CHEMICAL REACTION ANALYSIS

PRENTICE-HALL INTERNATIONAL SERIES
in the PHYSICAL and CHEMICAL ENGINEERING SCIENCES

Chemical Reaction Analysis

EUGENE E. PETERSEN

Department of
Chemical Engineering
University of California at Berkeley

PRENTICE-HALL, INC.

Englewood Cliffs, New Jersey

PRENTICE-HALL INTERNATIONAL, INC., *London*
PRENTICE-HALL OF AUSTRALIA, PTY, LTD., *Sydney*
PRENTICE-HALL OF CANADA, LTD., *Toronto*
PRENTICE-HALL OF INDIA (PRIVATE) LTD., *New Delhi*
PRENTICE-HALL OF JAPAN, INC., *Tokyo*

Englewood Cliffs, N.J.

Library of Congress Catalog Card Number: 64—66084

Printed in the United States of America

C—12872

Preface

Under the generic title "Chemical Reaction Analysis" this book deals with chemical kinetic processes and physical rate processes, and the manner in which these processes interact to govern the apparent overall behavior of chemically reactive systems. Although systems of this type are evident in many branches of science and engineering, the study and development of the field has remained largely within the sphere of chemical engineering; as a result, emphasis has been placed on serving the needs of the chemical industry. To an extent, such emphasis is justified. On the other hand, we cannot overlook the importance of many systems which lie outside the usual realm of chemical engineering, such as those supplying nutrients to the living cell or igniting solid propellants, all of which can be analyzed from a common set of principles. Accordingly, it seemed appropriate to shape this book to serve the needs of those interested in chemically reactive systems in general: to emphasize the chemical reaction itself and show how the behavior of the reaction system is modified when resistance to energy and material transport is large. By following this more general approach, I hope to have made the book valuable to a greater audience, who can adapt the principles and methods to fit specific cases rather than depend upon recipes.

Manifestly, this small book cannot cover all the topics which are concerned with heterogeneous chemical reactions and transport processes. The subject is too broad for this. However, the problem of what to select was quite naturally resolved for me: I could best deal with those topics which reflected my own interest and experience. Perhaps no one will completely agree with my selection of subject material; but I do not view this with any great alarm, because the subject matter is reasonably diverse and is developed from a unified point of view, thereby giving a perspective from which the vast and rich literature in this field can be evaluated. In fact, if the book stimulates the reader to probe deeper into this fascinating area, it will have served its purpose.

Certain prerequisite knowledge is assumed as part of the reader's background. He should have some familiarity with kinetics, and in particular with catalysis, because the treatment of the latter topic in this book is probably insufficient for the application of these methods to a specific problem. He must have had some experience with the theory of transport processes, and should have a working knowledge of ordinary differential equations. To understand the treatment of complex reactions, familiarity with vector and matrix operators is needed. The discussions in the two appendices should be sufficient for this purpose; however, to work confidently with these methods the suggested references should be consulted.

Many people have encouraged me and helped me in the writing of this book and to these people, many of whom must remain anonymous, I am indebted. I take pleasure in acknowledging the helpful comments of my colleagues Professors R. Aris, J. M. Prausnitz and T. Vermeulen on various parts of the book. I am sincerely grateful to two other colleagues, Professors A. Acrivos and M. Boudart, for helping me to shape ideas during the course of this project and for their comments on the finished manuscript. Their influence is evident in many parts of this book. I owe a great debt to Dr. J. C. Friedly who patiently and critically read the original manuscript. His comments and suggestions for improvement are too numerous to list in detail. To Mrs. Edith Taylor and Mrs. Jerilyn Schricker, who contributed far more to the final form of the manuscript than typing, I express my sincere thanks. Finally, this book would not have been possible without the efforts of my wife, Kay, who saw to it that large blocks of uninterrupted time were available to me for meditation.

E. E. PETERSEN

Berkeley, California

Contents

Introduction

1

The first aphorism of Sir Francis Bacon's *Novum Organum*, "Man, who is the servant and interpreter of nature, *can act and understand no further than he has observed*, either in operation or in contemplation, of the method and order of nature" [emphasis added], is almost a prophetic warning of special significance to the kineticist. He depends upon experimental measurements perhaps even more than does his counterpart in other areas of chemistry and chemical engineering. The rate of a chemical reaction *must* be measured experimentally. And yet, curiously, without theoretical interpretation, a set of measurements is often virtually useless. The bridge between theory and experiment is chemical reaction analysis: a subject concerned with the interaction of chemical kinetic and physical rate phenomena and having for its objective the resolution and evaluation of the importance of each of the individual processes in the over-all rate process.

