The Kinetics of the Adiabatic and Nonadiabatic Reactions at the Metal and Semiconductor Electrodes*

R. R. Dogonadze, A. M. Kuznetsov, and M. A. Vorotyntsev

Institute of Electrochemistry of the Academy of Sciences of the USSR, Moscow State University, Moscow, USSR

The basic results of the correct quantum-mechanical calculations of the probability of the elementary act of adiabatic homogeneous reactions are summarized. The calculations are carried out for the model of the one-dimensional potential energy curves without using the perturbation theory.

The adiabatic and nonadiabatic electrochemical reactions at the metal and semiconductor electrodes are considered. The physical picture of the process is discussed. The adiabatic electrochemical process is shown to be of the many-electron character. The expressions for the transition probability is derived for the metal and semiconductor electrodes. The redox reactions at the semiconductor are considered in the presence of the surface states.

The problem of the calculation of the probability of the adiabatic reaction elementary act at the metal and semiconductor electrodes is essentially different from the analogous problem for the homogeneous reactions. This difference is due to the many electron character of the electrochemical reaction. For the adiabatic electrochemical reaction, even in the case of the simplest process of only one electron transfer from the electrode to the reagent or back, the essential reorganization of the state of the many electrons in the electrode takes place, while in the homogeneous electron transfer reaction the state of only the transferred electron is changed.

To show clearly this difference, in the present paper firstly the main results for the homogeneous adiabatic reaction will be briefly summarized, and the adiabatic and nonadiabatic reactions at the metal and semiconductor electrodes will be considered.

1. Adiabatic Homogeneous Reactions

The problem of adiabatic and nonadiabatic course of the homogeneous reaction will be considered for the case of a simple outsphere electron transfer reaction between two ions A^{Z_1} and B^{Z_2}, located in the reaction zone at some distance R_0 apart from one another, as an example.

In this case the natural physical formulation of the problem is as follows. The Hamiltonian of the total system can be divided in two parts

$$H = H_i + V_i = H_f + V_f \qquad (1)$$

Here the Hamiltonian H_i describes the system in the initial state, which corresponds to the electron being in the ion A^{Z_1}. The term V_i represents the nondiagonal part of the electron and ion B^{Z_2} interaction, which is the cause of the electron transfer from ion A^{Z_1} to ion B^{Z_2}. Similarly, the Hamiltonian H_f describes the system in the final state, which corresponds to the electron in the ion B^{Z_2}, and V_f represents the nondiagonal part of the electron and ion A^{Z_1} interaction, causing the backward reaction.

The problem is to calculate the total probability of the transition between the states of the Hamiltonian H_i and H_f. By using the Born-Oppenheimer approximation in order to separate the electron and nuclear motions (including the inertia polarization fluctuations of the solvent) in the initial and final states, it is possible to introduce the concept of the electron terms (*i. e.* the potential energy surfaces) in the initial and final states U_i and U_f. The function U_i describes the dependence of the potential energy of the system in the initial state on the normal coordinates of all degress of the freedom of the solvent and does not include the interaction V_i of the electron with the ion B^{Z_2}. By analogous way, U_f describes the potential energy of the system in the final state and does not include the interaction V_f. The mutual arrangement of the potential energy surfaces depends on the electron state. The potential energies U_i and U_f for the ground and also for the first excited electron states in the ions A^{Z_1} and B^{Z_2} are shown schematically (as functions of one normal coordinate of the solvent) in Fig. 1. Since the electron excitation energies in the ions are very large ($\sim$ eV), the excited electron states may usually be neglected and one may consider the potential energy surfaces only for the ground electron states[1].
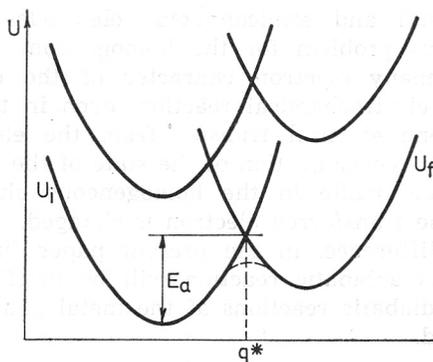
Fig. 1. The potential energy surfaces of the initial and final states for the ground and excited states of the electron in the ions A^{z1} and B^{z2} (the section along one of the normal coordinates of the solvent).

Depending on the properties of the specific system the different methods are convenient to use for the calculation of the transition probability. If the interactions V_i and V_f are small enough, the usual perturbation theory may be applied. For this case in the framework of the developed model of solvent[2] the correct quantum-mechanical calculation of the transition probability W_{if} can be carried out[3]. The expression derived for W_{if} in the case of the simple electron transfer reaction proved to be formally the same as in the absolute reaction rate theory[4]

$$W_{if} = \frac{kT}{h} \varkappa e^{-\frac{Ea}{kT} + \frac{Sa}{k}}$$

In this case the activation energy E_a proved to be determined by the saddle point on the intersection of the initial and final potential energy surfaces (Fig. 1). The transmission coefficient is determined by the formula[5]

$$\varkappa = \frac{2 |V_{if}|^2}{V_{cr}^2}$$

where $V_{if} = \int \varphi_i V_i \varphi_f \, dr$. Here φ_i and φ_f are the wave functions of the initial and final ground states of all the quantum subsystems. In the case under consideration when the quantum subsystem includes only the electrons, φ_i and φ_f represent the electron wave functions. The general expression for the critical value of the exchange integral V_{cr} and the formulae for the various specific cases are given[5,6]. Formula (3) is valid only in the case when the transmission coefficient is less than unity, $i.\,e.$ when the reaction is nonadiabatic. For these reactions the transmission coefficient determines the transition probability of the system from one (ground) initial potential energy surface U_i to one (ground) potential energy surface of the final state U_f after two-fold passing the system through their intersection region.

If the solvent polarization fluctuations are purely classical, one may use for the calculation the semiclassical method, which represents some generalization of the Landau-Zener method for the case of multidimensional terms, and is valid[5] both for the small and for the relatively large values of the interactions V_i and V_f. For small interaction values the results derived by this method coincide with those obtained in the framework of the perturbation theory.

