time. Between three points,

$$\int_{t_0}^{t_2} = \frac{h}{3} (x_0 + 4x_1 + x_2) \quad (12-31)$$

When n is even,

$$\int_{t_0}^{t_n} = \frac{h}{3} [x_0 + 4(x_1 + x_3 + \cdots + x_{n-1}) + 2(x_2 + x_4 + \cdots + x_{n-2}) + x_n] \quad (12-32)$$

A useful formula is obtained by differentiation of Eq. 12-31; thus

$$x_{n+1} - x_{n-1} = \frac{h}{3} (x'_{n+1} + 4x'_n + x'_{n-1}) \quad (12-33)$$

When the tabular data are not uniformly spaced, they can be plotted, and then uniformly spaced points can be taken off the smooth curve. Numerical integration is especially valuable when a very wide range in numerical values is covered since logarithmic plotting may then be used to help in obtaining uniformly spaced values; such plots are of course not adaptable to graphical integration.

Illustration 12-1. For the data of t versus x shown in Table 12-1, the derivatives and the integral over the entire interval will be evaluated by the several methods presented here. Figure 12-3 is a plot of the data and shows the normals drawn with the

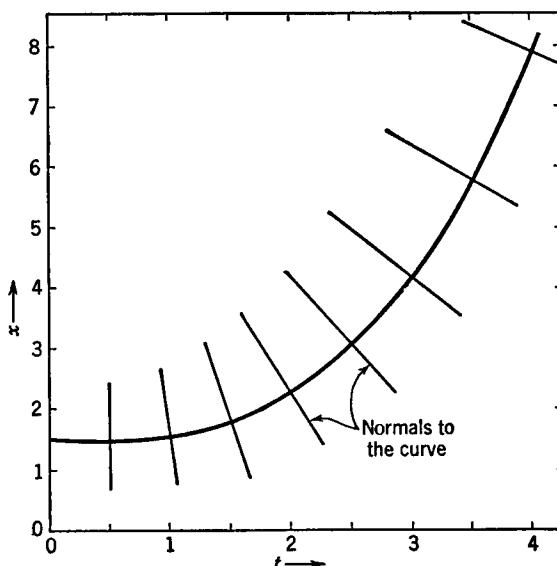


FIG. 12-3. Differentiation by the mirror method (Illustration 12-1).

aid of a mirror, from which the slopes are calculated and tabulated. Also shown are the results of calculations by the three-point and the five-point formulas and the true values from the equation $x = 1.5 + 0.1t^3$. Figure 12-4 shows the stepped curve from which the integral is evaluated. Comparison of integrals by the different methods follows:

Graphical:

$$A = 12.33$$

Trapezoidal rule:

$$A = 0.5 \left(\frac{1.500 + 7.900}{2} + 20.301 \right) = 12.501$$

Simpson's rule:

$$\begin{aligned} A &= \frac{0.5}{3} [1.500 + 4(12.201) + 2(8.100) + 7.900] \\ &= 12.401 \end{aligned}$$

True value:

$$A = 12.400$$

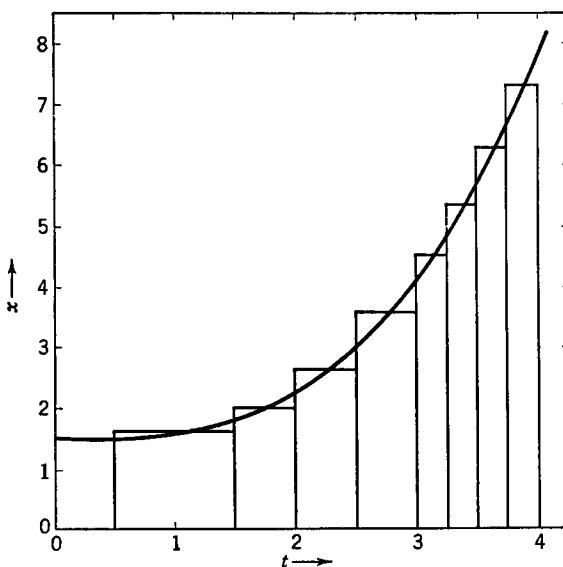


FIG. 12-4. Integration for Illustration 12-1.

