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Modern theories of chemical reactions in condensed phases

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ABSTRACT. The review is devoted to theoretical studies of the dynamics of chemical reactions in condensed phases. The fundamental differences in the description of the kinetics of gas-phase and liquid-phase reactions are demonstrated. The principal approaches, developed in the theory of liquid-phase reactions, are examined in detail: numerical modelling by Monte Carlo and molecular dynamics methods; numerical and analytical study of stochastic Langevin equations, the Fokker–Planck equation, and the kinetic Bohm–Gross equation. The possibilities and limitations of the modern theory are demonstrated in relation to examples of calculations of rate constants for specific isomerisation, substitution, addition, and electron transfer reactions.

The bibliography includes 114 references.

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The dynamics and kinetics of elementary chemical processes in condensed media constitute an important aspect of theoretical chemistry. It has developed vigorously during the last decade. The methodology for and calculations of potential energy surfaces and gas-phase reaction rate constants as well as dynamic calculations were developed in the previous decade on the basis of powerful computational techniques. Towards the end of the 1970's, the principal methodological aspects and problems of the gas-phase theory were exhausted and the interest of investigators shifted to the region of liquid-phase and solid-phase reactions.

This article deals with the present state of the problem. Without aiming at a complete survey of the literature, we concentrated attention on key factors in order to give the reader an idea, at an elementary level, about the advances in the theory and in its applications at the present time. Several reviews dealing with reactions in the condensed phase from current theoretical standpoints have been published.[1–7] Together with more specialised reviews, which will be quoted in the course of further exposition, they contain a complete bibliography.

Our exposition is restricted to reactions in non-ordered condensed media, primarily in molecular liquids, and only to those reactions whose dynamics can be adequately described within the framework of classical mechanics. Only processes occurring in the kinetic regime are described, i.e. diffusion kinetics are excluded. This in fact represents the situation, of fundamental importance for chemistry, where the medium influences directly the chemical step. New approaches and concepts, which are the subject of the present article, have been developed in this field.

I. Distinctive features of the dynamics of liquid-phase reactions

Under the influence of the medium, the rates of reactions can vary within a wide range. There exist fairly numerous chemical systems in which the interaction with the medium is weak. As a rule, these are reactions which occur in non-polar solvents under the usual conditions (room temperature, normal pressure). As a typical example, we shall quote data on the dimerisation of cyclopentadiene. Table 1 shows that different solvents hardly alter the Arrhenius parameters determined for the gas phase. There exist extensive experimental data also for other reactions. The established point of view is that, in the absence of polar effects, the liquid-phase reactions are usually faster by a factor of 2–5 compared with the gas phase and these slight differences between the rate constants are insufficient to detect reliably differences between the Arrhenius parameters in the gas phase and in solution and also when different non-polar solvents are compared.

One may quote an example of the opposite kind. For ionic reactions in polar solvents, i.e. for systems with a strong interaction, the rate constant is sometimes smaller by 10–20 orders of magnitude compared with the gas phase. There are well known S_N2 nucleophilic substitution reactions (Fig. 1) where the unusual gas-phase two-well PES profile is converted for an aqueous solution into a potential curve with a barrier (free energy profile),[10] which is familiar to chemists, while the activation energy increases from several units to 10–20 kilocalories per mole. However, the last example illustrates merely a change in the energetics of the elementary chemical process and at first sight does not require a revision of the principles governing its theoretical description. This aspect is not very interesting from the standpoint of the present review, whose subject is new approaches and concepts. S_N2 reactions will be examined below from new idealogical standpoints.

The transition state (TS) theory provides the standard method for the theoretical description of gas-phase reactions. The expression for the rate constant is

$$K = \kappa \frac{kTF^{\neq}}{hF^{(0)}} \exp(-\Delta U^{*}/kT), \qquad (I.1)$$

where k and h are the Boltzmann and Planck constants, T is the absolute temperature, $F^{\neq}$ and $F^{(0)}$ are the partition functions of the transition state and the reactants, and $\Delta U^{\neq}$ is the activation energy, usually identified with the height of the potential barrier on the PES.

Table 1. Experimental Arrhenius parameters and rate constants for the dimerisation of cyclopentadiene.

Medium	T, K	lg A (litre mol^{-1} s^{-1})	E_a, kcal mol^{-1}	lg$K$ (25 °C)
Gas phase	353—423	6.11	16.7	
	393—467	4.93	14.9	
	405—455	6.77	16.9	
Non-polar solvents				
C_6H_6	258—358	6.10	16.4	6.06
CCl_4	273—328	6.70	17.1	6.15
	273—295	5.90	16.2	6.00
paraffin	273—445	7.10	17.4	6.31
CS_2	273—308	6.20	16.9	7.80
	273—295	5.57	17.7	7.43
cyclopentadiene	271—308	5.80	16.2	7.90
	273—331	5.57	16.8	7.82

Note. The original literature on gas-phase reactions is quoted by Hynes[1] and the literature on liquid-phase reactions is quoted by Denisov.[9]

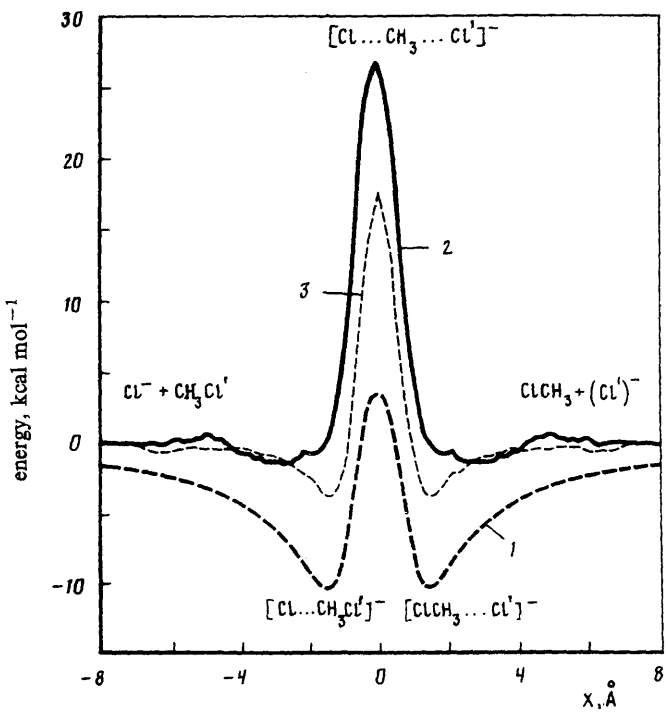


Figure 1. The calculated potential energy profile in the gas phase (curve *1*) and the free energy profile in water (curve *2*) and dimethylformamide (curve *3*) for an S_N2 reaction: $Cl^- + CH_3Cl'$.[10] The difference between the C—Cl and C—Cl′ distances is the reaction coordinate X.

The transmission factor $\varkappa$ cannot be calculated within the framework of the transition state theory and is usually assumed to be unity. The partition function is as a rule calculated in terms of the "harmonic oscillator—rigid rotator" approximation. It is useful to examine specially the isomerisation reactions (transition in a two-well system). Only the oscillator degrees of freedom change significantly in such reactions and, in terms of the classical approximation, the ratio of the partition functions is equal to the ratio of the products of the vibration frequencies ω at the minima for the reactants ($\omega_\nu^{\neq}$) and in the transition state (ω_ν^0) (ν = 0, 1, 2, ..., N):

$$K = \varkappa \frac{\Omega}{2\pi} \prod_{\nu=0}^{N} \frac{\omega_\nu^0}{|\omega_\nu^{\neq}|} \exp\left(-\Delta U^{\neq} / kT\right). \qquad (I.2)$$

The transition state frequencies include the purely imaginary frequency $\omega_0^{\neq} = i\Omega$. The modulus in the denominator of Eqn. (I.2) is necessary in order to eliminate the imaginary unity. A decomposition mode is known to correspond to the imaginary frequency, such modes being found by solving a standard vibrational problem in the vicinity of the saddle point on the PES.

For liquid-phase reactions with strong interaction, the harmonic approximation is inapplicable in principle.

We shall consider the S_N2 reaction already mentioned, for example:

$$\underset{\text{reactants}}{Cl^- + CH_3Cl} \rightarrow \underset{\text{TS}}{[Cl \cdots CH_3 \cdots Cl]^-} \rightarrow \underset{\text{products}}{ClCH_3 + Cl^-}. \qquad (I.3)$$

It is assumed that the reaction proceeds in the kinetic regime, i.e. the reactants in Eqn. (I.3) are in a solvent cage, their diffusion into the cage constituting a fast stage which does not affect the kinetics. Thus the reacting system is surrounded by a solvation shell consisting of a large number of molecules, the influence of which on the reaction has to be taken into account. The orientation motion of each solvent molecule is relatively free. It is found that the solvation shell has a multiplicity of configurations which correspond to different orientations of the solvent molecules. A minimum on the PES corresponds to each configuration; there is a set of minima with approximately equal energies separated by a low barrier (of the order of kT at room temperature). Rapid transitions occur between them and there are no grounds for differentiating any one of them as the "reactants minimum". Likewise in the region of the transition state there exists a set of first-order saddle points separated by higher-order saddle points whose relative height is of the order of kT and they must all be considered on an equal basis. This fundamentally anharmonic situation entails the breakdown of the usual ideas of the gas-phase theory, according to which its single minimum on the potential energy surface corresponds to the reactants and a single saddle point corresponds to the transition state.

Detailed study of each of the configuration minima of the solvation shell loses significance. The local frequencies corresponding to them have no direct bearing on the rate of the chemical reaction. An average description of the influence of the entire assembly of the configurations of the solvation shell on the reaction in the chemical subsystem (I.3) is necessary. This is formally achieved by a transition from the PES to the free energy surface (FES) with the corresponding modification of Eqn. (I.1):

$$K = \varkappa \frac{kT}{h} \exp(-\Delta G^{\neq}/kT), \qquad (I.4)$$

where $\Delta G^{\neq}$ is the height of the barrier on the FES. The use of Eqn. (I.4) presupposes the calculation of the anharmonic partition functions in Eqn. (I.1). The method for the theoretical description is then radically altered. For a gas-phase reaction, the central feature was the quantum-chemical calculation of the PES and the search for stationary points on the latter: the minima for the reactants and products as well as the saddle point corresponding to the transition state. This was sufficient to determine the activation energy as the height of the potential barrier and to establish the reaction mechanism. The dynamic calculations necessary for the evaluation of the pre-exponential factor reduced to the solution of the standard vibrational problem. After this, the dynamic calculation of the transmission factor, which is possible in principle, was assumed to be superfluous in the majority of applications. In order to find the activation energy and to establish the mechanism of reaction (I.3) in a polar medium, one has to construct the free energy profile. Thus the calculation of the anharmonic partition functions comes to the fore. As a rule this is a calculation by the Monte Carlo method.

The next stage is the calculation of the transmission factor $\varkappa$ by the method of molecular dynamics. One has to bear in mind that for a liquid-phase reaction the calculation of the transmission factor is more fundamental than for a gas-phase reaction. In the latter case, the decomposition mode, along which the reaction coordinate is directed at the saddle point on the PES, is chosen by the optimisation procedure as a result of the solution of the vibrational problem. On the other hand, the FES profile for a liquid-phase reaction is constructed as a rule along the reaction coordinate for the chemical subsystem found without taking into account the medium. When there is a strong interaction between the chemical subsystem and the medium, there are no grounds for the assumption that the coordinates of the medium (i.e. the orientation motions of the solvent molecules) do not contribute to the decompositon mode. Thus in the calculation of the FES profile the mode is not chosen by the optimum method. This constitutes an additional cause of the decrease in the transmission factor, which is characteristic only of a liquid-phase calculation.

II. Numerical modelling methods

The development of the computer technique, has made possible the direct modelling of systems comprising several hundreds of particles interacting in accordance with the laws of classical mechanics. The required values are calculated as averages over a large number of instantaneous configurations. Under certain conditions, such a model system describes successfully the properties of real microscopic objects. This is the essential feature of the method of molecular dynamics (MD).[11] The second approach in numerical modelling—the Monte Carlo (MC) method[11,12]—starts with the fundamental postulates of classical equilibrium statistical mechanics. It represents a procedure for calculating the average values $<A>$ of the observed quantity $A(\mathbf{r})$ for an equilibrium ensemble comprising n particles. Here $\mathbf{r}$ is the vector of the coordinates of the particles (r_1, r_2, r_3, ..., r_N). For example, in the case of a canonical ensemble, we have

$$<A> = \frac{\int A(\mathbf{r})\exp[-U(\mathbf{r})/kT]d\mathbf{r}}{\int \exp[-U(\mathbf{r})/kT]d\mathbf{r}}, \qquad \text{(II.1)}$$

where $U(\mathbf{r})$ is the potential function of the interaction.

A common feature of the method of molecular dynamics and the Monte Carto method is the absence of conceptual differences betweem them in the description of the interaction within the chemical subsystem, the interactions of the chemical subsystem with the molecules of the medium, and the interactions between the molecules of the medium themselves. The entire information about the system is included in the parameters of the classical particle interaction potentials and also in the masses of the particles in the method of molecular dynamics. By virtue of this factor, both methods are suitable, in principle, for the investigation of reactions occurring in any state of aggregation (gas, liquid, or solid) and for any densities and temperatures.

The test system is placed in a cell, which is frequently cubical or octahedral in shape. The system consists of molecules of the reactants and the solvent and their number ranges from several tens to several hundreds. Periodic boundary conditions are imposed on the cell, i.e. it is assumed that it is surrounded on all sides by exact copies. If in the course of modelling any one particle leaves the cell through one of its walls, then a similar particle from a neighbouring cell enters it through the opposite wall in the same direction (and with the same momentum in the method of molecular dynamics). This approach reduces to a minimum the edge effects and when the calculations are performed for a comparatively small number ($\sim 10^2$) particles, makes it possible to model successfully the properties of macroscopic systems containing $\sim 10^{23}$ particles.