For large interaction values, when $|V_{if}| > V_{cr}$, the calculation gives $\varkappa = 1$, $i.\,e.$ the reaction is adiabatic. However the semiclassical method leads to the same value of the activation energy as for the nonadiabatic reaction, $i.\,e.$ the activation energy is determined by the minimal energy on the intersection of the potential energies U_i and U_f. As it will be shown below this value may be somewhat higher than the correct activation energy. This difference is connected with the classical description of the motion along the coordinates of solvent, which is not valid in the energy region corresponding to the intersection point of the potential energy surfaces, where the quantum effects become essential.

To obtain the correct result for very large values of interactions V_i and V_f the quantum-mechanical consideration of this motion is necessary. However, because of the mathematical complexity of this problem for multi-dimensional potential energy surfaces of the rather arbitrary form, it has not yet been solved.

We succeeded in obtaining an exact solution of this problem for the model system of onedimensional potential energy curves, which may be considered as linear terms in the range of their intersection point

$$U_i = Fq; \qquad U_f = -F'q \qquad (4)$$

The expressions for the transition probability $P(E)$ from the initial to the final states at fixed energy E are different depending on the values of the dimensionless parameters

$$v = \frac{E}{\Delta E} ; \qquad S = \frac{2 \, | \, V_{if} \, | \, (FF')^{\frac{1}{2}}}{\Delta E \cdot (F + F')} ; \qquad \gamma = \frac{S^2}{8 \, \sqrt{\, | \, v \, |}} \qquad (5)$$

where

$$\Delta E = \left(\frac{\hbar^2}{2 \, m} \right)^{1/3} \cdot \left(\frac{1}{F} + \frac{1}{F'} \right)^{-2/3}$$

The expression for the total transition probability averaged over E may be written in the form of eq. (2), where the values of $\varkappa$ and E_a depend on the parameters $\lambda = \dfrac{kT}{\Delta E}$, S and γ_T, where γ_T is obtained from γ by substitution kT instead E.

It was found that in the region $\gamma \gg 1$ and $\gamma_T \ll 1$ the reaction is non-adiabatic ($\varkappa \ll 1$), and the activation energy is determined by the intersection point of the initial (U_i) and the final (U_f) terms. If the conditions $S^4 \gg \lambda \gg \gg S \gg 1$ ($\gamma_T \gg 1$) are fulfilled, the transmission coefficient becomes equal to unity, *i. e.* the reaction is adiabatic. However, as previously, the activation energy is determined by the intersection point of the terms U_i and U_f. Provided the conditions $S \gtrsim \lambda$, $\lambda \gg \dfrac{1}{\sqrt{S}}$ are fulfilled, the activation energy is diminished by $2 \, | \, V_{if} \, | \, (FF')^{1/2} (F + F')^{-1}$ in comparison with the value for E_a obtained by the semiclassical method. In this case the activation energy corresponds to the highest point of the potential barrier on the total potential energy surface (dashed curve in Fig. 1), taking account of the interaction of the electron with both ions.

It should be emphasized that these results were obtained by means of the rigorous quantum-mechanical calculation without making use of the perturbation theory.

The physical picture of the electron transfer process for the homogeneous reaction is as follows. Owing to the fluctuations of the solvation shells of the ions, *i. e.* as the values of the normal coordinates of solvent q_i are varying, the positions of the electron energy levels in the ions are also varying. At the values of the normal coordinates q^*, corresponding to the intersection of the potential energy surfaces, the electron energy levels in both ions become equal to one another, and the electron transition from one ion to another takes place.

Thus, in the case of the homogeneous reaction the main contribution to the probability of the elementary act of the reaction is due to the transitions of the system between the lowest initial and final potential energy surfaces, which correspond to the initial and the final states of the transferred electron.

2. Reactions at Metal Electrodes

In the case of the reaction of electron transfer from the metal electrode to an ion in solution the situation is quite different. Since the electron spectrum in the metal is practically continuous the spacing of the potential energy surfaces of the initial and final states, corresponding to different excited electron states in the metal, is very small (Fig. 2), so that there are practically continuous sets of the potential energy surfaces both in the initial and in the final states.
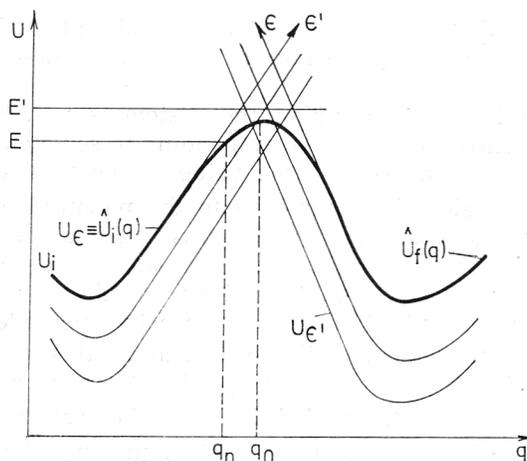
Fig. 2. The potential energy surfaces of the initial and final states for various excited states of the electrons in the metal. The solid curve represents the effective trajectory of the transition to the final state in the case of an *adiabatic* reaction at metal electrode.

Each final state differs from any initial one in that one electron has been transferred from metal to ion. It will be seen below that even in the approximation of the noninteracting electrons due to the transition of electron to the ion the change of the state of considerable number of the electrons in the metal can take place. Thus various potential energy surfaces in the initial and final states differ one from another not only in the energy of the transferred electron but also in the distribution of other electrons over the energy levels in the metal (in particular in the total electron energy in the metal).

It has been shown[1] that if there are several potential energy surfaces in the system their spacing being small, the transitions between various pairs of surfaces, in general, influence one another. However, it has been also shown[1] that under certain conditions the transitions between each pair of the surfaces may be considered as independent ones.

It is quite evident that in the case of the electrochemical reaction the transition between any potential energy surface of the initial state and any surface of the final state is always nonadiabatic. This is due to the delocalized electrons in the metal and hence the electron exchange integral V_{if} is small compared with $1/\sqrt{\Omega}$, where Ω is the volume of the electrode ($\Omega \rightarrow \infty$).

However, owing to the high electron state density in the electrode ($\sim \Omega$) the process as a whole, under sufficiently large values of the interaction between the electron in the electrode and that in the ion, can be similar to the adiabatic homogeneous reaction in the sense that the expression for the averaged transition probability is similar to eq. (2) with the transmission coefficient $\varkappa$ being equal to unity. However, it should be emphasized that the detailed physical picture of the transition is quite different.

The calculation will be carried out using the semiclassical method in the assumption that the polarization fluctuations of the solvent may be described classically.