Very few real systems involving chemical reactions can be analyzed, even in principle, with rigor, whereas certain systems, some of which have little practical importance, can be analyzed in a sophisticated fashion. While at first it may seem strange to be concerned with systems of little practical value, the real purpose of analysis is to find out which features of a reaction system are important. Can we neglect certain features which greatly complicate the analysis of the system and obtain a meaningful result? Unfortunately no unique answer can be given to this question because the importance of a particular effect often depends upon how the information is to be used as well as upon what property is being assessed. Intuition is often unreliable in making this decision. Thus, the systematic survey of the influence of certain coupled processes in modifying the over-all rate of chemical reactions combined with the development of techniques for analyzing such systems become the avowed objectives of chemical reaction analysis.

The task of the chemical reaction analyst may be rather idealistically divided into two phases: to measure and evaluate the chemical kinetic behavior of the particular system of interest, and to use this information to design equipment in which this reaction can be carried out economically on a commercial scale. Without minimizing the importance and difficulty of the latter phase, the former is by far the more difficult and important. Moreover, the first phase *should be* completed before the latter phase begins. It is for this reason that this book deals almost exclusively with the evaluation of chemical kinetic behavior.

Difficulties arise, however, when we endeavor to deal exclusively with chemical kinetics. A given chemical reaction will often occur only over a rather narrow range of conditions, and everywhere within this range other processes, such as transport of mass and energy, may influence the over-all rate. In these cases we are forced to analyze all of the processes simultaneously if we are to learn about the kinetics. Finally, chemical reaction rates are measured in reactors, and accordingly we shall find it necessary to analyze the characteristics of the particular reactor in which the rates are measured in order to obtain the desired information. Thus it follows that the principles necessary to carry out the first phase include those basic to reactor design.

In this book we shall progress systematically from simple to complex systems. First, we discuss chemical reactions as isolated processes: the determination of a chemical reaction rate from experiments, and the relationship between the functional form of the heterogeneous rate expression and reaction mechanisms. We progress to systems wherein transport phenomena modify the true kinetic behavior. In these sections, we seek criteria whereby the importance of physical phenomena can be assessed from experimental measurements. Later chapters emphasize the analysis of reactors.

Nowhere in this book will there be found a master key for the analysis of chemically reactive systems. Each system has peculiarities of its own. However, with a knowledge of the characteristic behavior of processes which mask the kinetic behavior, it should be possible to plan an experimental program to study the basic process—the kinetics—efficiently. Experience gained by analyzing the behavior of elementary systems is valuable in developing a perspective from which the important processes governing the behavior of complex systems are more quickly identified and isolated.

The Rate Expression 2

2.1 Rate of chemical reaction

Chemical reactions are interactions among molecules to alter the molecular species present. A chemical transformation results in a rearrangement of the atoms in a part of the original species present (reactants) to form other species (products) in such a way as to conserve atoms. The extent to which a particular chemical reaction has occurred is then associated with the number of the original molecular species which have been transformed into specified product molecules.

Chemical reactions may take place in a single phase, or in several phases or at phase interfaces, giving rise to their classification as either homogeneous or heterogeneous. In this chapter, we shall be interested in rate laws for both kinds of kinetics. The most useful quantitative description of a chemical rate process relates the specific reaction rate to the relevant intensive properties of the system. In the case of a homogeneous reaction, the specific reaction rate is a measure of the number of molecules undergoing a particular chemical transformation per unit time per unit volume. The heterogeneous reaction rate is similarly defined except that it is based upon a unit area rather than a unit volume. The desirable form of a specific reaction rate is therefore an *intensive property* of a system and care must be exercised in its mathematical formulation to preserve this property. Although the discussion immediately following applies in the strictest sense only to homogeneous reactions, we shall later recognize its applicability to heterogeneous systems.

