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Abstract

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ON THE THEORY OF MONOMOLECULAR REACTIONS IN SOLIDS

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Up to the present time there has been no microscopic theory of chemical reactions in solids. A number of works devoted to the macroscopic kinetics of the thermal decomposition of crystal lattices (see, for example, (1)) do not touch at all upon the nature of the elementary chemical act; therefore, for example, it is not even possible to calculate approximately the rate constants of nucleus formation. Meanwhile, the solution of the question of elementary chemical transformations would also substantially clarify the macrokinetic regularities. Here we shall consider a rather general formulation of monomolecular reactions in lattices of a general type, especially the differences between the latter and the corresponding reactions in the gas phase.

We shall adopt the general assumptions concerning the existence and conservation, in the course of the reaction, of a Maxwell–Boltzmann distribution. It is true that if in a gas it is established and maintained by collisions, then in solids a strong interaction between particles is responsible for it, of the order of magnitude of the binding energy of the particles in the lattice. We shall not detail this concept, since our consideration will be restricted to the transition-state method, while the question of a more precise formulation of a monomolecular transformation, including the study of activation and deactivation processes, may serve as the subject of a special discussion.

The rate constant of the elementary transformation, in the usual notation, has the form

$$\tilde{k} = \varkappa \frac{kT}{h} \frac{F^{\ddagger}}{F} e^{-E_0/kT}. \tag{1}$$

The elementary system under consideration directly includes the decomposing particle (for example, a molecule) with a sufficiently large number of nondecomposing neighbors. The number of the latter must be so large that in the final results one can pass to the limit $N \to \infty$ (N is the number of neighbors) without detriment to the description of the process in another such block of the lattice. This, of course, restricts the description to small degrees of transformation. If one introduces a potential V characterizing the deviation of the selected block of the lattice from the ideal one in the transition state, then the corresponding shift of the electronic energy will be (^{2})

$$\Delta E = \Delta E_{nl} + \Delta E_{loc}, \tag{2}$$

where the part ΔE_{nl}, associated with the nonlocalized electrons, has the form

$$\Delta E_{nl} = \frac{2}{\pi} \int_0^{E_F} \arg\det(1 - VG(E))\, dE \tag{3}$$

(E_F is the Fermi energy, $G(E)$ is Green' s function), while the electrons localized in the neighborhood of the defect give a contribution ΔE_{loc}

$$\Delta E_{loc} = 2 \sum_{i,m} \left(E_{gi} - E_{0i}^m\right); \tag{4}$$

E_{gi} is the boundary of band i; E_{0i}^m are the levels of localized electrons, which are found from the equation

$$\det(1 - VG(E)) = 0; \tag{5}$$

ΔE is the difference of the electronic energies in the initial and transition states and is therefore identical with E_0, up to the difference of the zero-point vibrational energies (phonons at $T = 0$). The latter can be written as

$$\Delta E'(0) = \frac{\hbar}{2} \sum_f (\nu^{\neq}(\mathbf{f}) - \nu(\mathbf{f})). \tag{6}$$

Here $\nu^{\neq}(\mathbf{f})$ and $\nu(\mathbf{f})$ are the phonon spectra in the initial and transition states; $\mathbf{f}$ are quasimomenta.

$\Delta E'$ can be calculated in exactly the same way as ΔE, but in this case the perturbation is the electronic shift already found (^{3})

$$\Delta E'_{nl}(0) = \frac{\hbar}{2} \int^{\nu_0} \arg\det(1 - \Delta E D(\nu))\, d\nu; \tag{7a}$$

$$\Delta E'_{loc}(0) = \frac{\hbar}{2} \sum_{i',\, m'} (\nu_{gi'} - \nu_{0i'}^{m'}); \tag{7b}$$

$$\det(1 - \Delta E D(\nu_{0i'}^{m'})) = 0. \tag{7c}$$

In these formulas ν_0 is the limiting frequency, and $D(\nu)$ is the phonon Green' s function. It should, of course, be remembered that in our problem the principal role is played by optical phonons.

