MOLECULAR DYNAMICS: COLLISIONAL AND STATISTICAL APPROACH TO REACTION RATE

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Summary

Experimental and theoretical studies of the dynamics of chemical reactions have as their objective the characterization of reactive events at the molecular level, proving the dependence of observable quantities from the nature of reagents and products, and from the distributions of velocities, internal energy, and angular momentum.

The observable quantities in this field are the rate constants and cross sections. The precision with which these quantities can be measured depends strongly on the system used and relies heavily on the progress of experimental techniques.

An important aspect of these investigations is the correlation of observable phenomena with intermolecular interaction forces (potential energy surfaces) beyond the simple early models of chemical kinetics.

Although the experiments that fostered the early developments were on simple processes in the gas phase, an ample phenomenology is now being accumulated, thanks to progress in experimental techniques. The modern interpretive tools now pave the way for the study of systems of increasing complexity, the program of molecular dynamics being that of describing complex systems of macroscopic interest from the characterization of the dynamics of elementary processes.

1. Introduction

The study of the velocity of chemical reactions is of primary importance not only from the viewpoint of basic research—to deepen our knowledge of the structure of matter and of the laws that underlay it—but also from the viewpoint of applications. For example, these studies open perspectives for the preparation of new compounds and the comprehension of the evolution of complex systems (combustion processes, planetary atmospheres, plasmas) and of the modalities governing energy transfer in chemical reactions.

Historically, chemical kinetics became an important part of chemistry in the second half of the nineteenth century. Initially, attention was paid to the assessment of the laws that determine the speeds of reactions and their dependence on quantities such as concentrations of reactants and temperature of the system. A further step was the determination of the mechanisms of chemical reactions, namely the characterization of complex reactions as a combination of elementary processes. A third step forward was in the modeling of macroscopic processes in terms of microscopic events.

While the interpretation of unimolecular reactions in terms of intermolecular energy transfer and of energy redistribution among molecular modes was advanced only at the beginning of the twentieth century, the role of collisions between reactant molecules in bimolecular reactions was recognized as soon as the kinetic theory of gases was formulated. Svante Arrhenius (1889) gave the general law, which describes the dependence on absolute temperature T of *the rate constant*

$$k = A \exp(- E_a/RT) \tag{1}$$

where R is the gas constant and the factor A varies only slightly with temperature; the meaning attached to the energy of activation E_a is as the minimum energy which molecules need have to overcome the threshold to reaction. 1889 can be considered as the birth date of reactive dynamics as the study of the motion of atoms and molecules in a reactive event. Eq. (1) was motivated by the 1884 discovery by Van't Hoff of the exponential dependence from the temperature of the equilibrium constants for most reactions: Eq. (1), when used for both a reaction and its inverse, agrees with Van't Hoff's equation interpreting chemical equilibrium as dynamical at the microscopic level. Therefore, the parameters in Eq. (1) can be discussed in a language borrowed from thermodynamics and can be estimated by the techniques of statistical mechanics (transition state theory, developed by M. Polanyi, E. Wigner, and H. Eyring in the 1930s).

The analogy with simple microscopic models that lie at the foundation of the kinetic theory of gases (models that satisfactorily reproduce their macroscopic behavior) is close, even though the ample variety in the phenomenology of chemical reactions calls for the consideration of a greater complexity of the interactions at play and thus for the

introduction of elaborate theoretical models. The advent of quantum mechanics and its early applications in the 1930s provided a sound theoretical basis for molecular dynamics. From the 1960s onwards, vigorous experimental progress allowed the accumulation of empirical information on chemical reactions at a microscopic level. Since then, molecular reaction dynamics has represented a basic area of modern research in chemistry, involving an increasing number of laboratories and leading to Nobel Prizes for Chemistry in 1986 to Dudley R. Herschbach (Harvard University, USA), Yuan T.Lee (University of California, Berkeley, USA), and John C.Polanyi (University of Toronto, Canada), and in 1999, to Ahmed Zewail (California Institute of Technology, USA).

2. Definitions and Models

A reactive event is often a three-center problem, while four-center reactions are rare, and those involving more than four centers are rarer still. Dynamical constraints (symmetry conservation, specificity, concentrations) controlling reactivity are particularly important in organic chemistry.

