



An Introduction to

Chemical Kinetics

Margaret Robson Wright

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0643
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Margaret Robson Wright

Formerly of The University of St Andrews, UK

江苏工业学院图书馆
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John Wiley & Sons, Ltd

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West Sussex PO19 8SQ, England

Telephone (+44) 1243 779777

Email (for orders and customer service enquiries): cs-books@wiley.co.uk
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John Wiley & Sons Inc., 111 River Street, Hoboken, NJ 07030, USA

Jossey-Bass, 989 Market Street, San Francisco, CA 94103-1741, USA

Wiley-VCH Verlag GmbH, Boschstrasse 12, D-69469 Weinheim, Germany

John Wiley & Sons Australia Ltd, 33 Park Road, Milton, Queensland 4064, Australia

John Wiley & Sons (Asia) Pte Ltd, 2 Clementi Loop #02-01, Jin Xing Distripark, Singapore 129809

John Wiley & Sons Canada Ltd, 22 Worcester Road, Etobicoke, Ontario, Canada M9W 1L1

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic books.

Library of Congress Cataloging-in-Publication Data

Wright, Margaret Robson.

An introduction to chemical kinetics / Margaret Robson Wright.

p. cm.

Includes bibliographical references and index.

ISBN 0-470-09058-8 (acid-free paper) – ISBN 0-470-09059-6 (pbk. : acid-free paper)

1. Chemical kinetics. I. Title.

QD502.W75 2004
541'.394—dc22

2004006062

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

ISBN 0 470 09058 8 hardback
0 470 09059 6 paperback

Typeset in 10.5/13pt Times by Thomson Press (India) Limited, New Delhi
Printed and bound in Great Britain by TJ International Ltd., Padstow, Cornwall
This book is printed on acid-free paper responsibly manufactured from sustainable forestry in which at least two trees are planted for each one used for paper production.

200701671

An Introduction to Chemical Kinetics

John H. E. Wright

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*Dedicated with much love and affection
to
my mother, Anne (in memoriam),
with deep gratitude for all her loving help,
to
her oldest and dearest friends,
Nessie (in memoriam) and Dodo Gilchrist of Cumnock, who,
by their love and faith in me, have always been a source of great
encouragement to me,
and last, but not least, to my own immediate family,
my husband, Patrick,
our children Anne, Edward and Andrew and our cats.*

Preface

This book leads on from elementary basic kinetics, and covers the main topics which are needed for a good working knowledge and understanding of the fundamental aspects of kinetics. It emphasizes how experimental data is collected and manipulated to give standard kinetic quantities such as rates, rate constants, enthalpies, entropies and volumes of activation. It also emphasizes how these quantities are used in interpretations of the mechanism of a reaction. The relevance of kinetic studies to aspects of physical, inorganic, organic and biochemical chemistry is illustrated through explicit reference and examples. Kinetics provides a unifying tool for all branches of chemistry, and this is something which is to be encouraged in teaching and which is emphasized here.

Gas studies are well covered with extensive explanation and interpretation of experimental data, such as steady state calculations, all illustrated by frequent use of worked examples. Solution kinetics are similarly explained, and plenty of practice is given in dealing with the effects of the solvent and non-ideality. Students are given plenty of practice, via worked problems, in handling various types of mechanism found in solution, and in interpreting ionic strength dependences and enthalpies, entropies and volumes of activation.

As the text is aimed at undergraduates studying core physical chemistry, only the basics of theoretical kinetics are given, but the *fundamental concepts* are clearly explained. More advanced reading is given in my book *Fundamental Chemical Kinetics* (see reading lists).

