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## CALCULATION OF THE KINETICS OF CHEMICAL REACTIONS IN POLAR LIQUIDS FOR ANHARMONIC MOLECULAR POTENTIALS*

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In calculating the probability of an elementary act of charge transfer in a polar liquid, the use of a harmonic approximation to describe the intramolecular degrees of freedom may be unsatisfactory in a number of cases. A reaction in which the state of one intramolecular degree of freedom R changes (due to a change in the length or formation or breaking of a chemical bond) is examined to clarify the problem of the effect of the form of the terms on the qualitative picture of the transition.

The probability of a nonadiabatic transition in unit time is calculated from the general formula of collision theory using the first Born approximation. Averaging and summation with respect to the vibrational states of the solvent (which is described within the harmonic approximation) gives for W the expression

$$W \sim \sum_{n,n'} \exp\left[-\frac{E_n}{kT}\right] |\langle \varphi'_{n'} | \varphi_n \rangle|^2 \exp\left[-\frac{(E_s - \Delta J + E_n - E'_{n'})^2}{4E_s kT}\right],$$

where $E_n$, $E'_{n'}$, $\varphi_n$, $\varphi'_{n'}$ are the excitation energies and wave functions of the intramolecular degree of freedom, and $E_s$ and $\Delta J$ are the solvent reorganization energy and the heat effect of the process.

Using quasi-classical wave functions for $\varphi_n$ and $\varphi'_{n'}$ it can be shown that, if the excitation energies $E_n$ and $E'_{n'}$ are sufficiently large, the term corresponding to unexcited intramolecular vibrations ($n = n' = 0$) makes a fundamental contribution to the summation with respect to n and n' in the region ($|\Delta J| \ll E_s$), i.e., the given degree of freedom in this case behaves in a quantum fashion. It is demonstrated that the excited states of the quantum degree of freedom play a substantial role only in the nonbarrier and nonactivation regions.

If the excitation energies $E_n$ and $E'_{n'}$ are sufficiently small, a large number of terms make a major contribution to the summation with respect to n and n', so that one can pass from summation to integration with respect to the energies. The following expression is obtained for the probability W of an elementary act of a chemical reaction after a number of transformations:

$$W \sim \int d\Delta j \exp\left[-\frac{(E_s - \Delta j)^2}{4E_s kT} - \frac{\varepsilon_a(\Delta J - \Delta j)}{kT}\right],$$

where $\varepsilon_a(\Delta J - \Delta j)$ is determined as the energy at the point of intersection of the initial U(R) and final U'(R) term (reckoned from the minimum of the initial term) under the condition that the minimum of the initial term is shifted upwards relative to the minimum of the final term by ($\Delta J - \Delta j$). Thus, in this case the intramolecular degree of freedom behaves classically, and the transition occurs through the common saddle point on the total surface of the electron terms.

The results obtained are directly correlated in the case of several noninteracting, intramolecular degrees of freedom.

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* Moscow (1970), 14 pp., bibliography : 6 citations.

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