The observed quantities are calculated as averages over a large number ($\sim 10^5 - 10^6$) of instantaneous configurations of this system. In the Monte Carlo method, the configuration is determined by the set of coordinates $\mathbf{r}$, while in the method of molecular dynamics it is determined by the set of coordinates $\mathbf{r}$ and the momenta $\mathbf{p}$ of the particles (the molecules of reactants and the medium) in the cell. Both methods were developed and have been widely used in relation to equilibrium chemical systems and have begun to be employed only recently in the study of the dynamics of chemical reactions. Studies on equilibrium chemical systems have shown that, despite the serious simplifications characteristic of the molecular dynamics and Monte Carlo methods (the ergodic hypothesis and the restrictions imposed on the number of particles in the cell and on the modelling time), both methods make it possible to calculate with satisfactory accuracy, using only the microscopic characteristics of the system (the interparticle interaction potentials and the masses of the particles), the equilibrium macroscopic characteristics of real chemical systems (heat capacity, density, equilibrium constants, etc.). Calculations by the Monte Carlo method are more economical as regards computer time than modelling of the same system by the method of molecular dynamics. On the other hand, the Monte Carlo method is applicable, because of its very nature, only to equilibrium systems. Therefore, in the study of the dynamics of chemical reactions in condensed phases the FES characteristics are calculated in the first stage by the Monte Carlo method and the rate constant is determined within the framework of the equilibrium transition state theory, while the transmission factor $\varkappa$ is calculated (but not always) in the second stage by the method of molecular dynamics. We shall consider both methods in greater detail, emphasising their applications to the dynamics of chemical reactions.

1. The Monte Carlo method

A random sequence of configurations of the system $\{\mathbf{r}_j\}$ is used in the Monte Carlo method.[11,12] Their energies obey the Boltzmann distribution $\exp[-U(\mathbf{r}_j)/kT]$ and Eqn. (II.1) is replaced by the average over the configurations realised:

$$<A> = \frac{1}{M}\sum_{j=1}^{M} A\{\mathbf{r}_j\}, \qquad \text{(II.2)}$$

where M is the number of configurations. The random sequence $\{\mathbf{r}_j\}$, sometimes called the trajectory of the Monte Carlo method, is generated with the aid of the Metropolis algorithm. The Metropolis algorithm and the details of the Monte Carlo method in relation to equilibrium chemical systems have been described in detail.[7,11,12] The texts of the Fortran and Basic programs, which employ the Monte Carlo method for equilibrium[13,14] and non-equilibrium[12] systems, have been published.[12–14] We shall consider below only the versions of the Monte Carlo method applicable to calculations for chemical reactions. The majority of the points on the Monte Carlo trajectory correspond to the configurations with energies close to the minimum value, precisely the configurations which make the main contribution to the partition functions used in the calculations of the equilibrium characteristics of the system. This approach is relatively ineffective in the calculation of the free energy of activation $\Delta G^{\neq}$.

We are interested in the free energy changes along the reaction coordinate x. In principle, they can be determined by averaging the probability of realising different values of x along the Monte Carlo trajectory. The distribution function $g(x)$, which yields the dependence of the free energy on x to within an additive constant C, is usually calculated:

$$G(x) = -kT\ln[g(x)] + C. \qquad \text{(II.3)}$$

The quantity $G(x)$ defined in this way is sometimes referred to as the average force potential. In order to achieve satisfactory statistics of the values in the vicinity of the transition state with a coordinate $x = x^{\neq}$ and a relative potential energy $\Delta U^{\neq}$, the Monte Carlo trajectory must pass fairly frequently through regions of the configuration space whose energies relative to the reactants minimum are close to $\Delta U^{\neq}$. The probability of the occurrence of such configurations for points on the Monte Carlo trajectory is proportional to $\exp(-\Delta U^{\neq}/kT)$ i.e. it is negligible when $\Delta U^{\neq} \gg kT$. In the usual version of the Monte Carlo method, it would therefore be either necessary to generate an extraordinarily long sequence of configurations or to be content with a very rough estimate of $G(x)$. There are two main ways of obviating this difficulty. The first is called the method of importance sampling[10,12] and the second is referred to as the statistical theory of perturbations.[10,13]

The method of importance sampling involves the imposition of an artificial external potential V, which "forces" the Monte Carlo trajectory to remain for most of the time in the region with the value of x in which we are interested. The potential V usually has a constant negative value within the range $(x - \Delta/2, x + \Delta/2)$ and is zero outside it. A sequence of configurations with a non-Boltzmann distributon of probabilities $\exp[-(U + V)/kT]$ is then generated and most of the points on the resulting Monte Carlo trajectory correspond to the range $(x - \Delta/2, x + \Delta/2)$. Within the range indicated, the relative probabilities of different values of V obey the Boltzmann distribution.

The imposition of the external potential V creates, as it were, a "window" which makes it possible to see the distribution of the probabilities of the values of x along the given section of the reaction coordinate. By carrying out a series of Monte Carlo calculations with window potentials V_j centred on different sections of the reaction coordinates which must partly overlap, we find for each window i its own distribution function $g_i'(x)$. The true distribution function $g(x)$ in the ith interval $(x - \Delta/2, x + \Delta/2)$ is related to distribution function in the corresponding window by the formula $g(x) = C_i g_i'(x)\exp(V_i/kT)$, where C_i is a normalised constant. The constants C_i are determined from the condition of the continuity of $g(x)$. By joining together the functions $g_i'(x)$ calculated for different intervals i, we obtain a single function $g(x)$ embracing the entire range of variation of x—from the reactants to the transition state.

An alternative to the importance sampling method is the statistical perturbation theory.[10,12,15] It is based on the formula:

$$G(H_0 + H_1) - G(H_0) = -kT\ln <\exp(-H_1/kT)>_0, \qquad \text{(II.4)}$$

where H_0 is the Hamiltonian of the initial system, H_1 is the perturbation, and the averaging $<\ldots>_0$ is carried out with respect to the distribution of the initial system. When applied to the Monte Carlo method, this means that trajectories corresponding to the Hamiltonian H_0 are generated. The expansion of the exponential function $\exp(-H_1/kT)$ in Taylor's series corresponds to the thermodynamic perturbation theory. In the calculation of the free energy profile, the configuration of the reactants minimum might be adopted as the initial system assuming that the non-equilibrium configurations along the reaction coordinate up to the transition state are perturbed systems. Eqn. (II.4) yields the exact computational algorithm, but, if the perturbation H_1 is large, the calculations converge slowly. The calculation is therefore carried out by scanning along x in several stages, so that in each step an acceptably small perturbation is achieved. The calculation requires careful optimisation of the length of the step and is refined in each step by the alternate replacement of the initial and final configurations.

The practical execution of the program for the evaluation of the free energy of activation in solution throughout the entire volume has been achieved for the simplest S_N2 substitution reaction [Eqn. (I.3)][16] and for the nucleophilic addition of OH^- to $H_2C{=}O$.[17] We shall consider the principle stages in the calculations and we shall discuss the results in relation to reaction (I.3).

1. The gas-phase reaction pathway corresponding to the potential energy minimum in the cross-section, i.e. the gas-phase reaction coordinate, was determined in the first stage with the aid of non-empirical quantum-chemical calculations. The parameters of the empirical analytical potential, describing the interaction in the chemical system along the reaction coordinate x, were selected.

2. Quantum-chemical calculations for the interaction of the reacting system with a single solvent molecule were carried out in the second stage for different values of x and the parameters of the solvent–reacting system interaction potentials were evaluated as functions of x. The potentials of the interaction between the solvent molecules had been calibrated previously.

3. The one-dimensional average force potential was calculated in the third stage by the importance sampling method and the activation energy $\Delta G^{\neq}$ was calculated with its aid.

Specific calculations have been carried out for two polar solvents—water and dimethylformamide (DMF).[16] The potential and free energy curves obtained are presented in Fig. 1. Evidently the section through the FES calculated for an aqueous medium has little in common with the gas-phase potential energy curve. On passing from the gas phase to the aqueous solution, the minima corresponding to the pre-reaction and post-reaction ion–dipole complexes vanish almost completely and the height of the activation barrier increases from 4 to 26 kcal mol^{-1}. For the reaction in DMF, the differences from the gas phase are not so large. The activation barrier increases to 18 kcal mol^{-1} and, in addition, in DMF there are distinct although not quite so deep as in the gas phase, minima for the ion–dipole complexes. The latter factor is important, since it requires a revision of the traditional ideas concerning the single-stage mechanism of the S_N2 reactions in solutions occurring without the formation of intermediates.

Similar results have been obtained[18,19] for the S_N2 reaction in a polar medium using semiempirical quantum-chemical approaches in the stage involving calculations for the interactions in the chemical subsystem and partly the interactions between the chemical subsystem and the solvent molecules in combination with the statistical perturbation theory in the stage involving the calculation of the free energy.

2. The method of molecular dynamics

Despite the apparently self-evident nature of the molecular dynamics method and the simplicity of the underlying idea, the theoretical aspects of its numerical application merit examination. It is known[20] that the differential equations of motion in the method of molecular dynamics with the intermolecular interaction potentials normally employed are locally unstable. This means that the solutions corresponding to similar initial conditions can differ very greatly. The numerical solution of the equations of motion inevitably introduces an error, which can be treated as a change in the initial conditions. It is therefore important to analyse the dependence of the results of the modelling on the characteristics of the system and on the selected algorithm for the solution of the dynamic equations. In estimating the errors of numerical methods, one usually compares the results of computer calculations carried out with the accuracy of the arithmetical operations and with twice such accuracy.

In the case of molecular dynamics, it is possible to estimate directly the accuracy of the method on the basis of the invariance of Newton's equations relative to changes in the sign of the time. The calculated trajectories for a specific time interval with subsequent inversion at the final point of the signs of the momenta of all the particles and the calculation of the trajectory of the reverse motion should lead to the initial point in the phase space. In reality, numerical calculation does not lead to the return to the exact starting point and the differences obtained between the initial and final points constitute an estimate of the accuracy of solving the equations of motion.

Systematic studies[20] on the forward and reverse trajectories for systems with a short-range interaction potential (Lennard-Jones) have led to a series of important conclusions concerning the errors in numerical modelling by the method of molecular dynamics. Analysis of the accumulated errors led to the conclusion that the results of the molecular dynamic experiment resemble in many respects the solutions of the stochastic Langevin equation, which will be examined in detail in the next Section. For short modelling times, the standard errors of the coordinates and momenta of the particles vary linearly with time, the duration of the linear interval depending on the algorithm for the solution of the differential equations, in particular on the degree of the equation fitted to the function to be integrated. With increase in the modelling time, the system becomes stochastic and the error of the calculation is found to depend solely on its physical characteristics and not on the numerical application of the method of molecular dynamics. The error is expressed in this case in terms of the entropy of the system by the Krylov–Kolmogorov procedure.[20]

The existence of errors in the method of molecular dynamics leads to a randomly migrating trajectory in a layer with a thickness ΔE resembling the trajectory of the Monte Carlo method. This means that the modelling in the method of molecular dynamics, formally carried out for a microcanonical ensemble taking into account the random scatter of the values of ΔE, possesses features of averaging with respect to a canonical ensemble. Thus the numerical application of the method of molecular dynamics introduces a series of fundamental factors which infringe the deterministic nature of the initial equations and which render the method of molecular dynamics similar to other approaches used in the modelling of multiparticle systems—the Monte Carlo method and stochastic equations. It is useful to bear these considerations in mind in comparing the results of various approaches to the description of the kinetics of chemical reactions in a condensed phase.

3. Calculation of the transmission factor by the reaction flux method

We shall consider how the complete dynamic theory, free from the limitations of the approximation of the transition state theory, is formulated within the framework of classical dynamics.[12,21] The idea of a "critical surface" in the configuration space, separating regions of the reactants and products, is introduced as a basis. The reaction coordinate x is normal to the surface. If this coordinate is known, then the equation of the surface in the vicinity of the transition state can be formulated as follows:

$$x = x^{\neq}. \tag{II.5}$$

The simplest and commonest is the selection of the top of the barrier on the FES profile as the coordinate $x^{\neq}$.

Another important factor is the introduction of the characteristic function

$$\eta[x(t)] = \begin{cases} 1 \text{ when } x(t) > x \\ 0 \text{ when } x(t) < x^{\neq} \end{cases} \tag{II.6}$$

i.e. η is a power function. It is a function of time and a functional of the classical trajectory $x(t)$. The starting point of the trajectory at $t = 0$ is selected on the critical surface. The distribution of the initial conditions is assumed to correspond to equilibrium. In particular, the initial rates $\dot{x}(t = 0)$ are taken from the equilibrium (Maxwell) distribution. In the course of dynamic evolution, the trajectory can intersect repeatedly the critical surface but ultimately, at $t \to \infty$, it always remains either in the reactants region or in the products region. In the former case

$$\eta[x(t)] = 1 \text{ when } t \to \infty, \tag{II.7}$$

while in the latter

$$\eta[x(t)] = 0 \text{ when } t \to \infty. \tag{II.8}$$

The conditions (II.7) and (II.8) can hold only in a multidimensional system (strictly speaking a macroscopic system), since otherwise even at $t\to\infty$ transitions from the reactants to the products region and conversely are inevitable on a two-well FES.

The classical rate constant is calculated from the equation

$$K = \lim_{t\to\infty}\left\langle \delta\left(x - x^{\neq}\right)\dot{x}(t=0)\,\eta\left[x(t) - x^{\neq}\right]\right\rangle. \qquad \text{(II.9)}$$

The angular brackets denote averaging with respect to the equilibrium distribution i.e. correspond to the equilibrium initial conditions on the critical surface. It can be shown that in the limit $t\to 0$ this average value reduces to the rate constant in terms of the approximation of the transition state theory:

$$K_{TS} = \lim_{t\to 0}\langle \delta(x^{\neq} = x)\,\dot{x}(t=0)\eta[x(t) - x^{\neq}]\rangle =$$

$$= \langle \delta(x = x^{\neq})\,\dot{x}(t=0)\eta\,\dot{x}(t=0)]\rangle .$$

We used the fact that $x(t) - x = t\dot{x}(t = 0)$ when $t\to 0$. Consequently the transmission factor $\varkappa$ is

$$\varkappa = \frac{\lim_{t\to\infty}\langle \delta(x = x^{\neq})\dot{x}(t=0)\eta[x(t) - x^{\neq}]\rangle}{\langle \delta(x - x^{\neq})\dot{x}(t=0)\eta[\dot{x}(t=0)]\rangle} . \qquad \text{(II.10)}$$

In fact, the calculation of the transmission coefficient reduces to studying an ensemble of the trajectories $x_i(t)$ with equilibrium initial conditions on the critical surface. In calculating the contributions of the trajectories to the transmission factor, one should take into account correctly their direction and the sign of the initial rate. Various recipes have been proposed for this purpose.[5,21–25] We shall consider one of them. For all the trajectories, the initial rate $\dot{x}(t = 0) = \dot{x}$ is positive. The trajectories extend both into the future ($t > 0$, $t\to\infty$) and into the past ($t < 0$, $t\to -\infty$). The evolution of each trajectory can be traced for a fairly long time (in practice for $\sim$3 ps). After this, a characteristic multiplier Q_i is attributed to each trajectory $x_i(t)$:

$$Q_i = 1, \text{ when } t>0 \;\; x_i > x^{\neq} \text{ at } t\to\infty ,$$

$$Q_i = -1, \text{ when } t<0 \;\; x_i > x^{\neq} \text{ at } t\to -\infty , \qquad \text{(II.11)}$$

$$Q_i = 0 \begin{cases} \text{when } t>0 \; x_i < x^{\neq} \text{ at } t\to\infty , \\ \text{when } t<0 \; x_i < x^{\neq} \text{ at } t\to -\infty . \end{cases}$$

The trajectories with $Q_i = 1$ are reaction trajectories, while those with $Q_i = 0$ are non-reaction trajectories. The trajectories with $Q_i = -1$ may be called anti-reaction trajectories since their contribution is subtracted from the total reaction flux. One can write for the transmission factor

$$\varkappa = \frac{\Sigma_i W_i \dot{x}_i Q_i}{\Sigma_i W_i \dot{x}_i} , \qquad \text{(II.12)}$$

where W_i is the Maxwellian weighting factor.

