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Use of the Classical Trajectory Method in Modelling the Dynamics of Atom-Molecule Collisions in Chemical Reactions

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This review discusses methods of modelling atom - molecule collisions in chemical reactions by calculating the classical trajectories, and the application of these methods in studies of the dynamics and kinetics of bimolecular and unimolecular reactions. The discussion includes methods of defining and analysing the potential energy surface, methods of calculating the trajectories in multidimensional phase space, and statistical methods of controlling numerical experiments (selection of initial parameters, calculation of the distribution function of the active molecule with respect to life-time, etc.). 154 references.

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I. INTRODUCTION. FORMULATION OF THE MOLECULAR DYNAMICS PROBLEM

Rapid progress is being made in experimental and theoretical studies of the kinetics of chemical reactions at the microscopic level. The exchange of energy between different degrees of freedom during molecular collisions and intramolecular motion are being studied as component parts of chemical reactions and of relaxation processes. The formulation of the problem is closely associated with practical aspects of non-equilibrium chemical kinetics: the determination of the rate constants of fast processes and of the role of different degrees of freedom in the kinetics of chemical reactions taking place in strong shock waves and in rarefaction waves, with controlled external stimuli applied to specified degrees of freedom of the reacting molecules, etc. On the other hand, rate constant data for these processes obtained by modern methods of diagnosing initial, intermediate, and final states of reacting gases can be used as the experimental foundations for the solution of the problem.

In addition to quantum-mechanical calculations of the probability of elementary transitions, the theory increasingly uses numerical methods of solving the equations of molecular motion (i.e. the methods of molecular dynamics). In a strict formulation of the problem the motion of an isolated molecule as a whole, and that of its component parts, are described by the Schroedinger equation, which takes into account the interactions of all electrons and nuclei. Molecular dynamics in the widest sense is concerned with the motion of both the nuclear and the electronic subsystem. However, a large class of problems in molecular dynamics and chemical kinetics can be solved by determining only the motion of the nuclei. Under these conditions the electronic subsystem acts as a field of forces in which the nuclear motion takes place, and no allowance for it is needed beyond determining this field.

In the Born–Oppenheimer adiabatic approximation the motions of electrons and of nuclei can be treated separately. The effective interaction between the nuclei is defined by the potential energy surface (PES), which depends on the internuclear distances and on the quantum state of the electronic subsystem. The conditions under which the adiabatic approximation is valid are determined by the difference in energy between the electronic levels and by the velocity of the nuclei, and are characterised by the Massey parameter[1].

The motion of nuclei in a potential field can be studied by classical mechanics. The error associated with the classical approximation can be evaluated by comparing the solutions of the quantum and of the classical motion problem. A detailed analysis of the approach to the classical limit in the theory of molecular collisions is given in Ref. 2.

Many workers[3–11] (for example, by using model PES of the LEPS type†) have solved the dynamics problem both within the framework of the classical equations of motion and quantum-mechanically. The two types of solution were used to calculate the probability of elementary transitions with different types of averaging over the initial and the final states. It follows from that work[3–11] that for "reasonable" PES with high activation barriers the difference between the averaged process parameters calculated in the classical approximation or quantum-mechanically is small. Only the classically forbidden processes (for example, tunnelling and reflection above barriers) are exceptional in this respect. These processes involve light atoms, and are very important for the kinetics of reactions at low temperatures. For a wide range of reactions with thermal energies of ~1000 K the classical approximation is adequate.

In Slater's dynamical theory[15] the molecule is treated as a set of classical harmonic oscillators. This model allows analytical treatment, but the harmonic approximation is not even qualitatively correct when used to describe the nature and rate of intramolecular energy redistributions and the localisation of energy along the reaction coordinate. The models used in modern molecular dynamics allow as far as possible for the real interactions in the molecule. Numerical studies of these models by computer calculations provide the modern "experimental" basis for further developments in

†The LEPS potential[12–14] is named after its proposers (London–Eyring–Polanyi–Sato). It is an empirical potential, with many adjustable parameters. In 1929 an attempt was made to construct the potential surfaces for three hydrogen atoms. Subsequently many empirical parameters were introduced into the potential, which gradually lost its quantum-mechanical significance. The LEPS potential is widely used at present to describe three-particle interactions.

dynamical theory. Dynamical calculations for molecules containing more than two nuclei are possible only with the most advanced computing techniques, even within the confines of the classical description (the "classical trajectories method"). The volume of the computational work is so enormous that even on the best computers the problem can be solved only by exploiting new and efficient methods of computing mathematics.

Several review articles on numerical modelling in molecular dynamics using classical trajectory calculations have appeared in the last decade[16–20]. The aim of the present review is to examine the most recent advances in this area and to acquaint the reader with practical results. The second section is devoted to methods of modelling atom–molecule collisions and chemical reactions by using classical trajectories, and the third section deals with the application of these methods to studies of the dynamics and kinetics of bimolecular and unimolecular reactions.