2.2 Simple reactions

In much of the early experimental work in chemical kinetics, investigators were concerned with closed, constant volume, homogeneous, isothermal, batch systems. In such a system consider the general simple reaction below:

$$\sum_{i=1}^{n} a_i A_i = 0, \tag{2.2-1}$$

where $a_i < 0$ and $a_i > 0$ are, respectively, the stoichiometric coefficients of reactants and products. The number of molecules of the ith species which react per unit time per unit volume will not in general be equal to the number of molecules of the jth species. However, these rates will be related by a simple ratio of the stoichiometric coefficients. The conservation equation for this system becomes

$$\frac{1}{a_i}\frac{dC_i}{dt} = \frac{1}{a_j}\frac{dC_j}{dt} = \bar{\mathscr{R}},^{*} \tag{2.2-2}$$

the specific rate of reaction, where C_i and C_j are the concentrations of A_i and A_j, respectively. Note that the form of Eq. 2.2-2 defines a reaction rate which is the same for all n species in the system. This, of course, is a direct consequence of the fundamental meaning of the stoichiometric equation.

The contention that the specific rate of the reaction $\bar{\mathscr{R}}$ is uniquely determined by a set of intensive properties of the system is supported by an overwhelming preponderance of experimental evidence as well as by complete consistency with kinetic theory. We shall consider the function $\bar{\mathscr{R}}$ to be of the form

$$\bar{\mathscr{R}} = \bar{\mathscr{R}}(T, C_{A_1}, C_{A_2}, C_{A_3}, \ldots, C_{A_n}), \tag{2.2-3}$$

i.e.,

$$\frac{\bar{\mathscr{R}}_i}{a_i} = \frac{\bar{\mathscr{R}}_j}{a_j} = \bar{\mathscr{R}}. \tag{2.2-4}$$

A chemical reactor designed to carry out the reaction of Eq. 2.2-1 on an industrial scale may not meet the restrictions imposed upon the system used to obtain the rate law $\bar{\mathscr{R}}$ from Eqs. 2.2-2 and 2.2-3; however, whether it does or does not is irrelevant, because the function $\bar{\mathscr{R}}$ is an intensive property of the particular system and can be used along with the appropriate equations

---

* The bar notation refers to reaction rate per unit volume or the rate in a reference volume. The absence of a bar refers to a heterogeneous rate expression.

for the conservation of species i and energy to obtain in principle the correct design. The danger in the restricted definition as given in Eq. 2.2-2 is, therefore, that an incorrect formulation of the function $\mathscr{R}$ will result if the experimental reactor does not meet the restrictions implicit in the equation used to interpret the experimental results.

In an effort to obtain a more general equation for determining $\mathscr{R}$, consider a closed, homogeneous, isothermal, batch system, but not constant volume. Figure 2.2-1(a) shows a cylindrical batch reactor of unit cross-sectional area fitted with a piston so that the volume of the reactor can be varied arbitrarily during the course of reaction by, say, varying the pressure on the external side of the piston. Suppose that there are $N(t)$ molecules of certain reactant species present at a time t, and at some later time, $t + \Delta t$, there are $N(t + \Delta t)$ molecules of the same species. Then during the time interval Δt, $N(t) - N(t + \Delta t)$ molecules have reacted. Now the conservation equation must be modified because the specific rate $\mathscr{R}$ is concerned with the number of molecules undergoing reaction per unit volume per unit time. Under the given set of conditions the value of $\mathscr{R}$ is given by Eq. 2.2-5:

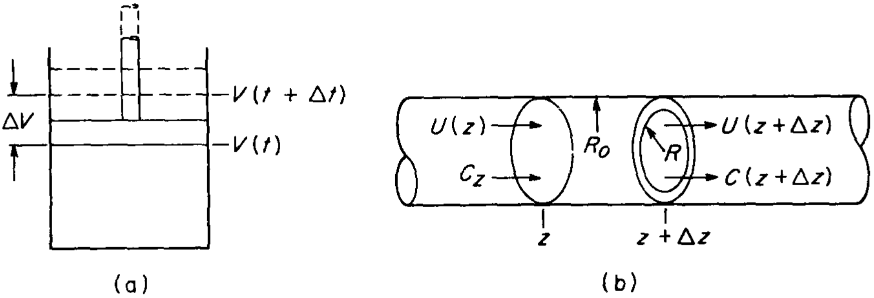

Fig. 2.2-1. Schematic diagrams of batch and piston flow reactors.

$$\lim_{\Delta t \to 0} \left\{ \frac{1}{V(t)} \frac{N(t + \Delta t) - N(t)}{\Delta t} \right\} = \frac{1}{V(t)} \frac{dN(t)}{dt} \tag{2.2-5}$$