4. Examples of calculations by the method of molecular dynamics

The first reaction in a condensed phase for which it was possible to carry out direct calculations of the rate constant by the method of molecular dynamics was the *gauche–trans* isomerisation of n-butane in liquid CCl_4.[26] The molecular dynamics calculations were performed for a unit cell containing a n-butane molecule and 122 CCl_4 molecules. The modelling conditions corresponded to a temperature of $\sim$300 K. The interactions of the solvent molecules with one another and with the solute were described by the Lennard-Jones potentials. The CCl_4 molecules were assumed to be spherically symmetrical, while the n-butane molecule was assumed to consist of a chain of four Lennard-Jones spheres rotating about the central axis.

The calculations were performed for two models of the medium: a liquid solvent with moving CCl_4 molecules and a "frozen" vitreous solvent, in which the positions of the CCl_4 molecules were fixed in one of the equilibrium configurations obtained by the Monte Carlo method. The time variation of the rate of reaction $K(t)$ and the transmission factor $\varkappa = K(t)/K(0)$ were calculated by the reaction flux method using the formula (II.12).[21] Here $K(0)$ is calculated in the initial instant and, as shown above, agrees with the rate constant in the transition state theory.

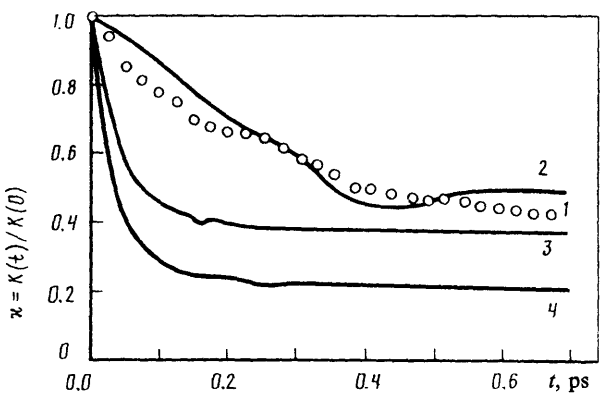


Figure 2. Time variation of the transmission factor $\varkappa = K(t)/K(0)$ calculated from Eqn. (II.12) by the method of molecular dynamics (curve *1*) and the method of stochastic dynamics (curves *2–4*) based on the kinetic Bohm–Gross equation (see text) for the isomerisation of n-butane in liquid CCl_4:[28] (*2*) $\nu = 0.2 \times 10^{13}$ s^{-1}; (*3*) $\nu = 4.0 \times 10^{13}$ s^{-1}; (*4*) $\nu = 10.0 \times 10^{13}$ s^{-1}.

The calculated relations are presented in Fig. 2. The points were obtained by numerical modelling and the continuous lines are a result of the solution of the stochastic equation (subsection II.5). The form of the curves obtained for the liquid and vitreous solvents is completely analogous. In both cases the $K(t)/K(0)$ curve reaches a plateau almost at the same time. The existence of the plateau makes it possible to consider the existence of a rate constant for the given reaction. The transmission factor in the region of the plateau for the liquid solvent ($\varkappa = 0.361$) does not differ greatly from the value $\varkappa = 0.276$ obtained for the vitreous solvent. This can be

partly explained by the fact that the mass of the solvent molecules is much greater than the mass of the n-butane units: $m_{CH_4}/m_{CCl_4} = 0.11$. The small molecules therefore move much more slowly than the methyl groups of n-butane.

One of the problems for the solution of which the application of the method of molecular dynamics is most fruitful is that of testing the applicability of the approximate models describing the influence the medium on the rate of reaction. Calculations for the chair–boat type of isomerisation of cyclohexane are instructive in this sense.

It was observed at the beginning of the 1980's[28,29] that the rate of isomerisation of cyclohexane increases with increase in pressure. The experimental pressure dependence of the free energy of activation, which determines the pressure dependence of the rates within the framework of the transition state theory, proved to be too weak to account for the observed relation. Calculation[30] by the method of molecular dynamics within the framework of the stochastic model (see the next Section) reproduced the observed effect.

The reason for the discrepancy between the predictions of the transition state theory and the stochastic calculation was elucidated by the Monte Carlo and molecular dynamic methods.[31] The modelling was carried out for the cyclohexane molecule in a cell containing 250 CS_2 molecules. An empirical intermolecular potential, which satisfactorily reproduced the geometry and conformational properties of the cyclohexane, was used. The solvent–solvent and solvent–cyclohexane intermolecular interactions were described by Lennard-Jones potentials. The energy of the system corresponded to a temperature of 300 K and the density (ρ = 1.0, 1.3, 1.4, and 1.5 g cm^{-3}) corresponded to the experimental pressure range. The calculations of the free energy of activation $\Delta G^{\neq}$ by the Monte Carlo method using window potentials showed that an increase in density from 1.0 to 1.5 g cm^{-3} does not alter $\Delta G^{\neq}$ to within the accuracy determined by the statistical scatter. A more detailed allowance for the influence of the medium at ρ = 1.5 g cm^{-3} yielded a positive contribution of solvation to the activation barrier, amounting to 0.08 $\pm$ 0.02 kcal mol^{-1}. This means that, according to the transition state theory, the rate of reaction should diminish only slightly with increase in pressure. The molecular dynamic calculation demonstrated that, on the contrary, the transmission factor $\varkappa$ increases from 0.34 to 0.47 with increase in density, which in fact produces an increase in the rate of reaction.

The establishment of the theory of gas-phase reactions, in particular the transition state theory, was in many respects based on theoretical and experimental studies of the substitution reaction:

$$A + BC \rightarrow AB + C, \qquad (II.13)$$

which is the simplest chemical reaction in which bonds are simultaneously ruptured and formed. Reactions (II.13) proved to be suitable for the elucidation of the mechanism of the elementary chemical step and the fundamental concepts of theoretical chemical kinetics were in fact first formulated in relation to these processes as an example. An enormous amount of experimental data, obtained in the gas and liquid phases, has accumulated for substitution reactions, indicating a wide variety of their mechanisms. These factors explain the interest in the study of reactions (II.13) by various theoretical methods, including the method of molecular dynamics.[32–34]

In the initial version,[32] the hypothetical reaction

$$X + X_2 \rightarrow X_2 + X \qquad (II.14)$$

was modelled in a cell containing 100 atoms of the medium [an inert gas (He, Ar, or Xe) with the density corresponding to the liquid state]. The interaction in the chemical subsystem X_3 was described by the London–Eyring–Polanyi–Sato (LEPS) potential, usually employed in theoretical studies on the gas-phase reactions involving triatomic sytems.

Three series of calculations were performed with the parameters of the LEPS potential corresponding to barrier heights of 20, 10, and 5 kcal mol^{-1} and frequencies of the decomposition mode at the top of the barrier of 419, 288, and 168 cm^{-1} respectively. The chemical subsystem–solvent and solvent–solvent interactions were described by the Lennard-Jones potentials. In calculations with high gas-phase activation barriers (20 and 10 kcal mol^{-1}), not one case of a repeated intersection of the critical surface by trajectories was observed. All the trajectories starting from the critical surface at velocities directed towards the reactants appeared at the reactants minimum, while all the trajectories with initial velocities directed towards the products appeared at the products minimum. This is a result of the weakness of the interaction of the X_3 system with a medium comprising a liquid inert gas. Only for a low barrier (5 kcal mol^{-1}) with a small curvature in the vicinity of the transition state did individual trajectories reintersect with the critical surface. In this case transmisison factors $\varkappa$ of 0.97, 0.91, and 0.91 were obtained respectively for the reactions in He, Ar, and Xe. Thus calculations by the method of molecular dynamics for reaction (II.14) in a system interacting weakly with the medium showed that, for sufficiently high barriers, the transition state theory constitutes a satisfactory approximation for the calculation of the rate constant. This estimate agrees with the conclusion known from the gas-phase theory.

In order to elucidate the limits of the applicability of the transition state theory, it is desirable to investigate chemical reactions by the method of molecular dynamics under the conditions of strong interaction with the medium. A good example is provided by the ionic version of the substitution reaction (II.14)–an S_N2 (I.3) reaction occurring in a polar medium.

The $Cl^- + CH_3Cl$ reaction in an environment comprising 64 H_2O molecules has been modelled[33,34] by the method of molecular dynamics. A potential of the LEPS type was adopted for the $Cl^- + CH_3Cl$ system. In the one-dimensional case, it reproduced the principal characteristics of the potential used in a study[16] of this reaction by the Monte Carlo method. The potential of the interaction of the solvent molecules with the chemical system depended on the charge distribution in the latter, which varied continuously along the reaction coordinate. The calculations yielded a transmission factor $\varkappa$ = 0.55.

The main qualitative result consisted in the description of the dynamic events occurring in the vicinity of the barrier. The outcome of the reaction is usually determined in the course of the first 0.02 ps after the start of the trajectory from the top of the potential barrier. This period is much shorter than the reorientation time of the solvent molecules. For a sufficiently high potential barrier, the reaction in the vicinity of the transition state is determined by the potential generated by the configuration of the solvent "frozen" in this state, which was the equilibrium configuration at an earlier stage but is a non-equilibrium configuration in relation to the transition state.

The presence or absence of ternary points on the trajectory depends on the configuration of the solvation shell in the initial instant. Having been selected at random this configuration makes an additional contribution to the potential barrier which is

asymmetric relative to the gas-phase top of the barrier. Whether the reaction occurs or not depends on the direction in which the given trajectories starts relative to this fluctuation barrier. The average picture corresponds to an effective decrease in the curvature of the potential barrier in the vicinity of the transition state, which reduces the transmission factor.

The situation described can be reproduced at the phenomenological level with the aid of the stochastic theory, which will be examined in detail in the succeeding Sections of the present review. Using the trajectories calculated by the method of molecular dynamics, the correlation function for a random external force acting on the variable reaction coordinate has been determined.[34] The principal dynamic characteristic of the corresponding generalised Langevin equation (GLE)—the friction kernel—is expressed directly in terms of this correlator.[33,34] The transmission factor, obtained as a result of the solution of the GLE by a standard approximate method (The Grote—Hynes method), agrees satisfactorily with the result of the direct dynamic calculation.

The dynamic study considered above constitutes undoubtedly an outstanding computational achievement. It demonstrates not only the possibilities of modern methods of the computer modelling of reactions but also their limitations. Thus the qualitative picture of the dynamics of the trajectories in the vicinity of the barrier, described in detail above, is incorrect or at least is only partly correct. The point is that in the method of molecular dynamics, which is applied using simplified potentials (atom—atom potentials) because of computational limitations, one cannot take into account the polarisation of the electrons of solvent molecules caused by the dynamic charge redistribution in the chemical subsystem in the course of evolution along the molecular dynamic trajectory. This, so called non-inertial polarisation, is almost instantaneously adjusted to the current charge distrubution, in contrast to the orientation polarisation associated with the motion of heavy molecular fragments, which, as shown above, remains frozen in the course of the reaction. Since the non-inertial polarisation is known to constitute not less than 40% of the total polarisation of the medium by the chemical subsystem, one may conclude that the inference concerning the "frozen" medium, which is undoubtedly valid within the framework of the given molecular dynamic study, cannot be extended to the real development of events in an S_N2 reaction.

In conclusion we may note that the problem of calculating the absolute rate constant for reaction (I.3) has not been fully exhausted. The point is that the calculation by the Monte Carlo method described above (subsection II.1) was carried out for a one-dimensional set of rigid configurations of the chemical subsystem located along the reaction coordinate. The corresponding free energy profile takes into account only the contribution of solvent molecules to the partition function. The contribution of the motions of the chemical subsystem to the pre-exponential factor has not so far been calculated. Thus the Arrhenius exponential function (the calculation of $\Delta G^{\neq}$ [16] yields the activation energy) and the transmission coefficient $\varkappa$ have been found,[33,34] but the contribution to the pre-exponential factor, calculated within the framework of the usual transition state theory, has not been determined. The difficulty is associated with the estimation of the corresponding partition functions for the chemical subsystem in solution. A well-founded solution of the problem requires an extremely complex calculation by the Monte Carlo method taking into account the configurations of the reactants with complete allowance for their interactions (and their internal structure) with solvent molecules on different bases.

5. Application of the method of molecular dynamics in the modelling of chemical kinetics by stochastic equations

The stochastic theory, which provides the most general and natural methods for the description of many-particle systems, is widely used in the study of the influence of the medium on chemical reactions. In the subsequent Sections of the present review, it is discussed in detail at a qualitative level. The direct numerical solution of stochastic equations constitutes a more complex problem, which can be solved by the method of molecular dynamics within a certain range of dynamic parameters. Calculations of the trajectories (the reaction flux method) have been used[35–39] to extract kinetic information from the Langevin equation (LE) and the generalised Langevin equation.

Here we shall describe in greater detail an alternative stochastic model based on the kinetic Bohm—Gross equation.[41] In this model, the phase point $(\mathbf{r}, \dot{\mathbf{r}})$ of a system comprising N particles evolves subject to the potential $U(\mathbf{r})$ in conformity with Newton's equations. At a random instant t', the velocity of the ith particle $\dot{r}_i$ changes abruptly to $\dot{r}'_i$. The evolution then continues until the time t'', when the velocity of the jth particle (this can be any particle including the ith particle) changes abruptly to $\dot{r}''$, and so on. The velocities $\dot{r}'$, $\dot{r}''$, ... are selected at random from the Maxwell distribution. The time intervals t' after which the velocities of the particles become stochastic are statistically independent and obey the Poisson distribution:

$$P_n(t) = \frac{(\nu t)^n}{n!} \exp(-\nu t),$$

where ν has the significance of the collision frequency. This algorithm is equivalent to the solution of the kinetic Bohm—Gross (BG) equation[36] for the distribution function $f(\mathbf{r}, \dot{\mathbf{r}}; t)$

$$\left[\frac{d}{dt} + \hat{L}\right] f(\mathbf{r}, \dot{\mathbf{r}}; t) = \hat{D}(\nu) f(\mathbf{r}, \dot{\mathbf{r}}; t), \qquad \text{(II.15)}$$

where $\hat{L}$ is the Liouville operator describing the evolution of the system in the absence of collisions and $\hat{D}(\nu)$ is an integral operator taking into account the influence of collisions. One may point to the relation between this approach and the stochastic theories discussed below. The Langevin equation can be reduced by a standard procedure to the Fokker—Planck equation.[42] On the other hand, the latter differs from Eqn. (II.15) only by its right-hand side: the corresponding collision operator describes the diffusion process subject to the external forces potential.