II. METHODS OF STUDYING INTRAMOLECULAR MOTION BY USING CLASSICAL TRAJECTORIES

Three basic tasks can be distinguished in the development of numerical methods of solving the molecular dynamics problem in the framework of the classical equations of motion.

1. Determining the PES. Numerical solution of the Schroedinger equation for complex molecules is impossible at present even on the most modern computers, and therefore the number of non-empirical PES calculations so far reported is very small. Model surfaces which adequately describe the molecular system in the asymptotic regions of phase space are usually employed: the models correctly describe the energetics of the main paths of the reaction, and the vibration frequencies and the geometries of the initial molecule and of the reaction products. By using these PES the general features of the dynamic behaviour of molecular systems can be identified, and methods of numerically modelling the dynamic processes can be developed.

2. Determining the initial conditions. In order to obtain kinetic expressions for analysing the molecular dynamics we must examine a set of trajectories to allow for the statistical nature of the initial data in a real physical experiment. At the same time the number of trajectories must not be too great, since the calculation of each trajectory is very costly in computer time. These conflicting requirements add to the difficulty of determining the initial conditions.

3. The choice of an effective numerical algorithm for solving the classical equations of motion, capable of calculating the trajectory of motion reliably over long integration times. The solutions usually show a large scatter of characteristic times, and are oscillatory functions, but they must keep the integrals of motion constant. As a result, a need for special numerical methods of calculating trajectories has arisen.

The PES can be adequately described in a number of ways. One of these is based on *ab initio* calculations of the potential in a limited region of configurational space.

Leforestier[21] calculated the dynamic characteristics of the reaction $H^- + CH_4 \rightarrow CH_4 + H^-$ by using an *ab initio* potential for a small region of the transition state, and obtained the classical trajectories of motion for a small translational energy along the reaction coordinate. This choice of initial conditions in the region of the transition state leads to rapid dissociation, and the motion is observed only in a limited region of configurational space. Hence this very interesting method does not allow us (unfortunately) to analyse the dynamics of a reaction over the whole of phase space.

From the potential energy at a few reference points, calculated by numerical solution of the Schroedinger equation, and knowing the asymptotic behaviour of the potential, a polynomial surface (called a spline[24]) was calculated[22,23]. This approximation allows wide variations in the PES, while keeping constant the reference points and the general structure, and therefore it offers detailed information on the effect of the shape of the PES on the dynamics and kinetics of the reaction.

As we have already pointed out, the Born–Oppenheimer adiabatic approximation is often used in the classical description of molecular dynamics. However, some molecular processes are strongly non-adiabatic, but this can be allowed for in the dynamical approach. The interactions between two adiabatic energy levels have been studied[25–30], and the classical problem has been solved by first considering only one potential surface but allowing for the probability of transition to another PES (calculated by the Landau–Zener formula[1]) in the region where the two surfaces approach each other closely or intersect. Further classical motion up to the next intersection lines takes place on the old and the new PES with probabilities $1 - P$ and P respectively, and so on. This method of allowing for non-adiabaticity is applicable when the section of the classical trajectory in which transitions between PES have a high probability is relatively short.

The first reported application of the classical trajectory method was to bimolecular collision processes between an atom and a diatomic molecule[31–33], i.e. a special case of the three-body problem. Because of the relatively small number of dimensions of the phase space for a three-body system, fairly detailed computer calculations of the trajectories are possible. The most successful numerical calculations and analyses of classical trajectories so far reported have been in studies of the three-body problem.

The classical trajectory method as applied to collisions between an atom and a diatomic molecule has been described in detail[34] for the exchange reaction $H + H_2 \rightarrow H_2 + H$. The choice of the coordinate system for the classical trajectories is considered in special detail. The initial conditions are chosen so as to describe the quantum states of the reactants as exactly as possible. Equations relating the initial and the final quantum states of the system to the classical variables are given.

Statistical treatment of the calculated trajectories yields kinetic information with a varying amount of detail. The probability of the reaction is first determined, and hence the full cross-section of the reaction as a function of the initial states of the reactants and the final states of the products are obtained. The rate constant of the reaction is then calculated as the integral of the full reaction cross-section for a given distribution of the initial states of the reactants. The thermal (equilibrium) rate constant is calculated by assuming a Maxwell distribution of the molecules with respect to velocity and a Boltzmann distribution with respect to the internal initial states.

