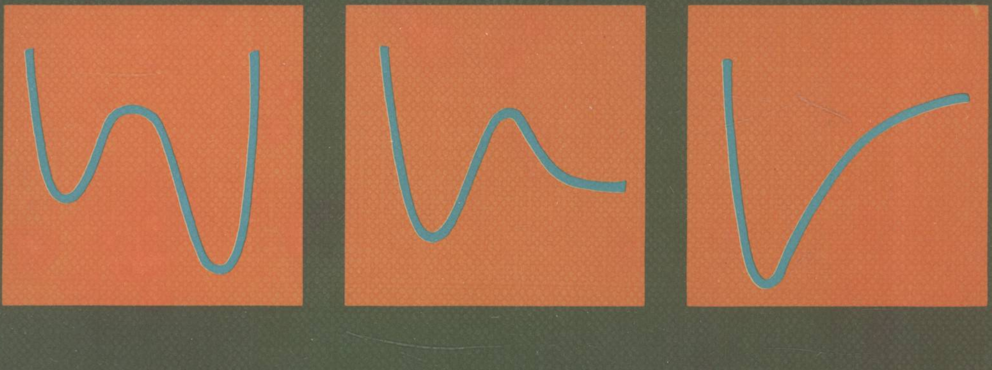
Modern Gas Kinetics

Theory, Experiment and Application

Edited by

M.J. PILLING and
I.W.M. SMITH



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Modern Gas Kinetics

To Gwen and Sue

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Preface

The origins of this book are in a Summer School on Gas-Phase Kinetics which was held in Cambridge between 26th June and 3rd July, 1985. The Summer School was sponsored by the Science and Engineering Research Council and was attended by 43 students whom they support with research studentships. In addition, 21 other British students and 18 students from abroad attended the course.

The intention of the organisers of the Summer School was to provide a course which would acquaint post-graduate students with the wide range of research activity in gas-phase kinetics, whatever was their own, necessarily narrow, research topic. The major—but certainly not the only—mode of instruction was a course of lectures. They were accompanied by a fairly extensive set of lecture notes which have served as the progenitor of this book. In addition to the lectures, there was a daily class session and two evenings when students presented short seminars on their research. The participants were divided into three groups, each with two lecturers, for the classes. The main focus for these sessions was the extensive problem sets which accompanied the lectures. These problems and their worked answers are reproduced here and are an unusual, and we hope valuable, feature of the book. We have also indicated in the list of contents how many lectures were devoted to the topics covered in each chapter. We believe that this feature along with the problems should make our text especially attractive to those planning, giving or taking a course of postgraduate lectures in chemical kinetics.

This book, like the course on which it is based, addresses the three main themes suggested in the title. Part A considers theories of elementary chemical reactions, both bimolecular and unimolecular. Although the calculation of potential energy surfaces for reaction systems is not treated explicitly, the role of the potential energy surface in controlling the dynamics by which reagent molecules are transformed to products is an underlying theme throughout this chapter. Space is also found for some comparisons of theoretical predictions with experimental data. The methods by which both the kinetics and dynamics of elementary reactions are studied experimentally are described in Part B, together with some case histories and the important, and so often neglected, matter of error analysis. Finally, in Part C, a number of chapters describe the kinetics of complex reactions particularly in commercially or environmentally important situations. Some stress is placed on the need for a good data base for the crucial elementary reactions in complex systems, and on the identification of which reactions are indeed crucial.

The first chapter of the book stands on its own. Written by Professor John Simons, it is based on the first lecture given at the Summer School. Its aim was to whet the appetite of the audience by describing the aims of the course, by providing a map of the terrain to be covered, and by highlighting some of the splendours to be encountered. In addition, the editors have written a short introduction to each part of the book. These paragraphs set the contents of that part in context and connect them with the topics covered in the other parts of the book. An attempt is also made to define the objectives of the chapters that follow and to specify what the serious student (and problem solver) should learn from them.

We conclude this preface with thanks to a number of people. First, to our four fellow-authors—who remain our very good friends even after this project! Secondly, to several people who helped in a variety of ways with the Summer School: Mrs S. Clements, whose office dealt efficiently with the arrangements in Christ's College; Mr Martin Woodman, whose cheerful assistance with the accounts was most welcome; and Drs A. B. Callear (Cambridge) and Dr. J. A. Kerr (Birmingham) who helped with tutorial sessions. Thirdly, Mr Navin Sullivan of Blackwell's. He has shown great enthusiasm for this book since the idea was first put to him. His firmness has done much to ensure that we have managed to keep to the timetable that we originally put forward.