The solution of the Bohm—Gross equation (II.15) with the aid of the Laplace transformation makes it possible to write formal expressions for the correlaton functions in terms of which the rate of the chemical reaction is expressed.[40,43] Analytical studies on the expressions obtained have been carried out for two limiting cases corresponding to low and high collision frequencies ν. In the diffusional limit for high values of ν, Eqn. (II.15) reduces to the Smoluchowski equation with a coefficient of friction ν/m [the equivalent of the intense friction limit in the Langevin equation (see sub-section III.2).

Within the framework of this technique, the reaction flux method (see sub-section II.3) was first applied to the study of chemical reaction kinetics.[40] The simplest unimolecular reactions were considered—conformational isomerisation of alkanes in a non-polar solvent.[27,40] The interaction with the medium was described by a single parameter—the collision frequency ν. In specific calculations a value with the same order of magnitude as the average collision

frequency in the modelling of the solvent by the method of molecular dynamics using the hard sphere potential was adopted as ν. The dependence of the result of the calculations on ν when the latter was varied in the range $(2-300) \times 10^{12}$ s^{-1} has been studied in detail.[27,40]

Fig. 2 presents the time variations of the rate constant $K(t)$ for the *trans–gauche* isomerisation of n-butane obtained by the reaction flux method[21] within the framework of the Bohm–Gross model[27] and by the method of molecular dynamics.[26] The values of $K(t)/K(0)$, where $K(0)$ is the rate in the initial instant equal exactly to the rate constant in the transition state theory, were plotted along the ordinate axis. After the initial transition period, the duration of which depends on the parameter ν, the value of $K(t)$ reaches a plateau, as in the usual molecular dynamics calculation. The quantity $K(t)/K(0)$ in the region of the plateau represents the transmission factor $\varkappa$. With increase in the collision frequency ν, the system reaches the plateau sooner and there is a simultaneous decrease in the transmission factor $\varkappa$, in agreement with the result derived from the Kramers theory in the high friction limit (see subsection III.2).

Fig. 2 shows that the results of calculations by the methods of stochastic and molecular dynamics agree best for $\nu = 2 \times 10^{12}$ s^{-1}, which agrees in terms of order of magnitude with the collision frequency in liquid CCl_4 for which the molecular dynamics calculation was carried out. Using certain assumptions, it is possible to determine for specific systems the $\nu(p, T)$ relation (p is the pressure and T the temperature) and thus to determine the dependence of the rate of reaction on the thermodynamic parameters of the system. It has been found[14] that, in the isomerisation of n-butane under normal conditions (T = 300 K, p = 1 atm), the change in the activation barrier $\Delta E^{\neq}$ owing to collisions is very small, while the contribution of collisions to the change in the activation volume $\Delta V^{\neq}$ is approximately an order to magnitude higher than follows from the transition state theory. Several calculations have been devoted to the study of the influence of pressure on the isomerisation of cyclohexane.[27–30]

III. Stochastic dynamics

1. Simplest stochastic equations

In the dynamic theory, an enormous number of coordinates of the medium have to be studied. An effective way of obviating this difficulty is to eliminate most of them from the equation of motion, leaving only significant dynamic variables. Among "significant variables", one includes the internal coordinates of the chemical subsystem and in the first place the reaction coordinate. It is sometimes necessary to examine explicitly one or several coordinates of the medium. This happens in those cases where the reorganisation of the medium is an important or even fundamental condition for the chemical reaction, as happens, for example, in electron transfer processes. The examples presented below illustrate the choice of significant coordinates.

The coordinates which have not been taken into account explicitly (these usually include all the coordinates of the medium with a few possible exceptions) are referred to as the thermostat. The explicitly considered significant coordinates interact (exchange energy) with the thermostat, forming a thermodynamically open system. The dynamics of open systems is described by stochastic equations. The simplest of these, the Langevin equation, deals explicitly with a single dynamic variable:

$$m\frac{d^2x}{dt^2} + \gamma\frac{dx}{dt} = -\frac{dU(x)}{dx} + (\text{random force}). \qquad \text{(III.1)}$$

The first terms on the left-hand and right-hand sides of this equation represent the usual Newtonian contributions: the kinematic term proportional to the acceleration (m is the mass) and the regular force $-dU(x)/dx$. The frictional force added to the left-hand side is proportional to the velocity (γ is the coefficient of friction)†. It describes the dissipation of energy as a result of the interaction of the dynamic variable x with the thermostat. The random force describes the irregular effect of the thermostat on the variable x. In the modelling of a chemical reaction by Eqn. (III.1), the random force ensures the thermal activation of the substrate which is necessary to overcome the potential of the barrier. Its intensity is related to the coefficient of friction in such a way that the joint effect of the random and dissipative forces leads to the establishment of the Boltzmann equilibrium for the variable x during a time significantly exceeding its relaxation period.

For chemical applications, it is necessary to examine a more complex stochastic equation—the so called generalised Langevin equation:[44,45]

$$m\frac{d^2x}{dt^2} + \int_{-\infty}^{t} f(t-\tau)x(\tau)d\tau = -\frac{dU(x)}{dx} + (\text{random force}). \qquad \text{(III.2)}$$

It differs from the Langevin equation (III.1) by a more complex structure of the term describing the dissipative force. The corresponding integral expression depends in each instant t on the entire preceding evolution of the dynamic variable $x(t)$. The quantity $f(t-\tau)$ is called the relaxation kernel or the memory kernel. Dynamic systems with such properties are referred to as non-Markov systems in contrast to the Markov systems in which the frictional force is local in terms of time, i.e depend only on the current instant t. Eqn. (III.2) is obtained when the linear response theory is applied to continuous dynamic models of the medium.[46]

An alternative form of the formulation of the generalised Langevin equation, where the integral term contains the velocity $\dot{x}(t)$ and not the coordinate $x(t)$, is also commonly used:[44]

$$m\frac{d^2x}{dt^2} + \int_0^t \beta(t-\tau)\,\dot{x}(\tau)d\tau = \frac{d\,\bar{U}(x)}{dx} + \text{random force}. \qquad \text{(III.3)}$$

The quantity $\beta(t)$ is called the friction kernel. The different lower integration limit compared with Eqn. (III.2) is in most cases insignificant. To within this difference, Eqns. (III.2) and (III.3) are mathematically equivalent and the integral kernels $f(t-\tau)$ and $\beta(t-\tau)$ as well as the potentials $U(x)$ and $\bar{U}(x)$ are linked by the relations:[44]

$$f(t) = d\beta/dt;\ \bar{U}(x) = U(x) + \frac{\beta(0)x^2}{2}. \qquad \text{(III.4)}$$

The Langevin equation (III.1) can be obtained both from Eqn. (III.2), when the memory kernel is the derivative of the Dirac delta function:

$$f(t) = \gamma\delta'(t), \qquad \text{(III.5)}$$

† The quantity γ/m is sometimes referred to as the coefficient of friction.[42–45]

and from Eqn. (III.3) if

$$\beta(t) = \gamma\delta(t). \tag{III.6}$$

The intensity of the random force on the right-hand side of Eqn. (III.2) is linked to the kernel $f(t)$ by the relation called the fluctuation-dissipative theorem (FDT). We shall designate the random force by $F(t)$ and its autocorrelation function by $<F(t)F(0)>$ [the averaging is over instances of the random process $F(t)$]. The Fourier transform of the autocorrelation function is designated by

$$\left(F^2\right)_\omega = \int_{-\infty}^{+\infty} \langle F(t)F(0)\rangle \exp(i\omega t)\mathrm{d}t.$$

Then FDT assumes the form[45–47]

$$(F^2)_\omega = -\frac{2kT}{\omega}\,[\mathrm{Im}f(\omega)], \tag{III.7}$$

where $f(\omega)$ is the Fourier transform of the kernel $f(t)$:

$$f(\omega) = \int_{-\infty}^{+\infty} f(t)\exp(i\omega t)\mathrm{d}t. \tag{III.8}$$

It can be shown that the imaginary component of $f(\omega)$ is always negative.

In the case of Eqn. (III.3), the FDT is written in the following form:[44,45]

$$<F(t)F(0)> = kT\beta(t). \tag{III.9}$$

The two forms of the FDT, namely Eqns. (III.7) and (III.9), are equivalent, which can be readily established using Eqn. (III.4). The FDT ensures the establishment in the system of a Boltzmann equilibrium for times exceeding the relaxation period. The analogous relation for the Langevin equation (III.1) mentioned above is a special case of the FDT.

Henceforth we shall always assume that the random force $F(t)$ is Gaussian.[43–45] In this case, it is fully determined by its autocorrelation function. If the friction kernel has been specified, then the FDT fully determines the Gaussian random force. This factor permits the description of the dynamics of the medium by only one friction kernel in a phenomenological study of reactions in a condensed medium. The Langevin equation was first used for the description of Brownian motion of colloidal (i.e. macroscopic) particles. In applying it in the theory of elementary chemical processes, it is essential to remember that the coordinate x in Eqn. (III.1) characterises the changes in the chemical subsystem and is a microscopic variable. Therefore the interpretation of γ as a macroscopic coefficient of friction is illegitimate although it is frequently used. The quantity γ as well as the integral kernels $f(t)$ and $\beta(t)$ should be regarded as phenomenological characteristics of the interaction between the chemical subsystem and the medium. Their microscopic interpretation is discussed below.

2. Extraction of kinetic information from stochastic equations

If the potential (more precisely the free energy profile) is represented by a two-well curve, then such equations decribe the dynamics of the transition through the barrier and can model the chemical reaction (Fig. 3). The corresponding frequencies (the frequency at the top of the barrier $\omega^{\neq}$ is imaginary) are:

$$\omega_0^2 = \lambda_0/2m, \qquad (\omega^*)^2 = -\lambda^*/2m.$$

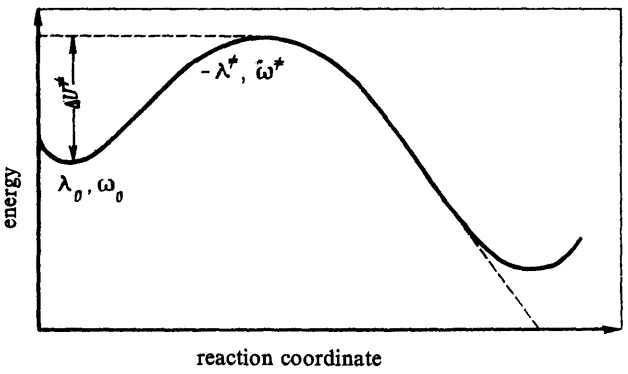


Figure 3. Potential curve (free energy profile) for a chemical reaction in a condensed medium; $\Delta U^{\neq}$ is the height of the barrier, λ_0 and $-\lambda^{\neq}$ are the force constants at the reactants minimum and at the top of the barrier ($\lambda_0 > 0$, $\lambda^{\neq} > 0$) and ω_0 and $\omega^{\neq}$ are the corresponding frequencies. In the Kramers theory, the presence of the second well is ignored (dashed straight line).

The rate constant in Eqn. (III.1) has been calculated by Kramers.[48] If the condition

$$\gamma/m\omega_0 >> 1, \tag{III.10}$$

has been fulfilled, then

$$K = \frac{\Omega}{2\pi}\sqrt{\lambda_0/\lambda^*}\exp(-\Delta U^*/kT),$$
$$\Omega = \sqrt{(\gamma/2m)^2 + (\omega^*)^2} - \gamma/2m. \tag{III.11}$$

When

$$\gamma/2m\omega^* >> 1 \tag{III.12}$$

the expression for the rate constant assumes a simpler form:

$$K = \frac{\omega_0\omega^* m}{2\pi\gamma}\exp\left(-\frac{\Delta U^*}{kT}\right). \tag{III.13}$$

This is the so called high friction limit in the Kramers theory, where the rate constant is inversely proportional to the coefficient of friction. If Eqn. (III.11) is extended to the region of low friction, formally ignoring the limitation (III.10), then the well known result

$$K = \frac{\omega_0}{2\pi}\exp(-\Delta U^{\neq}/kT) = K_{\mathrm{TS}}, \tag{III.14}$$

is obtained, which is equivalent to the application of the transition state theory without taking into account the influence of the medium.

The condition (III.10) defines the regions of intermediate and high friction. In the region of very low friction, where

$$\gamma/m\omega_0 << kT/\Delta U^*, \tag{III.15}$$

a different expression is valid for the rate constant. It differs from Eqn. (III.11) by the pre-exponential factor, which is directly proportional to the coefficient of friction. In this region the kinetics are limited by the thermal activation of the chemical system. The rate constant increases in proportion to the intensity of the random force ensuring activation, which is proportional to γ according to the FDT.

The overall dependence of the rate constant on γ, predicted by the Kramers theory, is presented in Fig. 4. Between its two-branches, corresponding to the increase and decrease in K, there is a transition region; in order to find the solutions in this region, use is made of numerical methods for the solution of the generalised Langevin equation.[3,5–39] The exact value of the constant K is always less than that calculated by Eqn. (III.14) obtained in the primitive transition state theory without taking into account the influence of the medium.

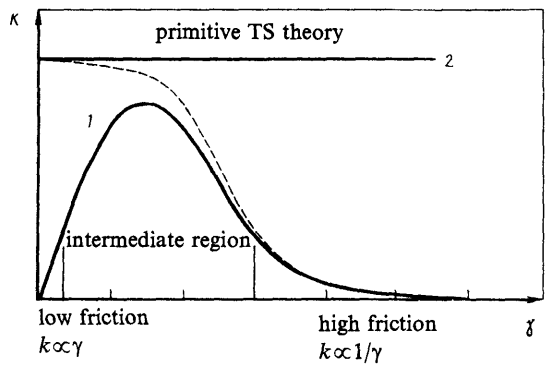


Figure 4. Dependence of the rate constant K on the coefficient of friction γ in the Kramers theory (curve *1*) and in the primitive transition state theory (curve *2*). The regions of high and low friction are described by simple formulae. Dashed curve—calculation by Eqn. (III.11). Upper horizontal line (primitive transition state theory)—calculation by Eqn. (III.14).