Obviously, the results of dynamical calculations can be used in the same way to calculate the rate constants under non-equilibrium conditions, for example for different temperatures of the different degrees of freedom, or for other stated deviations from the Maxwell–Boltzmann distribution. This allows us, in particular, to apply the classical trajectory treatment to non-equilibrium processes in the upper layers of the atmosphere, and also (under laboratory conditions) to the excitation of molecular degrees of freedom by laser radiation or to the excitation of a gas by a laser, by powerful shock waves, or by chemical activation.

Raff and coworkers[35] have developed a method of calculation for the four-centre problem which allows (by a special choice of coordinate system and of initial conditions) the following collisions to be studied: atom–atom, atom–diatomic molecule, atom–triatomic molecule, and diatomic molecule–diatomic molecule. The method has been used to examine various alternative mechanisms of the $I_2 + H_2$ reaction and to calculate the rate constant of the recombination reaction $I + I + H_2 \rightarrow I_2 + H_2$. The calculated constant agrees exactly with experiment.

These methods are valid only for systems in which the number of atoms taking part in the reaction is small. They cannot be applied to reactions involving polyatomic molecules.

A method which can be applied to studies of the dynamics and kinetics of those reactions has been described[36]. Within the limits of the proposed model schemes, different mechanisms for the decomposition of excited molecules can be examined and the conditions for selective and for thermal activation can be defined. For modelling the decomposition of a polyatomic molecule over an activation barrier the following procedure is used to define the initial conditions: the origin of each trajectory is chosen in the region of phase space corresponding to the activated complex, and the trajectories are calculated twice (once for positive and once for negative time changes). By "fusing" these two trajectories the trajectory of the motion of the molecule leading to decomposition is obtained. This method of defining the initial conditions allows a correct choice of the trajectories leading to decomposition, and can be used to calculate the maximum spontaneous decomposition time for each trajectory. The method can also be used to model reactions such as $(AB)^* \rightarrow A + B$ and $A + BC \rightarrow (ABC)^* \rightarrow AB + C$, including those in which the fragments A, B, and C have a complex structure. It has been applied to studies of the decomposition of molecules such as N_2O and CHF_3.[37,38] The practical application of the method requires a knowledge of the geometry of the activated complex. In reactions with a well defined activation barrier the position of the activated complex is usually given by the saddle point of the PES. The directions of the reaction coordinates at the saddle point are the directions of decreasing potential energy.

In dynamic studies of chemical reactions the configuration of the activated complex (reaction path) often needs to be known. If the saddle point of the PES is known, and if the configuration of the activated complex is determined by the saddle point, the identification of the reaction path presents no difficulty. We only need to follow the potential energy surface downwards from the saddle point to the valleys of products and of reactants in the direction of the reaction coordinate. However, the most difficult part of the procedure is to find the saddle point, because paths leading to extrema and to saddle points are not easily identified by using local methods of describing the energy surface.

A localised method of studying the energy surface which nevertheless allows the saddle point to be identified has been described[39]. The step of the algorithm consists in moving along the constant energy surface and searching for the point where the surface is least steep. This method is a mathematical realisation of the idea put forward by Pencir[40]. Another method of searching for the saddle point of the PES[36] relies on a global description of the surface. The PES is intersected by a hyper-plane passing through the valleys of products and of reactants. The descent to the saddle point begins at the point in the section where the potential energy is a maximum. The saddle point in the PES is easily located by this procedure.

If the initial conditions are chosen arbitrarily not all the trajectories lead to reaction: in other words, phase space can be divided into reaction-active and reaction-inactive regions. Dynamical studies[41–43] have established the general condition for distinguishing these two types of region in phase space for reactions of the $A + BC \rightarrow AB + C$ type. This condition depends on the activation energy and on the form of the saddle point in the region of the activated complex.

Statistical methods of evaluating multidimensional integrals are used to calculate rate constants by the classical trajectory methods. The first attempts at calculating the constants relied on the standard Monte Carlo procedure, in which each variable was arbitrarily associated with one particular distribution law, irrespectively of the other variables[34]. More exact methods of calculating the integrals from a limited number of chosen trajectories were subsequently developed. These include a Monte Carlo scheme[44] for modelling the three-particle interaction act. By specifying the initial conditions as suggested it is possible to choose trajectories in the part of phase space which makes the most substantial contribution to the wanted kinetic parameters. The method was used to calculate the rate constant for the $H + H + H \rightarrow H_2 + H$ recombination reaction, which was found to agree with experiment for temperatures between 2000 and 5000 K, as well as giving the distribution in energy of the hydrogen molecules.

A recently developed method of evaluating multidimensional integrals for calculating reaction rate constants[45,46] relies on a non-random sampling of the initial conditions. The error in the calculation of the integral was shown to be smaller than in the standard Monte Carlo method. This allows a smaller number of trajectories to be used to achieve a prescribed level of accuracy in the evaluation of the integrals.

