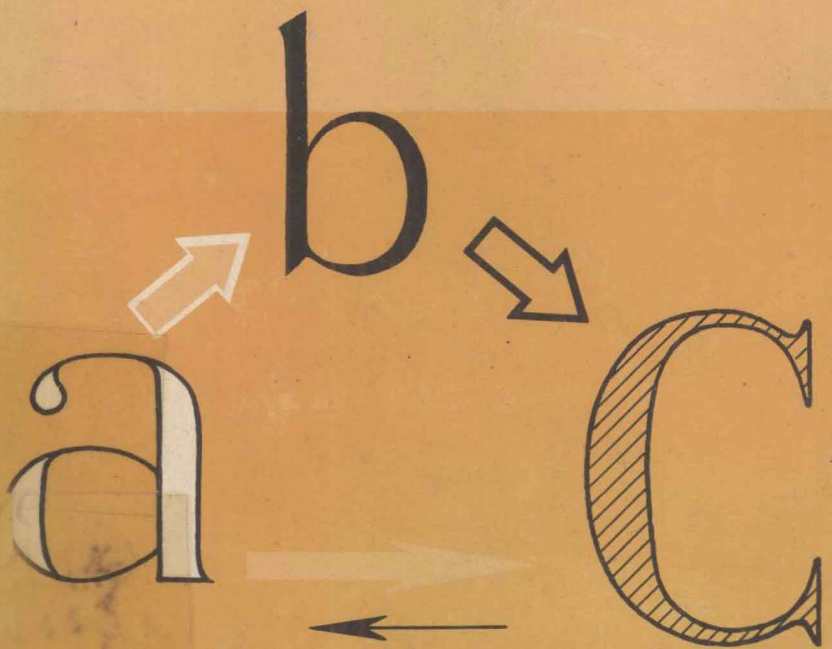
Edward L. King

HOW CHEMICAL REACTIONS OCCUR



How Chemical Reactions Occur

An Introduction to Chemical Kinetics and Reaction Mechanisms

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How Chemical Reactions Occur

THE GENERAL CHEMISTRY MONOGRAPH SERIES

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Editor's Foreword

The teaching of general chemistry to beginning students becomes each day a more challenging and rewarding task as subject matter becomes more diverse and more complex and as the high school preparation of the student improves. These challenges have evoked a number of responses; this series of monographs for general chemistry is one such response. It is an experiment in the teaching of chemistry which recognizes a number of the problems that plague those who select textbooks and teach chemistry. First, it recognizes that no single book can physically encompass all the various aspects of chemistry that all instructors collectively deem important. Second, it recognizes that no single author is capable of writing authoritatively on *all* the topics that are included in everybody's list of what constitutes general chemistry. Finally, it recognizes the instructor's right to choose those topics that he considers to be important without having to apologize for having omitted large parts of an extensive textbook.

This volume, then, is one of approximately fifteen in the General Chemistry Monograph Series, each written by one or more highly qualified persons very familiar with the current status of the subject by virtue of research in it and also conversant with the problems associated with teaching the subject matter to beginning students. Each volume deals broadly with one of the subdivisions of general chemistry and constitutes a complete entity, far more comprehensive in its coverage than is permitted by the limitation of the standard one-volume text. Taken together, these volumes provide a range of topics from which the individual instructor can easily select those that will provide for his class an appropriate coverage of the material he considers most important.

Furthermore, inclusion of a number of topics that have only recently been considered for general chemistry courses, such as thermodynamics, molecular spectroscopy, and biochemistry, is planned, and these volumes will soon be available. In every instance a modern structural point of view has been adopted with the emphasis on general principles and unifying theory.

These volumes will have other uses also: selected monographs can be used to enrich the more conventional course of study by providing readily available, inexpensive supplements to standard texts. They should also prove valuable to students in other areas of the physical and biological sciences needing supplementary information in any field of chemistry pertinent to their own special interests. Thus, students of biology will find the monographs on biochemistry, organic chemistry, and reaction kinetics particularly useful. Beginning students in physics and meteorology will find the monograph on thermodynamics rewarding. Teachers of elementary science will also find these volumes invaluable aids to bringing them up to date in the various branches of chemistry.

Each monograph has several features which make it especially useful as an aid to teaching. These include a large number of solved examples and problems for the student, a glossary of technical terms, and copious illustrations.