Our final and most heartfelt thanks must be reserved for Mrs Margot Long. Her efforts in typing all the material for the Summer School were quite astonishing. They might have been described as unbelievable, except they have been repeated during the preparation of the manuscript for this book. For this Herculean effort, all six authors are extremely grateful.

June 1986

Michael Pilling
Ian Smith

Contents

A Theories of elementary reactions

B Kinetics and dynamics of elementary reactions

C Kinetics of complex reactions

*Figures in parentheses after each chapter title refer to the number of lectures on which that chapter is based.

Introduction
The Interplay Between Theory and Experiment in the Kinetics of Gas-Phase Reactions

J. P. SIMONS

The patterns of enquiry in gas kinetics range from (i) the microscopic study of the dynamics of elementary reactive collisions, seen as individual scattering events at selected collision energies involving reagents in selected quantum states, to (ii) the study of elementary reaction rates at selected bulk temperatures, averaged over all populated internal quantum states and collision energies, to (iii) the study of complex reactions—often at high temperatures—the anatomy of which involves extended sequences of elementary reactions. Examples of complex reactions include pyrolysis (e.g., hydrocarbon cracking, which is dealt with later in Chapter C5), combustion (Chapter C2), atmospheric chemistry (Chapter C1) at altitudes ranging from the troposphere to the stratosphere, or, if complex sequences of ion–molecule reactions are also included, into the ionosphere, comet tails, interstellar clouds and—closer to home—gas laser media (Chapter C6). The levels of enquiry implicit in these patterns form a hierachy which links many talents, ranging from those of the quantum mechanic to those of the chemical engineer, and this diversity is reflected in the design of this book which addresses three interrelated topics:

Section A: theories of elementary gas-phase reactions;
Section B: experimental methods for the study of the kinetics and dynamics of elementary reactions;
Section C: the kinetics of complex gas-phase reactions.

1 Interplay between theory and experiment

In scientific enquiry one may choose to follow, at one extreme, the Baconian inductive approach: that is, collect as much observational data as possible and hope that a pattern of comprehension and thence understanding will eventually emerge. Experimental data are valueless, however, unless set against some working theoretical model or hypothesis. This leads to the other extreme, the deductive (inspirational) approach of Descartes, where a basic theoretical model is developed to be tested by subsequent experiment (see Fig. 1). Experimental activity in the kinetics of gas-phase reactions lies somewhere between these two extremes, whilst theoretical activity tends towards the approach of Descartes.

