Elementary Reaction Kinetics

Latham · Burgess

Third Edition

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BUTTERWORTHS
LONDON - BOSTON
Sydney - Wellington - Durban - Toronto

The Butterworth Group

United Kingdom Butterworth & Co (Publishers) Ltd
London 88 Kingsway, WC2B 6AB

Australia Butterworths Pty Ltd
Sydney 586 Pacific Highway, Chatswood, NSW 2067
Also at Melbourne, Brisbane, Adelaide and Perth

South Africa Butterworth & Co (South Africa) (Pty) Ltd
Durban 152–154 Gale Street

New Zealand Butterworths of New Zealand Ltd
Wellington 26–28 Waring Taylor Street, 1

Canada Butterworth & Co (Canada) Ltd
Toronto 2265 Midland Avenue
Scarborough, Ontario, M1P 4S1

USA Butterworth (Publishers) Inc
Boston 19 Cummings Park, Woburn, Mass. 01801

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First published 1962
Reprinted 1964
Reprinted 1968
Second edition 1969
Reprinted 1976
Third edition 1977

ISBN 0 408 46102 0

© Butterworth & Co (Publishers) Ltd 1977

LIBRARY OF CONGRESS CATALOGING IN PUBLICATION DATA

Latham, Joseph Lionel.
Elementary reaction kinetics.
Bibliography: p.
Includes index.
1. Chemical reaction, Rate of. I. Burgess, A.E., joint author. II. Title.
QD502.L38 1977 541'.39 77-902
ISBN 0-408-46102-0

Printed in England by Billing & Sons Limited,
Guildford, London and Worcester

Preface

The object of this book is to provide an introduction to the main ideas of chemical reaction kinetics. It is intended for students reading the subject for the first time, and should be particularly useful to the undergraduate in providing a less rigorous introduction to the subject than is found in specialist texts. The book, however, does deal with a wide range of topics with the intention of giving the reader a broadly based understanding of this rapidly developing subject area.

Thus the book should prove to be suitable not only for the student of chemistry, but also for students following courses in physical or life science who require an understanding of elementary reaction kinetics.

The first three chapters cover the concepts and terminology of chemical kinetics, the basic rate laws and an introduction to the methods of measuring reaction rates. Chapter 4 deals with the effect of temperature on reaction rate and the concept of activation energy. This leads into chapters on the basic theories of reaction rate, the special problem of unimolecular reactions and the kinetic investigation of reaction mechanisms.

The importance of catalysis is emphasized by separate chapters on heterogeneous, homogeneous and enzyme catalysis. The subject of chain reactions and free radical processes is treated in Chapter 11, and then the reader is introduced to the techniques used for studying fast reactions. Examples of the analysis of experimental results are given in Chapter 13. The concluding chapter has sections giving a summary of useful mathematics, the least-squares method of line fitting and an outline of the thermodynamic concept of chemical equilibrium which is fundamental to the theory of reaction rates.

To deal with the fact that reaction rates vary continuously with time, it is necessary to have some knowledge of the mathematical technique specially devized to deal with continuously varying quantities – namely infinitesimal calculus. To help the reader who cannot readily bring to mind the mathematical results required in this text, a compact summary of such results is given in Chapter 14. When quoted in the text, these results are referred to by the letter M (for Mathematical Result).

The most important equations developed in the text are placed in a rectangular box on the first occasion on which they occur. This has been done to help the reader to pick out the important points that can usefully be committed to memory.

The authors have felt it justifiable in certain cases to simplify (some might say over-simplify) complex topics. One of the failings of students of reaction kinetics is that they sometimes cannot see the wood for the trees! Many excellent specialist texts exist which deal with kinetic topics with thoroughness and mathematical rigour. These, however, tend to be somewhat overpowering for a beginner. It is hoped that this book will enable the reader to realize the scope of reaction kinetics, and will be a useful introduction to the specialist texts dealing with those topics for which greater sophistication is needed. Suggestions for additional reading are made at the end of the book.

The IUPAC recommendations for the units of physical quantities have been used throughout. In naming compounds classical or recommended names are used, depending on which seemed the more appropriate.

