# THEORY OF MOLECULAR ELECTRODE KINETICS

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## I. INTRODUCTION

In the past decade considerable progress has been made in the theory of electrode processes, both in understanding the physical mechanism of an elementary act and in obtaining quantitative data in calculations of the current and other kinetic parameters. Naturally, the theoretical results obtained at present are applicable only to a limited class of electrode reactions. It should be stressed, however, that some of the conclusions of the theory are of a general nature and valid for all reactions occurring under the conditions when the slow step of the process is the discharge or ionization of ions. On the other hand, the theoretically studied class of reactions is broad enough and their consideration is of great practical interest.

This paper is concerned with the quantum theory of electrode processes for reactions of two types:

(1) redox reactions involving electron exchange between electrode and ion in solution; and

(2) hydrogen ion discharge reactions.

Now we have at our disposal theoretical prerequisites for calculating even more complex electrode reactions, but here we shall confine ourselves to the description of semi-phenomenological theory based on rather general assumption (Section II). In spite of this theory being practically free of any assumptions about the nature of the model, it permits us to draw some very important conclusions regarding the nature of the course of an electrochemical reaction. On the other hand, for this semi-phenomenological theory to be complete, it is necessary to determine the parameters contained in it by comparing them with experimental data. With such a treatment, however, the true physical mechanism of the course of the electrochemical reaction remains unexplained. Therefore in two subsequent sections we shall proceed from a specific model for each component of the total system participating in the elementary act of ion discharge. Naturally, we shall thus lose some accuracy in the quantitative results of the theory, but in the author's opinion, the main object of the theory now is to elucidate the physical mechanism of the course of electrode reactions and to obtain fundamental qualitative results.

Among the assumptions about the model of the theory, the dielectric continuum model used by us to describe the solvent stands apart. As will be shown later, a polar solvent plays an important dynamic role in the charge transfer process. Apparently the importance of the medium in homogeneous electron transfer reactions in polar liquids was first stressed by Libby.[1] He pointed out that due to the fluctuation motion of the solvent atoms during electron transfer, the system has to pass through the Franck–Condon barrier. This idea was later developed and applied to various homogeneous charge transfer processes in polar liquids by Platzman and Franck,[2] who used a dielectric continuum model for the description of the solvent. It is of interest to note that it was the above authors[2] who suggested the possibility of applying the theory of radiationless transitions developed in the theory of polyatomic molecules[3] and polar crystals.[4] The radiationless transition theory was elaborated by Pekar,[4] Lax,[3] Huang, and Rhys,[5] Krivoglaz,[6] Fröhlich,[7] Kubo[8] and others. In fact analysis of different charge transfer processes in polar systems shows the physical mechanism to be quite similar in liquids and crystals. The first attempt to extend the theory to polar liquids was made by Davydov[9] and Deygen[10] in the investigation of the absorption spectra and electric conductivity of metal ammonia solutions. The most consistent theory of homogeneous redox reactions within the framework of the classical theory was given by Marcus.[11–12] Though the method used by Marcus differs somewhat from Pekar's approach based on non-equilibrium thermodynamics, the final result for potential energy of non-equilibrium polarization is the same for both theories. Later Marcus generalized his theory for the case of redox reactions on metal electrodes[13–14] (see also[15–19]). In Section III we shall discuss in detail a polar solvent model to the approximation of a dielectric continuum. The expression for the potential energy and quantum-mechanical Hamiltonian of the solvent given there is more accurate than those in the theories of Pekar and Marcus. Besides it will be shown to what approximation it is possible to derive the results of the above authors from our formulae. In our opinion, the results in Section III are better in that a more accurate expression is obtained for the basic parameter of the theory—the reorganization energy of the solvent $E_s$—than in earlier theories. In Pekar and Marcus's theory the quantity $E_s$ depends only on the geometric dimensions of ions. In the formula obtained by us however, the reorganization energy proves to be dependent on such an important parameter as the space correlation of dipole moments of solvent molecules. It is to be hoped from this result that the possibilities of comparing physical results of the theory with experimental data will be better in the future.

In addition, Section III gives an adiabatic perturbation theory for the estimation of the electron transfer probability in unit time. The last Section IV deals with the calculations of electrochemical kinetics for redox and hydrogen ion discharge reactions.

In conclusion, we shall discuss two basic assumptions of the theory, which will be considered valid for all the processes treated in the present paper. The first assumption is that total current is made up of mutually independent individual ion discharge acts. According to this assumption, estimation of the current presents two independent problems:

(1) Determination of the concentration of the discharging ions and the electrical potential distribution in the region near the electrode.

(2) Calculation of the specific electrode reaction rate constant.

The first problem is of a purely statistical nature. It is one of the most important problems in modern theoretical electrochemistry. In this paper, however, we shall be only concerned with the second problem. It will be clear from what follows that calculation of the current can be formally completed, the resulting expression containing the discharging ion's concentration $C_s$ and the electrical potential $\varphi_s$ in the reaction region as given parameters.