Generally speaking, Simpson's rule is sufficiently superior to the trapezoidal or the graphical methods to warrant the extra trouble. The three-point formula appears to be inaccurate when one of the three points is much different from the others, as in the first group of three in this illustration. When a calculating machine is available, the five-point formulas are distinctly worthwhile.

TABLE 12-1. DATA AND RESULTS FOR ILLUSTRATION 12-1

t	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
x	1.500	1.513	1.600	1.838	2.300	3.062	4.200	5.788	7.900
dx/dt , mirror	0	0	0.29	0.67	1.08	1.80	2.80	3.53	4.45
dx/dt , 3-point...	0.050	0.100	0.250	0.624	1.224	1.824	2.652	3.700	4.748
dx/dt , 5-point...	-0.0091	0.0937	0.306	0.664	1.227	1.8753	2.7013	3.6753	4.7973
dx/dt , true value.....	0	0.0750	0.3000	0.6750	1.2000	1.8750	2.7000	3.6750	4.8000

78. Numerical Solution of Differential Equations

First-order ordinary differential equation $dx/dt = f(x,t)$, $x = x_0$ when $t = t_0$. From Taylor's theorem,

$$x_1 = x_0 + hx'_0 + \frac{h^2}{2!}x''_0 + \frac{h^3}{3!}x'''_0 + \dots$$

Succeeding values of x are obtained by repeated application of the formula

$$x_{n+1} = x_{n-1} + 2hx'_n \quad (12-34)$$

and the original differential equation (to evaluate x'). Geometrically, this formula states that the slope of a chord connecting two points on a curve is equal to the slope of the curve midway between these two points. This is approximately true and becomes more nearly so the closer the two points are together. The accuracy of the method is improved by taking the interval h smaller.

Illustration 12-2. To solve the equation $x' = (1 - x^2)^{1/2}$ with the initial conditions $x_0 = 0$ and $t_0 = 0$, choose $h = 0.1$. Evaluating the derivatives for use in Taylor's formula,

$$\begin{aligned}x_0' &= (1 - x_0^2)^{1/2} = 1 \\x_0'' &= -(1 - x_0^2)^{-1/2}x_0x_0' = 0 \\x_0''' &= -(1 - x_0^2)^{-1/2}[x_0x_0'' + (x_0')^2] - (x_0x_0')^2(1 - x_0^2)^{-3/2} = -1\end{aligned}$$

Accordingly,

$$x_1 = 0 + 0.1(1) + \frac{(0.1)^2}{2}(0) + \frac{(0.1)^3}{6}(-1) + \dots = 0.100$$

$$x_1' = [1 - (0.1)^2]^{1/2} = 0.995$$

$$x_2 = 0 + 2(0.1)(0.995) = 0.199$$

Calculations for the first five points are shown in Table 12-2 and compared with the true values obtained by direct integration.

TABLE 12-2. CALCULATIONS FOR ILLUSTRATION 12-2

t	Calculated x	x'	True value of x
0	0.000	1.000	0
0.1	0.100	0.995	0.0999
0.2	0.199	0.980	0.1985
0.3	0.296	0.950	0.2957
0.4	0.390	0.921	0.3894
0.5	0.480	0.877	0.4795

Second order, $x'' = f(x', x, y)$, with x_0 and x_0' specified. The second derivative is approximated by the second difference divided by h^2 . Consequently,

$$x_{n+1} = 2x_n - x_{n-1} + h^2x_n'' \quad (12-35)$$

Taylor's theorem is applied to finding x_1 and x_1' , the latter from the derivative of the theorem. In case it is necessary to evaluate first derivatives beyond this point, Eq. 12-33 will be found convenient.