The authors of the several monographs deserve much credit for their enthusiasm which made this experiment possible. Professor Rolfe Herber of Rutgers University has been of invaluable assistance in the preparation of this series, having supplied editorial comment and numerous valuable suggestions on each volume. Thanks are also due to Professor M. Kasha of the Florida State University for many suggestions during the planning stages and for reading several of the manuscripts.

RUSSELL JOHNSEN

Tallahassee, Florida
October 1962

Preface

This book provides an introduction to the dynamic aspects of chemical change—the rates of chemical reactions and the pathways by which they occur. These dynamic aspects are fundamental facets of chemistry. Knowledge of how chemical reactions occur is important from both theoretical and practical points of view. The effectiveness of a chemical process in industry may depend upon the rate of a particular reaction: an increase in rate by a factor of 10 can change red ink to black ink.

The material in this book is meant to be part of a first course in college chemistry. Beginning students should obtain a fairly sophisticated background in chemical kinetics and the meaning of rate laws in terms of reaction mechanisms so they can use these principles to understand the chemistry of both inorganic and organic substances. Because it is a basic part of chemistry, an introduction to chemical reactivity is important for the first-year student who will pursue the study of chemistry no further. To the first-year science major, the subject is crucial; and certainly to defer its instruction until a junior- or senior-level course in physical chemistry is to defer it too long.

I have attempted to present those theoretical and experimental aspects of the subject that can be understood by the intelligent student with a background of high school chemistry plus part of what is customarily covered in first-year college chemistry. The simplest ideas about the calculus notation are introduced, but it is not assumed that students using this book will have had calculus. It is more important for the beginning student to understand the meaning of a rate law than to be able to integrate rate laws of a variety

of forms. This is as true for the terminal student as it is for the chemistry major.

It is hoped that this book will also be a useful introduction, or reintroduction, to the subject for those at more advanced levels in related fields.

EDWARD L. KING

Boulder, Colorado
February 1, 1963

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I

Introduction

Some chemical reactions occur very rapidly and others occur very slowly. Most chemical reactions occur more rapidly the higher the temperature. One objective of this book is to explain these observations. Chemical kinetics is the part of chemical science dealing with the velocity of chemical reactions. The subject includes both the experimental study of reaction velocity and the development of theories to explain experimental results and to predict the outcome of experiments which have not yet been performed. Recent advances in experimental techniques have opened whole new areas of study. This is particularly true in the field of very fast reactions; measurement of the velocity of a reaction which occurs in one-thousandth of a second or even less is now possible. One experimental setup for studying fast reactions is shown in Fig. 1–1. Also, the theories of chemical kinetics continue to be improved, in some instances as the result of new high-speed computers making calculations which were once practically impossible.

Chemical kinetics has relevance in space technology. Chemical reactions of components of the air occur at the high temperatures realized when a space capsule reenters the atmosphere, Fig. 1–2. The rates of these endothermic reactions are pertinent in the dissipation of heat generated upon reentry. And, of course, before the problems of reentry are faced, the space vehicle has to get off the