We shall assume that only the vibrational degrees of freedom are essential, and therefore write the distribution function in the transition state in the form

$$F^{\neq} = \prod_f \left(1 - e^{-\hbar\nu^{\neq}(\mathbf{f})/kT}\right)^{-1}. \tag{8}$$

The frequencies of the nonlocalized vibrations may be represented in the form

$$\nu^{\neq}(\mathbf{f}) = \nu(\mathbf{f}) + \frac{1}{N}\Delta(\mathbf{f}), \tag{9}$$

where $\Delta(\mathbf{f})$ can be found from (6) and (7a). The frequencies of the localized vibrations are determined by equation (7c). One (in the simplest case) of the latter vibrations will have an imaginary frequency, which corresponds to motion along the decomposition coordinate. This frequency is formed from some boundary frequency, and therefore in (8) there is one boundary frequency fewer than in the initial state.

Restricting ourselves, for simplicity, to a single branch, we find

$$F^{\neq} = (1 - e^{-\hbar\nu_g/kT}) \exp - \left[-\sum_f \left(\ln(1 - e^{-\hbar\nu(\mathbf{f})/kT}) + \frac{1}{N}\frac{\hbar\Delta(\mathbf{f})}{kT}\frac{1}{e^{\hbar\nu(\mathbf{f})/kT} - 1} \right) \right]. \tag{10}$$

Here the expansion in the small quantity $1/N$ has been used twice. Thus, for the ratio of the distribution functions we obtain

$$\frac{F^{\neq}}{F} = (1 - e^{-\hbar\nu_g/kT}) \exp\left[-\frac{\hbar}{kT}\int_0^{\pi} \frac{\Delta(\mathbf{f})}{e^{\hbar\nu(\mathbf{f})/kT} - 1}\, d\mathbf{f} \right]. \tag{11}$$

It is not difficult to see that, also for localized frequencies differing from the imaginary ones, (11) remains valid with the only change that the exponent contains the total phonon energy shift $\Delta E'(T)$ at a temperature T different from zero, less the zero-point shift,

$$\frac{F^{\neq}}{F} = \left(1 - e^{-\hbar\nu_g/kT}\right) \exp\left(-\frac{\Delta E'(T) - \Delta E'(0)}{kT} \right). \tag{12}$$

If the sum (6) is included in the pre-exponential factor A, then for (1) we find

$$\tilde{k} = Ae^{-\Delta E/kT}; \tag{13}$$

$$A = \varkappa \frac{kT}{\hbar} e^{-\Delta E'(T)/kT} \left(1 - e^{-\hbar\nu_g/kT}\right). \tag{14}$$

At sufficiently high temperatures,

$$A = \nu_g e^{-\Delta E'(T)/kT} \qquad (\varkappa \sim 1). \tag{15}$$

It is interesting to compare the expression obtained with the pre-exponential factor for the gas phase. Omitting the zero-point energy and once again expanding in (15), for $T \to \infty$, to order of magnitude we obtain

$$A \sim \nu_g e^{-2\Delta\nu/\nu_1}, \tag{16}$$

where $\Delta\nu$ is the half-width of the vibrational band; $\hbar\nu_1$ is some mean energy within it, whereas in the gas phase

$$A' \sim \nu_0, \tag{17}$$

and ν_0 is the frequency of some fundamental vibration in the molecule. If one takes into account that $\nu_g \sim \nu_1 + \Delta\nu$ and $\nu_1 - \Delta\nu \sim \nu_0$, it is clear that the pre-exponential factors are in fact close to one another. As for the activation energy, as is seen from (2), the part of it associated with the nonlocalized electrons, equal in order of magnitude to ΔE_{loc}, is specific only to the solid phase. This shows that the activation energy in the solid phase is, generally speaking, higher than for the corresponding reactions in the gas.

The consideration carried out is restricted to the case of purely homogeneous decomposition. As is known, reactions in the solid phase most often begin at various kinds of lattice defects. In this connection it should be noted that the principal features of the method used do not change in this case; it is true, however, that it becomes necessary to know the spectra and eigenfunctions in the real lattice. If the defects are sufficiently localized, the problem reduces to changing the corresponding Green' s functions in the presence of the defect potential V_d. Thus, for example, for electrons

$$G'(E) = \frac{G(E)}{1 - V_{dG}(E)}. \tag{18}$$

In the case of extended defects (for example, dislocations) the same method is applicable, but the direct solution of the new zero-order problem is very complicated.

Let us also note that the reaction may proceed through various excited electronic states of the lattice (for example, excitons). A different technique should be applied to the consideration of this possibility.

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Note: Figure translations are in progress. See original paper for figures.

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