KINETIC THEORY OF CHEMICAL REACTIONS

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In [1] a calculation was made of the probability of the elementary action of a nonadiabatic reaction in a solution, under the assumption that the surface potential energies of the initial and final states (i.e., the electronic therms of the inlet and outlet channels of the reaction) have the form of arbitrary multidimensional parabolas (the harmonic approximation). Physically, such a picture corresponds to the postulation that, with different degrees of freedom of the system, the motion in the reaction channel can be resolved into noninterreacting normal vibrations. The authors of [2, 3] proposed a method which took account of the anharmonic nature of the vibrations and of the interaction between the motions with different classical degrees of freedom; however, in the calculation made in [2, 3], the interaction between the motions with respect to classical and quantum degrees of freedom was essentially neglected.

The present work proposes a method for considering the more general case of a chemical reaction; the method involves the use of a double adiabatic approximation. The scheme of the proposed approach will be presented below, and the possible effects arising with calculation of the interaction between the motions with respect to classical and quantum degrees of freedom will be discussed. The details of the calculation will be set forth in a separate article. We shall begin with consideration of the simplest case of a chemical reaction in a polarized liquid such that, during the course of the reaction, the state of polarization of the solvent, which was performing classical vibrations, changes, and there takes place the transfer of a single particle A which, in the reagents and in the products, performs quantum vibrations with an excitation energy $\Delta E \gg kT$. The interaction between the quantum and the classical degrees of freedom V (R, q) which can arise in the reaction zone (the region of the intersection of the initial and final therms) leads to a situation in which the form of the potential energy surfaces in the reaction zone becomes more complex. [Figure 1 gives schematic representations of cross sections of the initial and final therms by the surfaces U = const as a function of two coordinates, describing the state of polarization of the solvent (q) and the position of the particle A(R).] Since the frequency of the vibrations ω_R with respect to the coordinate R considerably exceeds the frequency of the vibrations ω_q with respect to the coordinate q, a double adiabatic approximation can be used, considering the solvent as a slow subsystem, and the particle A, which performs the transition, as a rapid subsystem. Solving the Schrödinger equation with fixed values of the coordinate q gives the wave functions $\Phi_m(R; q)$ of the particle A and the energy levels $\varepsilon_m(q)$ which depend on q as a parameter. In accordance with the standard method of an adiabatic approximation, the functions $\varepsilon_m(q)$ represent the potential energy of the slow subsystem $U_m(q) = \varepsilon_m(q)$, whose form depends on the quantum state of the subsystem (m). Figure 2 gives qualitative curves of the potential energy for the ground ($m = 0$) and excited ($m \neq 0$) vibrational states of the quantum subsystem in the initial and final states. The dependence of ε_m on q in the general case can be different. The most important case is evidently that in which, in the reaction zone, the chemical bond between the particle A and the starting reagent is weakened. This means that with motion along the coordinate q toward the region of intersection of the therms, the levels $\varepsilon_m(q)$ approach each other (Fig. 2).

The first consequence arising from this circumstance consists of an increase in the role of the excited states during the course of the reaction, since the closer the approach of the therms in the reaction zones the less becomes the difference in the activation energies for transitions with the participation of the ground and excited vibrational states, while the transmission coefficients rise with a rise in the excitation energy of the vibrations along the coordinate R, due to the greater degree of overlapping of the wave functions. A quantitative calculation of this effect for the case in which the transitions between the different therms can be assumed independent [4] can be carried out

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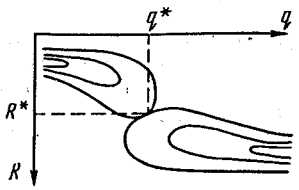

Fig. 1

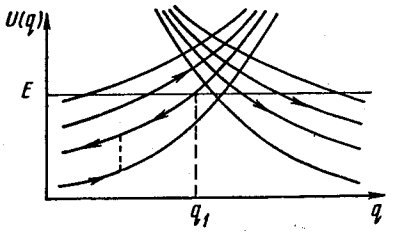

Fig. 2

using formula (1.31) of [3]. It can be stated qualitatively that this effect should become considerable if the distance between the therms in the reaction zone becomes comparable with kT. In the case in which the distance between the therms in the reaction zone becomes considerably less than kT, the transition takes place through the common saddle point at the intersection of the electronic therms (Fig. 1). If the distance between the therms in the reaction zone remains great in comparison with kT, the principal role (in the normal region [3]) will be played by transitions between therms corresponding to unexcited vibrational states.