At first we shall calculate the transition probability of the system to any potential energy surface as the result of a single transition of the system

through the region of the intersection of the initial and final potential energy surfaces, while moving along the normal coordinates, describing the solvent polarization state (Fig. 2).

Far from the intersection region the system is moving on one of the initial terms U_ε (»entrance« term), corresponding to some electron distribution in the metal $\{n_i^o\}$ and hence to some value of the total electron energy ε. In the intersection region the transitions to the potential energy surfaces of the final state become possible. If such transition has occured at the intersection point of the term U_ε and of some term of the final state $U_{\varepsilon'}$, in further moving along the coordinate q the transition from the term $U_{\varepsilon'}$ to some other term of the initial state, is in principle possible etc.

To describe the movement of the system along this set of the terms, we introduce the probability densities $r(\varepsilon, \varepsilon', \{n_i^o\})$ and $r'(\varepsilon, \varepsilon' \{n_i^o\})$. The quantity $r(\varepsilon, \varepsilon' \{n_i^o\}) d\varepsilon$ is the probability that the system reaches the intersection point $(\varepsilon, \varepsilon')$ of the terms $U_{\varepsilon'}$ and U_ε, moving along either term of the initial state, corresponding to the total electron energy in the metal in the interval from ε to $\varepsilon + d\varepsilon$, provided that at first the system was moving along the entrance term, corresponding to the electron distribution in the metal $\{n_i^o\}$. In a similar fashion $r'(\varepsilon, \varepsilon', \{n_i^o\}) d\varepsilon'$ is the probability of that the system reaches the point $(\varepsilon, \varepsilon')$ along either term of the final state in the energy interval $d\varepsilon'$. Considering the change of the probability $r(\varepsilon, \varepsilon', \{n_i^o\}) d\varepsilon$ in the interval from ε' to $\varepsilon' + d\varepsilon'$, one can obtain the differential equation for $r(\varepsilon, \varepsilon', \{n_i^o\})$:

$$\frac{\partial r(\varepsilon, \varepsilon', \{n_i^o\})}{\partial \varepsilon'} = \varkappa \varrho(\varepsilon^*)[1 - n^o(\varepsilon^*)] r'(\varepsilon, \varepsilon', \{n_i^o\}) - \varkappa \varrho(\varepsilon^*) n^o(\varepsilon^*) r(\varepsilon, \varepsilon', \{n_i^o\}) \qquad (6)$$

The second term in the right side of eq. (6) describes the reduction of $r(\varepsilon, \varepsilon', \{n_i^o\})$ due to transitions to the terms of the final state. The first term describes the increase of $r(\varepsilon, \varepsilon', \{n_i{}^o\})$ due to backward transitions. Here $\varrho(\varepsilon^*)$ and $n^o(\varepsilon^*)$ are the one electron density of states and the probability of the level ε^* in the metal, from (or to) which the electron transfer at the given values of ε and ε' is possible, being occupied by electron, respectively. The requirement of the conservation of the total probability leads to

$$\frac{\partial r'(\varepsilon, \varepsilon' \{n_i^o\})}{\partial \varepsilon} = \frac{\partial r(\varepsilon, \varepsilon', \{n_i^o\})}{\partial \varepsilon'} \qquad (7)$$

As the electron transfer to the ion or back is possible provided the levels in the metal and in the ion are equal, and since the position of electron level in the ion depends on the solvent polarization, i. e. on q, it is clear that the position of the level ε^* will also depend on the q, and in the coordinates $(\varepsilon, \varepsilon')$ it will depend only on the difference $\varepsilon - \varepsilon'$. The origin of the coordinates for the energies ε and ε' is convenient to be chosen so that for the entrance term the equation $\varepsilon = 0$ be fulfilled ,and the relationship

$$\varepsilon^* - \varepsilon_F = \varepsilon - \varepsilon' \qquad (8)$$

be valid, where ε_F is the Fermi level, since the potential energy surfaces of the initial and final states can be written as

$$U_\varepsilon = \hat{U}_i + \varepsilon; \quad U_{\varepsilon'} = \hat{U}_f + \varepsilon'$$

In this case the boundary conditions to the eqs. (6)—(7) have a form

$$\varepsilon > 0 \qquad r(\varepsilon, \varepsilon', \{n_i^o\}) = r'(\varepsilon, \varepsilon', \{n_i^o\}) = 0$$

$$\varepsilon' \to -\infty \qquad r(\varepsilon, \varepsilon', \{n_i^o\}) \to \delta(\varepsilon); \quad r'(\varepsilon, \varepsilon', \{n_i^o\}) \to 0 \qquad (9)$$

Now we introduce the probability densities $r(\varepsilon, \varepsilon')$ and $r'(\varepsilon, \varepsilon')$ averaged over the initial distribution of the electrons in the metal $\{n_i^o\}$ at fixed values of ε and ε'. The equations and the boundary conditions for the averaged probability densities have the same form as those for the unaveraged ones with the substitution the Fermi distribution function $f(\varepsilon^*)$ instead of $n^o(\varepsilon^*)$:

$$f(\varepsilon^*) = \left[1 + \exp\frac{\varepsilon^* - \varepsilon_F}{kT}\right]^{-1} \qquad (10)$$

$$\frac{\partial r(\varepsilon, \varepsilon')}{\partial \varepsilon'} = \frac{\partial r'(\varepsilon, \varepsilon')}{\partial \varepsilon} = \varkappa \varrho [1 - f(\varepsilon^*)] r'(\varepsilon, \varepsilon') - \varkappa \varrho(\varepsilon^*) f(\varepsilon^*) r(\varepsilon, \varepsilon') \qquad (10a)$$

$$\varepsilon > 0 \qquad r(\varepsilon, \varepsilon') = r'(\varepsilon, \varepsilon') = 0$$

$$\varepsilon' \to -\infty \qquad r(\varepsilon, \varepsilon') \to \delta(\varepsilon); \quad r'(\varepsilon, \varepsilon') \to 0 \qquad (10b)$$

For metals the dependence of $\varkappa$ and ϱ on ε and ε' in these equations may be neglected since they vary more smoothly that the Fermi function does.