Many students veer rapidly away from topics which are quantitative and involve mathematical equations. This book attempts to allay these fears by guiding the student through these topics in a step-by-step development which explains the logic, reasoning and actual manipulation. For this reason a large fraction of the text is devoted to worked examples, and each chapter ends with a collection of further problems to which detailed and explanatory answers are given. If through the written word I can help students to understand and to feel confident in their ability to learn, and to teach them, in a manner which gives them the feeling of a direct contact with the teacher, then this book will not have been written in vain. It is the teacher's duty to show students how to achieve understanding, and to think scientifically. The philosophy behind this book is that this is best done by detailed explanation and guidance. It is understanding, being able to see for oneself and confidence which help to stimulate and sustain interest. This book attempts to do precisely that.

This book is the result of the accumulated experience of 40 very stimulating years of teaching students at all levels. During this period I regularly lectured to students, but more importantly I was deeply involved in devising tutorial programmes at all levels where consolidation of lecture material was given through many problem-solving exercises. I also learned that providing detailed explanatory answers to these exercises proved very popular and successful with students of all abilities. During these years I learned that being happy to help and being prepared to give extra explanation and to spend extra time on a topic could soon clear up problems and difficulties which many students thought they would never understand. Too often teachers forget that there were times when they themselves could not understand, and when a similar explanation and preparedness to give time were welcome. To all the many students who have provided the stimulus and enjoyment of teaching I give my grateful thanks.

I am very grateful to John Wiley & Sons for giving me the opportunity to publish this book, and to indulge my love of teaching. In particular, I would like to thank Andy Slade, Rachael Ballard and Robert Hambrook of John Wiley & Sons who have cheerfully, and with great patience, guided me through the problems of preparing the manuscript for publication. Invariably, they all have been extremely helpful.

I also extend my very grateful thanks to Martyn Berry who read the whole manuscript and sent very encouraging, very helpful and constructive comments on this book. His belief in the method of approach and his enthusiasm has been an invaluable support to me.

Likewise, I would like to thank Professor Derrick Woollins of St Andrews University for his continued very welcome support and encouragement throughout the writing of this book.

To my mother, Mrs Anne Robson, I have a very deep sense of gratitude for all the help she gave me in her lifetime in furthering my academic career. I owe her an enormous debt for her invaluable, excellent and irreplaceable help with my children when they were young and I was working part-time during the teaching terms of the academic year. Without her help and her loving care of my children I would never have gained the continued experience in teaching, and I could never have written this book. My deep and most grateful thanks are due to her.

My husband, Patrick, has, throughout my teaching career and throughout the thinking about and writing of this book, been a source of constant support and help and encouragement. His very high intellectual calibre and wide-ranging knowledge and understanding have provided many fruitful and interesting discussions. He has read in detail the whole manuscript and his clarity, insight and considerable knowledge of the subject matter have been of invaluable help. I owe him many apologies for the large number of times when I have interrupted his own activities to pursue a discussion of aspects of the material presented here. It is to his very great credit that I have never been made to feel guilty about doing so. My debt to him is enormous, and my most grateful thanks are due to him.

Finally, my thanks are due to my three children who have always encouraged me in my teaching, and have encouraged me in the writing of my books. In particular, Anne

and Edward have been around during the writing of this book and have given me every encouragement to keep going.

List of Symbols

Margaret Robson Wright
Formerly Universities of Dundee and St Andrews
October, 2003

| | |
|---------------|---|
| A | absorption coefficient |
| A | Arrhenius pre-exponential factor |
| A | Debye-Hückel parameter |
| a | activity |
| B | osmotic virial coefficient |
| E | internal energy |
| b | osmotic virial coefficient |
| b | lumped parameter |
| c | concentration |
| c° | standard concentration |
| d | distance |
| d | distance |
| E_A | activation energy |
| E_0 | mean-field energy |
| E_1, E_{-1} | activation energies of forward and reverse steps |
| e | exponent |
| f | fraction of species |
| G | Gibbs free energy |
| H | enthalpy |
| h | Planck's constant |
| I | ionic strength |
| I_0 | initial concentration |
| I_{obs} | observed intensity |
| I | moment of inertia |
| I | ionic strength |
| K | equilibrium constant |
| K' | equilibrium constant for reaction involving reactants |
| K'' | equilibrium constant for reaction involving reactants |
| K_M | Michaelis constant |
| k | rate constant |

