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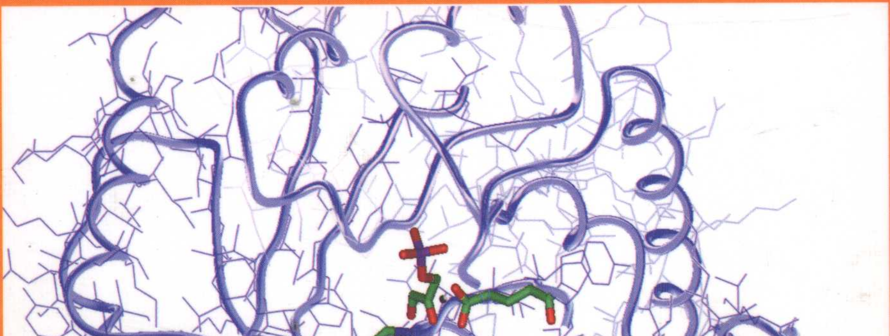

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Preface

Chemical kinetics is the area of science devoted to the study of the rates as well as the mechanisms of reactions. Its applications range from the understanding of the interplay between metabolic processes, where the intricate control of the rates of enzymatic processes is fundamental for the overall wellbeing of biological systems, through industrial synthesis of both fine and heavy chemicals to the long-term geological and atmospheric changes occurring on our planet since the evolution of the Universe and those expected to occur in future. At the economic level, the overwhelming majority of industrial chemical syntheses involves heterogeneous or homogeneous catalysis, and an understanding of the inherent processes and interactions is fundamental for the optimisation of reaction conditions. Moreover, a kinetic and mechanistic understanding of the complex series of interrelated reactions occurring between molecules such as oxygen, carbon dioxide, hydrogen, nitrogen and its oxides in the stratosphere and the study of processes induced by the absorption of light or high-energy radiation is fundamental to our appreciation of effects such as global warming or the depletion of the ozone layer. The timescales involved in these dynamic processes vary by many orders of magnitude, from less than the time of vibration of a chemical bond up to the age of the Universe.

All textbooks in physical chemistry have sections dedicated to kinetics. However, generally, owing to space constraints, they cannot treat the topic in the depth that is necessary for its full appreciation, and frequently, they treat its mechanics rather than its practical applications or its relations to the other areas of physical sciences such as thermodynamics and structural studies. Further, although a number of excellent student texts (at the undergraduate as well as postgraduate levels) are devoted to this topic, some of the most important ones were published several decades ago and cannot be expected to reflect the numerous significant research advances that have been acknowledged by the award of many Nobel prizes and other important distinctions in this area.

This book aims to provide a coherent, extensive view of the current situation in the field of chemical kinetics. Starting from the basic theoretical and experimental background, it gradually moves into specific areas such as fast reactions, heterogeneous and homogeneous catalysis, enzyme-catalysed reactions and photochemistry. It also focusses on important current problems such as electron-transfer reactions, which have implications at the chemical as well as biological levels. The cohesion between all these chemical processes is facilitated by a simple, user-friendly model that is able to correlate the kinetic data with the structural and the energetic parameters.

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While the book is primarily meant for chemists, we feel that it can also be useful to students and research workers in related disciplines in the physical sciences, the biological and biomedical areas and in the earth and atmospheric sciences. It is hoped that this text will be beneficial to students at the undergraduate as well as postgraduate levels. In addition, the programs available free of cost at a dedicated website (http://www.ism.qui.uc.pt:8180/ism/) will be valuable to many research workers whose investigations necessitate the use of the tools of chemical kinetics.

The task of compiling this book would have been impossible without the excellent collaboration of many of our colleagues and co-workers, whose studies have been cited throughout the text. The feedback on the earlier versions of this text from our students at the University of Coimbra have contributed greatly to the improvement of the same. Very special thanks are due to Dr. Carlos Serpa and Dr. Monica Barroso for their contribution to the design of experiments and models that have helped us to understand the relationship between chemical structure and reactivity.

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1.1 INITIAL DIFFICULTIES IN THE DEVELOPMENT OF CHEMICAL KINETICS IN THE TWENTIETH CENTURY

One of the major difficulties in the development of chemical kinetics stemmed from the lack of mathematical preparation of chemists of that period. For example, Morris Travers [4,5,15] in his biography of William Ramsey noted that his lack of mathematical preparation was the determining factor that made him decide not to become a physicist. Harcourt also notes his own mathematical weakness and his inability to understand many of the mathematical treatments that were made on his experimental data on chemical reactions. These were due to the mathematician Esson, professor of geometry at Oxford. Such developments were sufficiently complex that they were not even understood by many of his contemporary mathematicians, let alone by the chemists of the period. Also, the work of Guldberg and Waage in this area resulted from a collaboration between a professor of applied mathematics and a chemist, while the extremely promising work of Berthelot and Péan de St Gilles on kinetics was finally abandoned by the premature death of the latter scientist at the age of 31.