The solutions of these equations are

$$r(\varepsilon, \varepsilon') = -\frac{\partial g}{\partial \varepsilon}; \quad r'(\varepsilon, \varepsilon') = -\frac{\partial g}{\partial \varepsilon'} \qquad (11)$$

Here

$$g(\varepsilon, \varepsilon') = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{dz}{z} e^{-\frac{\varepsilon z}{kT}} \; F(\varkappa \varrho kT, z, 1 + \varkappa \varrho kT + z; -e^{\frac{\varepsilon' - \varepsilon}{kT}}) \qquad (12)$$

where $F(a, b, c; y)$ is the hypergeometric function.

The general expressions (11—12) are simplified in two limiting cases.

a) Nonadiabatic Reactions

Let the nonequality

$$\varkappa \varrho kT \ll 1 \qquad (13)$$

be fulfilled. In this case the solutions (11—12) can be written in the form

$$r(\varepsilon, \varepsilon') \simeq \delta(\varepsilon) \{1 - \varkappa \varrho kT \ln(1 + e^{-\frac{\varepsilon'}{kT}})\}$$

$$r'(\varepsilon, \varepsilon') \simeq \Theta(-\varepsilon) \varkappa \varrho f(-\varepsilon' + \varepsilon_F) \qquad (14)$$

These expressions are valid provided $\varkappa \varrho \varepsilon' \ll 1$ and mean that in this interval of ε' the system with the probability approximately equal to unity is moving along the coordinate q on the *entrance* term, corresponding to the Fermi distribution of the electrons in the metal. The probability of the transitions to the other final terms are small even after passing the system across the

whole intersection region of the initial and final terms. The above result corresponds to the independent onefold transitions from *entrance* term to the terms of the final state, *i. e.* corresponds to the independent transitions of the electrons from each level in the metal to the ion.

Averaging over the total energy of the system gives the expressions for the probability of the elementary act of the reaction (or for current density) which are identical with those derived earlier for the nonadiabatic electrochemical reactions[6,7].

b) Adiabatic Reactions

The reverse limiting case corresponds to the condition

$$\varkappa \varrho\, kT \gg 1 \tag{15}$$

being fulfilled. The formulae have the simplest form in the limit

$$\varkappa \varrho\, kT \to \infty \tag{16}$$

In this case one obtains from eqs. (11)—(12)

$$r\,(\varepsilon, \varepsilon') = \beta\, e^{\beta\varepsilon}\; \delta\,(1 - e^{\beta\varepsilon} - e^{\beta\varepsilon'}) \tag{17}$$

$$r'\,(\varepsilon\, \varepsilon') = \beta\,(1 - e^{\beta\varepsilon})\, \delta\,(1 - e^{\beta\varepsilon} - e^{\beta\varepsilon'}) \tag{18}$$

where $\beta = 1/kT$.

Thus in this limit $r\,(\varepsilon, \varepsilon')$ and $r'\,(\varepsilon, \varepsilon')$ are not zero only on the curve (Fig. 2)

$$e^{\beta\varepsilon} + e^{\beta\varepsilon'} = 1 \tag{19}$$

The physical meaning of the result derived is that in this case the manyfold transitions of the system between the terms of the initial and final states take place.

If the parameter $\varkappa \varrho\, kT$ is a large, but finite number, *i. e.* if the nonequality (15) is fulfilled, the expressions for $r\,(\varepsilon, \varepsilon')$ and $r'\,(\varepsilon, \varepsilon')$ are more cumbersome. However, it can be shown that in this case $r\,(\varepsilon, \varepsilon')$ and $r'\,(\varepsilon, \varepsilon')$ are also essentially nonzeroth only in small region near the line (19). Near this line they can be approximated by the expressions:

$$r\,(\varepsilon, \varepsilon') \simeq \sqrt{\frac{\varkappa \varrho}{4\,\pi\, kT\, \eta\,(\eta + 1)}}\; \exp\left\{-\varkappa \varrho\, kT\, \frac{(X - X_{max})^2}{4\,(1 + \eta)}\right\} \tag{20}$$

$$r'\,(\varepsilon, \varepsilon') \simeq \eta \cdot r\,(\varepsilon, \varepsilon') \tag{21}$$

where

$$X = e^{-\beta\frac{\varepsilon + \varepsilon'}{2}}\,;\quad X_{max} = \frac{\eta + 1}{\sqrt{\eta}}\,;\quad \eta = e^{\beta\,(\varepsilon' - \varepsilon)} \tag{22}$$

It should be noted that $r\,(\varepsilon, \varepsilon')$ and $r'\,(\varepsilon, \varepsilon')$ differ essentially from zero in the narrow band, the width of which near the maximum of the curve (19) is much smaller than kT. Thus in this case the system is also moving practically along the »trajectory« determined by eq. (19). The equation of this trajectory in the coordinates (U, q) has a form

$$U = \check{U}_i(q) + \frac{1}{\beta} \ln \frac{e^{\beta \check{U}_f(q)}}{e^{\beta \check{U}_i(q)} + e^{\beta \check{U}_f(q)}} \qquad (23)$$

where $\check{U}_i(q)$ is the potential energy surface of the initial state corresponding to the Fermi distribution of the electrons in the metal, $\check{U}_f(f)$ is the potential energy surface of the final state corresponding to the electron distribution in the metal, for which the total energy of the electrons is smaller than the total electron energy for the Fermi distribution by the Fermi energy ε_F.

Thus, if the total energy of the system E does not exceed the value of the energy at the upper point of the trajectory (23) (Fig. 2), the motion of the system will be reversed at the point q_n (Fig. 2) and the system will return to the initial state, i. e. the total probability of the transition to the final state for these values of the energy is equal to zero. The energy is above $U(q_0)$, the system will go to the final state with the probability equal to unity. In this case the process as a whole can be refered to as an adiabatic one. However unlike the homogeneous reaction this adiabatic transition occurs owing to the manyfold nonadiabatic transitions between large number of the initial and final terms.

Physical picture of the process is as follows. Due to the variation of the values of the normal coordinates of the solvent (including the polarization fluctuations) the electron energy level in the ion is lowered and passes through the electron levels in the metal. Thereby the electron transition from some level to the ion becomes possible, which leads to the transition of the system to one of the terms of the final state. In further lowering the electron level in the ion the backward transition from the ion to a lower unoccupied level in the metal is possible, which leads to the transition of the system to the another term of the initial state etc.

3. Reactions at Semiconductor Electrodes

Considering redox reactions at the semiconductor electrode one should distinguish two possible processes: 1) the electron exchange between the ion and the zones of the semiconductor, and 2) the electron exchange between the ion and the local surface states of the semiconductor. In this section the first process is considered.