A statistical procedure (the modified method of moments) has been used[47] to calculate the distribution functions with respect to the spontaneous disintegration time of excited molecules. The modification of the standard method of moments consists in limiting the region for which the changes in the arbitrary quantity are calculated. This modification was introduced because the distribution of spontaneous decomposition times for excited molecules gave a set of random values concentrated in a limited range of time, although the true range of spontaneous decomposition times extends over the whole of the positive time axis.

A new procedure[48,49] for choosing initial conditions (importance sampling) offers an even lower error in the calculation of multidimensional integrals. It has been used to calculate the rate constants of the bimolecular reactions $F + H_2$, $C + H_2$, and $O(^3P) + H_2$, and shown to be superior to the standard method.

Some workers[50–52] have avoided the direct calculation of multidimensional integrals by expanding the differential scattering cross-section into a Legendre polynomial series. The coefficients of the expansion are obtained by statistical methods. In this case the evaluation of the multidimensional integral reduces to a statistical calculation of a discrete set of one-dimensional quantities. It has been shown that this method differs from the methods based on the direct calculation of multidimensional integrals in not causing a loss of information when the averaging is carried out over small angles. Some calculations[53–57] of the rate constants of various reactions in terms of flows through the critical surface in phase space have been based on Keck's variational theory[58].

The postulates of the statistical theories can be tested by combining the methods of molecular dynamics with estimates of the kinetic parameters. Dynamical calculations can be

used to confirm the hypothesis of an equilibrium distribution of active molecules in the region of the transition complex, and also to evaluate the transmission coefficients, i.e. to test the interpretation of the rate constant as a flow of representative points through the critical surface in the direction of the reaction products, and finally they can also be used to test the assumed statistical nature of the redistribution of energy in the active polyatomic molecule.

In some recent papers[59-63] the results of the classical trajectory method are compared with those obtained by applying statistical theories to the same PES. Good agreement between the two theories is obtained if the surface has a relatively simple structure, without sharp curvatures or excessively steep slopes.

Other recent papers[64-66] examine the relationship between the redistribution of energy and the stability of the classical motion. An analogue of the Lyapunov function, describing the behaviour of a specially defined gap between trajectories, is used as a criterion of the degree of randomisation of the system. A statistically randomised energy is revealed by an exponential increase in this distance. The degree of ergodicity of the system is determined by the nature of the PES.

A detailed dynamical analysis of the statistical behaviour of molecular systems has been published[67,68]. The degree of ergodicity of a polyatomic molecule is characterised by the spectra of the autocorrelation functions of the generalised momenta of the normal vibrations, obtained in the calculation of the classical trajectories. The area under the spectrum defines the energy of the given normal mode, and energy redistribution processes within the molecule can be characterised by the time-changes in the shape of the spectrum. At low energies the molecule behaves as a set of weakly coupled harmonic oscillators, and the spectra consist of discrete lines, but at higher energies additional lines and a continuum appear in the spectrum.

The autocorrelation function method has been applied in studies of the dynamics of intramolecular energy redistribution in a model of the CD_3X molecule (where X = H, Cl). Different PES were used to model the reaction with and without an activation energy barrier. Initial excitation of the molecule was by chemical or by thermal activation. It was found that the possibility of randomising the initial energy distribution of the active molecule depends on the characteristic features of the PES and on the total energy of the system. An equilibrium distribution of energy among the products is observed if the PES has no barrier in the output channel, and also in cases of strong intermolecular interactions.

Modelling studies of unimolecular reactions of complex molecules are reviewed in Refs.69 and 70. Some universal principles for the construction of model PES are formulated: they allow the equilibrium structure of the molecule, the force constants, and the relative masses of the particles to be varied. Three methods of selecting the initial conditions for polyatomic molecules are discussed: 1) selective excitation of normal modes, 2) non-selective (equal-probability) filling of phase space along the coordinates, 3) gradual selection, each set of initial conditions being used to generate the next set. The last two methods of defining the initial conditions ensure that all additions to the phase space are equally probable (if the number of samples is large enough), and can be used for modelling thermal activation. These principles have been used in a study[70] of the unimolecular decomposition of CD_3Cl, and the results have been compared with those of Ref.68. For small excitation energies it was shown that the polyatomic fragment CD_3 can be treated as a heavy structureless particle.

We should note that in a phase space with a large number of dimensions (~12–15 measurements) the modelling of thermal activation by equal-probability or by gradual selection requires an extremely large number of initial points for filling the phase space with a dense and uniform distribution of trajectories. A dynamical-statistical description of the excited molecules, applicable to barrierless unimolecular decomposition reactions, has been proposed[71] in order to overcome the need to calculate a large number of trajectories to obtain adequate kinetic information. This description is based on assessments of the stability of the distribution of spontaneous decomposition times with respect to variations in the configuration of the critical surface, and it allows the distribution function to be calculated from a relatively small number of trajectories. The distribution over maximum times for spontaneous decomposition can also be obtained from this description of the excited molecules.