Illustration 12-3. Solve $x'' = -2xx'$ with $x_0 = 0$, $x_0' = 1$, and $h = 0.1$. The higher derivatives are

$$\begin{aligned}x_0'' &= -2x_0x_0' = 0 \\x_0''' &= -2[x_0x_0'' + (x_0')^2] = -2 \\x_0^{(4)} &= -2[x_0x_0''' + 3x_0'x_0''] = 0 \\x_0^{(5)} &= -2[x_0x_0^{(4)} + 4x_0'x_0''' + 3(x_0')^2] = 16\end{aligned}$$

Substituting into Taylor's theorem,

$$\begin{aligned} x_1 &= 0 + 0.1(1) + \frac{0.01}{2}(0) + \frac{0.001}{6}(-2) + \frac{0.0001}{24}(0) + \frac{0.00001}{120}(16) + \dots \\ &= 0.0997 \end{aligned}$$

$$x'_1 = 1 + 0.1(0) + \frac{0.01}{2}(-2) + \frac{0.001}{6}(0) + \frac{0.0001}{24}(16) + \dots = 0.9901$$

Also

$$x''_1 = -2(0.0997)(0.9901) = -0.1974$$

From Eq. 12-35,

$$x_2 = 2(0.0997) - 0 + 0.01(-0.1974) = 0.1974$$

To evaluate x'_2 , eliminate the second derivative from the equations

$$x''_{n+1} = -2x_{n+1}x'_{n+1} \quad (\text{the original DE})$$

$$x'_{n+1} = x'_{n-1} + \frac{h}{3}(x''_{n+1} + 4x''_n + x''_{n-1}) \quad (\text{derivative of Eq. 12-33})$$

with the result

$$x'_{n+1} = \frac{x'_{n+1} + \frac{h}{3}(4x''_n + x''_{n-1})}{1 + \frac{2h}{3}x_{n+1}}$$

Then

$$x'_2 = \frac{1 + \frac{0.1}{3}[4(-0.1974) + 0]}{1 + \frac{2(0.1)}{3}(0.1974)} = 0.9610$$

$$x''_2 = -2(0.1974)(0.9610) = -0.3794$$

By repeated application of these formulas, the results in Table 12-3 are obtained.

Simultaneous equations, $x' = f(x, y, t)$ and $y' = g(x, y, t)$. Each equation is solved independently, with necessary substitution of values calculated from the other. The procedure will be illustrated for two first-order equations. Another example is in Sec. 17.

Illustration 12-4. Solve the two equations $x' = (1 - x^2)^{1/2}$ and $y' = x + ty$ with $t_0 = x_0 = y_0 = 0$ and $h = 0.1$. The solution of the first equation is in Illustration 12-2. For the other,

$$\begin{aligned} y'_0 &= x_0 + t_0 y_0 = 0 \\ y''_0 &= x'_0 + y_0 + t_0 y'_0 = 1 \\ y'''_0 &= x''_0 + 2y'_0 + t_0 y''_0 = 0.1 \\ y^{(4)}_0 &= x'''_0 + 3y''_0 + t_0 y'''_0 = 4.01 \end{aligned}$$

Therefore

$$y_1 + 0 + 0.1(0) + \frac{0.01}{2}(1) + \frac{0.001}{6}(0.1) + \frac{0.0001}{24}(4.01) + \dots = 0.0052$$

Continue with Eq. 12-34 and the procedure of Illustration 12-2, utilizing the values of x calculated from the other equation. Results are in Table 12-4.

TABLE 12-3. RESULTS FOR ILLUSTRATION 12-3

t	x	x'	x''	x'''	$x^{(4)}$	$x^{(5)}$
0	0	1.0000	0	-2.0000	0	16.0000
0.1	0.0997	0.9901	-0.1974	-1.9206	1.5550	13.1440
0.2	0.1974	0.9610	-0.3794			
0.3	0.2913	0.9151	-0.5332			
0.4	0.3780	0.8556	-0.6502			
0.5	0.4621	0.7865	-0.7269			

TABLE 12-4. RESULTS FOR ILLUSTRATION 12-4

t	x	x'	y	y'
0	0	1	0	0
0.1	0.100	0.995	0.0052	0.1052
0.2	0.199	0.980	0.0210	0.2032
0.3	0.296	0.950	0.0458	0.3097
0.4	0.390	0.921	0.1005	0.4300
0.5	0.480	0.877	0.1318	0.5459