The main difference in considering such processes from the electron exchange processes at the metal electrode is that for the semiconductor the dependence of the state density ϱ on ε^* may not be neglected. This is due to the fact that the Fermi level in the semiconductor lies in the forbidden zone where $\varrho \equiv 0$. Hence the small regions near the edges of the valence and conduction bands, where ϱ approaches to zero rather sharply, are of essential importance.

The general equations for the probability densities $r(\varepsilon, \varepsilon')$ and $r'(\varepsilon, \varepsilon')$ and boundary conditions are also given by (10a)—(10b). However, the density of states ϱ is not constant now, but has a form qualitatively shown in Fig. 3. In this case the parameter essentially influencing the character of the process is also $\varkappa \varrho kT$. Here ϱ means some intermediate value of the state densities near the edges of the zone, which will be given below.
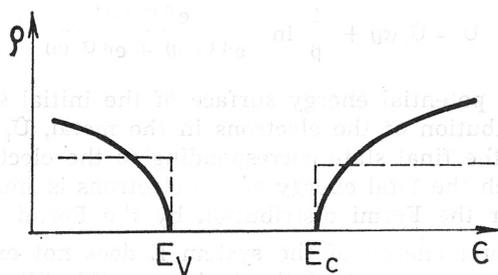
Fig. 3. The state density for the electrons in the semiconductor.

1) Nonadiabatic Transition. — Let the condition (13) be fulfilled. In this case the solution can be obtained in the same manner as in the case of the metal electrode in previous section, but here we shall give another derivation leading to more general results. The results of **the previous section show that** under condition (13) the backward transitions (from the terms of final state to the terms of the initial state) can be neglected. Omitting the first term in the right side of eq. (10a) and integrating, one has for $r(\varepsilon\,\varepsilon')$ and $r'(\varepsilon,\varepsilon')$

$$r(\varepsilon, \varepsilon') \simeq \delta(\varepsilon) \exp\left\{-\varkappa \int_{-\infty}^{\varepsilon'} \varrho\, f(-\varepsilon'' + \varepsilon_F)\, d\varepsilon''\right\} \tag{24}$$

$$r'(\varepsilon, \varepsilon') \simeq \Theta(-\varepsilon)\, \varkappa\, \varrho\, f(-\varepsilon' + \varepsilon_F) \exp\left\{-\varkappa \int_{-\infty}^{\varepsilon'} \varrho\, f(-\varepsilon'' + \varepsilon_F)\, d\varepsilon''\right\} \tag{25}$$

These expressions in general form are valid both for the semiconductor and for the metal electrodes. In part, the expansion of the exponentials in the power series gives expression (14).

Since in this case the probability of transition to the terms of the final state is small, the total probability $W(E)$ of the transition to the terms of the final state after twofold passing the intersection region of the terms at the fixed energy of the system E, may be assumed equal to the double transition probability after onefold passing the intersection region in the positive direction of the q-axis up to the turning point $\hat{q}$

$$W(E) = 2 \int_{-\infty}^{\overset{\wedge}{\varepsilon'}} r'(\varepsilon, \varepsilon')\, d\varepsilon' \tag{26}$$

where the integration goes to the level $\underset{v}{\varepsilon'}$, determined by the equation

$$E = \hat{U}_i(q) = \hat{U}_{\varepsilon'}\overset{\wedge}{(q)} \tag{27}$$

and $r'(\varepsilon, \varepsilon')$ is determined by eq. (14). Averaging the probability $W(E)$ over energy E leads to the following expression for the reaction rate constant or for the current density $\vec{i}$

$$\vec{i} = e\, C_s \int \varrho(\varepsilon)\, f(\varepsilon)\, W(\varepsilon)\, d\varepsilon \tag{28}$$

where C_s is the surface concentration of the oxidizer, $W(\varepsilon)$ is the probability of the elementary act of the electron transfer from the level ε in the electrode

to the ion. Formally this expression is identical with the analogous expression for the metal electrode[6,7], but actually the integral in (28) splits into two integrals (over the valence and conduction bands), i. e. the total current density $\vec{i}$ splits into two currents, one the electron and the other the hole current: $\vec{i} = \vec{i^e} + \vec{i^p}$. The experimentally observed transfer coefficients: $\alpha^e_{exp} = -$ $- d \ln i^e / d e \eta / kT$ and $\alpha^p_{exp} = - d \ln i^p / d e \eta / kT$ can be related to the mean values of the microscopic transfer coefficiens $\alpha^e = - d E^e_a / d \Delta J_{if}$ and $\alpha^p = -$ $- d E^a_e / d \Delta J_{if}$, or to the mean value of the occupation of the electron levels, as it was in the case of the metal electrode. However, it is now necessary to take into account the dependence of state density on ε near the edges of the zones:

$$\varrho_e \sim (\varepsilon - E_c)^{1/2}; \quad \varrho_p \sim (E_V - \varepsilon)^{1/2}$$

For example the expression for α^e_{exp} has a form

$$\alpha^e_{exp} = \langle \alpha^e(\varepsilon) \rangle + \left\langle \frac{kT}{2(\varepsilon - E_c)} \right\rangle \cdot \left(1 - \frac{d \eta_c}{d \eta} \right) \tag{29}$$

or

$$\alpha^e_{exp} = 1 - \langle f(\varepsilon) \rangle - \left\langle \frac{kT}{2(\varepsilon - E_c)} \right\rangle \cdot \frac{d \eta_c}{d \eta} \tag{30}$$

where η_c is the overvoltage at the contact, and $< \ldots >$ denotes averaging over the partial currents $i^e(\varepsilon) \, d\varepsilon$. Thus unlike the metals the value α_{exp} for the semiconductor is not equal to the mean value $< \alpha(\varepsilon) >$ of the microscopic transfer coefficient.

The main contributions to the integrals over ε for electron and hole currents are due to the transitions from small groups of the levels in the semiconductor near some levels ε^*_e and ε^*_e. To determine values ε^*_e and ε^*_p one should take into account the dependence of ϱ_e and ϱ_p on ε. The criterium of and adiabatic and nonadiabatic course of the process contains the values $\varrho_e(\varepsilon^*_e)$ and $\varrho_p(\varepsilon^*_p)$.