It is sometimes assumed that the quantity γ is proportional to the hydrostatic viscosity of the medium. The Kramers theory stimulated the experimental search for the relation between the reaction rates and the viscosity‡.[49,50] The decrease in K with increasing viscosity has been observed in a number of cases. On the other hand, the question of the existence of a kinetic regime for which the rate of reaction increases with increasing viscosity still remains open. The point is that the thermal activation of a fairly complex chemical subsystem can be achieved not only through the interaction with the medium but also as a result of energy exchange within the subsystem itself. This effect, which is not taken into account within the framework of the simple model (III.1), is independent of the viscosity and can render the Kramers model insignificant in the region of very low friction [Eqn. (III.15)].

‡ This concerns the effect of the viscosity on the kinetics of an elementary chemical process and not its trivial effect, which is always observed for diffusion-controlled reactions.

For the generalised Langevin equation (III.3), the rate constant for a system with a two-well potential was calculated by Grote and Hynes.[51] It has the form of Eqn. (III.11) with a modified expression for the decomposition frequency Ω. This quantity is determined as the single positive root of the characteristic equation

$$m\Omega^2 + \Omega\beta(\Omega) + \lambda^{\neq} = 0,$$

where

$$\beta(\omega) = \int_0^{\infty} \beta(t)\exp(-\omega t)dt$$

represents the Laplace transformation of the kernel $\beta(t)$.

The characteristic equation for the generalised Langevin equation (III.2) assumes the form:[2,9]

$$m\Omega^2 + f(i\Omega) + [\lambda^{\neq} - f(\omega = 0)] = 0, \qquad \text{(III.17)}$$

where $f(\Omega)$ is the Fourier transform of the kernel $f(t)$ defined in Eqn. (III.8). If Eqn. (III.4) holds, then Eqns. (III.16) and (III.17) yield the same decomposition frequency Ω and the same rate constant K. The Grote–Hynes equation for the rate constant is obtained on the same assumptions as those underlying the derivation of the Kramers formulae (III.11). For the reactions occurring in complex chemical subsystems, these postulates are found to be justified in many cases. Eqns. (III.11), (III.16), and (III.17) are widely used in modern literature and are known as the Kramers–Grote–Hynes (KGH) approximation.

An alternative formulation of the KGH theory, in which the characteristic equation (III.17) plays a key role, is also possible. It can be conveniently rewritten by introducing the notation $\omega = i\Omega$:

$$\begin{aligned} -m\omega^2 + f(\omega) + [\lambda^{\neq} - f(\omega = 0)] = 0, \\ -m\omega^2 + f(\omega) + [\lambda_0 - f(\omega = 0)] = 0. \end{aligned} \qquad \text{(III.18)}$$

The second equation analogous to the first, was formulated for the reactants minimum. We shall consider all the roots of these equations, designating them by $\Omega_{\nu}^{\neq}$ and $\Omega_{\nu}^{(0)}$ (ν = 0, 1, ..., N) respectively. For the first equation, the decomposition frequency is

$$\Omega_0^{\neq} = i\Omega; \quad \Omega > 0. \qquad \text{(III.19)}$$

All the remaining roots $\Omega_{\nu}^{\neq}$ and $\Omega_{\nu}^{(0)}$ are complex and have negative imaginary components. This fact implies that the characteristic equations (III.18) describe decaying oscillations, whose energy is dissipated. It follows from the property of causality of the core $f(t)$.[45,47] The rate constant can now be represented in the form[52]

$$K = \frac{\Omega}{2\pi}\left(\left|\prod_{\nu=0}^{N}\frac{\Omega_{\nu}^{0}}{\Omega_{\nu}^{\neq}}\right|\right)^{1/2}\exp\left(-\Delta U^{\neq}/kT\right). \qquad \text{(III.20)}$$

This formulation corresponds to the generalised transition state theory, because, as in the usual harmonic transition state theory [Eqn. (I.2)], it uses only the energies and characteristic frequencies at stationary points. It also has a deeper significance, based on the equivalence of the KGH and transition state theories, which is discussed in the next Section. Here one considers of course the transition state theory taking into account the influence of the medium, in contrast to the primitive version of this theory which completely ignores the medium [see Eqn. (III.14)].

3. Relation between the dynamic and stochastic descriptions. Generalised transition state theory as a multidimensional extrapolation of the KGH approximation

Hitherto, in speaking of dynamics, we had in mind the study of equations of motion, both classical Newtonian and stochastic Langevin equations. In this Section, the dynamic systems will be understood as conservative systems retaining the total energy and obeying the equations of classical mechanics. In contrast to them, stochastic systems, being open, dissipate energy, exchanging it with the thermostat.

Stochastic systems permit an abbreviated description of dynamic systems with a large number of degrees of freedom (ideally a macroscopically large number). They can be obtained rigorously from Newtonian equations formulated for the complete dynamic system, differentiating one or several "significant" variables for explicit examination, excluding all others in succession. The exclusion of "insignificant" variables represents a mathematical procedure, the application of which results in the subdivsion of the initial dynamic system into a subsystem having a small number of dynamic degrees of freedom and the thermostat interacting with it.[44,45,53] We shall consider the result of the application of this procedure to the model dynamic system "coordinate x + set of harmonic oscillators q_j with linear interaction in terms of q_j. The system Hamiltonian is

$$H = \frac{p_x^2}{2m} + U(x) + \sum_{j=1}^{N}\left\{\frac{p_j^2}{2\mu_j} + \frac{\mu_j}{2}\left[\omega_j q_j + \frac{C_j}{\mu_j \omega_j} x\right]^2\right\}, \quad \text{(III.21)}$$

where m is the mass of a "one-dimensional particle" x, $U(x)$ its potential, and p_x its momentum. The oscillator variables q_j are characterised by masses μ_j, frequencies ω_j, and momenta p_j ($j = 1, 2, ..., N$). The interaction of the dynamic variable x with the oscillator variables q_j has the form of the linear combination $x\sum_{j=1}^{N} C_j q_j$, where C_j are coupling constants. In essence one considers harmonic oscillators the equilibrium positions of which depend linearly on x.

The equation of motion for the variable x, obtained as a result of the exclusion of the oscillator variables,[54] reduces to the generalised Langevin equation (III.3) with the friction kernel.

$$\beta(t) = \sum_{j=1}^{N} \frac{C_j^2}{\mu_j \omega_j^2} \cos(\omega_j t). \quad \text{(III.22)}$$

The random force is determined by the initial conditions for oscillator variables and satisfies the FDT.

For a continuous medium, $N \to \infty$ and the set of oscillators is characterised by a spectral density defined as follows:[55]

$$J(\omega) = \frac{\pi}{2}\sum_{j=1}^{N} \frac{C_j^2}{\mu_j \omega_j} \delta(\omega - \omega_j), \quad \text{(III.23)}$$

$$\beta(t) = \frac{2}{\pi}\int_{-\infty}^{+\infty} \frac{J(\omega)}{\omega} \cos(\omega t) d\omega. \quad \text{(III.24)}$$

Eqns. (III.23) and (III.24) specify the mutually single-valued correspondence between the phenomenological generalised Langevin equation, specified by the friction core $\beta(t)$, and the dynamic system described by Eqns. (III.21) and (III.23). This correspondence permits a deeper understanding of the significance of the KGH approximation. If $U(x)$ is a one-dimensional two-well potential, then the Hamiltonian (III.21) describes transitions in a model two-well system. By applying to it the canonical transition state theory, it is possible to calculate the rate constant defined by Eqns. (I.2). Here one observes that, if the friction core satisfies Eqns. (III.22) and (III.24), the result agrees with the rate constant based on the KGH theory. Thus the following general assertion is valid:[56–59] the KGH approximation for the generalised Langevin equation (III.3) is equivalent to taking into account the medium within the framework of the dynamic model (III.21) to which the canonical transition state theory has been applied.

However, as mentioned in Section I, the medium is in principle anharmonic. The application of the oscillator model therefore requires explanation. We shall consider a completely different method for the microscopic modelling of the generalised Langevin equation (III.3) on the basis of a dynamic system of equations. For a real medium, having a PES with a complex anharmonic structure with a multiplicity of shallow (with a depth of $\sim kT$) minima, it is possible to construct a smooth free energy profile along a "significant" variable, which we designate by x. It corresponds to the two-well curve of stochastic models. Then, on the basis of the complete system of dynamic equations, it is possible to calculate the friction kernel for the generalised Langevin equation, which is achieved by statistical mechanical methods within the framework of the linear response theory.

The molecular-dynamic calculation permits the study of the fluctuating force $F(t)$ acting on the variable x and, in particular, permits the calculation of the autocorrelation function $\langle F(t)F(0)\rangle$. Then, having identified $F(t)$ with the random force included in the generalised Langevin equation, and applying the FDT [Eqn. (III.9)], we obtain the friction kernel $\beta(t)$ for the generalised Langevin equation (II.9).[33,34,60] Thus, when the methods of molecular dynamics and the FDT are used jointly, the generalised Langevin equation can be fully reproduced for a specific dynamic model reaction in the given medium. Having compared the Hamiltonian (III.21) with the generalised Langevin equation obtained, one can now show that the oscillator variables included in it have no direct microscopic interpretation. They arise on transition, within the framework of the linear response theory, from the strongly anharmonic microscopic PES to the smooth FES, because the dissipative force in the generalised Langevin equation is linear in x. This is only one of the indirect methods for describing the influence of the medium on the variable x. It is not essential to resort to it, because all the results are obtained by studying the phenomenological generalised Langevin equation without employing a particular interpretation.

We obtained two important corollaries from the above discussion. Firstly a practical recipe has been formulated for the microscopic evaluation of the friction kernel. Secondly, the assertion that the KGH approximation is a version of the transition state theory with allowance for the medium has acquired a profound significance. We demonstrated that the KGH method permits the extrapolation of the harmonic version (I.2) of the transition state theory to the description of fundamentally anharmonic models within the framework of the linear response theory.

In chemical applications, one cannot restrict the treatment to one-dimensional stochastic equations (III.1)–(III.3). It is frequently necessary to examine explicitly several "significant" variables, whose dynamics are described by a system of stochastic equations. An equivalent of the Kramers theory for a system of Markov–Langevin

equations of type (III.1) as well for a system of non-Markov equations of type (III.3) is known.[63–66] An alternative solution of the problem[52] is provided by employing the generalised transition state theory in the form defined by Eqn. (III.20). This universal expression for the rate constant is independent of the dimensions of the system. It can be obtained by applying the canonical transition state theory to the oscillator Hamiltonian of type (III.21) containing any number of oscillator variables $x_1, x_2, \ldots$ At the phenomenological level, these variables evolve on a multidimensional two-level FES $U(x_1, x_2, \ldots)$ in conformity with the specified system of generalised Langevin equations.

In order to apply the generalised transition state theory, it is necessary to find initially the reactants minimum and the saddle point on the FES. The difference between their energies yields the activation energy $\Delta U^{\neq}$ in Eqn. (III.20). The force constants matrices are then calculated at both points. The linearisation of the system of generalised Langevin equations in the vicinity of the stationary points makes it possible to obtain two systems of linear integrodifferential equations, whose coefficients are the matrices of masses, friction kernel (they are assumed to be known), and the calculated force constants. Two characteristic equations are derived from these quantities by a standard method. They are analogous to Eqn. (III.18), whose roots are the characteristic frequencies for the reactants and the transition state. The roots are complex and have the same properties as the roots in the one-dimensional case. The pre-exponential factor in Eqn. (III.20) is derived from the frequencies obtained. This method makes it possible to obtain the rate constant in terms of an approximation analogous to the one-dimensional KGH approximation for systems of any complexity.

An alternative method of calculating the rate constant in a multidimensional stochastic system is also known.[63–66] It reduces the calculation to the one-dimensional expression (III.11), the ratio of the two force constants is replaced by the ratio of the corresponding determinants, and the decomposition frequency Ω is calculated from the multidimensional characteristic equation. The result is equivalent to the calculation by Eqn. (III.20).

IV. Examples of the application of stochastic models

1. Charge transfer reactions. Formulation of the continuous model of the medium in relation to outer-sphere electron transfer

The electron transfer between the donor D and the acceptor A in a polar solvent

$$D^- + A \rightarrow D + A^- \qquad \text{(IV.1)}$$

is the simplest chemical process in which the specific features of the influence of the medium are fully manifested. The kinetics of a multiplicity of reactions (IV.1), in which D and A are transition metal complexes, organic substrates, and fragments of biomolecules, have now been investigated. The term "outer-sphere electron transfer" presupposes that the internal coordinates of the chemical subsystem do not change in the rate-limiting stage of the reaction. Changes occur in the configuration of the solvation shell surrounding the reaction complex. The solvation shell is adjusted to the charge distribution in the chemical subsystem, which changes significantly during the reaction. The rearrangement of the solvation shell for a fixed geometry of the chemical subsystem occurs mainly as a result of the orientation motions of the solvent molecules. The study of reaction (IV.1) makes it possible to investigate in relation to a specific example and in a pure form the dynamic behaviour of the coordinates of the medium in the chemical process.

We shall designate the coordinates of the solvent by Q_v. It is necessary to examine the dependence of the free energy $G(Q_v)$ on these coordinates. In the continuous model of the medium, one introduces as Q_v not the elementary orientation motions of individual solvent molecules but collective modes describing concerted combinations of a large number of elementary displacements. This approach permits, in principle, the differentiation of one or several collective coordinates significant for the description of the reaction and the restriction of the treatment to their explicit study.

In a purely electrostatic interaction of the medium with a donor–acceptor pair, the inertial polarisation $P(r)$, i.e. the part of the total polarisation of the medium from which the polarisation due to electrons has been excluded, may be conveniently adopted as the variable.[67,68] The inertial polarisation varies from point to point in the three-dimensional space. Its values at each point are independent variables. Such quantities are referred to as field variables. A field variable actually represents a three-dimensional continuum of variables of the usual type. For a given charge distribution $\rho_a(r)$ in the pair $[D + A]^-$, one may consider the dependence of the FES on the variable $P(r)$ modelling the collective motions of the solvent molecules. This dependence is quadratic: the FES represents a paraboloid, with an infinite number of dimensions, in the polarisation space. Its minimum corresponds to the polarisation $P^{(a)}(r)$ adjusted by an equilibrium procedure to the charge ρ_a. For a different charge distribution $\rho_b(r)$, the minimum in the FES paraboloid shifts to another point in the polarisation space $P^{(b)}(r)$. If, during the reaction, the charge distribution in the substrate changes from ρ_a to ρ_b, then the FES has the form of two intersecting paraboloids. It describes the reorganisation of the polar solvent taking into account only electrostatic forces and has an activation barrier whose height is

$$\Delta U^{\neq} = (E_r + Q)^2/4E_r. \qquad \text{(IV.2)}$$

This is the familiar Marcus formula,[67,68] where Q is the difference between the free energies of the products and the reactants (it is assumed that $Q < 0$ for exothermic reactions) and E_r is the so called solvent reorganisation energy (an important parameter characterising the change in the FES on passing from the ρ_a to the ρ_b charge distribution). It is assumed that $|Q| \leqslant E_r$.