A second circumstance which can be considered substantial, if the interaction $V_{1,2}$ between the reagents, leading to a transition of the particle A from one molecule to another, is sufficiently great (an adiabatic reaction), consists in the fact that the proposed method permits taking account of multiple transitions in the reaction zone between therms corresponding to different excited vibrational and electronic states of the reagents (Fig. 2). A method described in [5] can be used to take these transitions into account quantitatively, under the assumption of independent transitions between the different therms.

Finally, the proposed method using a double adiabatic approximation permits taking quantitative account of still one more effect, connected with interaction between motions with respect to both classical and quantum degrees of freedom. The above interaction can lead to the mutual conversion of translational motion along the coordinate q to vibrational energy along the coordinate R [6]. In the proposed method these conversions of translational and vibrational energy are taken into account as follows. As a result of the dependence of the wave function Φ_m (R; q) on q, solutions of the Schrödinger equation, found using a double adiabatic approximation, are approximate. Taking this dependence into account leads to transitions between states corresponding to different therms $U_m(q)$, i.e., to transitions between therms. Therefore, if at the start (at $q \to -\infty$) the system is located on a therm corresponding to an unexcited vibrational state (m = 0) along the coordinate R, with motion along the coordinate q toward the reaction zone, there can be a transition to the therm of the first excited vibrational state (m = 1). If the connection between the therms in the reaction channels is not too small, with further motion along the coordinate q there is the possibility of transitions to therms with higher excited vibrational states (m = 2, 3, . . .). Taking account of the above transitions in the language of the classical description, in the generally accepted sense, is equivalent to taking account of the zigzag motion of a system over the surface of an electronic therm [6].

In particular, within the framework of the concepts of quantum mechanics the proposed method permits a quantitative description of the phenomenon of a reflection of the system into the entrance channel, connected with a complete conversion of translational energy into vibrational [6]. In practice, let a system move along the unexcited therm $U_0(q)$ with an energy E, sufficient to overcome the potential barrier determined by the intersection of the ground initial (U_0) and final (U_0') therms (Fig. 2). If, with motion along the coordinates q, there is a transition of the system to the first excited therm $U_1(q)$, further motion of the system along this therm will take place only up to a point q_1 which, with a given energy E, is a point of inflection for the given therm. At this point, the velocity of the translation motion along the coordinate q reverts to zero, the direction of the motion of the system changes to the reverse, and the system returns to the starting channel.

Use of the double adiabatic approximation to describe motion in the coordinates R and q is convenient for practical calculations, in the case in which the interaction L, leading to transitions between therms in the channels, is not great. In principle, this method is applicable also with a large degree of interaction L; however, in this case the calculations become very complicated. Here it is more convenient to go over from the coordinates R and q to some curvilinear coordinates r and Q and to use a double adiabatic approximation, assuming that the translational motion along the curvilinear coordinate Q is slow compared with the motion in a perpendicular direction. The therms $U_m(Q)$ obtained in this case will, in the general case, have quantitatively a form analogous to that shown in Fig. 2. The system of curvilinear coordinates must be chosen so as to diminish as far as possible the interaction L,

which leads to transitions between therms in the channels.* In addition, in the general case, the systems of coordinates for the initial (r, Q) and final (r', Q') channels cannot coincide. In such a form, with the necessary generalizations for the case of participation of a large number of degrees of freedom in the reaction, this method can be used to calculate the rates of a rather broad class of reactions, in both the liquid and gas phases.

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* In contrast to [7], which used curvilinear coordinates to treat the adiabatic transition of a system from its initial state into its final state on the surface of adiabatic electronic therms, we are considering channel therms.