To conclude this section we should stress that dynamical descriptions of unimolecular reactions usually deal with long-lived (in comparison to the molecular vibration period) polyatomic systems. This imposes very stringent requirements on the numerical solution procedure applied to the differential equations of motion. The effectiveness of the solution of the classical equations of motion has been improved[45] by an algorithm which allows a system of differential equations to be solved by local linearisation. At each integration step the initial PES is fitted to a parabolic expression. The resulting new system of differential equations is linear, and therefore can be solved exactly. By improving the approximation (i.e. by shortening the integration step) the new solution of the problem can be made convergent over the whole integration range. The additive integrals of motion of the original problem are retained (within the stated precision) in the numerical solution by choosing a parabolic approximation for the PES.

We have described[36] a procedure which allows neighbouring trajectories to be calculated, once the trajectory for the specified initial conditions has been obtained, by expanding the solution of the equation of motion in a Taylor series in increments of the initial data. This procedure allows new trajectories of motion to be obtained at a small additional cost in computer time, and thus it offers a substantially greater volume of data and an effectively filled initial phase space. The effectiveness of these new programs has been compared with that of the previously most widely used procedure: that of Kutta and Meerson. The algorithm proposed in Ref.45 was found to be the most effective for trajectories of motion of polyatomic systems extending over long times and showing a large scatter of characteristic times.

Practical applications of different methods of calculation based on classical trajectories have shown that surfaces which adequately describe experimental results can be constructed by varying the PES parameters and by comparing the results of model calculations with kinetic data.

III. DYNAMIC BEHAVIOUR OF MOLECULES AND KINETIC ASPECTS OF REACTIONS

1. Dynamics of Bimolecular Reactions

The rate constants of chemical reactions and the relaxation times of the associated processes calculated by the classical trajectory method are relatively insensitive to the lack of precision of the classical approach, to the errors of the numerical integration, and to the detailed features of the PES, since they are averaged over many trajectories.

However, both the rate constants and the relaxation times are sensitive to the overall characteristics of the PES.

Polanyi and coworkers[72-82] have carried out an extensive investigation of the effect of the position of the PES barrier on the kinetic behaviour of a molecular system. For exchange reactions such as A + BC → AB + C the PES is classified into different sections along the reaction path. Depending on whether the kinetic energy of the system is converted into internal energy of the products during the approach of the reactants or during the separation of the products, the PES is said to be of the attractive or of the repulsive type. In the intermediate case the surface is called "mixed". PES of the attractive type are shown to be characteristic of exothermic reactions, and those of the repulsive type of endothermic reactions. The energy distribution functions for the products have been determined as a function of the type of surface. Thus, for exothermic reactions the attractive nature of the potential causes strong vibrational excitation of the products. The degree of vibrational excitation of the products is determined also by the mass ratio of the reactants. The effectiveness of rotational and of vibrational excitation in overcoming an activation barrier has also been analysed as a function of the location of the barrier. It was found that the translational energy of the reactants is more effective than their vibrational energy in overcoming barriers located in the reactant region. The vibrational energy of the reactants is converted into vibrational energy of the products with a high efficiency.

Classical trajectory analysis has been used to study a large number of molecular collision processes and to identify their kinetic features. The vibrational transitions in the exchange reactions

$$\begin{aligned} H + H_2(v = 1,2) &\rightarrow H_2(v = 1,2) + H \\ H + HCl(v = 1,2) &\rightarrow HCl(v = 1,2) + H \\ Cl + HCl(v = 1,2) &\rightarrow HCl(v = 1,2) + Cl \end{aligned}$$

have been studied[83] by using the LEPS potential. Vibrational excitation of the initial molecules are shown to lower the activation energy in every case, the magnitude of this effect depending on the combination of nuclear masses. It was also shown that this path to changes in vibrational energy is an efficient vibrational relaxation mechanism in sufficiently dense atomic gases.

The displacement reactions

$$\begin{aligned} Br + HBr &\rightarrow H + Br_2 \\ Cl + HX &\rightarrow HCl + X \\ X &= I, Br \end{aligned}$$

have also been studied[84-88], together with the vibrational relaxation of HCl and DCl in the gas phase. The rate of the reactions was found to be increased by a preliminary vibrational excitation of the reactants. The agreement of these results with those of molecular beam experiments is good on the whole, and confirms the validity of the theory.

Several papers[89-95] deal with vibrational relaxation processes and the role of vibrational energy displacement reactions.