Equation 2.2-6 extends this definition to give a rate expression which is the same for all species. This equation is more general than Eq. 2.2-2 and may be used together with Eq. 2.2-1 to predict the rate of reactions in most batch reactors and from which $\mathscr{R}$ can be obtained from experimental data.

$$\frac{1}{V(t)a_i} \frac{dN_i(t)}{dt} = \frac{1}{V(t)a_j} \frac{dN_j(t)}{dt} = \mathscr{R}(T, C_{A_1}, C_{A_2}, \ldots, C_{A_n}) \tag{2.2-6}$$

There seems to be considerable confusion in the literature on the formulation and use of the rate law. The difficulty appears to stem from a conflict in the intended use of kinetic equations. At the risk of being repetitious, attention should again be called to several points which follow directly from the discussion in the introduction to this chapter. The rate function $\bar{\mathscr{R}}$ is a well-defined intensive property of the system. To determine values of $\bar{\mathscr{R}}$, it is necessary to measure how many molecules of a species (for simple reactions of the type in Eq. 2.2-1) react per unit time in a unit volume. Under the conditions of the first system discussed (constant volume), the number of molecules reacted is directly proportional to the concentration and Eq. 2.2-2 correctly describes the system. In the second system, the concentration of a species may vary for two reasons; reaction of the species and a volume change. We must, therefore, account for volume changes in the conservation equation in such a way that only the reacted molecules of the species are measured and equated to $\bar{\mathscr{R}}$. To determine the nature of the $\bar{\mathscr{R}}$ function, it is necessary to compute the corresponding concentrations of all species and temperature for each value of $\bar{\mathscr{R}}$. Since the determination of the rate function is the objective of most kinetic studies, the equation used to interpret kinetic data should be formulated to apply to the particular apparatus used.

As a final illustration consider the open, isothermal flow system shown in Fig. 2.2-1(b). If $U = U(z)$ is uniform across a given cross section at z, then the equipment is generally referred to as a piston or plug-flow reactor. Under steady-state conditions, conversion is a function of position z, rather than time. Then

$$\frac{1}{a_i}\operatorname{div}(UC_i) = \frac{1}{a_j}\operatorname{div}(UC_j) = \bar{\mathscr{R}}, \tag{2.2-7}$$

where $-\operatorname{div}(UC)$ is equal to the net accumulation per unit volume per unit time in the differential volume owing to the flow flux, UC_i.* For this one-dimensional system Eq. 2.2-7 becomes

$$\frac{1}{a_i}\frac{d(UC_i)}{dz} = \frac{1}{a_j}\frac{d(UC_j)}{dz} = \bar{\mathscr{R}}. \tag{2.2-8}$$

Note that $\Delta z/U$ is a measure of residence time in the differential volume.

Equation (2.2-8) is not a particularly useful expression when the number of moles in a reference mass of feed changes with chemical reaction. This latter condition can be expressed mathematically as

$$\sum_{i=1}^{n} a_i \neq 0. \tag{2.2-9}$$

When the number of moles changes during the course of reaction, the velocity becomes a function of z, the distance along the reactor. For such systems, an alternate expression will be adopted at this time and used

---

* Readers not familiar with vector notation should refer to the brief discussion in Appendix I.

throughout the remainder of the book. Take as a basis a mass of feed equal numerically to the average molecular weight of the feed stream, $\bar{M}$. The concentration variable Y_i is then defined as the number of moles of the ith species in a mass of reacting mixture numerically equal to $\bar{M}$. Thus, Y_{i0}, the concentration of i in the initial feed mixture, corresponds to the mole fraction of i therein. Substituting into Eq. 2.2-7,

$$\frac{1}{a_i}\operatorname{div}(UC_i) = \frac{1}{a_i}\operatorname{div}\left\{\frac{\rho_T U}{\bar{M}}\frac{\bar{M}C_i}{\rho_T}\right\} = \frac{G_0}{a_i\bar{M}}\operatorname{div} Y_i, \tag{2.2-10}$$

where ρ_T = the density at any point within the flow reactor,
$G_0 = \rho_T U$ = the mass velocity—a constant throughout the plug-flow reactor.

Eq. 2.2-8 becomes

$$\frac{G_0}{a_i\bar{M}}\frac{dY_i}{dz} = \mathcal{R}, \tag{2.2-11}$$

which may be used to obtain $\mathcal{R}$ in an isothermal flow reactor in which the number of moles of reactants in the stoichiometric equation differs from the number of moles of products.