2) *Adiabatic transition.* — Let the condition (15) is fulfilled. To solve the equations (10a) we assume one simplification. The dependence of ϱ_e and ϱ_p on ε within the zones will be neglected, i. e the function $\varrho(\varepsilon)$ will be replaced by the model one (see dashed curve in Fig. 3). Then for the values $\varepsilon - \varepsilon'$, corresponding to those of ε^* in the conduction band (see eq. (8)), the equations and boundary conditions are determined by eqs. (10a — 10b). The solution in this region is described by eqs. (11 — 12). For the values of $\varepsilon - \varepsilon'$, corresponding to those of ε^* in the forbidden zone, the equations are simplified. In this region the equation for the Laplace transform $G(p, \varepsilon' - \varepsilon)$ of the function $g(\varepsilon, \varepsilon')$ (see eq. (II)) has a form

$$\frac{d^2 G}{d y^2} + p \frac{d G}{d y} = 0 \tag{31}$$

where $y = \varepsilon' - \varepsilon$. The solution of this equation

$$G = a_1(p) e^{-py} + b_1(p) \tag{32}$$

should be conjugated with the solution in the conduction band at the point $y = -E_c + \varepsilon_F$ (E_c is the edge of the conduction band). The coefficients a_1 (p) and b_1 (p) can be determined by using the conditions of the solution and its derivative continuity. As a consequence the solution corresponding to the forbidden zone has a form

$$g(\varepsilon, \varepsilon') = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{dp}{p} e^{-p\varepsilon} \left[F\left(\frac{p}{\beta}, \varkappa \varrho\, kT, 1 + \frac{p}{\beta} + \varkappa \varrho\, kT; -e^{\beta(\varepsilon_F - E_c)}\right) + \right.$$

$$+ \frac{\varkappa \varrho}{\varkappa \varrho + \beta + p} e^{\beta(\varepsilon_F - E_c)} \{e^{+p(\varepsilon - \varepsilon' + \varepsilon_F - E_c)} - 1\} \times$$

$$\left. \times F\left(1 + \frac{p}{\beta}, 1 + \varkappa \varrho\, kT, 2 + \frac{p}{\beta} + \varkappa \varrho\, kT; -e^{+\beta(\varepsilon_F - E_c)}\right) \right] \qquad (33)$$

In the region corresponding to the valence band the solution for $G(p, \varepsilon' - \varepsilon)$ is

$$G(p, \varepsilon' - \varepsilon) = a_2(p)\, F\left(\frac{p}{\beta}, \widetilde{\varkappa \varrho}\, kT, 1 + \frac{p}{\beta} + \widetilde{\varkappa \varrho}\, kT; -e^{+\beta(\varepsilon' - \varepsilon)}\right) +$$

$$+ b_2(p)\, (-e^{\beta(\varepsilon' - \varepsilon)})\frac{p}{\beta} + \widetilde{\varkappa}_2\, kT \; F\left(-\frac{p}{\beta}, -\widetilde{\varkappa \varrho}\, kT, 1 - \frac{p}{\beta} - \widetilde{\varkappa \varrho}\, kT; -e^{\beta(\varepsilon' - \varepsilon)}\right) \qquad (34)$$

where $\widetilde{\varkappa \varrho}$ denotes the value of $\varkappa \varrho$ in the valence band, and the coefficients $a_2(p)$ and $b_2(p)$ are determined by the conditions of the conjugation with eq. (33). In the limit $\varkappa \varrho\, kT \to \infty$ these expressions are simplified and $r(\varepsilon, \varepsilon')$ and $r'(\varepsilon, \varepsilon')$ were proved not to be zero only along the certain curves (Fig. 4). In the conduction band $r(\varepsilon, \varepsilon')$ and $r'(\varepsilon, \varepsilon')$ are not zero along the curve determined by eq. (19) as for metals. In the forbidden zone the curves where
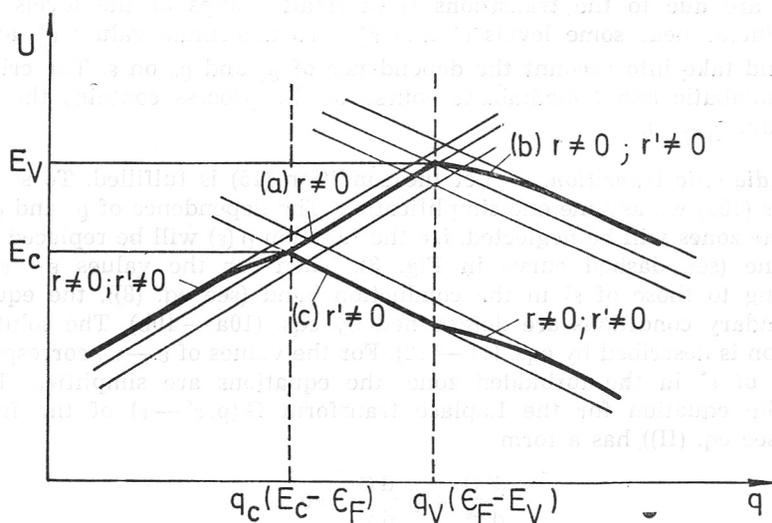
Fig. 4. The diagram of the potential energy surfaces and the effective trajectories of the transition in the case of an *adiabatic* reaction at the semiconductor electrode. The points q_c and q_v show the positions of the bottom of the conduction band and the top of the valence band.

$r(\varepsilon, \varepsilon')$ and $r'(\varepsilon, \varepsilon')$ are not zero are different. In the forbidden zone $r(\varepsilon, \varepsilon')$ is not zero along the curve

$$e^{\beta \varepsilon} + e^{\beta(\varepsilon - \Delta_e)} = 1 \tag{35}$$

and $r'(\varepsilon, \varepsilon')$ is not zero along the curve

$$e^{\beta \varepsilon'} + e^{\beta(\varepsilon' + \Delta_e)} = 1 \tag{36}$$

where $\Delta_e = E_c - \varepsilon_F$. In the valence band $r(\varepsilon, \varepsilon')$ and $r'(\varepsilon, \varepsilon')$ are not zero along two curves

$$e^{\beta \varepsilon} + e^{\beta \varepsilon'} = \frac{1 + e^{\beta \Delta_p}}{1 + e^{-\beta \Delta_e}}$$

$$e^{\beta \varepsilon} + e^{\beta \varepsilon'} = \frac{1 + e^{-\beta \Delta_p}}{1 + e^{\beta \Delta_e}} \tag{37}$$

where $\Delta_p = \varepsilon_F - E_V$.