Berthelot and St Giles, in their kinetic study of esterification reactions, showed that the amount of ester formed at each instant was proportional to the product of the "active masses" of the reactants and inversely proportional to the volume. Rather inexplicably, these authors did not take into account the role of these factors in defining the rate law of the reaction [4,5,15]. A possible explanation for this can be seen in a note on the life and work on Marcelin Berthelot [16]. In this work, indications are given of Berthelot's understanding of the role of mathematics in chemistry: "the mathematicians make an incoherent block out of physical and chemical phenomena. For better or for worse, they force us to fit our results to their formulae, assuming reversibility and continuity on all sides, which, unfortunately, is contradicted by a large number of chemical phenomena, in particular the law of definite proportions."

Guldberg and Waage arrived at the concept of chemical equilibrium during 1864–1867 through the laws of classical mechanics: that there are two opposing forces, one owing to the reactants and the other to the products, which act during a chemical reaction to achieve equilibrium. In an analogy with the theory of gravity, such forces will be proportional to the masses of the different substances; actually, they established two separate laws, one relating to the effect of masses and the other to that of volume, and it was only later that they were combined into a single law, involving concentrations or "active masses".

Guldberg and Waage also initially experienced difficulties in finding the proper exponents involved in the description of the variations in the concentrations of the different substances; this problem was resolved in 1887, in terms of molecular kinetic theory. However, far more importantly, these authors did not manage to distinguish the rate laws (what we would call today the initial conditions) from the derivatives of the equilibrium conditions. This considerably complicated and delayed the future development of chemical kinetics. The dynamic nature of chemical equilibrium was never in doubt. However, the complexity of the systems was far from being considered and the link between equilibrium and kinetics was weak. The works of Harcourt and Esson are models of meticulous experimental and theoretical work, but on reading them, it is also obvious that these authors had to confront many conceptual and technical problems. Their kinetic studies needed fairly slow reactions that could be started and stopped quickly and easily. The reactions that best satisfied these experimental conditions were, in fact, fairly complex in mechanistic terms. In spite of the fact that Harcourt knew that such reactions did not happen in a single step, he was far from being able to recognise all their complexities. It was this difficulty in seeing simplicity in the macroscopic observations and extending it to the corresponding microscopic interpretation that became one of the main obstacles to the proper development of chemical kinetics.

Another area of chemical kinetics that has been the focus of various historical studies, involved the interpretation of the effect of temperature on the rates of chemical reactions. For rates measured under standard concentration conditions, Arrhenius expressed this effect by the equation

$$k = A\mathrm{e}^{-(E_\mathrm{a}/RT)} \tag{1.1}$$

where k is the rate under standard conditions and A and E_a constants, which are practically independent of temperature. A is called the *frequency factor* or *pre-exponential factor* and E_a the *activation energy*.

The Arrhenius law took a long time to become accepted; many other expressions were also proposed to explain the dependence of rate on temperature [17–19]. However, the Arrhenius expression eventually became dominant, as it was the model that was the easiest to relate to in terms of physical significance. Nevertheless, its acceptance did not come quickly, and was compounded by great difficulties in scientific communication at the time, with lack of interaction between different research groups often carrying out similar, and often parallel studies, instead of drawing on the progress that had already been achieved in this area.

Many of these conceptual and experimental difficulties would disappear with the brilliant work of van't Hoff [20], who introduced the concept of order of reaction and, through it, the possibility of knowing the mechanism of a chemical reaction just on the basis of chemical kinetics [21]. In fact, van't Hoff used the term *molecularity* for what we would call today reaction *order* (the power to which a concentration of a component enters into the rate equation). When referring to the actual concept of *molecularity*, this author used the explicit expression "the number of molecules that participate in the reaction" [6]. The term *order* is due to Ostwald. Van't Hoff received the first Nobel Prize in 1901 for his discovery of the laws of chemical dynamics.

During this period, interest in chemical kinetics remained fairly high until 1890, and then declined "due to the lack of stimulus from kinetic theories which could suggest appropriate experiments, sufficient to stimulate a discussion" [22] and, in essence, it needed something to allow a connection between molecular structure and chemical reactivity. This is true, not just of chemical kinetics: all areas of science suffer in the absence of appropriate theories, which help to guide development of experiments.