List of Symbols

| | |
|------------------|---|
| A | absorbance $\{ = \log_{10}(I_0/I) \}$ |
| A | A factor in Arrhenius equation |
| A | Debye-Huckel constant |
| a | activity |
| B | constant in extended Debye-Huckel equation |
| B' | kinetic quantity related to B |
| b | number of molecules reacting with a molecule |
| b | impact parameter |
| c | concentration |
| c^\ddagger | concentration of activated complexes |
| d | length of path in spectroscopy |
| d | distance along a flow tube |
| E_A | activation energy |
| E_0 | activation energy at absolute zero |
| E_1, E_{-1} | activation energy of reaction 1 and of its reverse |
| e | electronic charge |
| f | constant of proportionality in expression relating to fluorescence |
| G | Gibbs free energy |
| H | enthalpy |
| h | Planck's constant |
| I | intensity of radiation |
| I_0 | initial intensity of radiation |
| I_{abs} | intensity of radiation absorbed |
| I | moment of inertia |
| I | ionic strength |
| K | equilibrium constant |
| K^\ddagger | equilibrium constant for formation of the activated complex from reactants |
| $K^{\ddagger*}$ | equilibrium constant for formation of the activated complex from reactants, with one term missing |
| K_M | Michaelis constant |
| k | rate constant |

| | |
|-------------------|--|
| k_1, k_{-1} | rate constant for reaction 1 and its reverse |
| k | Boltzmann's constant |
| m | mass |
| n | order of a reaction |
| N^\ddagger | number of activated complexes |
| p | pressure |
| p_i | partial pressure of species i |
| p | p factor in collision theory |
| Q | molecular partition function per unit volume |
| Q^\ddagger | molecular partition function per unit volume for the activated complex |
| $Q^{\ddagger*}$ | molecular partition function per unit volume for the activated complex, but with one term missing |
| R | the gas constant |
| r | internuclear distance |
| r_\ddagger | distance between the centres of ions in the activated complex |
| S | entropy |
| s | half of the number of squared terms, in theories of Hinshelwood and Kassel |
| T | absolute temperature |
| t | time |
| U | energy |
| V | volume |
| V | velocity of sound |
| V_s | term in Michaelis-Menten equation |
| v | velocity |
| v | relative velocity |
| v | vibrational quantum number |
| Z | collision number |
| Z | collision rate |
| z | number of charges |
| α | order with respect to one reactant |
| α | branching coefficient |
| α | polarisability |
| β | order with respect to one reactant |
| γ | activity coefficient |
| Δ | change in |
| ΔG^θ | standard change in free energy |
| ΔH^θ | standard change in enthalpy |
| ΔS^θ | standard change in entropy |
| ΔV^θ | standard change in volume |

| | |
|------------------------|---|
| $\Delta G^{\ddagger*}$ | free energy of activation with one term missing |
| $\Delta H^{\ddagger*}$ | enthalpy of activation with one term missing |
| $\Delta S^{\ddagger*}$ | entropy of activation with one term missing |
| $\Delta V^{\ddagger*}$ | volume of activation with one term missing |
| δ | distance along the reaction coordinate specifying the transition state |
| ε | molar absorption coefficient (Beer's Law) |
| ε | energy of a molecule |
| ε_0 | energy of a molecule in its ground state |
| ε_0 | universal constant involved in expressions for electrostatic interactions |
| ε_r | relative permittivity |
| η | viscosity |
| θ | angle of approach of an ion to a dipole |
| κ | transmission coefficient |
| λ | wavelength |
| λ | collision efficiency |
| μ | chemical potential |
| μ | dipole moment |
| μ | absorption coefficient for ultrasonic waves |
| ν | frequency |
| σ | cross section |
| $\sigma_{(R)}$ | cross section for chemical reaction |
| τ | relaxation time |
| τ | time taken to pass through the transition state |
| τ | lifetime |

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