The first attempt at describing the vibrational relaxation of diatomic molecules by classical trajectories related to the O_2 + Ar reaction[96,97]. The potential of the molecule was approximated by the Rydberg–Klein–Rees method. The probabilities of changes in vibrational states and of dissociation of the molecules were calculated over a wide temperature range (from 1000 to 20000 K), in which the probability of one-quantum and two-quantum transitions decreases as the vibrational level number n increases, and for $n \geq 20$ it is independent of temperature. The calculations were satisfactorily consistent with scattering experiments in molecular beams and with direct measurements of relaxation times.

The classical trajectory method has been applied to the relaxation processes in the Br_2 + Ar system[98]. The effect of molecular rotation on the rate of vibrational relaxation was examined, and $V-R$ exchange was shown to be more effective than $V-T$ exchange in this system. Results obtained by the "breathing sphere" and the "rough sphere" model[99] were compared, and recommendations on the relative merits of these models were given.

Another group of papers[100-109] discusses the redistribution of vibrational, rotational, and translational energy in excited diatomic molecules (H_2, N_2, KBr) in their own atmosphere or in an atmosphere of inert gas (Ar, He). The differential transition cross-sections were calculated as a function of the vibrational and rotational quantum numbers, together with the full cross-sections of the transitions from the given quantum states. The effect of variations in the PES on these cross-sections was estimated, and it was shown that the full cross-section is less sensitive to these variations than the differential cross-section. The probability of a vibrational–rotational transition and the characteristic vibrational relaxation time were studied as a function of the initial vibrational energy of these diatomic molecules and of temperature. The limiting value of the total collision energy, for which the rotational relaxation of the diatomic molecule can be expressed in the rigid rotator approximation, was also calculated.

The classical trajectory method has been used in models of interatomic interactions in molecular systems[99,110-112].

Another series of papers[113-116] discusses the reactions

$$\begin{aligned} H + F_2 &\rightarrow HF + F \\ F + H_2 &\rightarrow HF + F \\ HF + H &\rightarrow HF + H \end{aligned}$$

and the corresponding reactions of the deuteriated analogues. The differential reaction cross-sections and the deactivation rate constants were calculated, the distribution of energy among the products was found, and the relative role of translational and rotational energy in the reactions was determined. In the deactivation of HF and DF the vibrational energy was found to be converted mainly into translational energy of the products, i.e. the relaxation occurs by the $V-T$ mechanism, but at higher levels of rotational energy the $V-R-T$ mechanism contributes increasingly to the deactivation.

The effect of the vibrational state of the molecule on the reactive scattering characteristics has been studied[117] for the reactions

$$\begin{aligned} O + N_2 &\rightarrow NO + N \\ O + H_2 &\rightarrow OH + H \\ N + O_2 &\rightarrow NO + O, \end{aligned}$$

and an analytical expression for the rate constant in terms of the initial vibrational energy and of the translational temperature of a diatomic molecule was obtained.

Numerical solutions of the classical equations of motion by the Monte Carlo method have been used[118-126] to calculate the rate constants and the angular and energy distributions of the products for various reactions in triatomic systems:

$$\begin{aligned} H_2 + H &\rightarrow H + H_2 \\ D_2 + F &\rightarrow DF + D \\ O + N_2^* &\rightarrow NO + N \text{ etc.} \end{aligned}$$

Isotope effects and the dependence of the kinetic parameters on the type of PES were also investigated.

The classical trajectory method can be applied to the analysis of reaction mechanisms as a function of the type of PES. From the solution of the dynamical problem the reaction mechanism corresponding to the given PES is determined. The inverse problem can also be solved: to construct a PES consistent with the experimentally established mechanism.

A series of papers[127-131] discusses the study of reaction mechanisms on the basis of dynamical calculations. A special study was made of the recombination reaction Br + Br + E (where E = He, Ar, Xe), assuming:

a) an energy transfer mechanism, i.e.

$$\mathrm{Br} + \mathrm{Br} \rightleftarrows \mathrm{Br}_2^*$$
$$\mathrm{Br}_2^* + \mathrm{E} \rightarrow \mathrm{Br}_2 + \mathrm{E},$$

or b) a radical–molecule complex mechanism, i.e.

$$\mathrm{Br} + 2\mathrm{E} \rightleftarrows \mathrm{BrE} + \mathrm{E}$$
$$\mathrm{BrE} + \mathrm{Br} \rightarrow \mathrm{Br}_2 + \mathrm{E}.$$

In a He atmosphere the first mechanism is predominant, and in an Ar or Xe atmosphere the opposite is true. By allowing for both these mechanisms the calculations can be satisfactorily reconciled with experimental data. Dynamical calculations have shown that when the reaction takes place by the energy transfer mechanism the pre-exponential factor of the rate constant is almost independent of temperature, whereas if the radical–molecule mechanism is predominant this factor decreases as the temperature increases.