The physical picture of the transition is as follows. As the system is moving along the coordinate q (in the left of the point q_c in Fig. 4) the manyfold transitions between the terms of the initial and final states take place that corresponds to the electron transfer from the conduction band to the ion and back to the conduction band. If the system reaches the point q_c, corresponding to the edge of the conduction band, on the initial term (i. e. the electron level in the ion is not occupied) it will be further moving along this term up to the point q_V (curve a in Fig. 4), corresponding to the edge of the valence band, since the electron level in the ion, lying in the forbidden zone, the transitions are impossible. After passing the point q_V the transitions between the terms of the initial and final states, corresponding to the manyfold electron exchanges between the valence band and the ion, are possible again (curve b in Fig. 4). If the system reaches the point q_c along one of the terms of the final state, it will move along this term up to the point q_V. After passing this point the transitions between the initial and final terms become possible again (curve c in Fig. 4). The probability of the system going along the upper trajectory after reaching the point q_c is equal to $f(E_c)$. The probability of the system going along the lower trajectory after the point q_c is equal to $1 - f(E_c)$, i. e. the ratio of these probabilities is determined by that of the electron and hole concentrations at the edge of the conduction band.

In averaging over the energy one should take into account that if the system is moving along the lower trajectory at the energy $E < E_c$, the transition probability is equal to zero, i. e. the system will reverse to the initial state. At the energies $E > E_c$ the transition probability to the final state is equal to unity. For the system moving along the upper trajectory the transition to the final state occurs provided $E > E_V$. Taking account of the probability of one or another trajectory one obtains for the averaged probability of the elementary act of the reaction the following expression

$$W_{if} = \frac{\omega_{eff}}{2\pi} \left[f(E_c) e^{-\frac{E_a^e}{kT}} + \{1 - f(E_c)\} e^{-\frac{E_a^p}{kT}} \right] \tag{38}$$

where E_a^e and E_a^p are the activation energies for the transition of the electron from the bottom of the conduction band and the top of the valence band, respectively.

4. *The Electron Exchange in the Presence of the Surface States*

The electron exchange is possible between the ion and surface states if these are present. In the steady state this process must consist of two steps: 1) the electron exchange between the ion and the surface level, and 2) the electron exchange between the surface level and the bands.

Depending on the rate of each step, one step or another will be slow. Firstly, the case will be considered when the electron exchange between the surface levels and the ion is slow enough. It will be assumed for simplicity that there is only one surface level at the energy E_l in the gap. Generalization to the surface zone is not difficult.

Several different cases can take place.

1) Let the process as a whole be nonadiabatic. It is so provided the conditions (13) are fulfilled for the conduction and valence bands, and also the condition

$$\varkappa_l \ll 1 \tag{39}$$

is fulfilled, where $\varkappa_l$ is the transmission coefficient for the electron transfer from the surface level to the ion. In this case the expression (28) for the current is formally valid, but in integrating over the electron spectrum one should take into account that in the forbidden zone $\varrho(\varepsilon)$ is not zero and is proportional to $\varrho(\varepsilon) \sim N_l \, \delta(\varepsilon - \varepsilon_l)$, where N_l is the surface state concentration. This leads to that besides the electron and hole components in the total current, the term $\overrightarrow{i_l}$ arises, which is due to the nonadiabatic transitions of the electron from the surface level:

$$\overrightarrow{i_l} \sim N_l \cdot W(E_l) \cdot f(E_l) \tag{40}$$

2) Let the condition (13) for the conduction and valence bands be fulfilled, but the condition (39) be violated, *i. e.* the transition from the surface level is an adiabatic one. In this case the transition goes as follows. In the region $q < q_c$ (Fig. 5) the system with the probability approximately equal
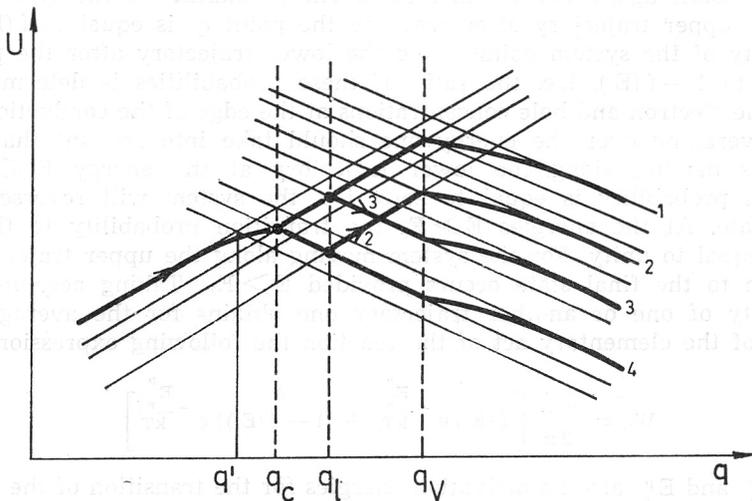
Fig. 5. The diagram of the potential energy surfaces and the effective trajectories of the transition in the case of an *adiabatic* reaction at the semiconductor electrode in the presence of the surface states; q_l shows the position of the surface level.

to unity is moving along the *entrance* term. The transitions to the terms of the final state occur with a small probability. In the absence of the surface level these lead directly to the transition of the system to the final state, *i. e.* they fully determine the value of the electron current. Now the situation is quite different. Let us assume that in some point q' the transition of the system to the term of the final state has occurred. After the transition the system is moving along the final term up to the point q_l where the electron energy level in the ion is equal to that of the surface state. If the surface state is not occupied, the backward transition of the electron will occur with the probability equal to unity and the system will return to the initial state. If the surface level is occupied, the system will go on moving along the final term and will go to the final state. Thus the factor $f(E_l)$, determining the probability of the surface level being occupied, must be introduced in the expression for the electron current.

In the region $q_c < q < q_V$, corresponding to the forbidden zone, the transitions to the terms of the final state are impossible and the system is moving along the entrance term. The surface level being occupied the transition to the term of the final state occurs at the point q_l with the probability equal to unity and after that the system is moving along this term to the final state. The current, which is due to these transitions, is described by eq. (40) with $\varkappa_l = 1$. If the surface level is not occupied the system goes on its movement along the entrance term, since in the region $q_l < q < q_V$ the transitions to the final terms are impossible. On the right from the point q_V the transitions to the final terms, determining the value of the hole current, are possible with a small probability. However the factor $1 - f(E_c)$, determining the probability of that in the point q_l the transition to the final state does not occur, must be introduced now in the expression for the hole current.