The second assumption refers to the choice of the slow step of the total electrochemical process. Everywhere in this paper we shall consider the discharge process to be the rate determining step. This assumption can be quantitatively formulated as the condition

$$\tau_e \gg \tau_d \tag{1}$$

where $\tau_e$ is the mean time necessary for one discharge act (the reciprocal of the discharge probability in unit time) and $\tau_d$—the mean time between diffusion jumps of a discharging ion in solution. The physical significance of condition (eqn (1)) is that before discharging ion must 'impinge' many times on the electrode. The violation of this condition means that the slow step is the diffusion transport of ions to the electrode, for in that case each 'impingement' of the ion on the electrode should result in a discharge act (probably with an 'adhesion' coefficient). Actually at $\tau_e \ll \tau_d$ the ion resides so long in the reaction region that the charge exchange process can be considered as being a semi-equilibrium one and the current will be determined mainly by the number of 'impingements' of ions upon the electrode.

## II. SEMI-PHENOMENOLOGICAL THEORY

In studying an electrode process, it is convenient to analyse it first with the aid of a semiphenomenological theory which should be based only on sufficiently obvious assumptions. Though the physical ideas and mathematical methods used in this section are of a rather general nature and applicable to many electrochemical processes involving charge transfer, for convenience we shall make a number of particular assumptions later to obtain a closed expression for the current and to illustrate the basic assumptions of the semiphenomenological theory.

It is characteristic of all processes considered by us that during a charge transfer in an elementary electrochemical act one or several electrons in the electrode must undergo a change in quantum state. For example, if a redox reaction occurs on the electrode, such as

$$\mathrm{Ox} + \mathrm{e}_f \rightarrow \mathrm{Red} \tag{2}$$

(electron $\mathrm{e}_f$, which at first is at an arbitrary quantum energy level $\varepsilon_f$ in the electrode, passes to the ion in solution to the level $\varepsilon_i$). Similarly, during ionization of a particle adsorbed on the electrode

$$A_{\mathrm{ads}} \rightarrow A^{+}_{\mathrm{sol}} + \mathrm{e}_f \tag{3}$$

the electron, which is initially at the adsorption level $\varepsilon_a$ and ensures the chemical bond of particle $A$ with the electrode, may pass after ionization to an arbitrary level $\varepsilon_f$ in the bulk of electrode, etc. Henceforth the qualitative nature of the energy spectrum of an electron in initial and final states will be of importance for us. For example, if the electron is in the bulk of the electrode, two basic cases should be distinguished when the electrode material is either metal or insulator, intrinsic or impurity semiconductors being particular cases of these. A qualitative type of structure of the electron energy spectrum for metals and insulators (semiconductors) is given in Figs. 1 and 2. Continuity of the energy spectrum is characteristic of both cases, but the values of the energy level density $\rho(\varepsilon_f)$ near the Fermi level are essentially different for

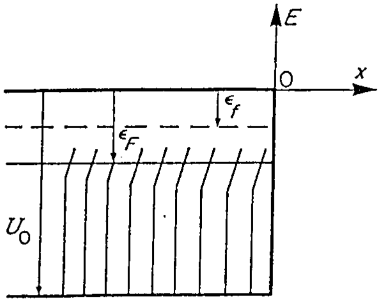

Fig. 1. Schematic diagram of the electron energy spectrum in metal; $U_0$ is the depth of the potential well for electrons.

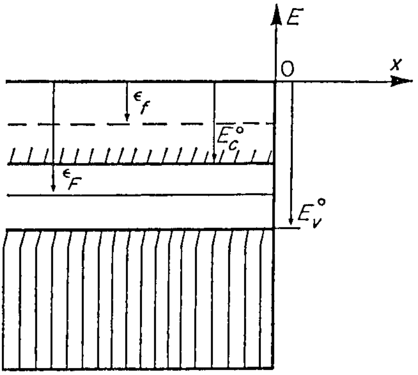

Fig. 2. Schematic diagram of the electron energy spectrum in semiconductor (insulator).

metals and insulators. For metals $\rho(\varepsilon_f)$ changes smoothly near $\varepsilon_F$. For example, in the free electron model

$$\rho_m(\varepsilon_f) = \frac{m_e V_e}{2\pi^2\hbar^3}\sqrt{(2m_e(\varepsilon_f - U_0))} \tag{4}$$

where $m_e$ is the electron mass, $U_0$ is the depth of a potential well in the metal, and $V_e$ is the metal volume. As will be shown below, an essential role in the kinetics of electrode processes on metals is played only by the energy levels located near $\varepsilon_F$:

$$|\varepsilon_f - \varepsilon_F| \sim kT \tag{5}$$

In this energy range the relative change of $\rho(\varepsilon_f)$ is very small:

$$\frac{\Delta\rho_m}{\rho_m} \simeq \frac{kT}{2(\varepsilon_F - U_0)} < 1 \tag{6}$$

For example, at room temperature ($kT \simeq 0{\cdot}025$ eV) and $(\varepsilon_F - U_0) \simeq 6$ eV this quantity is equal to 0·002 and at $(\varepsilon_F - U_0) = 3$ eV, $\Delta\rho_m/\rho_m \simeq 0{\cdot}004$. This means that in electrochemical kinetics for metal electrodes we can consider $\rho(\varepsilon_f) \simeq \rho(\varepsilon_F) \equiv \rho_F$, i.e. the electron level density for a given electrode is constant.