Partial differential equations. One method of solution of many of the partial differential equations occurring in reaction kinetics is based on central differences. Using the notation

$$z_{m,n} = z(x_m, y_n)$$

$$h = \Delta x$$

$$k = \Delta y$$

the various partial derivatives are expressed as follows in terms of the point values shown in Fig. 12-5:

$$\frac{\partial z}{\partial x} = \frac{z_{m+1,n} - z_{m,n}}{h} \quad (12-36)$$

$$\frac{\partial z}{\partial y} = \frac{z_{m,n+1} - z_{m,n}}{k} \quad (12-37)$$

$$\frac{\partial^2 z}{\partial x^2} = \frac{1}{h} \left(\frac{z_{m+1,n} - z_{m,n}}{h} - \frac{z_{m,n} - z_{m-1,n}}{h} \right) = \frac{z_{m+1,n} - 2z_{m,n} + z_{m-1,n}}{h^2} \quad (12-38)$$

$$\frac{\partial^2 z}{\partial y^2} = \frac{z_{m,n+1} - 2z_{m,n} + z_{m,n-1}}{k^2} \quad (12-39)$$

$$\frac{\partial^2 z}{\partial x \partial y} = \frac{2z_{m+1,n+1} - 3z_{m+1,n} - 3z_{m,n+1} + 2z_{m,n} - z_{m-1,n} - z_{m,n-1}}{2hk} \quad (12-40)$$

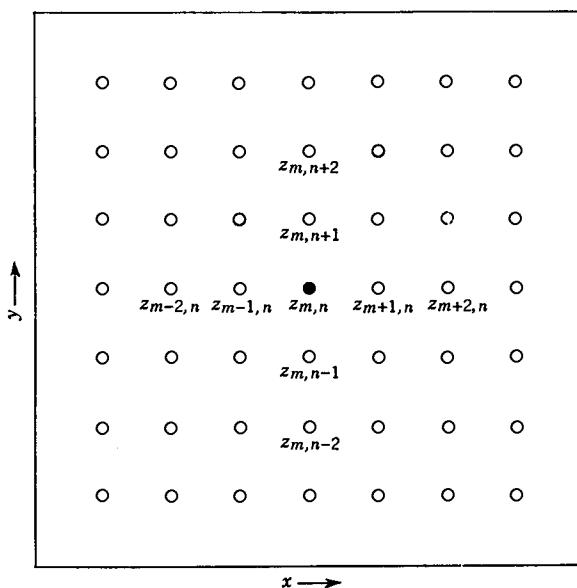


FIG. 12-5. Points used in forming differences to substitute for partial derivatives.

Sometimes a simplification of the difference equation results from proper choice of h and k . Thus the PDE for heat transfer,

$$\frac{\partial z}{\partial y} = a \frac{\partial^2 z}{\partial x^2}$$

becomes in difference form

$$\frac{z_{m,n+1} - z_{m,n}}{k} = \frac{a}{h^2} (z_{m+1,n} - 2z_{m,n} + z_{m-1,n})$$

Upon setting $h^2/ak = 2$ and rearranging, the difference equation assumes the simple form

$$z_{m,n+1} = 0.5(z_{m+1,n} + z_{m-1,n})$$

The sizes of the increments h and k affect the accuracy and labor of the solution. For some PDEs the errors resulting from substitution of differences for derivatives can be calculated by repeating a portion of the numerical solution with another value of h (Scarborough, 194). Available criteria for the stability and convergence of numerical solutions of linear PDEs with constant coefficients have been reviewed by Mickley, Sherwood, and Reed (154).

When the solution appears to be inaccurate, because the successive results oscillate or are physically unreasonable, probably the first move should be to repeat the solution with smaller increments. It may be possible to apply some of the criteria in the references just cited. Other

methods of solution are more stable than the one described here, though they are more laborious for a single application. These may be found in the references cited in this chapter.

Examples of numerical solutions of partial differential equations are shown in Secs. 52 and 58.

PROBLEMS

In the following, solve the differential equations. Answers are given in some instances as a check.