An example of the determination of the PES parameters from experimental data is given in Ref.132. The parameters of the PES in the LEPS form for the reaction $O + H_2 \rightarrow OH + H$ were found by minimising the target function $\Phi = \ln(k_r/k_e)$, where k_r is the rate constant of the reaction, calculated by the classical trajectory method, and k_e is the experimental rate constant.

The PES have been constructed[133-135] for four classes of chemical reaction mechanisms of the exchange type $A + BC \rightarrow AB + C$. The influence of special features of the PES on the energy distribution of the reaction products and on the type of reactive scattering was clearly revealed.

We have discussed[37] a model of the decomposition of linear molecules of the N_2O type. The aim was to find the distribution function of the spontaneous decomposition time of the molecules and to investigate the distribution of energy among the reaction products. The distribution function was determined from the maximum spontaneous decomposition times, and it was found (by a numerical experiment) to have two maxima. The first maximum corresponds to the trajectories for elastic scattering, whereas the other trajectories describe the behaviour of the excited molecules. The distribution function of the maximum lifetimes $[f_m(\tau)]$ for these trajectories is satisfactorily described by a gamma-distribution. We found that $f_m(\tau)$ depends on the initial kinetic energy of the vibrational degrees of freedom and on the kinetic energy along the reaction coordinate. According to the assumed model, the initial kinetic energy of the vibrational degrees of freedom (including the reaction coordinate) is converted, on average, into internal energy of the N_2 molecule, whereas the rotational energy appears as kinetic energy of the relative (translational) motion of the products.

A detailed dynamical study of the following reactions has been reported[136,137]:

$$\mathrm{Br} + \mathrm{H}_2 \rightarrow \mathrm{HBr} + \mathrm{H}$$
$$\mathrm{H} + \mathrm{H}_2 \rightarrow \mathrm{H}_2 + \mathrm{H}.$$

The results were compared with those of the statistical theory for the same reactions. The reaction probability P_r was calculated by the classical trajectory method. The probability P_s of the system reaching the transition state was also calculated, and compared with the probability of the reaction obtained by the transition state method (P_{ts}). The transmission coefficient P_r/P_s and the distribution of active molecules in the region of the transition state were found to be strongly dependent on the structure of the PES, and in particular on the location of the barrier. The distribution function of the active molecules in the region of the transition state was determined. For an endothermic reaction with a relatively low barrier located in the valley of the products the probabilities were found to decrease in the sequence $P_{ts} > P_r \cong P_s$. For the reverse reaction ($H + HBr \rightarrow Br + H_2$), on the other hand, we have $P_{ts} \cong P_s < P_r$. For an endothermic reaction with a barrier in the valley of products the transmission coefficient is close to unity, but the distribution function of the active molecules for reactants in their equilibrium state differs from the equilibrium distribution. For exothermic reactions with a barrier in the valley of reactants, e.g.

$$\mathrm{H} + \mathrm{H}_2 \rightarrow \mathrm{H}_2 + \mathrm{H}$$
$$\mathrm{HBr} + \mathrm{H} \rightarrow \mathrm{H}_2 + \mathrm{Br},$$

the opposite situation exists: the transmission coefficient is smaller than unity, and an equilibrium distribution exists.

2. Dynamics of Unimolecular Reactions

Many recent publications describe studies of unimolecular reactions by numerical methods. A detailed formulation of the problems in the theory of unimolecular reactions which can be solved by the classical trajectory method has been given[138]. One of these problems is the calculation of the distribution function $f(\tau)$ in time (τ) of spontaneous decomposition of molecules. In the RRKM (Rice–Ramsperger–Kassel–Marcus) statistical theory[139] this function is assumed to be exponential for τ values greater than the average vibration period of the thermally activated molecule. To test the validity of this hypothesis and to calculate $f(\tau)$ for a specific molecule as a function of the type of activation and of the parameters of the potential is one of the fundamental problems in molecular dynamics, to which the classical trajectories method is applicable. This problem is very closely related to the validity of the model of weakly coupled harmonic oscillators and of the model of free redistribution of energy between normal vibrations.

The effect of the initial vibrations on the form of the function $f(\tau)$ as a function of the assumed model of the potential has been studied[140] in the case of the dissociation of a triatomic molecule. The calculation was carried out for two models of the potential: harmonic, and anharmonic. Two types of initial state were also considered: 1) a random initial distribution of total internal energy, and 2) the total internal energy is initially finite, and only the kinetic energy is randomly distributed. In the former case the function $f(\tau)$ is found to decrease exponentially with increase of τ for either type of potential, whereas in the latter case this function has a sharp maximum for a harmonic potential and a diffuse maximum for an anharmonic potential.