A revival of interest in this area began around 1913 with the "radiation hypothesis", due to M. Trautz, Jean Perrin and William Lewis. The particular challenge they tackled would probably have escaped notice of the scientific community, except for the fact that Perrin and Lewis were two highly respected scientists. Their developments required a strong mathematical preparation. Lewis was the first chemist to develop a theory of chemical kinetics based on statistical mechanics and quantum theory. It is clear that Lewis was an exception in terms of mathematical background to the majority of British chemists, who even in the 1920s had a mathematical background that was insufficient to address, or even understand such problems.

The "radiation theory", which was received with enthusiasm, was later seen to be mistaken. However, it was important as it stirred up a lively debate that greatly contributed to the development of the correct theories of chemical kinetics.

In this first phase of development, the theories of chemical kinetics tried to resolve the problem of the calculation of the pre-exponential factor and activation energy in the Arrhenius equation. The difficulties in calculating A stemmed in large part from the confusion that had existed ever since the first quarter of the nineteenth century over the role of molecular collisions on the rates of reaction. Today, we know that molecular collisions lead to the distribution of energy between molecules, but the rate of chemical reactions is determined both by the frequency of these collisions and the factors associated with the distribution of energy.

Max Trautz in 1916 and William Lewis in 1918 developed mathematical expressions that allowed the formulation of a collision theory for pre-exponential factors. In 1936 Henry Eyring, and almost independently, Michael Polanyi and M.G. Evans came to develop the transition state theory, having as its bases thermodynamics and statistical mechanics.

The concept of potential energy surface (PES) was developed to calculate the activation energy. Based on quantum mechanics, the first PES was constructed, at the start of the 1930s by Eyring and Polanyi for the reaction $H + H_2$. But the concept of PES is much more comprehensive because it allows the dynamic study of the rates of elementary reactions. This is based on the study of the forces that cause molecular motions that will lead to chemical reaction.

1.2 CHEMICAL KINETICS: THE CURRENT VIEW

Chemistry is concerned with the study of molecular structures, equilibria between these structures and the rates with which some structures are transformed into others. The study of molecular structures corresponds to study of the species that exist at the minima of multidimensional PESs, and which are, in principle, accessible through spectroscopic measurements and X-ray diffraction. The equilibria between these structures are related to the difference in energy between their respective minima, and can be studied by thermochemistry, by assuming an appropriate standard state. The rate of chemical reactions is a manifestation of the energy barriers existing between these minima, barriers that are not directly observable. The transformation between molecular structures implies varying times for the study of chemical reactions, and is the sphere of chemical kinetics. The "journey" from one minimum to another on the PES is one of the objectives of the study of molecular dynamics, which is included within the domain of chemical kinetics. It is also possible to classify nuclear decay as a special type of unimolecular transformation, and as such, nuclear chemistry can be included as an area of chemical kinetics. Thus, the scope of chemical kinetics spans the area from nuclear processes up to the behaviour of large molecules.

The range of rates of chemical reactions is enormous. Figure 1.1 gives a general panorama of the variety of reaction rates of processes in the world around us. Nuclear transformations and geological processes can be considered to be some of the slowest reactions that we come across. The corrosion of some metals frequently takes place during the life expectancy of a human (80 years = 2.5×10^9 sec). The time of cooking food is readily measurable simply by visual observation, and extends from minutes to hours. We can contrast this with the case of reactions such as the precipitation of a salt or neutralisation of an acid that occur in <0.1 sec, because visually we can no longer distinguish images on this timescale. There are, however, special techniques which allow much shorter time resolution in our observation window, and which allow study of extremely rapid reactions. The limit of time resolution of interest for chemical kinetics is defined by the movement of nuclei in molecules in their vibrational or rotational motion.