To define a three-center reactive collision, we write:

$A + BC \rightarrow (A\ldots B\ldots C) \rightarrow AB + C$,

where A, B, and C are atoms or radicals. In an idealized experiment a flow of A particles impinges on BC with a relative kinetic energy $E = \frac{1}{2}\mu v^2$, where v is the relative velocity of A and BC, and $\mu = (m_A m_{BC})/(m_A + m_{BC})$ is their reduced mass (see Section 5 for experimental details). The quantum states of species at play will be collectively indicated as i for reactants and f for products, to identify electronic, vibrational, and rotational states and possibly polarization—as referred to relative orientation of species and their spins and orbital angular momenta when they approach at the beginning of the reaction or separate at the end. Although experimentally elusive, none the less basic is the role of the overall orbital angular momentum of the collision L. Quantum mechanically, it is defined as $L = (h/2\pi)\sqrt{\ell(\ell+1)}$, where h is Planck's constant and l the orbital quantum number, or classically as $L = \mu v b$, where b is the impact parameter (see Figure 1); therefore all possible values of L contribute to measurable quantities.
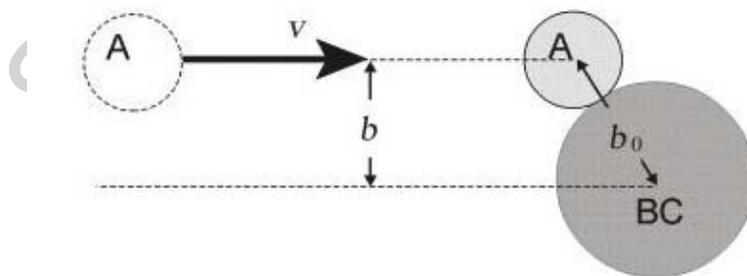

Figure 1. The A+BC collision according to the "rigid sphere" model: b is the impact parameter and v the relative velocity. In the simplest model a reaction occurs if b is smaller than the sum of the radii of the two spheres. In the model that reproduces Arrhenius equation (Eq. (1)), there is the additional requirement that the kinetic energy along the line joining A to BC be larger than a threshold value, E_o: this leads to Eq. (4).

2.1. Cross Section for Reactive Collisions

In dynamics the measurable quantities associated to a reactive event are the *cross sections* (German *Querschnitt*): its meaning is illustrated with reference to an experimental configuration (see Section 5) where two reactants A and BC cross in a volume τ with relative velocity *v*.

The measurement of the number *N* of particles of any of the products collected within a solid $d\Omega$ angle allows us to write down the time derivative:

$$dN/dt = \sigma_{i,f}(E,\Omega)\, vn_A n_{BC} \tau d\Omega \tag{2}$$

where n_A e n_{BC} are the densities of reactant particles and $\sigma_{if}(E,\Omega)$ is the differential cross section for the reaction from state *i* to state *f*. This is a basic quantity in reaction dynamics.

By integration of differential cross section over the whole solid angle Ω, one obtains the total (or integral) cross section $Q_{if}(E)$, which is a measure of the probability of the reactive event, a quantity often amenable to direct measurement using a variety of experimental configurations.

2.2. From Cross Sections to Rate Constants

The total cross section $Q_{if}(E)$ is connected to the microcanonical rate constant by the equation $k_{if}(E) = vQ_{if}(E)$. If reagents follow a velocity distribution according to the Maxwell–Boltzmann statistics, the average over the distribution $<k_{if}(E_r)>=k_{if}(T)$ is the "state-to-state" rate constant.

The weighted sum of constants $k_{if}(T)$ over all available final states *f* and the average over actual distribution of initial states *i* give the rate constant *k(T)*, which is the standard measurable quantity in the macroscopic experiments of chemical kinetics.