12-1. $\frac{dy}{dx} + 2xy = 4x.$ $y = 2 + Ce^{-x^2}.$

12-2. $x \frac{dy}{dx} = y + x^3 + 3x^2 - 2x.$ $2y = x^3 + 6x^2 - 4x \ln x + Cx.$

12-3. $\frac{dy}{dx} + \frac{1}{3}y = \frac{1}{3}(1 - 2x)y^4.$ $y^{-3}e^{-x} = -2xe^{-x} - e^{-x} + C.$

12-4. $x \frac{dy}{dx} + (1 + x)y = e^x.$ $xye^x = \frac{1}{2}e^{2x} + C.$

12-5. $\left(\frac{dy}{dx}\right)^2 + y^2 = 1.$ $y = \sin(x + C) \quad \text{or} \quad y = \cos(x + C).$

12-6. $\frac{d^2y}{dx^2} - 3 \frac{dy}{dx} + 2y = 0.$ $y = C_1 e^x + C_2 e^{2x}.$

12-7. $4 \frac{d^3y}{dx^3} - 3 \frac{dy}{dx} + y = 0.$ $y = (C_1 + C_2 x)e^{x/2} + C_3 e^{-x}.$

12-8. $\frac{d^2y}{dx^2} - 6 \frac{dy}{dx} + 25y = 0.$ $y = e^{3x}(C_1 \sin 4x + C_2 \cos 4x).$

12-9. $\frac{d^2y}{dx^2} - 3 \frac{dy}{dx} + 2y = e^x.$ $y = C_1 e^x + C_2 e^{2x} - xe^x.$

12-10. $\frac{dx}{dt} + \frac{dy}{dt} - x = 2t + 1.$ $x = -t - \frac{1}{3}.$

$2 \frac{dx}{dt} + 2 \frac{dy}{dt} + x = t.$ $y = \frac{t^2}{2} + \frac{4t}{3} + C.$

12-11. By numerical methods, show that the solution of the differential equation $dy/dt = 2.3746 - 1.8y - 0.5746y^3$, with the initial condition $y(0) = 0$, is as follows:

t	0	0.05	0.10	0.15	0.20	0.25
y	0	0.1135	0.2169	0.3113	0.3966	0.4738

12-12. The solution of the rate equations for a complex reaction is

$$C_a = 2.0e^{-k_1 t}$$

$$C_b = \frac{2k_1}{k_1 - k_2} (1.5 - e^{-k_1 t})$$

Given the condition that $C_a = 0.5$ and $C_b = 4.5$ when $t = 5.0$, find the numerical values of k_1 and k_2 .

12-13. From the following data on a reacting system, find the rate of reaction by several of the methods described in this chapter, as a function of the time.

<i>Time,</i> <i>min</i>	<i>Concentration,</i> <i>lb moles/cu ft</i>	<i>Time,</i> <i>min</i>	<i>Concentration,</i> <i>lb moles/cu ft</i>
0	1.25	9	0.590
1	1.11	10	0.555
2	1.01	15	0.435
3	0.910	20	0.357
4	0.825	25	0.303
5	0.770	30	0.264
6	0.715	40	0.208
7	0.670	50	0.172
8	0.625		

APPENDIX 1

THE LITERATURE OF REACTION KINETICS

In this text it has not been possible to treat any topics exhaustively and some have had to be omitted entirely. These shortcomings can be remedied in part by reference to other publications, so the present guides to the literature of reaction kinetics are offered. These bibliographies and specific references are not meant to be scholarly in the sense of citing original sources, but they are meant to be immediately useful in providing background or amplification. Wherever original sources are not cited in this text, they may certainly be found in some of the many articles and books listed here. The references are grouped in the following categories.

Literature cited. Specific references made throughout the text have been arranged alphabetically by the first author's name and have been given numbers by which they are referred to in the text. Page references to the text are given, so this list serves as a partial author index.

Further readings are suggested for individual sections or chapters. Mostly they are either parallel or supplementary treatments in other books or comprehensive review articles. They are listed by author with a letter-and-number reference to items in Sec. 81 or are complete with title and date if the item is not listed there.

Books and reviews list most of the recent books relating to kinetics and some on catalysis, since it is not possible to dissociate these two topics. Included are a few books of more general character with substantial portions devoted to kinetics, as well as references to certain annual reviews in this field.

Serial works. In order to make these valuable works more accessible, the tables of contents have been included from Emmett, "Catalysis," and the series "Advances in Catalysis."

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- Mechanisms of polymer formation and decomposition
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* Various editors, Academic Press, Inc., New York.