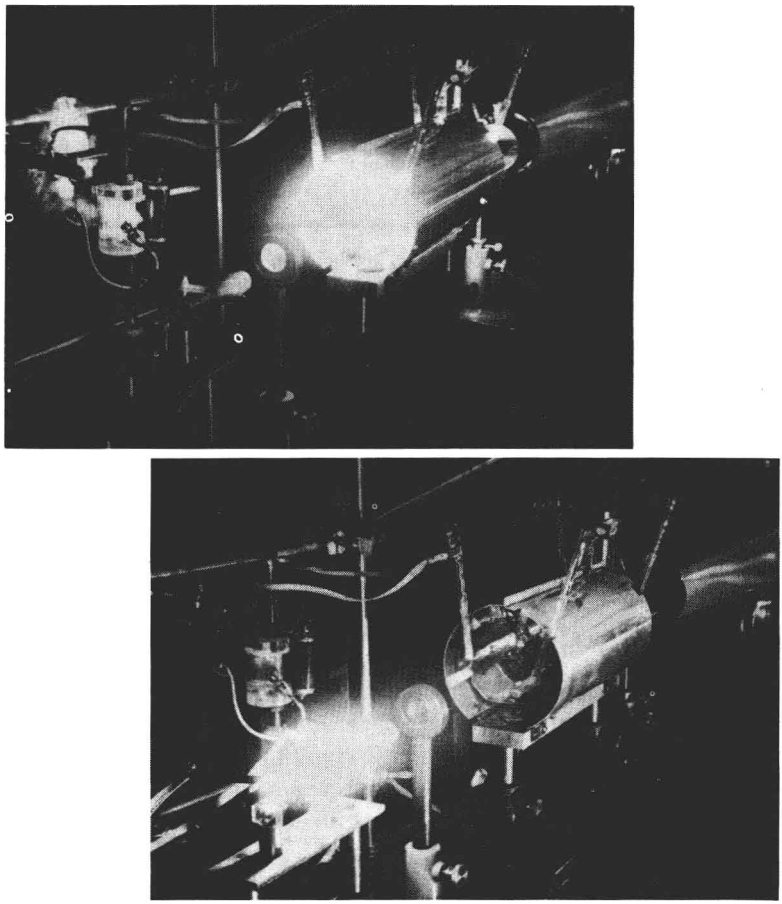

Figure 1–1. Flash photolysis. The upper photograph shows the intense flash of light which causes a photochemical reaction to occur in the reaction cell. The lower photograph shows the monitoring flash of light which is set off a short time interval later. Light from this flash goes through the reaction cell to the spectrograph at the upper right. Short-lived species formed in the reaction cell by the intense flash of light are detected by their characteristic spectra. The subject of flash photolysis is discussed in Chapter 9. (These photographs appeared in *Scientific American*, May, 1960, and are reproduced with permission of the publisher.)

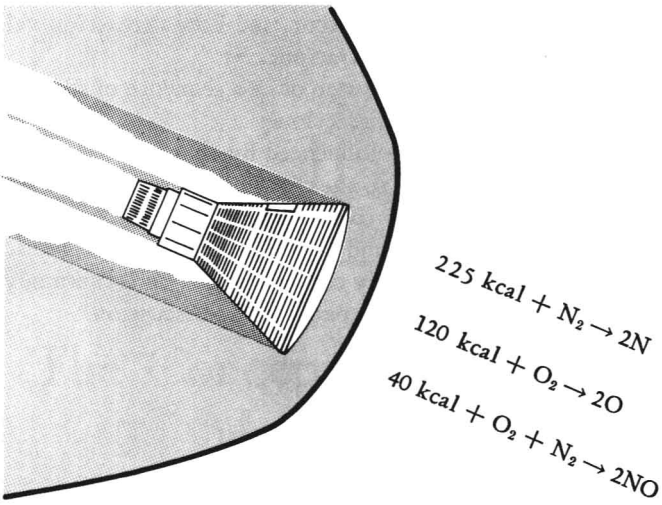

Figure 1–2. Endothermic chemical reactions which occur in the atmosphere at the high temperatures generated during reentry of a space capsule.

ground. This involves the kinetics of the exothermic chemical reactions that provide thrust to the rocket.

In an introduction to discussion of the rates of chemical reactions, the fundamental questions which can be posed should be reviewed. The composition of reactants and products must be known before a reaction can be considered characterized in even the simplest manner. The molecular structure of reactants and products should also be established; this is a problem of a varying degree of difficulty. In addition to asking for information regarding the composition and structure of reactants and products in a reaction, one may pose the questions:

1. To what extent does reaction go before chemical equilibrium is reached?
2. What heat effect accompanies chemical reaction?
3. How is the position of equilibrium influenced by changes in temperature?

4. How rapidly does reaction occur, and how is reaction velocity influenced by changes in concentration?

5. Does reaction occur in one step or in a sequence of steps the net result of which is the over-all reaction?

6. How is the reaction rate influenced by changes in temperature?

Questions 1 to 3 are related to the thermodynamics of the chemical reaction, and questions 4 to 6 to the kinetics and mechanism of the reaction. It is the kinetics and mechanism of chemical reactions with which we will be primarily concerned, but both thermodynamics and structure are relevant in parts of the discussion.

II

The Concept of Reaction Mechanism

Chemical reactions involve the forming and breaking of chemical bonds. The geometrical relationships of the atoms in the products are different from those in the reactants. A mixture of gaseous hydrogen and iodine is a simple example. In this mixture, pairs of hydrogen atoms are bonded together and pairs of iodine atoms are bonded together. Chemical reaction in this system produces hydrogen iodide,[1]

$$H_2 + I_2 = 2HI,$$

and after reaction the system contains molecules of hydrogen iodide in which an atom of hydrogen is bonded to an atom of iodine. Examination of the system before reaction and after reaction (Fig. 2–1) does not disclose the pathway by which the transformation occurs. The same point can be made with reference to the chemical equation for the change. A balanced equation for a net chemical change indicates only what species are consumed and what species are produced.

[1] An equality sign is used in a chemical equation if only the stoichiometry of the reaction is given by the equation.