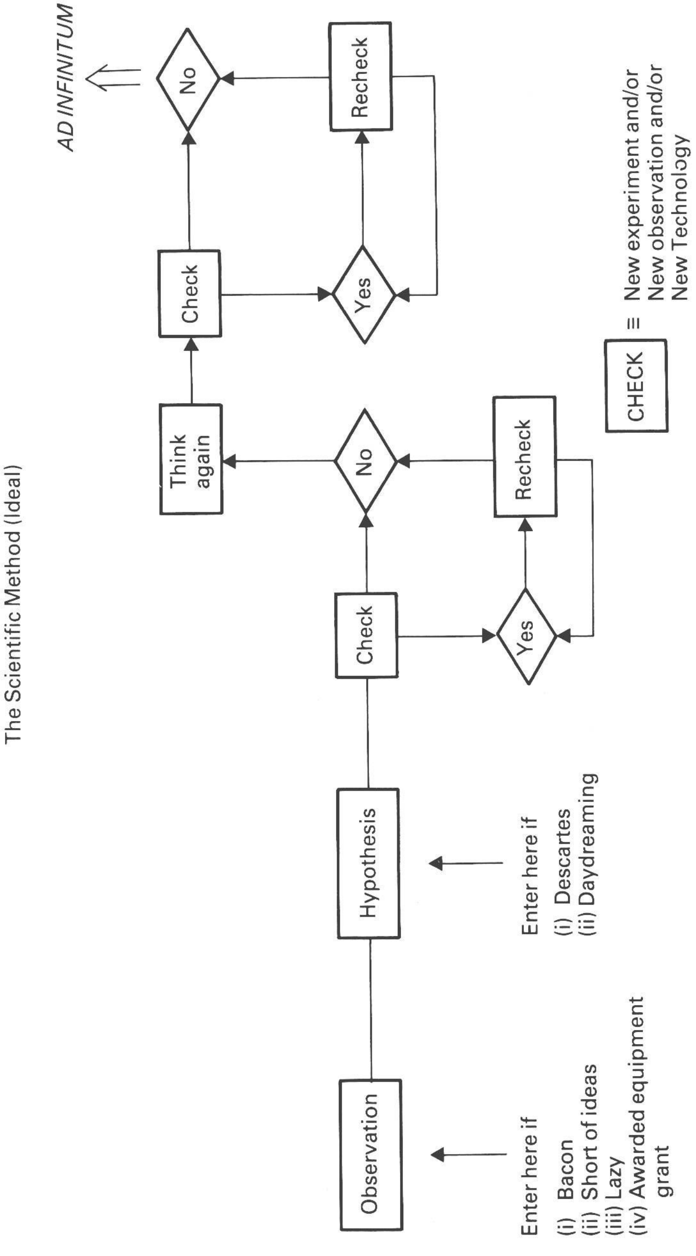

Fig. 1. The scientific approach: intuition versus exploration.

At its most basic, theory attempts the *ab initio* calculation of the potential energy hypersurface for the reactive system and the quantum mechanical description of the reactive scattering events that may occur under its influence. This approach is at present constrained, by its very difficulty, to a few simple, model systems. At a more tractable and practical level, molecular events can be simulated using the equations of classical, rather than quantum, mechanics to describe the scattering. The computation of such trajectories (see Chapter A2) can provide an adequate description of the reaction dynamics in systems of only a few atoms, but where molecular complexity or dynamical ignorance prevails (i.e., in most of chemistry) statistically based models, such as transition state theory (Chapters A1 and A3), must complement experimental measurement. The main aim of such models is the prediction of elementary reaction rates in advance or in place of direct experimental measurement. The realistic predictive precision of theory was provocatively (and characteristically) questioned at a conference a few years ago by Professor Fred Kaufman.[1] If elementary reaction rate theory is not quantitatively predictive, so putting the experimenters out of business, is it of any practical use as a tool for the analysis of more complex reacting systems? The conclusion, at least for unimolecular reactions (Chapter A4), seems to be a guarded 'Yes!', though qualified by uncertainties in critical parameters such as the efficiency, quantum state dependence, and temperature dependence of collisional energy transfer processes, and by ignorance of the details of the potential energy hypersurface.[2]

Even in the absence of quantitative reliability there is a deeper motive for 'theoretical understanding' that is based on simple curiosity. At its most fundamental level the theory of elementary gas-phase reactons seeks to understand the way chemical bonds are made and broken during energetic atomic, molecular or ionic collisions or following single or multiple photon absorption. There is a continuum between the 'core' science of the chemical physicists and its applications to the 'strategic' science of the chemical engineers. Gas-phase kineticists lie somewhere in the middle.

2 Bimolecular reactions

In the macroscopic world of reactions in bulk between reagents at thermal equilibrium (Chapter B1), the crucial parameters are the temperature-dependent rate constant $k(T)$ and the activation energy E_{act} defined by

$$E_{act} = -\mathrm{d}\ln k(T)/\mathrm{d}\,(1/\boldsymbol{R}T). \tag{1}$$

When the internal quantum states of the reagents and products, denoted collectively by the quantum numbers n and n', are selected and observed (in bulk systems), we enter the realm of state-to-state kinetics (Chapter B2) in which the rates are described by sets of detailed rate constants $k(n'|n;T)$. If we increase the resolution of the experiment still further and enter the microscopic world of individual reactive collisions at energy E_t, usually by studying reactive scattering under molecular beam conditions, the counterparts to the bulk world of rate constants and activation energies become the set of energy-dependent reactive cross-sections $S_{\mathrm{reac}}(n'|n;E_t)$ and the threshold energy E_t^0. Averaging over the thermal distributions of relative velocity (or collision energy) at temperature T, links the two worlds through the Laplace transform:

$$k(n'|n;T) \propto \int_{E_t^0}^{\infty} S_{\mathrm{reac}}(n'|n;E_t)\, E_t \exp(-E_t/k_B T)\, \mathrm{d}E_t. \qquad (2)$$

A knowledge of $S_{\mathrm{reac}}(n'|n;E_t)$, the state-to-state reactive excitation functions, would allow, in principle, the calculation of the detailed rate constants $k(n'|n;T)$ and, after appropriate averaging, the evaluation of the thermal rate constant $k(T)$.

$$k(T) = \sum_{n'} \sum_{n} g(n)\, k(n'|n;T) \qquad (3)$$

where n defines the internal quantum states of the reagents and $g(n)$ is the initial reagent state Boltzmann distribution for the temperature T.