Looking back through this section, we note that in Eqs. 2.2-2, 2.2-6, and 2.2-11 the specific rate function $\mathcal{R}$ has been set equal to three different expressions. Throughout the remainder of this book, many more expressions will appear which contain this function. To argue that any one of these is more correct than all of the others as its defining equation is to confuse a conservation equation with a definition. The function $\mathcal{R}$ is a source term in a conservation equation and the remaining terms in the above equations vary with the type of system in question. In this respect, it is instructive to note that every design equation in this book in which $\mathcal{R}$ appears may be viewed as a possible means of determining it, but none of them is its defining equation.

We see that the $\mathcal{R}$ function is independent of the system in which it was obtained. Its functional dependence upon the relevant intensive properties of the system will be most reliably determined in simple systems wherein the kinetic phenomena are emphasized and transport phenomena minimized. Conversely, it is usually unreliable to infer the kinetics from the over-all performance of equipment encumbered by complex transport mechanisms. Thus the design engineer is faced generally with two problems: finding the $\mathcal{R}$ function from an experimental apparatus making use of valid conservation equations for that system, and its subsequent combination with the relevant equations of motion and conservation for a particular reactor to predict the latter's performance.

2.3 Complex reactions

Reactions of industrial importance are frequently not simple and cannot, therefore, be represented by a single stoichiometric equation of the form shown in Eq. 2.2-1. The departure from the simple system may arise for a variety of reasons. As examples, the formation of a given set of products may occur by more than one reaction path, or a given set of reactants may go to several sets of products, or a reaction may take place between the reactants and the intermediate products to form additional products. The analysis of such systems may be undertaken by writing a set of stoichiometric equations each of which corresponds to a reaction which is known to occur in the system. Let us assume that the number of such equations corresponds to m. A careful survey of these equations may show that they are not all linearly independent, i.e., it may be possible to obtain one of the stoichiometric equations by adding or subtracting two or more of the other members of the set. Should this be the case, then it is possible to reduce the m equations to, say, k equations which are now linearly independent. The system can be represented completely by the set of k equations.

A simple example which illustrates this point is the reaction of graphite with oxygen. Three reactions may be presumed to take place:

$$\left.\begin{aligned} C + \tfrac{1}{2}\,O_2 &= CO &\quad (1)\\ C + O_2 &= CO_2 &\quad (2)\\ CO + \tfrac{1}{2}\,O_2 &= CO_2 &\quad (3) \end{aligned}\right\} \qquad (2.3\text{-}1)$$

In this case $m = 3$. By inspection, we can see that these three equations are not linearly independent because adding (1) and (3) of Eq. 2.3-1 gives (2). Thus, we say one of the equations is linearly dependent and $k = 2$. The choice as to which two equations are retained is arbitrary from the standpoint of stoichiometry, although all may be valid paths mechanistically.

If the original set of m equations included all of the reactions which take place to an appreciable extent, it then follows that it is necessary to know the rates of appearance or disappearance with respect to k components in order to determine the rate at which each reaction of the original scheme has occurred at a particular point. The analysis of the system has been reduced to the problem of solving k simultaneous equations in k unknowns. Obviously, if the system is small (k is small), there is no compelling reason to develop a formal system of analysis and the familiar algebraic methods for handling such equations are adequate. However, a formal method of analysis offers some computational advantages when k is large for two reasons: it minimizes the opportunity for computational errors, and it makes use of standard programs available for large digital computers.

Consider the general set of stoichiometric reactions

$$\sum_{i=1}^{n} a_{ij}A_i = 0 \qquad (j = 1, 2, 3 \ldots m), \tag{2.3-2}$$

which is a shorthand representation of the following set of equations:

$$\left.\begin{aligned} a_{11}A_1 + a_{21}A_2 + a_{31}A_3 + \ldots + a_{n1}A_n &= 0 \\ a_{12}A_1 + a_{22}A_2 + \ldots\ldots\ldots + a_{n2}A_n &= 0 \\ a_{1k}A_1 + a_{2k}A_2 + \ldots\ldots\ldots + a_{nk}A_n &= 0 \\ a_{1m}A_1 + a_{2m}A_2 + \ldots\ldots\ldots + a_{nm}A_n &= 0 \end{aligned}\right\} \tag{2.3-3}$$

where values of a_{ij} are the stoichiometric coefficients and where $a_{ij} < 0$ refer to reactants and $a_{ij} > 0$ refer to products. As before, assume that the first k of these m equations are linearly independent, where of course $m > k$. Another way of saying this is that we form an n by m matrix of the stoichiometric coefficients and determine the rank of the largest *nonsingular* matrix* which for the above case will be k.