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LIST OF SYMBOLS

(i) Roman Letters

A	reactant species
A	pre-exponential factor of Arrhenius equation or Debye–Hückel constant
a	concentration of A
a_{A}	activity of A
B	reactant species
b	concentration of B
$\mathrm{C}^{\ddagger}$	transition state species C
c	molecular velocity
$c^{\ddagger}$	concentration of transition state species C
d	differential operator
E	enzyme
$E^{\ddagger}$	energy of activation
exp	exponential function, i.e. $\exp(x) = \mathrm{e}^{x}$
F	mathematical function (general form)
f	activity coefficient
G	Gibbs free energy or conductance
H	enthalpy
h	Planck's constant
I	integration constant
J	joule
K	kelvin (unit of absolute temperature)
K	equilibrium constant
k	rate constant (forward reaction) or force constant
k_{-1}	rate constant (back reaction)
kJ	kilojoule
l	litre
log	logarithm (to the base 10)
ln	logarithm (to the base e)
M	molar mass
m	metre
m	molecular mass or proportionality constant
mol	mole
N	newton
N	Avogadro constant

n	molecular concentration
Pa	pascal (= 1 N m^{-2})
p	pressure
P	probability factor (in collision theory)
Q	ratio of actual to most probable velocity
R	gas constant
S	substrate
S	entropy
s	second
s	number of vibrational degrees of freedom
T	temperature
t	time
$t_{\frac{1}{2}}$	half-life
V	molar volume
X	experimental value
x	change in concentration due to reaction
Z	collision constant
z	charge on an ion

(ii) Greek Letters

Δ	operator meaning 'final value of . . . minus initial value of . . .'
σ	molecular collision diameter
π	circumference divided by diameter of circle
μ	ionic strength, chemical potential
ρ	density
τ	relaxation time
θ	fraction of surface covered
η	viscosity

(iii) Miscellaneous

$\propto$	proportionality sign
∞	infinity sign
$\int$	integral sign
∂	partial differential operator
subscript $_0$	refers to initial state
subscript $_{-1}$	refers to back reaction
superscript ‡	refers to transition state
!	factorial sign
$[\cdots]$	molar concentration of ...

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INTRODUCTION

The subject of reaction kinetics is concerned with the detailed study of the rates of chemical reactions. The experimental part of the subject deals with ways of measuring precisely the variation of the concentrations of reacting substances with time. These measurements are carried out in such a way that the effects of temperature, pressure, catalysts, isotopes, radiation, etc. on the rate of reaction can be assessed.

Interpretation of the experimental results leads to a better understanding of the mechanism of reactions. The combination of the results of a large number of experiments gives rise to general theories of chemical reactivity.

From a fundamental point of view there are two important aspects to any process of change. The first is the extent of the change; the second is the time taken to accomplish the change. It is no consolation to the master of a ship which has struck an iceberg, to be told that if only he had waited a few years for equilibrium to be reached, the iceberg would have melted and the ship would have been safe!

In chemical reactions, the problem of predicting the products when equilibrium is eventually reached is dealt with in chemical thermodynamics. The equilibrium constant can in principle be predicted from free energies obtained from measurements made in calorimeters. When equilibrium is achieved rapidly, it is possible to predict quite accurately the relative proportions of the reactants and products in simple cases. Thermodynamics has, however, nothing to say about the *rate* at which a chemical reaction will occur. An analogy may be drawn with the case of a stone falling under gravity. Knowledge that its ultimate position will be on the ground (a 'thermodynamic' result) enables no deductions to be made about the rate of fall (a 'kinetic' result).

The limitation of thermodynamics in explaining chemical processes is seen by considering the reaction of hydrogen and oxygen at one atmosphere pressure and room temperature. The reaction appears to occur instantaneously when the mixture is sparked. On the other hand, in the absence of a spark or a catalyst, no reaction is detectable after several years. Thermodynamic calculations show, however, that the reaction is accompanied by a large decrease in free energy, and so should be capable of occurring spontaneously with some vigour. (The kinetic explanation of why one does not look for a gas leak with a lighted candle is discussed in Chapter 11.)

There are many examples of chemical reactions that occur at a measurable rate. It is worth noting that the process of life itself depends on the combined effect of many thousands of chemical reactions, each proceeding at a steady rate at body temperature. The dramatic effect of temperature on rate of reaction (see Chapter 4) is illustrated by the fact that a 10 °C rise in temperature of the human body invariably leads to death.