In practice, the procedure just outlined is not yet technically viable and there is no microscopic substitute for the direct experimental measurement of macroscopic rate constants. (Similarly, the inverse transform from the macroscopic rate constant and its temperature dependence to the microscopic cross-sections places such demands on the precision of the measurements of $k(T)$ as to be also non-viable.) The real value of excitation function measurements lies in their direct probing of the detailed reaction dynamics, which are controlled by the potential energy surface over which the elementary reactions proceed. At a higher level of averaging this control is also reflected in the temperature dependence $k(n'|n;T)$ or ultimately, $k(T)$. If one wants to understand the temperature dependence one is inevitably led back to the potential energy hypersurface and the nature of the transition state(s) of the reactive collisions proceeding under its influence. The surface lies at the heart of reaction kinetics and is the meeting ground of the experimentalists and the theoreticians. Figure 2 summarises these converging patterns of enquiry and also some of the interactions between the various aspects of gas-phase reaction kinetics discussed in this book. We turn now to the question of the transition state.

If one assumes that the motion of atoms can be described by classical equations of motion, then the transition state of an elementary reaction can be identified with a 'dividing surface' (within the complete potential energy hypersurface) which separates the reagent and product regions of the configuration space and through which all reactive trajectories must pass for reagents to be transformed to products. Classical transition state theory chooses the dividing surface through which the total calculated flux is least, in order to minimise the number of trajectories which pass through the dividing surface but then return through it

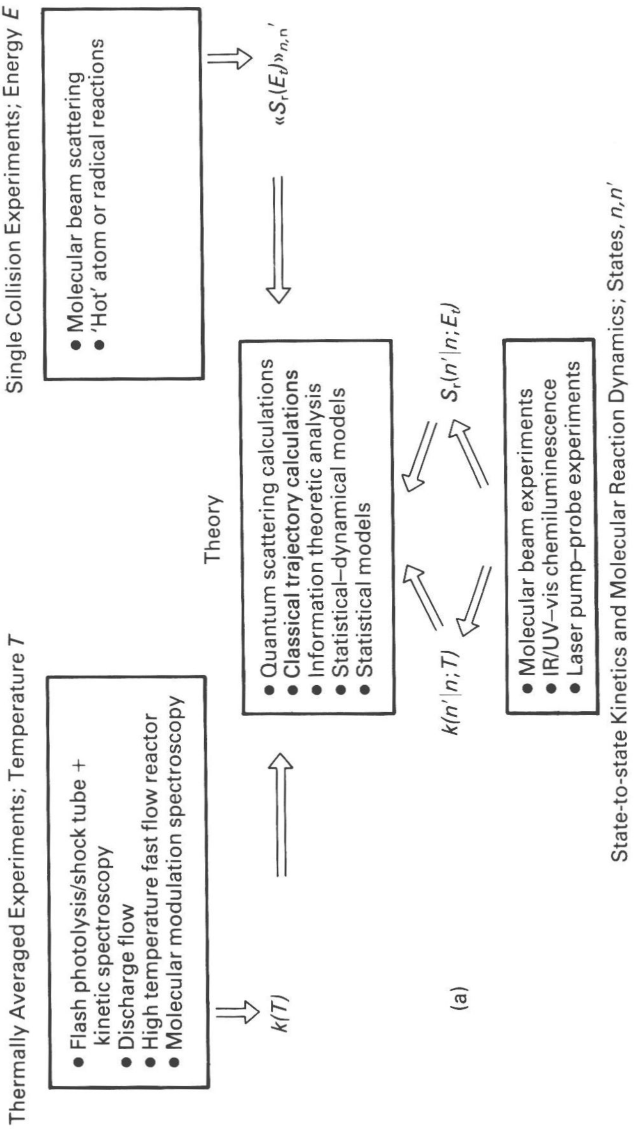
Thermally Averaged Experiments; Temperature T
• Flash photolysis/shock tube + kinetic spectroscopy
• Discharge flow
• High temperature fast flow reactor
• Molecular modulation spectroscopy
$k(T)$
Single Collision Experiments; Energy E
• Molecular beam scattering
• 'Hot' atom or radical reactions
$\langle\langle S_r(E_t)\rangle\rangle_{n,n'}$
Theory
• Quantum scattering calculations
• Classical trajectory calculations
• Information theoretic analysis
• Statistical–dynamical models
• Statistical models
$k(n'|n;T)$
$S_r(n'|n;E_t)$
• Molecular beam experiments
• IR/UV–vis chemiluminescence
• Laser pump–probe experiments
State-to-state Kinetics and Molecular Reaction Dynamics; States, n,n'
(a)

Fig. 2(a).