To carry out experiments to study reaction dynamics, control is required over at least some of the relevant parameters, such as velocities, internal states, and relative orientations of reactants and products, to disentangle information lost in the averaging involved in rate measurements. Such a control is typically only partially achieved. Thus, one obtains differential or integral cross sections for ensembles of particles, for which some of the degrees of freedom are only partially defined, or not defined at all. Although this implies that full dynamical information is rarely achieved because of some unavoidable averaging, dynamical experiments carry more information than rate measurements, which imply the concept of temperature and thus a canonical distribution of translational and internal degrees of freedom of reactants and products. Therefore, rate constants can be obtained (at least in principle) by Boltzmann averaging of cross sections, while the inverse process (namely, deconvolution from rate constants to cross sections) is impossible. Indeed, information on cross sections is required in order to interpret the velocity of reactive processes or transport phenomena under conditions

where the hypothesis of thermal equilibrium does not hold, and temperature is not a significant parameter.

The simplest microscopic model that illustrates the dynamics of elementary chemical reactions assumes a reaction takes place with a probability that depends only on the requirement (Figure 1) for reactants (approximated as spheres) to come close to each other within a range b (impact parameter) smaller than a distance b_o, which is the sum of the two molecular radii (hypothesis of rigid spheres). The total cross section is then taken as πb_o^2. It can be easily demonstrated, averaging over a Maxwell–Boltzmann distribution, that in this case the rate constant depends only slightly on temperature, $k(T) \propto T^{1/2}$, in disagreement with experimental evidence that the dependence is typically exponential (Eq. (1)).

The dependence of the probability of a reactive event on collision energy can be introduced in the simplest way by assuming that a requisite for reactivity is not only that reagents come close at a distance lower than b_o (as in the previous model), but also that the collision energy is higher than a threshold value Eo: as we will see, this threshold value for energy represents the microscopic interpretation of the activation energy E_a that appears in Eq. (1) and accounts for the temperature dependence of the kinetics of macroscopic processes. Therefore assuming that the total cross section is a "step function" of energy—namely, equal to zero for $E<E_o$ and to πb_o^2 for $E>E_o$ one obtains:

$$k(T) = \pi b_o^2 \, (8k_B T/\pi\mu)^{1/2} \, (1+E_o/k_B T)\exp(-E_o/k_B T) \tag{3}$$

where k_B is the Boltzmann's constant, the ratio of the gas constant is R, and Avogadro's number is N ($k_B = R/N$).

The simplest microscopic model that can adequately interpret Arrhenius law (see Eq. (1)) can be obtained by introducing in the rigid-sphere model the condition that reaction takes place if the collision energy along the line that joins the centers of the rigid spheres, is larger than the threshold value: then, the total cross section is equal to zero for $E<E_o$ and equal to $\pi b_o^2 \, [1-(E/E_o)^2]$ for $E>E_o$ one gets:

$$k(T)= A(T)\exp(-E_o/k_B T) \tag{4}$$

in close agreement with Eq. (1), identifying the activation energy as the macroscopic analogue of the threshold energy, and thus $E_a = NE_o$.

The models currently utilized in chemical reaction dynamics go beyond the simple rigid-sphere assumptions and explicitly consider more realistic descriptions of the interactions at play. For example, reactions that do not present an activation energy can be interpreted by two-body models interacting at long range with a potential that can be approximated as $V(R) \propto r^{-s} \, (s>2)$, the only obstacle to reaction being the need for

reactants to overcome a centrifugal barrier of height Eb^2/r^2, where E is the kinetic energy for the collision and b the impact parameter. This model has been applied to the reactions between an ion and a neutral molecule (s=4) (George Gioumousis and D.P Stevenson) and the cross section for these reactions takes the simple form $\sigma = \pi(2\alpha/E_T)^{1/2}$ (where α is the polarizability of the molecule) and the specific rate constant k in this case turns out to be independent of temperature. For many of these reactions, experiments confirm the weak decrease of the cross section as the collision energy increases, and also the numerical values of cross sections calculated according to this model, or its simple generalization, are in good agreement with experimental observations.

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Biographical Sketch

Vincenzo Aquilanti is full professor of General Chemistry in the University of Perugia, Italy. He has carried out teaching and research activities in numerous universities worldwide. His scientific achievements in the fields of radiation and reactive collisions between atoms and simple molecules of atmospheric and astrophysical interest, and of quantum and semiclassical chemical physics are reported in more than 250 papers in scientific journals and book chapters. He is the leader of a research group where experimentalists and theoreticians cooperate, and act in collaboration with international institutions. He is active in editorial committees of several scientific periodicals, and has organized many International Meetings. He is married and has three children; his interests also include history and philosophy of science.