The interaction between the donor and the acceptor is introduced into the theory within the framework of the two-level model. A matrix Hamiltonian of the following type is considered:

$$H = \begin{pmatrix} H_{aa} & H_{ab} \\ H_{ba} & H_{bb} \end{pmatrix}. \qquad \text{(IV.3)}$$

The diagonal matrix elements depend parametrically on the polarisation $P(r)$:

$$H_{aa} = \alpha_a - \frac{1}{2} f_0 \int [P_a^2 - (P - P_a)^2] \mathrm{d}^3 r,$$
$$H_{bb} = \alpha_b - \frac{1}{2} f_0 \int \left[P_b^2 - (P - P_b)^2\right] \mathrm{d}^3 r. \qquad \text{(IV.4)}$$

The electronic matrix elements α_a and α_b characterise the intrinsic energy of the chemical subsystem in the states "a" and "b" without taking into account the interaction with the inertial polarisation. The effects of the polarisation of the electrons of the medium (non-inertial) are assumed to be implicitly included in α_a and α_b. The non-diagonal matrix element is a parameter of the electronic interaction:

$$H_{ab} = H_{ba} = \beta. \tag{IV.5}$$

The coefficient $1/f_0$ is called the Pekar multiplier:[69]

$$\frac{1}{f_0} = \frac{1}{4\pi}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right), \tag{IV.6}$$

where ε_0 and ε_∞ are the static and optical dielectric constants. The quantity f_0 is the coefficient of the linear response for the inertial polarisation (response)—induction field (external force) pair:

$$f_0 P(r) = D(r). \tag{IV.7}$$

In particular, one may consider the equilibrium induction fields D_a and D_b related to the charges ρ_a and ρ_b by the Poisson equation.

We shall consider the adiabatic theory in greater detail. The lowest eigenvalue of the matrix H plays the role of the FES in it:

$$U[P] = -\sqrt{\alpha^2/4 + \beta^2} + \alpha/2 + H_{aa}. \tag{IV.8}$$

Here $\alpha = H_{bb} - H_{aa} = Q + E_r - X$, where

$$Q = \alpha_b - \alpha_a - \frac{1}{2}f_0\int(P_b^2 - P_a^2)\mathrm{d}^3r, \qquad E_r = \frac{1}{2f_0}\int(D_b - D_a)^2\mathrm{d}^3r,$$
$$X = X[P] = \int(P - P_a)(D_b - D_a)\mathrm{d}^3r. \tag{IV.9}$$

The free energy of the reaction Q and the reorganisation energy E_r were discussed above. The quantity X is a variable of the usual type (a non-field variable), which is a functional of the field variable $P(r)$.

The quantity $U[P]$ is called the free energy functional. It depends on $P(r)$ solely via the usual variable X, which makes it possible to obtain a closed dynamic equation for this variable.

The dynamic properties of the continuous model are specified phenomenologically through the complex dielectric constant $\varepsilon(\omega)$.[70,71] This function of the frequency ω is determined experimentally from the relation between the variable periodic electric field $E(\omega)$ and the induction $D(\omega)$. The form of $\varepsilon(\omega)$ usually employed in practice is the Debye approximation:

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\tau_D\omega}, \tag{IV.10}$$

where the parameter τ_D (the Debye time) characterises the time scale of the relaxation processes determined by the polarisation of the medium. The renormalised quantity

$$\tau_L = \tau_D(\varepsilon_\infty/\varepsilon_0), \tag{IV.11}$$

called the longitudinal relaxation time, is frequently employed subsequently.

The dynamic theory starts with the equation of motion for polarisation. In the absence of external charges, it assumes the following form for the Debye model:[71]

$$(\tau_L f_0 \frac{\mathrm{d}}{\mathrm{d}t})P = -f_0 P + \text{random force}, \tag{IV.12}$$

where $f_0 P$ is a regular force generated by the change in the intrinsic energy of the polarisation field. In the presence of external charges, the regular force is modified. It can be found[46] as the variational derivative of the functional $U[P]$ [Eqn. (IV.8)]. The following equation is obtained as a result:[72]

$$\tau_L f_0 \frac{\mathrm{d}}{\mathrm{d}t}(P - P_a) = -f_0(P - P_a) + G(X)(D_b - D_a) + \text{random force}, \tag{IV.13}$$

where

$$G(x) = \frac{1}{2}[1 - \alpha/\sqrt{\alpha^2/4 + \beta^2}\,].$$

We have to determine the reaction rate constant from Eqn. (IV.13).

2. Kinetics of the outer-sphere electron transfer within the framework of the stochastic continuous model

The principal concepts of the continuous model of a polar solvent in relation to the simplest charge transfer reaction—the outer-sphere electron transfer—were introduced in the previous subsection. This is an essential preparatory stage before proceeding to the kinetic problems proper. For a number of reasons, the theory of such processes has nowadays advanced further than others and is essentially complete. It is useful to trace, in relation to this example, the logical structure of the complete dynamic theory of an elementary chemical process in a condensed phase.

A simplifying factor, characteristic of the two-level model described by Eqns. (IV.8) and (IV.9), is the dependence, mentioned above, of the free energy functional $U[P]$ on the field variable P through the coordinate X of the usual type. By virtue of this, the stochastic equation (IV.13) for the field variable P reduces to the incomparably simpler equation of X:[72,73]

$$\tau_L f_0 \frac{\mathrm{d}}{\mathrm{d}t} X = -X + 2E_r G(X) + \text{random force}. \tag{IV.14}$$

In this equation it is easy to recognise the generalised Langevin equation (III.1), from which the kinematic term, containing the acceleration (mass equal to zero), has been omitted. The first two terms on the right-hand side of the equation are functions of X representing the regular force. The corresponding one-dimensional potential $U(x)$ is represented by a two-well curve over a wide range of parameters§. The positions of the reactants minima and of the top of the barrier as well as the force constants are calculated for this potential. After this, it is possible to apply immediately the Kramers formula (III.11). Furthermore, since the inequality (III.12) is valid for $m = 0$, it is sufficient to use the high friction approximation (III.13). In this case the rate constant is given by:[46,72,73]

$$K = \frac{1}{2\pi\tau_L}\left(\frac{E_r}{2|\beta|}\right)^{1/2}\left(1 - \frac{Q^2}{E_r^2}\right)^{3/4}\exp(-\Delta U^*/kT), \tag{IV.15}$$
$$(E_r >> |\beta| >> kT;\ |Q| \leqslant E_r).$$

§ More precisely, the condition $2|\beta|/E_r < 1$ should hold. If it is infringed, the two-well potential becomes a one-well potential.

The activation energy $\Delta U^{\neq}$ is given by Eqn. (IV.2) in the zeroth approximation; it can be refined by subtracting $|\beta|$ from it. An important feature of Eqn. (IV.15) is the presence in the pre-exponential factor of a dynamic characteristic of the medium—the relaxation time τ_L.

Hitherto we have considered the adiabatic theory. It is valid subject to the condition

$$2|\beta|/kT \gg 1. \qquad \text{(IV.16)}$$

The numerator contains the minimal energy splitting of the two electronic terms of the two-level model described by Eqns. (IV.3)–(IV.5). The condition (IV.16) means that thermal fluctuations (i.e. the random force in the stochastic model are incapable of populating effectively the electronically excited state. If the condition (IV.16) has broken down, it is necessary to solve the electronic-non-adiabatic problem, which involves the consideration of a coupled system of two stochastic equations.[74] The dynamics of the outer-sphere electron transfer was first considered by Levich and Dogonadze[4,68,75] precisely within the framework of the non-adiabatic approach. Their calculations were based on perturbation theory. Current studies[74,76,77] were able to overcome this serious limitation. [It is noteworthy that the collective variable X, defined by Eqn. (IV.9), first appeared as a significant element of the dynamic theory in Zusman's study[74] within the framework of the non-adiabatic approach.] The expression recommended on the basis of the modern non-adiabatic theory for the rate constant has the Arrhenius form with an activation energy described by Eqn. (IV.2). The pre-exponential factor is usually formulated thus:

$$A = \frac{\beta^2}{\hbar}\sqrt{\frac{\pi}{E_r kT}}\,\frac{1}{1+\beta^2\tau_L B}. \qquad \text{(IV.17)}$$

The quantity B differs somewhat in the studies of different workers.[74,76–81] We shall quote the simplest (albeit not the best founded) version of the definition of B:[79]

$$B = 4\pi/\hbar E_r. \qquad \text{(IV.18)}$$

If the electronic matrix element β is sufficiently small in absolute magnitude, then the well known result based on perturbation theory in the classical limit is obtained from Eqn. (IV.17).[4,75] However, one can show directly that in the opposite limiting case where $\beta^2\tau_L B \gg 1$, Eqn. (IV.17) does not reduce to the correct Eqn. (IV.15) of the adiabatic theory. The approximate non-adiabatic theory, underlying Eqn. (IV.17), describes only cases of weak and intermediate linkages between the diabatic terms H_{aa} and H_{bb} in the two-level mode (IV.3). Thus Eqns. (IV.15) and (IV.17) supplement one another.

In conformity with the criterion (IV.16), the question of the mechanism, adiabatic or non-adiabatic, involved in electron transfer reduces to the estimation of the matrix element β. On the basis of the results of published calculations and their discussion,[82–83] one may conclude that the adiabatic condition in intermolecular electron transfer holds in many cases, while in intramolecular transfer it holds in all cases. In the study of more complex charge-transfer reactions, where internal motions of the chemical subsystem play a significant role (see subsection IV.3), the application of the adiabatic theory is natural and promising.

The scheme described for the outer-sphere electron transfer involves simplifications which are undesirable in the solution of specific problems. The most serious of them is the homogeneous medium approximation, on which the electrostatic formulae of subsection (IV.1) are based. A more realistic approximation is called the Born–Kirkwood–Onsager (BKO) model, it involves the cutting out of a cavity in the continuous medium in which the chemical subsystem is placed. The dielectric constants within and outside the cavity are different. In the dynamic theory, the complex dielectric constant has two values:

$$\varepsilon = \begin{cases} 1 \text{ (within the cavity)}, \\ \varepsilon(\omega) \text{ (outside the caivity)}. \end{cases} \qquad \text{(IV.19)}$$

In the static theory $\varepsilon(\omega)$ outside the cavity is replaced by the static constant ε_0.

The introduction of an inhomogeneity in the form of a cavity complicates the theory, but its structure remains the same as before.[84] The inhomogeneity leads to the renormalisation of the parameters: the expressions for the energy effect Q, the reorganisation energy E_r, and the principal dynamic variable X in Eqn. (IV.9) are altered. In particular, the reorganisation energy is[4,67,85]

$$E_r = \frac{1}{2f_0}\int_{V_e}(\nabla\varphi_b - \nabla\varphi_a)^2 d^3r, \qquad \text{(IV.20)}$$

where V_e is the volume outside the cavity and $\varphi_a(r)$ and $\varphi_b(r)$ are the vacuum potentials ($\varepsilon = 1$) generated by the diabatic charge distributions $\rho_a(r)$ and $\rho_b(r)$ and calculated from the Poisson equation. The general expressions (IV.15) and (IV.17) for the rate constant remain in force.

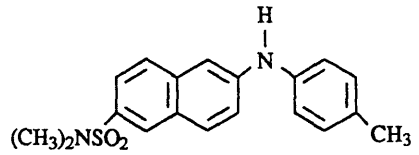
On going outside the framework of the Debye model of the solvent described by Eqn. (IV.10), a dynamic equation is arrived at in the adiabatic approximation,[46] which differs from Eqn. (IV.13) by its left-hand side: instead of the derivatives dP/dt, a linear integral operator acting on the polarisation variable P appears. This dynamic equation is the generalised Langevin equation (IV.2). A similar rate constant, defined by Eqn. (IV.15), can be calculated in terms of the KGH theory [Eqns. (III.11), (III.17), and (III.20)]. A non-adiabatic version of the non-Debye theory has also been formulated.[76,77,86]

Allowance for the internal degrees of freedom of the chemical subsystem, i.e. the extension of the treatment outside the framework of the outer-sphere model, means in essence that electron transfer is regarded as a reaction with charge redistribution in the chemical subsystem. We shall consider such processes in the next Section. Finally, the question of the extension of the treatment outside the framework of the two-level model (IV.3)–(IV.5) by improving the wave function describing the chemical subsystem has been discussed recently.[84,87,88] The wave function of the two-level model is linear and consists of two terms, i.e. contains only one variational parameter. In many cases this is insufficient. The problem is of current interest in applications of the theory to intramolecular processes in complex chemical substrates.

Experimental kinetic studies have confirmed the dependence of the rate constant for the outer-sphere electron transfer on the longitudinal relaxation time τ_L [see Eqns. (IV.11) and (IV.15)]. The distinct inverse proportionality observed for organic radical-ion donors and acceptors[89,90] constitutes convincing evidence in support of the adiabatic process mechanism. For a reaction involving

ruthenium complexes in different aliphatic alcohols and glycerol, a weaker relation $K \propto \tau_L^{-0.6}$ was observed.[91] This result can be explained in different ways: either on the basis of the non-adiabatic formula (IV.17),[92,93] or within the framework of the non-Debye approximation for $\varepsilon(\omega)$,[93,94] or by including in the dynamics the internal degrees of freedom of the chemical subsystem.[52]

The correlation between the kinetic measurements and the quantity τ_L is complicated by the fact that, together with τ_L, other factors change in different solvents, and their effect on the kinetics cannot be excluded. We may mention in the first place the change in solvent polarity, which is capable of altering the potential barrier in the reaction. In this respect, the study of intramolecular electron transfer in systems of the type



is instructive. The reaction was investigated in aliphatic alcohols in the temperature range 168–338 K.[95] Comparison of the temperature variations of the reaction rate constants and of the quantity τ_L itself in the same solvent (the influence of the change in polarity is excluded) demonstrated quite convincingly the transition of the kinetics from the regime in which there is no dependence on τ_L to one where it does obtain. The authors identified these two regimes as "non-adiabatic" and "adiabatic". However, we may note that, for the systems investigated, the electron transfer is accompanied by an appreciable change in intramolecular geometry, i.e. can be hardly classified as a purely outer-sphere process. Allowance for the internal degrees of freedom would make it possible to describe both regimes within the framework of the two-dimensional adiabatic model examined in the next subsection.