It is fairly easy to show experimentally that the rates of chemical reactions vary with time, but careful experiments are needed to show that this variation is regular and can be described by a mathematical equation. The first accurate kinetic study of a chemical reaction was carried out in 1850 by Wilhelmy, who measured the rate of conversion of an acidic solution of sucrose into glucose and fructose. This reaction was especially suitable for kinetic study as the amount of reaction could be found at any time by measuring the optical rotation of the solution in a polarimeter. Wilhelmy found that, at a given concentration of acid, the rate of reaction at any instant was proportional to the amount of sucrose remaining in solution.

In 1862, Berthelot and St. Gilles made a careful study of the equilibrium between acetic acid, ethyl alcohol, ethyl acetate and water:

$$CH_3CO_2H + C_2H_5OH \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$

They were able to show that in this reversible reaction the rate of the forward reaction was proportional to the concentration of ethyl alcohol multiplied by the concentration of acetic acid.

The idea that the rate of a chemical reaction at a given temperature depends on concentration was generalized by Guldberg and Waage who, in 1863, stated the *Law of Mass Action.* In modern terms this states that *the rate of a chemical reaction is proportional to the concentration of each reactant.* This law provides a quantitative basis for kinetic investigations.

One point that may cause confusion is that the Law of Mass Action is defined in some textbooks in terms of 'active mass'. This is for historical reasons as Guldberg and Waage used the term in their original publication. 'Active mass' has, however, no connection with the thermodynamic concept of 'activity'. In fact the rates of chemical reactions are proportional to the concentrations of the reagents rather than to their thermodynamic activities. To avoid confusion it is best to state the Law of Mass Action in terms of concentration or for gas reactions in terms of partial pressure*. Guldberg and Waage further showed that the position of chemical equilibrium can be explained quantitatively for a reversible reaction by assuming a *dynamic* rather than a *static* equilibrium, in which the rate of the forward reaction is equal to the rate of the reverse reaction.

The Law of Mass Action may be given a molecular interpretation when applied to a reaction of the type

$$A + B \rightarrow \text{products}$$

in which one molecule of A reacts with one molecule of B. Before the two molecules can react with one another to form a compound they must first meet. The number of collisions between the molecules of A and of B on simple probability theory is proportional to the number of molecules of A multiplied by the number of molecules of B, which in turn is proportional to the concentration of A multiplied by the concentration of B. The Law of Mass Action thus follows from the reasonable assumption that the number of molecules of A and B that react is proportional to the number of collisions between them.

In *one-stage reactions* the law of mass action may be applied directly to the concentrations of the reactants. If, however, a reaction occurs in a series of consecutive stages, the law must be applied successively to each individual stage of the reaction.

These simple ideas do not apply to all reactions, but they lead to the principle which is basic to the quantitative study of chemical reaction kinetics. This is that, at a given temperature and pressure, the reaction rate is a function of the concentrations of the reactants. It is this theme that is pursued in the following chapters of this book.

---

*It may be recalled that for a gas obeying the ideal gas law, the partial pressure is proportional to the molar concentration.

1

CONCEPTS AND TERMINOLOGY OF CHEMICAL KINETICS

The purpose of this chapter is to introduce the main concepts in reaction kinetics in such a way that they can be easily referred to later. These ideas are used and explained in more detail in the subsequent chapters.

1.1 Kinetics

The word *kinetic** was originally used to mean 'pertaining to motion'. For example, the kinetic theory of gases deals with properties of gases which are dependent on molecular motion. In chemical reactions there is no apparent motion, but there are changes in concentration. The phrase 'chemical kinetics', which is often abbreviated to 'kinetics', is used to describe the quantitative study of change in concentration or pressure with time brought about by chemical reaction.