3) Let the condition (15) is fulfilled for the conduction and valence bands, and for the surface level the condition reversal to eq. (39) is fulfilled, *i. e.* the transition is adiabatic. In this case the transition will proceed as follows (Fig. 5). At $q < q_c$ the probabilities $r(\varepsilon, \varepsilon')$ and $r'(\varepsilon, \varepsilon')$ are not zero only near the curve (19). In the gap in the region $q_c < q < q_l$ the probability $r(\varepsilon, \varepsilon')$ is not zero along the line (35), and $r'(\varepsilon, \varepsilon')$ along the line (36). In the region $q_l < q < q_V$ the probability $r(\varepsilon, \varepsilon')$ is not zero along the line (35) and along the line

$$e^{\beta(\varepsilon - \Delta_l + \Delta_e)} + e^{\beta(\varepsilon - \Delta_l)} = 1 \tag{41}$$

too. The probability $r'(\varepsilon, \varepsilon')$ is not zero along the line (36) and along the line

$$e^{\beta(\varepsilon' + \Delta_l)} + e^{\beta(\varepsilon' - \Delta_e + \Delta_l)} = 1 \tag{42}$$

In the valence band (in the region $q > q_V$) the probabilities $r(\varepsilon, \varepsilon')$ and $r'(\varepsilon, \varepsilon')$ are not zero along four curves. Two curves are described by eqs. (37), and two others by the equations

$$e^{\beta\varepsilon} + e^{\beta\varepsilon'} = \frac{e^{\beta\Delta_p} + e^{\beta\Delta_l}}{1 + e^{\beta\Delta_e}}$$

$$e^{\beta\varepsilon} + e^{\beta\varepsilon'} = \frac{e^{-\beta\Delta_l}(1 + e^{-\beta\Delta p})}{1 + e^{-\beta\Delta e}} \tag{43}$$

Thus moving along the coordinate q the system can move along four trajectories, shown in Fig. 5. The probability of the system moving along some

trajectory is determined by the probabilities of occupation of the electron levels near the bottom of the conduction band $f(E_c)$ and the surface level $f(E_l)$. Thus the probabilities of the trajectories 1, 2, 3 and 4 are equal to

$$f(E_c) \cdot f(E_l); \quad [1 - f(E_c)] f(E_l); \quad f(E_c) [1 - f(E_l)] \quad \text{and} \quad [1 - f(E_c)] [1 - f(E_l)]$$

respectively. To obtain the transition probability averaged over the energy of the system one should take into account that the transition into the final state along a given trajectory occurs only provided the energy of the system is larger than the highest energy values for this trajectory. As a consequence one obtains for the averaged probability of the elementary act of the reaction the following expression

$$W_{if} = \frac{\omega_{eff}}{2\pi} \left\{ f(E_c) f(E_l) e^{-\frac{E_a^c}{kT}} + [1 - f(E_c)] f(E_l) e^{-\frac{\tilde{E}_a}{kT}} + \right.$$

$$+ f(E_c) [1 - f(E_l)] \exp\left[-\frac{E_a^c \cdot \Theta(E_c - \hat{E}) + \hat{E}_a \cdot \Theta(\hat{E} - E_c)}{kT} \right] +$$

$$\left. + [1 - f(E_c)] [1 - f(E_l)] \exp\left(-\frac{E_a^v}{kT} \right) \right\} \qquad (44)$$

Finally, let us consider the case of slow electron exchange between the surface states and the bands. Due to the interaction of the electron, occupying the surface level, with the medium, the position of the surface level depends strongly on the configurations of the molecules of the medium. The physical mechanism of the electron transfer process from the surface state to the band or back is similar to that of the electron exchange between the bands and the ion in the solution, and all the results obtained for the latter are valid also for the former with the substitution in the formulae of all the parameters of the ion to the corresponding parameters of the surface state. In particular, it should be noted that the lower is the energy of the surface state, the larger is the electron transfer probability from the conduction band to the surface level and the less is the electron transfer probability from the surface level to the ion.

REFERENCES

1. M. A. Vorotyntsev, R. R. Dogonadze, and A. M. Kuznetsov, *Fiz. Tverd. Tela* **12** (1970) 1605.
2. R. R. Dogonadze and A. M. Kuznetsov, *Elektrokhimiya* **7** (1971) 763.
3. M. A. Vorotyntsev, R. R. Dogonadze, and A. M. Kuznetsov, *Dokl. Akad. Nauk USSR* **195** (1970) 1135.
4. S. Glasstone, K. J. Laidler, and H. Eiring, *The Theory of Rate Processes,* New York, 1944.
5. R. R. Dogonadze and A. M. Kuznetsov, *Teor. Eksp. Khim.* **6** (1970) 298. R. R. Dogonadze and Z. D. Urushadze, *J. Electroanal. Chem.* **32** (1971) 235.
6. R. R. Dogonadze and A. M. Kuznetsov, *Electrochemistry: the Universal Science,* 1967 (Russian edition) (VINITI, Moscow, 1969).
7. R. R. Dogonadze and A. M. Kuznetsov, *Elektrokhimiya,* **7** (1971) 172.

IZVOD

Kinetika adiabatskih i neadiabatskih reakcija na metalnim i poluvodičkim elektrodama

R. R. Dogonadze, A. M. Kuznetsov i M. A. Vorotyntsev

Opisan je problem kvantno-mehaničkog izračunavanja vjerojatnosti elementarnog akta adiabatske reakcije prijenosa elektrona na metalnim i poluvodičkim elektrodama. Teorijskim razmatranjima pokazano je, da je osnovna razlika između homogenih i heterogenih reakcija u tome, što u prvom slučaju dolazi samo do promjene stanja prenesenog elektrona, dok u drugom dolazi do značajne reorganizacije mnogih elektrona u metalnoj ili poluvodičkoj elektrodi. Razmotreni su i adiabatički i neadiabatički procesi na poluvodičkim elektrodama uz prisustvo površinskih stanja.

INSTITUT ZA ELEKTROKEMIJU
AKADEMIJA NAUKA SSSR
MOSKVA, SSSR