What we generally seek in the analysis is to determine the rate at which each of the k independent equations occurs under a prescribed set of conditions and to compute the compositions of each of the components and the temperature corresponding to these rates. Similar analyses are carried out for a wide variety of conditions in order to establish the rate at which each reaction occurs as a function of concentrations of the various species present, the temperature, and other conditions such as catalyst activity, etc., in order to establish the nature of the $\mathscr{R}$ function for each reaction. The hope is that this information will lead to some kinetic model. It may be pertinent to remark at this point that the mechanistic equations which describe the kinetic path model, if indeed they are obtained, will almost certainly be different from the set of k stoichiometric equations as written. In the absence of a kinetic model, the $\mathscr{R}$ functions may be represented as an empirical function of reaction conditions.

This objective cannot be realized without taking into account the type of reactor in which the rate data are determined. By analogy with our earlier discussion of simple reactions; compositions, temperature, and rates of complex reactions are related by a system of conservation equations. Because these latter equations contain terms corresponding to transport processes which vary with the type of reactor, we cannot give a general analysis of complex reaction systems. However, we shall develop a general relationship among the rates of complex reactions which will serve as the basis for analyzing all types of reactors. Then, as was done for simple reactions, the

---

* The largest nonsingular matrix of the n by m matrix of the stoichiometric coefficients is the k by k matrix of the set of independent reactions. See Appendix II.

analysis will be applied to differential and piston flow reactors as examples. In later sections we shall make further use of the following section when particular types of reactors are considered.

With the above objective in mind the formal analysis will be presented. The analysis is concerned with the independent sub-set k of the m equations shown in Eq. 2.3-2 which may be written as

$$\sum_{i=1}^{n} a_{ij} A_i = 0 \qquad (j = 1, 2, 3, \ldots, k), \tag{2.3-4}$$

where k is the order of the largest nonsingular matrix of the original matrix formed from the coefficients of the set of m reactions.

The rate at which the ith component is produced as a result of the jth reaction is

$$\bar{\mathscr{R}}_{ij} = \bar{\mathscr{R}}_{ij}[C_1, C_2, C_3, \ldots, C_n, T]. \tag{2.3-5}$$

These rates are related through the stoichiometric equations as shown below:

$$\frac{\bar{\mathscr{R}}_{ij}}{a_{ij}} = \frac{\bar{\mathscr{R}}_{kj}}{a_{kj}} = \bar{\mathscr{R}}_j \qquad (j = 1, 2, 3, \ldots, k). \tag{2.3-6}$$

Suppose now that we know the values of $\bar{\mathscr{R}}_j$ for each of the k reactions. To find the production rates of ith species P_i as a result of all the reactions we would simply multiply the stoichiometric coefficient of the ith species in each of the reactions times its corresponding rate and add these products. The mathematical equivalent of this statement is

$$P_i = \sum_{j=1}^{k} a_{ij} \bar{\mathscr{R}}_j. \tag{2.3-7}$$

However, we are generally faced with the problem in reverse, i.e., we are given, or we must obtain experimentally, the production rates of the various species and compute values of $\bar{\mathscr{R}}_j$ from the measurements. Since by supposition we have k independent equations, we need the independent determination of the production rates of k components of the mixture. Writing Eq. 2.3-7 in matrix* form to include the production rates of each of the k components:

$$[P_k] = [\bar{\mathscr{R}}_k][a_{kk}], \tag{2.3-8}$$

where

$$\left.\begin{aligned}
[P_k] &= [P_1 \quad P_2 \quad P_3 \quad \ldots \quad P_k] \\
[\bar{\mathscr{R}}_k] &= [\bar{\mathscr{R}}_1 \quad \bar{\mathscr{R}}_2 \quad \bar{\mathscr{R}}_3 \quad \ldots \quad \bar{\mathscr{R}}_k] \\
[a_{kk}] &= \begin{bmatrix} a_{11} & a_{21} & a_{31} & \cdots & a_{k1} \\ a_{12} & a_{22} & & & \\ a_{13} & & & & \\ a_{1k} & \cdots & \cdots & \cdots & a_{kk} \end{bmatrix}
\end{aligned}\right\} \tag{2.3-9}$$

---

* Readers not familiar with matrix multiplication should refer to the brief discussion in Appendix II.