1.2 Categories of Reactions

Chemical reactions can be divided into two broad categories: *homogeneous* and *heterogeneous*. In the former only one phase is present and the system is uniform in composition throughout. Reactions in a single solvent in which no solid catalyst is used are homogeneous. So, too, are gas reactions other than those occurring at a catalytic surface. Some examples of homogeneous reactions are:

$$H_2 + I_2 \rightarrow 2HI \text{ (in the gas phase)}$$

$$CH_3COCl + CH_3OH \rightarrow CH_3COOCH_3 + HCl \text{ (in the liquid phase)}$$

In heterogeneous reactions the mixture is not uniform throughout, and reaction occurs at phase boundaries. This is typically the case when solid catalysts are used, as in the following examples:

---

*This word is not restricted to the scientific field, e.g. kinetic art.

$$C_2H_5OH \xrightarrow{\text{alumina}} C_2H_4 + H_2O$$

$$2NH_3 \xrightarrow{\text{tungsten}} N_2 + 3H_2$$

Enzyme reactions have some of the features of both homogeneous and heterogeneous reactions.

1.3 Rate of Reaction

The precise meaning of the term 'rate of reaction' is not self-evident. A simple definition might be the mass of product formed in a given time under stated conditions. There are, however, two objections to this interpretation:

(a) the concentration of reactants changes as the reaction proceeds, and hence constant conditions cannot be maintained;

(b) the amount of product formed depends on the initial quantity of reactants as well as on their concentrations and chemical reactivities.

These difficulties can be overcome by defining the *rate of reaction* as the *decrease in concentration per unit time of one of the reactants.* Concentrations are usually expressed in moles per litre (written as mol l^{-1}); the time in seconds.

This definition may be expressed more concisely using the notation of the differential calculus. If [A] represents the concentration of the reactant A, measured at time t, then the rate is defined as

$$\boxed{\text{rate} = -\mathrm{d}[A]/\mathrm{d}t} \qquad (1.1)$$

The minus sign occurs because the concentration of the reactant *decreases* with increasing time.

An alternative definition of the rate of reaction is in terms of the *product.* If a represents the initial concentration of A and x represents the concentration of product at time t then

$$\boxed{\begin{aligned} &\text{rate} = +\mathrm{d}x/\mathrm{d}t && (1.2)\\ &\text{or}\\ &\text{rate} = \frac{-\mathrm{d}(a-x)}{\mathrm{d}t} && (1.3)\end{aligned}}$$

In equation 1.2 the sign is positive since the concentration of products *increases* with time (see M18).

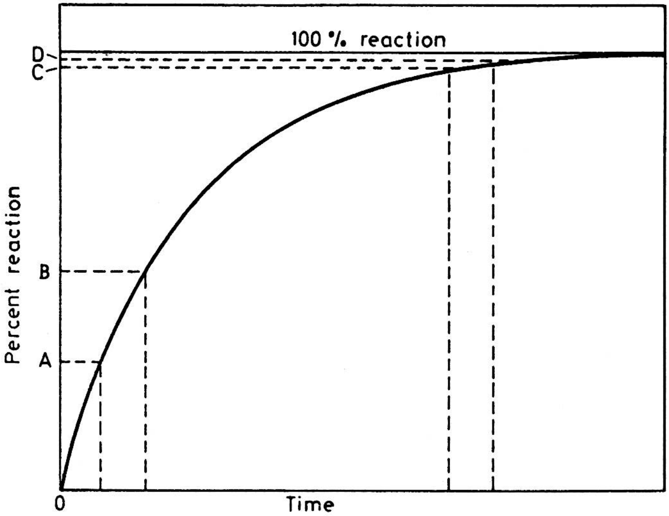

Figure 1.1 Variation of reaction rate with time

A typical curve of percentage reaction plotted against time is shown in *Figure 1.1.* It illustrates two general features of chemical kinetics. The first is that the amount of reaction in a given time interval decreases as the reaction proceeds. The amounts of reaction for two equal time intervals are shown on the graph. AB, which corresponds to the earlier time, is much greater than CD. The rate of reaction, using equation 1.2, is given by the slope of the curve, which clearly decreases with increasing time.

The second point is that there is no definite instant of time at which the reaction is completed, as the curve approaches 100% reaction asymptotically.

1.4 Rate Constant

The rate constant is a measure of the rate of a given chemical reaction under specified conditions. It may be defined in words as *the rate of change in concentration of reactant or product with time for a reaction in which all the reactants are at unit concentration.* The definition is helpful in that it gives some physical meaning to the rate constant.

As an example, in the decomposition of benzenediazonium chloride in water:

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