The chemical reaction can be considered as a voyage on a multi-dimensional PES (Figure 1.2). The definition of the PES has its origin in the separation of the movement of electrons and nuclei. This separation is justified on the basis of the difference in mass between an electron and a proton (the mass of the former is 1/1800 times the rest mass of the second), which means that the movement of electrons is much more rapid than that of the nuclei. Because of this, the electrons can be considered to re-adjust *instantaneously* to each of the geometries that the nuclei might adopt. The PES results from solving the Schrödinger equation for each of the possible nuclear geometries. The sum of the electronic energy and the nuclear repulsion governs the movement of the nuclei. Ideally, the Schrödinger equation must be solved for a great number of nuclear geometries using only the laws of quantum mechanics and the universal constants, which are given in Appendix 1. From this, a set of points will be obtained, and the energy determined for each of the possible geometries. This type of calculation, known as *ab initio*, is very time consuming

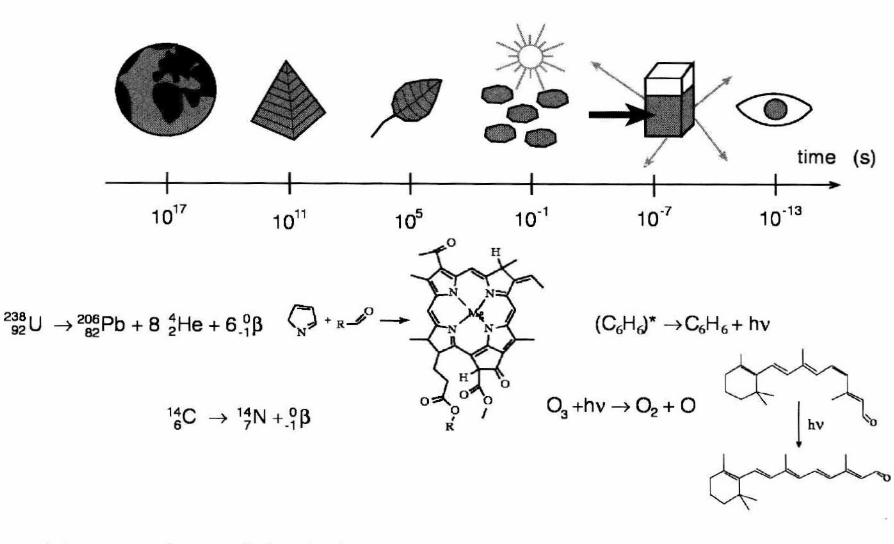

Figure 1.1 Range of rates of chemical reactions.

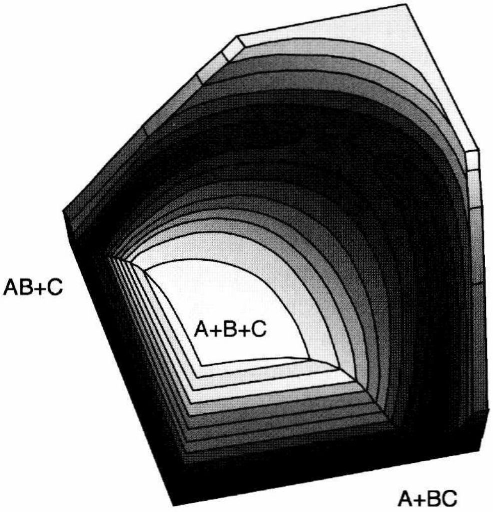

Figure 1.2 PES for collinear approach of atom A to the diatomic molecule BC in the triatomic system A+BC → AB+C, with the most important topographical regions: reactant valley (A+BC), transition state (‡), product valley (AB+C), dissociation plateau for all bonds (A+B+C) and lowest energy pathway from reactants to products (dashed line).

and difficult for polyatomic systems. As a consequence, many PESs include experimental information and are described by more or less complex functions, which are fitted to results of *ab initio* calculations and experimental information on the system.

In a hypersurface of a polyatomic system there can exist a number of more or less stable structures, which correspond to deeper or shallower potential wells. The separation between these wells is made up of hills, that is, potential barriers with variable heights. The height of the potential barriers determines the energy necessary to convert from one structure into another, that is, for a chemical reaction to occur. In the passage from a reactant well, or valley, to that of products, there is normally one that goes by a path, whose point of highest energy is termed the saddle point, given the topographic similarity to the saddle of a horse. A saddle point corresponds to a maximum energy on the route that leads from reactants to products, but a minimum one on the direction orthogonal to this. The reaction pathway, which goes through the lowest energy path, is called the *minimum energy path*. It is natural that a chemical reaction, which occurs on a single PES will follow preferentially the minimum energy pathway or route. The surface orthogonal to the minimum energy pathway between reactants and product and which contains the saddle point, corresponds to a set of nuclear configurations that is designated the *transition state*. Its existence can be considered as virtual or conceptual, because the transition state corresponds to a region on the potential energy hypersurface from which the conversion of reactants to products leads to a decrease in the potential energy of the system. The transition state is, therefore, intrinsically unstable.

The minimum energy pathway for a given reaction can be defined by starting from the transition state as being the path of the largest slope that leads to the reactants valley on

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