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Electronic properties and catalytic activity

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Homogeneous catalysis

Corrosion and surface reactions

Chemisorption of oxygen

Adsorption phenomena

Catalytic cracking and cracking catalysts

Isomerization and other reactions of hydrocarbons

Reactions of carbon monoxide

Tracer and other techniques

Miscellaneous catalytic reactions

APPENDIX 2

CONSTANTS AND CONVERSION FACTORS

CONSTANTS

Acceleration due to gravity:

$$\begin{aligned}g &= 32.2 \text{ ft}/(\text{sec})^2 \\&= 4.18(10^8) \text{ ft}/(\text{hr})^2\end{aligned}$$

Gas-law constant:

$$\begin{aligned}R &= 1.987 \text{ Btu}/(\text{lb mole})(^{\circ}\text{R}) \\&= 1.987 \text{ cal}/(\text{g mole})(^{\circ}\text{K}) \\&= 0.729 \text{ (atm)(cu ft)}/(\text{lb mole})(^{\circ}\text{R}) \\&= 10.71 \text{ (psi)(cu ft)}/(\text{lb mole})(^{\circ}\text{R}) \\&= 0.082 \text{ (liter)(atm)}/(\text{g mole})(^{\circ}\text{K})\end{aligned}$$

Ideal-gas specific volume:

$$\begin{aligned}V &= 379 \text{ cu ft}/\text{lb mole at 1 atm and } 60^{\circ}\text{F } (520^{\circ}\text{R}) \\&= 359 \text{ cu ft}/\text{lb mole at 1 atm and } 32^{\circ}\text{F } (492^{\circ}\text{R}) \\&= 22.4 \text{ liters/g mole at 1 atm and } 0^{\circ}\text{C } (273^{\circ}\text{K})\end{aligned}$$

Temperature:

$$\begin{aligned}^{\circ}\text{C} &= 0.556(^{\circ}\text{F} - 32) \\^{\circ}\text{F} &= 1.8(^{\circ}\text{C}) + 32 \\^{\circ}\text{K} &= ^{\circ}\text{C} + 273 \\&= 0.556(^{\circ}\text{R}) \\^{\circ}\text{R} &= ^{\circ}\text{F} + 460 \\&= 1.8(^{\circ}\text{K})\end{aligned}$$

CONVERSION FACTORS

To convert from	To	Multiply by
angstroms	meters	10^{-10}
angstroms	microns	10^{-4}
atmospheres	inches of mercury	29.92
atmospheres	millimeters of mercury	760
atmospheres	pounds per square foot	2,112
atmospheres	pounds per square inch	14.696
barrels (oil)	gallons (U.S.)	42
barrels per day	gallons per hour	1.75
barrels per day	gallons per minute	0.02917
Btu	kilocalories	0.252
Btu per pound	calories per gram	0.556
Btu per pound per degree	calories per gram per degree centigrade	1.00
Fahrenheit		
calories per gram	Btu per pound	1.8
centimeters	inches	0.3937
centipoises	pounds per foot per hour	2.42
centipoises	pounds per foot per second	0.000672
cubic feet	cubic meters	0.02832
cubic feet	gallons (U.S.)	7.481
cubic feet	liters	28.316
cubic meters	cubic feet	35.314
feet	centimeters	30.48
feet	meters	0.3048
gallons (U.S.)	cubic feet	0.1337
gallons (U.S.)	liters	3.7853
gallons per minute	barrels per day	34.28
grams	pounds	0.002205
kilocalories	Btu	3.969
kilograms	pounds	2.205
liters	cubic feet	0.03531
liters	gallons (U.S.)	0.2200
meters	angstroms	10^{10}
meters	feet	3.281
meters	microns	10^6
microns	angstroms	10^4
microns	meters	10^{-6}
microns	millimeters	10^{-3}
pounds	grams	453.6
pounds	kilograms	0.4536
square centimeters per second	square feet per hour	3.875
square feet	square inches	144
square feet	square centimeters	929.03
square feet	square meters	0.0929
square feet per hour	square centimeters per second	0.2581
square meters	square feet	10.76
tons (long)	pounds	2,240
tons (metric)	pounds	2,204
tons (short)	pounds	2,000

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