Thus the uncertainty in the interpretation of the experimental results within the framework of stochastic theories is difficult to overcome at the present time.

3. Reactions in polar and non-polar media

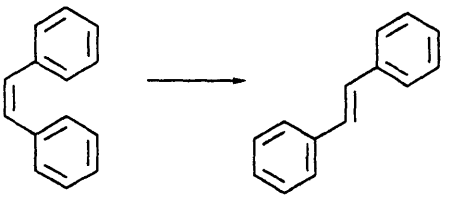
Transition to chemical reactions implies explicit study of the variables of the chemical subsystems together with the variables of the medium. For example, for charge transfer reactions in a polar solvent, one introduces the free energy functional $U[x_i, P(r)]$, which is a functional in relation to the variables of the medium [i.e. the polarisation $P(r)$] and is a normal function of the chemical variables x_i. We shall formulate the corresponding system of dynamic equations for the case of a single coordinate x[52] and the Debye approximation for $\varepsilon(\omega)$:

$$\tau_L f_0 \mathrm{d}P/\mathrm{d}t = -\delta U/\delta P + \text{random force}, \qquad (IV.21)$$

$$m\mathrm{d}^2x/\mathrm{d}2t = -\mathrm{d}U/\mathrm{d}x.$$

The functional $U[x_i, P(r)]$ plays the same role in the adiabatic theory of reactions in a condensed medium as the potential energy surface in the theory of gas-phase electronically adiabatic reactions. The variational derivative $\delta U/\delta P$ plays the role of the regular force. The rate constant for the system of Eqns. (IV.21) can be calculated on the basis of the generalised transition state theory [Eqn. (III.20)].[52]

Such a consistent theoretical programme of study, ranging from the construction of the energetic functional to the calculation of the rate constants for specific reactions in the medium, has not so far been realised. Fully phenomenological models are commonly used nowadays. The simplest of these arises from the Kramers Eqn. (III.1) and the corresponding expressions (III.11) and (III.13) for the rate constant. The isomerisation of cyclohexane[29,30] and the *cis–trans* isomerisation of stilbene and of its analogues in an excited state[49,50,96] have been frequently discussed at this theoretical level:



(IV.22)

In reaction (IV.22), the coordinate x of the Kramers model is identified with rotation about the central bond and a macroscopic quantity, directly proportional to the viscosity of the medium η and inversely proportional to the diffusion coefficient D, is used as the coefficient of friction γ. In order to observe the dependence of the rate constant on the viscosity, systematic studies have been carried out on the reaction kinetics in the gas phase and in non-polar liquids over a wide pressure range.[49,50] The observed relation is illustrated in Fig. 5. The right-hand side of this figure reveals a decrease in the rate constant with increasing viscosity, which is slower than would follow from the Kramers relation in the region of high friction. Considerable efforts have been made to observe the branch of the Kramers solution which ascends with increasing viscosity. Fig. 5 shows that its presence has not been convincingly confirmed. In this connection, one must recall the limitations of the Kramers model in the region of low friction when it is applied to complex molecular systems which were discussed in Section III.

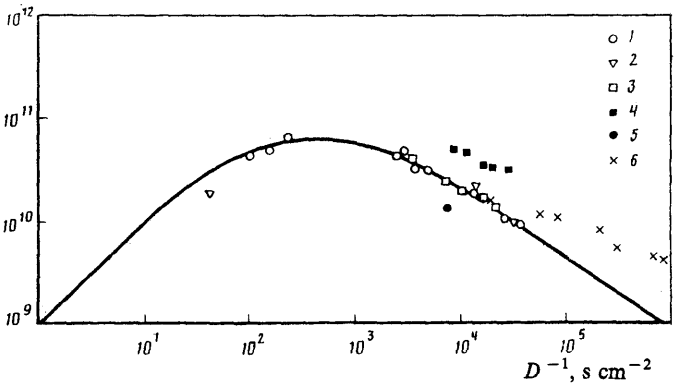


Figure 5. Correlation between the rate constant K for the photochemical isomerisation of stilbene and the reciprocal of the diffusion coefficient D^{-1}.[49] Experimental points obtained in the gas and liquid phases over a wide pressure range at 298 K: *1*, ethane; *2*, propane; *3*, CO_2; *4*, xenon; *5*, SF_6; *6*, n-hexane. Continuous curve — calculation based on the Kramers theory.

The phenomenological approach based on the Kramers equation encounters fundamental difficulties. We have seen that the role of the medium does not reduce only to the introduction of stochastic elements (the dissipative and random forces) into the description but

also involves the modification of the regular force. The interaction of the chemical system with the medium, superimposed on the intrinsic potential surface of the latter can distort appreciably both the height of the potential barrier and its shape (see, for example, Fig. 1). In the study of the role of friction, this side effect must be excluded, which requires accurate calculation of the interaction potential. For systems of type (IV.22), serious calculations have never been performed and the change in barrier height has been taken into account using an empirical method.[49]

Finally, in many cases the application of the one-dimensional generalised Langevin equation (III.1) as a model of the reaction in the given medium cannot be regarded as justified. In particular, using the hydrodynamic viscosities as a means of estimating the coefficient of friction γ, one frequently postulates a macroscopic description of the interaction in the spirit of the hydrodynamic Stokes formula

$$\gamma \sim \eta l, \qquad \text{(IV.23)}$$

where l is the characteristic distance over which the benzene rings migrate in reaction (IV.22).

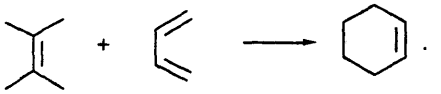
An attempt has been made to refine the dynamic description of isomerisation reactions with the aid of a two-dimensional stochastic model.[97,98] It was postulated that the process actively involves two angular variables with two different coefficients of friction. A study was made of the dynamic behaviour of the system as a function of the ratio of these parameters. The corresponding system of stochastic equations was solved in the high friction limit for both variables, where the kinematic contributions to the dynamics (proportional to the acceleration) are insignificant.

A consistent microscopic description of reactions in a given medium leads to a different two-dimensional dynamic model, in which the roles of both dynamic variables are fundamentally different:

$$\begin{aligned} &m\mathrm{d}^2x/\mathrm{d}^2t + \mathrm{d}U/\mathrm{d}x = 0, \\ &\gamma\mathrm{d}Q/\mathrm{d}t + \mathrm{d}U/\mathrm{d}Q = \text{random force}. \end{aligned} \qquad \text{(IV.24)}$$

The chemical coordinate x, obeying Newtonian dynamics, and the medium coordinate Q, the dynamics of which are introduced at the level of the simplest version of the Kramers theory (the high friction limit in which the kinematic term, proportional to the mass, has been omitted), are considered explicitly. The two variables are linked by the interaction included in the regular two-well potential $U(x, Q)$. By specifying this potential, it is possible to take into account the microscopic interaction explicitly. The significant factor is that in the two-dimensional model the coefficient γ characterises the interaction of the differentiated medium coordinate Q with the remaining degrees of freedom of the medium (thermostat) and its interpretation in the spirit of Eqn. (IV.23) is not open to objection.

We shall illustrate the application of the model (IV.24) in relation to the study of the pressure dependence of the Diels–Alder reaction.[8] For a typical reaction of this type



(IV.25)

dienophile diene adduct

The distance between the reactants is adopted as the chemical coordinate x. This leads to the simple model illustrated in Fig. 6. The chemical subsystem x is placed at the centre of a cylindrical cavity with a cross-section σ_0 and a length L. The medium coordinate Q is identified with the quantity L. During the reaction, the distance x diminishes and this entails also the diminution of the cavity. The dynamics is described by Eqns. (IV.24). An advantage of the two-dimensional model is the possibility of taking into account non-equilibrium solvation, i.e. the situation in which there is insufficient time for the medium coordinate Q to become adjusted to the change in the coordinate x, which is assumed to be faster. This effect can be described only by considering explicitly both coordinates—x and Q. The corresponding kinetic theory goes beyond the framework of the KGH approximation and the generalised transition state theory. It will be examined in Section V.

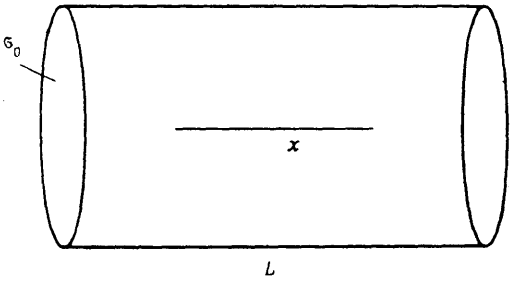
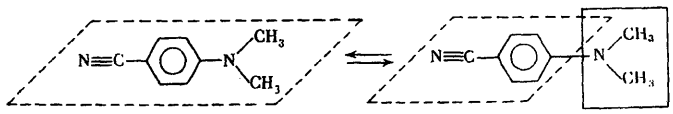


Figure 6. Model of the addition reaction in a condensed medium. x = distance between reactant molecules (reaction coordinate), L = coordinate of the medium; σ_0 = cross-section.

The experimental kinetic characteristics obtained for reaction (IV.25), investigated in the pressure range 0–6 kbar, have been interpreted[8] in terms of the non-equilibrium theory based on Eqns. (IV.24) and the reaction scheme adopted in Fig. 6. It was found that the majority of reactions can be regarded as reversible and that the rare anomalies in the pressure dependence of the rate constant could be interpreted as non-equilibrium effects.

Adopting the two-dimensional theory [Eqns. (IV.24)], we emphasised the difference between isomerisation reactions (IV.22) and addition reactions (IV.25). In the former case, the volume of the cavity hardly changes but its shape is altered. The latter case is characterised by a sharp decrease in the volume of the cavity during the elementary process. Accordingly, pressure affects addition reactions to an incomparably greater extent than isomerisation reactions. In the latter, the influence of the pressure is manifested mainly indirectly—through a change in the coefficient of friction γ.[28,29] The construction of a two-dimensional theory of isomerisation reactions would require the specification of a special medium coordinate the changes in which should model the change in the shape of the cavity. Without an explicit representation of coordinates x and Q, it is impossible to derive the energetic functional $U(x, Q)$.

Among charge-transfer reactions in polar media, photochemical isomerisation and nucleophilic substitution processes have been discussed in the literature. In the typical isomerisation reaction,[99]



planar structure perpendicular structure

(IV.26)

the molecule is excited to the first singlet state and there is rotation about the central C—C bond by 90° with alteration of the relative orientations of the terminal fragments. This conformational transition is accompanied by a strong polarisation of the molecule: according to a quantum-chemical calculation, its dipole moment increases from 6 to 16 D. A consistent dynamic description of reaction (IV.26) must include at least the angle of the conformational rotation and the polarisation of the medium as the dynamic variables.

It would also be necessary to examine the photochemical *cis—trans* isomerisation of non-polar conjugated molecules of the type of stilbene [reaction (IV.22)] when the latter occurs in a polar solvent, because it is known that the corresponding intermediate structures are highly polarised. However, all such reactions have been discussed theoretically hitherto at the elementary level of the one-dimensional Kramers model.[96,99,100] As in the electron transfer reaction, the coefficient of friction γ was assumed to be proportional to the relaxation time τ_L.

Methods for the explicit introduction of the medium coordinates into the two-dimensional model have been discussed in connection with the S_N2 reaction (I.3). In this case the antisymmetric motion in the complex

$$[Cl \cdots CH_3 \cdots Cl]^-$$

in the vicinity of the transition state is assumed to be the reaction coordinate. The form of the medium coordinate is determined by the form of the functional $U(q, P]$. One can imagine two limiting versions of the structure of this functional in the vicinity of the saddle point. In the first case, the section along x contains a barrier, while the section along the medium coordinate in the polarisation space consists of a paraboloid. This version corresponds to an insignificant modification of the gas-phase reaction coordinate in the presence of the polar solvent. A discrete coordinate corresponds to it:[101]

$$Y = \frac{\int D'(r)[f_0 P - D(r,\tilde{x})]d^3r}{\int [D'(r)]^2 d^3r}. \qquad (IV.27)$$

It is postulated that the regular electrostatic force $D(r,x)$, (the induction field which depends on the chemical coordinate x), has been linearised in the vicinity of the point $x = \tilde{x}$—for example, $\tilde{x}$ can correspond to the reactants minimum or to the saddle point of the potential $U[x, P(r)]$:

$$D(r, x) = D(r, \tilde{x}) + D'(r)(x - \tilde{x}),$$

$$D'(r) = \left.\frac{\partial D(r, x)}{\partial x}\right|_{x=\tilde{x}}.$$

In the second case, the section along x is a fragment of a parabola and that in the polarisation space is a two-well curve. In the vicinity of the transition state, the reaction proceeds mainly as a rearrangement of the medium, i.e. via the same mechanism as the outer-sphere electron transfer discussed above. The use of the variable X [Eqn. (IV.9)], which occurs in the electron transfer theory, as the reaction coordinate is most justified. Both variables, X and Y, correspond to the homogeneous medium approximation. The improvement of this simplest model by introducing a cavity would require the modification of both variables.[84]

Yet another procedure for the introduction of the medium variable, designed for a two-level electron transfer model, is possible. We designate by $P_a(r)$ and $P_b(r)$ the equilibrium polarisation of the medium corresponding to the reactants and reaction products. The current polarisation $P(r)$ can be specified by a linear interpolation:[67]

$$P(r) = \lambda P_a(r) + (1 - \lambda)P_b(r), \quad 0 < \lambda < 1. \qquad (IV.28)$$

This relation defines λ as the medium coordinate. It has been used for an S_N2 reaction[102] on the assumption of a one-well parabolic dependence of the free energy on λ. Such a scheme is not free from contradictions, since Eqn. (IV.28) was initially designed for a two-well model of the potential of the type which occurs in the electron transfer reaction.

The examples quoted in this Section show that theoretical studies on chemical reactions in a solvent are in their initial stage. The importance of the explicit consideration of the coordinates of the medium and their specific character has now been recognised. For reactions in non-polar media, these coordinates characterise the size or shape of the cavity in which the chemical subsystem is enclosed. In a polar solvent, the medium variables are represented by a particular functional of the inertial polarisation. In any version, such variables are collective modes, i.e. are concerted combinations of elementary motions of a large number of solvent molecules. The specific form of such a collective variable is defined within the framework of a particular model. Ultimately it follows from the concrete form of the energetic functional, just as the form of the usual vibrational modes is determined by the nature of the PES in the vicinity of its stationary points. In particular, in order to achieve a consistent solution of the problem of the medium coordinate in charge-transfer reactions, one has to establish the form of the cross-section of the functional $U[x, P]$ in the vicinity of the transition state. This requires the development of a method for quantum-chemical calculations with allowance for the effect of the medium.