The influence of anharmonicity on the exchange of energy between modes in unimolecular reactions has been studied[141] in the triatomic CO_2 molecule. The bond energies in this molecule were fitted to a harmonic potential and to a Morse potential. The initial conditions were chosen to give the

molecule a zero total momentum. The interaction between the rotational and the vibrational motion was found to be greater in the case of an anharmonic potential.

The exchange of energy between the normal vibration modes of the triatomic molecules H_2O, O_3, and ClNO has also been studied[142] for different initial excitations of the vibrational and rotational degrees of freedom. According to these calculations there is no exchange of energy between modes when the excitation energy is of the order of one vibrational quantum. As the initial energy of the vibrations increases, the energy of each mode begins to vary, both the amplitude and the rate of this variation increasing with the initial vibration energy.

The spontaneous decomposition of X–C–C–X molecules (where X = H, Cl) has been studied[143–145]. The stretching vibration energy of the bonds for this type of molecule was approximated by a Morse potential, and the bending energy by a potential proportional to the square of the angular variable. The function $f(\tau)$ was calculated for different initial excitations of the molecule. For an equal-probability distribution of the energy over the initial states the distribution function is exponential, i.e. the decomposition is a random process. If only some of the bonds are affected by the initial excitation the function $f(\tau)$ is no longer monotonic, and one of the initially excited bonds is usually the first to break. If the molecule lives long enough, this type of excitation is converted into equal-probability excitation, and the decomposition of the molecule becomes random. From the position of the maximum of the $f(\tau)$ function the duration of the non-statistical behaviour of the system can be calculated. If the maximum occurs at a value of τ significantly shorter than the average lifetime of the molecules the non-statistical behaviour of the system occupies a time much shorter than the decomposition time.

Intramolecular energy redistribution processes have been studied, and the function $f(\tau)$ has been calculated, for the unimolecular decomposition reactions[146,147]

$$C_2H_6 \rightarrow CH_3 + CH_3$$
$$C_2H_6 \rightarrow C_2H_5 + H \ .$$

Calculations by the classical trajectory method and by the statistical theory give divergent results, suggesting that in these reactions the dynamic effects play a predominant role in intramolecular relaxation and unimolecular decomposition processes. Similar conclusions were reached from a study of the methyl isocyanide molecule[148–150].

The dynamical–statistical description has been used[71] to model the unimolecular decomposition of the CH_2FI molecule, which produces[151] strong branching in the fluorination of methyl iodide. The distribution function of the lifetime under chemical activation was obtained for the system: it was found to go through a maximum, and to be satisfactorily approximated by a gamma-distribution. Statistical processing of the experimental results yielded the coefficients of the gamma-distribution, and their dependence on the parameters of the potential. Varying the adjustable parameters of the potential, without affecting the fundamental characteristics of the unexcited molecule, was shown to affect the rate constant of the dissociation by C–I bond breaking. The values of these parameters corresponding to the maximum rate of dissociation were calculated.

The decomposition of the penta-atomic CHF_3 molecule by the biradical mechanism

$$CHF_3 \rightarrow CF_2 + HF$$

has also been modelled[38] for given initial conditions of the activation barrier. Decomposition by a biradical mechanism is typical of a large group of (unimolecular) reactions, and is also important in chain reactions[152]. Modelling a decomposition which yields polyatomic fragments is also of theoretical interest. The main feature of the model used[38] for this reaction is the presence of two negative eigenvalues in the parabolic approximation of the PES at the saddle point, so that the reaction coordinate becomes "two-dimensional". The dynamics of decomposition along a two-dimensional reaction coordinate were studied by numerical methods. Even with this more complex model it was confirmed that when the reaction has a sharply defined activation barrier the position of the activated complex is determined by the saddle point of the PES. Under these conditions the reaction coordinates correspond to eigenvectors of quadratic form which approximate the PES at the saddle point and have negative eigenvalues. The distribution in energy of the reaction products was studied: most of the energy evolved by the decomposition of CHF_3 was shown to be converted into vibrational excitation of the HF molecule. The CF_2 molecule remains practically unexcited.

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The practical realisation (by computer calculations) of the classical trajectory method has provided answers to a number of important problems in the dynamics of polyatomic systems whose solution could not previously be attempted.

Our analysis of recent publications has shown that the study of atom–molecule collisions and of intramolecular motions by the classical trajectory method is potentially applicable to a wide range of chemical reactions.

The number of publications dealing with calculations of classical trajectories is continually rising as a result of the more general availability of powerful computers, of improvements in modelling techniques, and of the easier access to detailed information on the elementary chemical act.

The large fund of data on different classes of reaction, with different potential energy surfaces, allows us to define some general relationships between the fundamental laws of the kinetic process and the characteristic features of the PES. This leads, in turn, to the development of improved models of the PES.

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