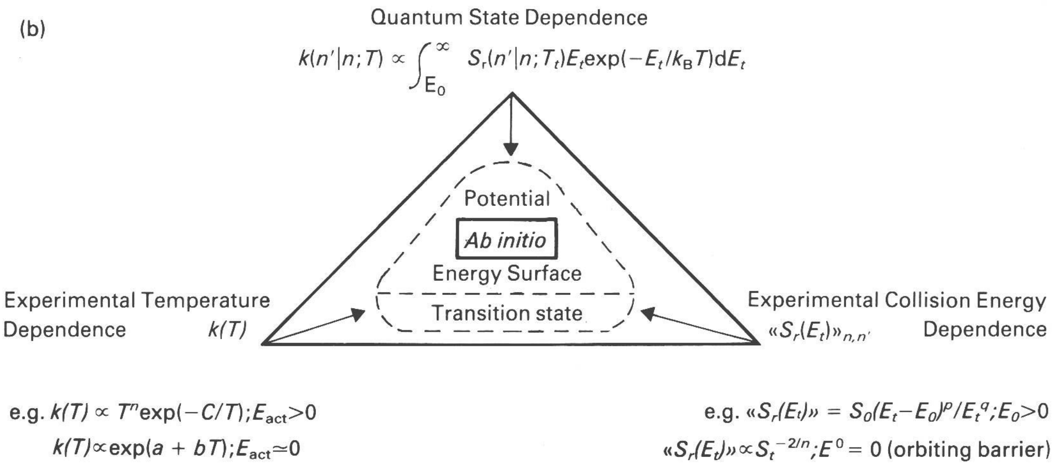

Fig. 2(b).

Fig. 2. The interface between theory and experiment: bimolecular reactions.

rather than continue on and yield separated products. If the product region of the potential energy hypersurface lies behind an energy barrier, then at energies near the reaction threshold the conventional choice of a dividing surface which passes through the saddle point of the potential energy surface is likely to be the best—that is, to be the surface through which the flux is a minimum. However, at higher collision energies, this may not remain the optimum choice. At least for collinear collisions, the best dividing surfaces can be defined by sections through the potential energy surface associated with 'trapped' classical trajectories. These trajectories oscillate continuously, crossing the reaction coordinate at right angles, and veering towards neither the reagent nor the product region of the potential energy surface. They are known as PODS—periodic orbit dividing surfaces. Examples are shown in Fig. 3 and they are discussed in detail in Chapter A1. Variational transition state theory chooses the 'best' transition state to estimate an upper bound to the reaction probability (even with the best choice of dividing surface some trajectories may 'return' through it); a lower bound is obtained by eliminating all trajectories which cross the surface through the saddle point more than twice (see Chapter A1).

Once the notion of trapped trajectories has taken root it is a short step to the notion of resonant periodic orbits—classical trajectories which correspond to quasi-bound quantum states in the collision complex and which can be related to dynamical scattering resonances—and then to the notion of a 'spectroscopy of the transition state'.[3] This could be an optical spectroscopy such as resonance Raman or fluorescence emission from bimolecular collision complexes or from molecules that are in the process of dissociating from an electronically excited state.[3,4] Alternatively, it could be scattering spectroscopy, as in the marvellously detailed angle and state-resolved crossed molecular beam scattering studies of the HF/DF products generated through the reaction of $F + H_2/HD/D_2$.[5]

Unimolecular reactions

The average rate of decomposition or isomerisation of a critically energised molecule (i.e. one that has an internal energy $E > E^0$, where E^0 is a threshold or critical energy) depends upon its internal energy distribution, its environment and possibly on its method of preparation. If this is collisional, as in a thermal unimolecular reaction, the distribution is controlled by the dynamical balance of intermolecular energy transfer from highly excited vibrational–rotational levels, and reaction. As Luther and Troe point out[6] 'the (principal) dilemma of thermal unimolecular rate theory is the lack of understanding of this elementary process', i.e. the intermolecular energy transfer. At sufficiently high pressures, of course, the Boltzmann distribution is maintained, but at lower pressures, in the absence of the strong collision assumption (section A4.3), we are in trouble. New techniques of activation have been developed which avoid this problem (as well as new experimental methods which address the problem of relaxation) though the question of