V. Dynamics of multidimensional stochastic systems. Non-equilibrium solvation and its kinetic consequences

We shall consider in greater detail the equation of motion (IV.24) describing the stochastic dynamics of a system with two degrees of freedom. One of them, the Newtonian coordinate x, refers to the motion within the chemical subsystem. The second, the stochastic coordinate Q, is one of the modes of the medium. These variables are related via the potential $U(x, Q)$, which corresponds to the simplest version to a harmonic model with a quadratic term containing a linear combination of x and Q:

$$U(x, Q) = V(x) + \frac{\lambda}{2}(Q - ax)^2, \qquad (V.1)$$

where $V(x)$ is a one-dimensional two-well potential characterising a gas-phase reaction. The second term of Eqn. (V.1), containing the coordinates Q, corresponds to a harmonic oscillator with a force constant λ and an equilibrium position which depends linearly on x.

The two-dimensional equation (IV.24) is the simplest model suitable for the description of non-equilibrium solvation. In order to extend the treatment beyond kinetics under non-equilibrium conditions, it is necessary to abandon the KGH approximation. We shall introduce two characteristic periods τ_x and τ_Q related to the time scales of the motions of the corresponding variables. The period τ_x is assumed equal to the reciprocal of the frequency for two reactant wells subject to the one-dimensional potential $V(x)$. In certain cases, τ_x is determined in terms of the residence time of the system near the barrier. The period τ_Q characterises the relaxation of the variable Q; it is proportional to the coefficient of friction γ. If the time scales for τ_x and τ_Q are comparable in magnitude, then the non-equilibrium effects are insignificant and the multi-dimensional KGH theory yields a satisfactory approximation for the rate constant. Another situation arises if τ_x and τ_Q are quantities of the same order of magnitude. We shall assume that Q is the slow coordinate, having put

$$\tau_x/\tau_Q << 1. \qquad (V.2)$$

Then in the course of an elementary process, there is insufficient time for the coordinate Q to become adjusted to the changes in the faster coordinate x, which in fact entails non-equilibrium effects.[86,103] The mathematical situation described by the inequality (V.2) is treated by averaging the system of Eqns. (IV.24) over the period of fast motion ν_x.[103–105] As a result of the averaging, the two-dimensional potential function is converted into a one-dimensional effective potential $\tilde{U}(Q)$, which governs the motion of the slow variable of the medium Q. The kinetic evolution of Q is expressed in terms of the Fokker–Planck equation for the distribution function $R(Q, t)$:[103–107]

$$\frac{\partial R}{\partial t} = D_Q \frac{\partial^2 R}{\partial Q^2} + \frac{D_Q}{kT}\frac{\partial}{\partial Q}\left[R\frac{\partial}{\partial Q}\tilde{U}(Q)\right] - K(Q)R. \qquad (V.3)$$

Here the first two terms on the right-hand side describe diffusion subject to a potential U with a diffusion coefficient D_Q. The last term on the right-hand side describes the departure of the particles from the reactants region at each point Q with a rate constant $K(Q)$, i.e. a chemical reaction subject to a two-well potential, which is represented by the section along the variable x through the two-dimensional potential $U(a, Q)$ [Eqn. (V.1)] parametrically dependent on Q. The local rate constant is given by

$$K(Q) = \frac{\omega(Q)}{2\pi}\exp\left(-\frac{\Delta U(Q)}{kT}\right). \qquad (V.4)$$

The frequency in the pre-exponential factor and the height of the barrier are functions of Q. Under these conditions, the diffusion coefficient D_Q is proportional to τ_Q^{-1} and the frequency $\omega(Q)$ is proportional to τ_x^{-1}. Eqn. (V.3) gives rise to a range of kinetic regimes.[107–109] Even more varied kinetics are generated by the initial system of Eqns. (IV.24), from which Eqn. (V.3) is obtained in the limit represented by Eqn. (V.2). Each kinetic regime operates in a different range of parameters of Eqn. (IV.24) and can be derived within the framework of a particular approximate model.

Fig. 7 represents the regions of applicability of different approximate descriptions of the kinetics of reaction (IV.24) as a function of the ratio τ_Q/τ_x. For a fixed τ_x, the above parameter increases with increase in τ_Q and is therefore proportional to the coefficient of friction γ and inversely proportional to the diffusion coefficient D_Q. The exact solution of Eqn. (IV.24) would make it possible to cover the entire range of values of the parameter τ_Q/τ_x.

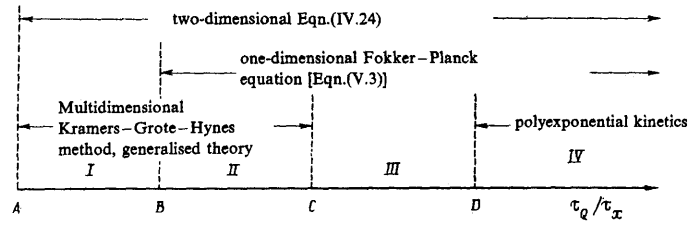


Figure 7. Schematic illustration of the changes in kinetics with increasing viscosity of the medium in the two-dimensional model of the reaction (IV.24). Points *A*, *B*, *C*, and *D* represent the conventional boundaries of different kinetic regimes.

The point B constitutes the left boundary of the region of applicability of the average quasi-one-dimensional equation (V. 3). To the left of this point, the solution is significantly two-dimensional (region I). Here τ_x and τ_Q are of the same order of magnitude and the two-dimensional KGH theory[94] or, what amounts to the same thing, the generalised transition state theory [Eqn. (III.20)] is applicable in this case. The next section of the horizontal axis (region II) corresponds to the situation where the quantity τ_Q/τ_x is now so large that the averaging of Eqn. (IV.24) is legitimate, but the KGH theory is still applicable. The rate constant in this region constitutes the quasi-one-dimensional limit of the two-dimensional KGH theory, is independent of γ, and is given by the simple Arrhenius expression

$$K_e = \frac{\omega_e}{2\pi}\exp\left(-\Delta U^{\neq}/kT\right), \qquad (V.5)$$

where ω_e is the frequency determined by the parameters of the two-dimensional potential.

The approximate solution of Eqn. (V. 3), which represents the equilibrium distribution $R_e(Q)$ and is obtained for fixed values of τ_Q and D_Q in the limit $\Delta U^{\neq}/kT \gg 1$, also corresponds to Eqn. (V. 5). The maximum in the reaction flux, described in Eqn. (V.3) by the term $K(Q)R(Q)$, is then found at the point $Q = Q^{\neq}$, i.e. the saddle point on the surface specified by the function (V.1). At the point $Q^{\neq}$, the quantity $K(Q)$ is a maximum and the reaction passes through the saddle point.

On passing to the region III, the distribution $R(Q)$ ceases to correspond to equilibrium. Movement along the coordinate Q becomes so slow that it has insufficient time to compensate for the decrease in the density of particles owing to the reaction in the vicinity of the point $Q^{\neq}$. The maximum in the reaction flux therefore shifts to the region $Q < Q^{\neq}$, the shift being extended further the greater the ratio τ_Q/τ_x. This increases the effective

potential barrier, which now depends on the coefficient of friction and temperature. A viscosity-dependent rate constant K with a non-Arrhenius temperature variation is thus obtained[103,104] and we then always have

$$\kappa = K/K_e < 1. \quad (V.6)$$

The non-equilibrium rate constant is always smaller than the equilibrium constant and there exists a range of parameters of the potential where the ratio (V.6) is extremely small ($\kappa \simeq 10^{-3}$ and less).[104,109]

Region IV is particularly interesting. Here the kinetics are of a polyexponential type; in other words, they cannot be described with the aid of a single rate constant.[107,108] The extreme case of polyexponential kinetics represents the "frozen" medium limit ($\tau_x/\tau_Q \to \infty$, $D_Q \to 0$) in which the rate of reaction is

$$Q(t) = \int \exp[-K(y)]R(y, 0)dy,$$

where $R(y, 0)$ is the distribution in the initial instant (it is determined by the conditions in the preparation of the reaction system). The dependence of the rate of reaction on the initial distribution is a distinctive property of the polyexponential regime. Eqn. (V.7) means that at each point on the Q axis a chemical reaction is generated with its own rate constant $K(Q)$ and the initial concentration of the reactants at each point is specified by the initial distribution $R(y, 0)$. Polyexponential kinetic regimes, especially the limit (V. 7), have been frequently observed in media with a low mobility. For example, they are typical for low-temperature chemistry.[110] Thus the simple two-dimensional model (IV.24) gives rise to a whole range of kinetic regimes, which are observed experimentally. In this respect, it is incomparably more elaborate than the primitive one-dimensional model (III.1). It can apparently be usefully employed as the phenomenological basis of the description of reactions in condensed media.

The description of effects due to the non-equilibrium nature of the medium is possible in a highly simplified form within the framework of a unique generalised Langevin equation.[34,60,111] We shall consider the dissipative term of Eqn. (III.3):

$$\int_0^t \beta(t - \tau)\dot{x}(\tau)d\tau.$$

Suppose that the time interval $\bar{\tau}$ during which the friction kernel $\beta(t)$ decays is sufficiently long compared with the reciprocal of the decomposition frequency Ω^{-1} [Ω is the solution of the characteristic equation for (III.3)]:

$$\bar{\tau}\Omega >> 1. \quad (V.8)$$

The multiplier $\beta(t-\tau)$ can then be taken outside the integral sign at the point $\tau = t$. This yields the additional term $\beta(0)x(t)$ in the expression for the regular force $(-\partial U/\partial x)$ in Eqn. (III.3), which effectively diminishes the absolute magnitude of the negative force constant in the transition state region. Such description is fully equivalent to the "frozen" medium picture mentioned in Section II.4 in connection with the calculation for the S_N2 reaction by the reaction flux method. Indeed, according to the inequality (V.8), the characteristic relaxation time of the medium $\bar{\tau}$ is much longer than the characteristic time of the motion of the chemical system in the vicinity of the barrier Ω^{-1}. In the other limiting case $\beta(t-\tau) = \delta(t-\tau)$, one obtains the usual Kramers equation; the intermediate case is characterised by a gradual change in the type of kinetics as a function of the ratio of the characteristic times indicated. In this abbreviated description many important results of the more complete two-dimensional theory are lost—for example the polyexponential kinetic regime.

VI. Certain problems and prospects

According to standard textbooks of chemical kinetics concerned with gas-phase reactions,[112,113] the calculation of the reaction rate constant is preceded by three stages:

1. calculation of the potential energy surface;
2. dynamic calculation on this surface;
3. calculation of the distribution function of the initial conditions in the reactants region with the aim of incorporating such conditions in the dynamic calculation.

After this, the rate constant is obtained by averaging the reaction flux in the reactant region on the basis of the initial conditions found.

The transition state theory eliminates the last two stages (dynamic and statistical) using the reaction flux in the region of the saddle point (i.e. the transition state) with the equilibrium distribution function. Modern gas-phase dynamic calculations involve as a rule the first two stages using the hypothesis of the equilibrium Boltzmann distribution in order to average the initial conditions.

Theoretical studies on the kinetics of reactions in condensed media have introduced significant modifications into the programme of operations indicated. In its numerical application, all its three stages are closely intertwined and their artificial separation is undesirable. Thus the calculation of the FES by the Monte Carlo method already involves the equilibrium estimate of the rate constant, which is more or less consistent with the transition state theory. In the stage involving the calculation of the transmission coefficient (i.e. the correction to the Monte Carlo calculation) by the method of molecular dynamics, the dynamic (calculation of reaction trajectories) and statistical (correction of the equilibrium distribution function) stages are virtually inseparable.

A similar situation occurs also in stochastic models: the search for the distribution function for a system of stochastic dynamic equations (we have in mind classical theories) reduces to the solution of the corresponding Liouville (or Fokker–Planck) equation, in which the dynamic and statistical aspects have merged into one.

Research has confirmed the striking vitality of the transition state theory. It was unexpectedly reborn in a generalised form, taking into account the medium, as the multidimensional KGH theory. After such radical modification, its application to a wide variety of kinetic chemical and biological problems promises to be fruitful.

From the standpoint of the development of the theory of chemical kinetics, it is of interest to go beyond the framework of the transition state and KGH methods, i.e. to investigate non-equilibrium effects. This concerns the small transmission factors $\kappa \ll 1$ in classical systems where tunnelling effects are ruled out. The search for the corresponding chemical objects constitutes a special task and this confirms yet again the advantages of the transition state theory in relation to reactions with thermal activation.

At the microscopic level, highly non-equilibrium situations have not so far been observed under thermal conditions. It is sufficient to point out that the calculation for an S_N2 reaction,[33,34] described in subsection II.4, which constitutes a record as regards the thoroughness and volume of computations, yielded only $\kappa = 0.55$ as

the transmission factor. However, even this quantity can be almost completely reproduced within the framework of the KGH theory,[34,60] i.e. it has no bearing on true non-equilibrium effects.

A general study of a model microscopic chemical system[114] showed that it is hardly possible to obtain $\varkappa < 10^{-1}$ retaining the hypothesis, usual for gas-phase reactions, that the initial distribution function in the reactants region corresponds to equilibrium. However, pronounced non-equilibrium effects arise naturally in the phenomenological description of the kinetics in the language of stochastic equations. Two examples were examined above: the region of low friction in the one-dimensional Kramers theory (subsection III.2) and the region of high friction in the two-dimensional stochastic model [Eqn. (IV.24)] (Section IV). Both cases are characterised by the breakdown of the Boltzmann distribution in the reactants zone, which is in fact the source of the disequilibrium.

Thus the next task to be tackled involves the calculation of the distribution functions for thermal reaction systems, under conditions where they deviate markedly from the Boltzmann equilibrium, and the experimental search for the corresponding natural objects. In this connection, we may note that the existing versions of the molecular dynamics calculations are unsuitable for such purposes. They are designed specially for the calculation of transmission factors close to unity under the conditions of small deviations from equilibrium in the transition state region. A converging (i.e. attaining a plateau) calculation of a low transmission factor within the framework of this method is impossible.

An evident aspect of theoretical studies is the application of the approaches already developed to specific chemical and biological systems. The next task on these lines is the development of continuous stochastic models for systems with non-electrostatic interaction by analogy with electron transfer theory. A promising procedure involves the combination of continuous models with numerical approaches: with Monte Carlo and molecular dynamic methods for the determination of the parameters of stochastic equations and with quantum-chemical methods for the calculation of interaction potentials. Finally, it is essential to develop quantum stochastic theories and their numerical application. Without such an instrument, it is impossible, for example, to investigte seriously electron transfer in a polar environment. Studies in this field are nowadays developing vigorously,[55,59] but their discussion is outside the framework of the present review.

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