For theoretical calculations condition eqn (5) viz. that only the electrons at energy levels near $\varepsilon_F$ participate in the passage of the current, is of fundamental importance. This is due to the fact that owing to the large concentration of the conduction electrons it is not always the case that one particle (one electron) states can exist in the system. It has been rigorously proved, however, that near the Fermi level electron states in all metals are always one particle ones (see e.g. Reference 20). In this case for the probability of the occupation of level $\varepsilon_f$ by an electron we must make use of the Fermi distribution function

$$n(\varepsilon_f) = \left[\exp\left(\frac{\varepsilon_f - \varepsilon_F}{kT}\right) + 1\right]^{-1} \tag{7}$$

The electron concentration in the conduction band and the hole concentration in the valence band being small, there is no doubt about the use of the one-electron approximation for semiconductors being justified. Therefore, just as with metals, the occupation of levels by electrons is determined by eqn (7). The one-electron approximation may become invalid only in highly doped semiconductors, which are not considered in this article. It is a specific feature of semiconductors that the electron level density near $\varepsilon_F$ is zero (see Fig. 2):

$$\rho(\varepsilon_f) = 0, \quad E_v^0 \leqslant \varepsilon_f \leqslant E_c^0 \tag{8}$$

Therefore, the main contribution to the current is made by the electrons localized at the levels near the bottom of the conduction band $E_c^0$ and by the holes localized at the levels near the top of the valence band $E_v^0$. This shows that in semiconductors the dependence of the level density $\rho$ on $\varepsilon_f$ cannot be neglected. The concentrations of electrons in the conduction band and holes in the valence band being small, the following equations can be used:

$$\rho_e(\varepsilon_f) = \frac{m_e^* V_e}{2\pi^2\hbar^3}\sqrt{(2m_e^*(\varepsilon_f - E_c^0))}, \quad \varepsilon_f \geqslant E_c^0; \tag{9}$$

$$\rho_p(\varepsilon_f) = \frac{m_p^* V_e}{2\pi^2\hbar^3}\sqrt{(2m_p^*(E_v^0 - \varepsilon_f))}, \quad \varepsilon_f \leqslant E_v^0, \tag{10}$$

where $m_e^*$ and $m_p^*$ are effective masses of electrons and holes respectively.

In considering the electron states in an ion or adsorbed particle, we shall everywhere in this article assume the quantum energy level of the electron to be discrete and isolated. In the case of an ion, this means that the electron is localized at the level with the least possible energy $\varepsilon_i$ and that the excited energy levels are located high enough for their occupation to be neglected. If one or more excited levels are located near $\varepsilon_i$, they can be taken into account by a method described later.

The spectrum of an electron in the adsorbed state is much more complicated. Let us consider this problem for metal electrodes in a strictly qualitative manner (for more detailed treatment, see References 21–23). The physical nature of adsorption will differ significantly depending on whether the electron energy in the adsorbed particle is larger ($\varepsilon_a > \varepsilon_F$) or less ($\varepsilon_a < \varepsilon_F$) than the

Fermi energy. In the former case ($\varepsilon_a > \varepsilon_F$) the electron is practically delocalized in the metal and the adsorbed particle is present on the surface as a relatively weakly bound ion. This state somewhat resembles physical adsorption. In this case, the effect of adsorbed particles on the electrode only amounts to some insignificant changes in the electron density and energy spectrum distributions. In this article for simplicity we shall consider only local adsorption levels ($\varepsilon_a < \varepsilon_F$). At $\varepsilon_a < \varepsilon_F$ the electron density distribution has a maximum near the adsorbed particle. In this sense, the corresponding energy value can be called a local level. If the adsorbed particle forms a local level, on the average, the total charge of electron and particle is zero. Owing to this sharp screening effect there is practically no interaction between adsorbed particles. Therefore, at fairly small fractional coverage of the electrode surface, the local adsorption level does not form a band structure.

For a description of the electrode process, it is necessary to know the number of elementary acts occurring per unit time, i.e. the transition probability per unit time, assuming the initial and final electron states to be given. The basic assumption of the semi-phenomenological theory is that in order to express the transition probability we assume as being valid the Arrhenius equation

$$W = \text{constant} \exp\left(-\frac{E_a}{kT}\right) \tag{11}$$

or the equation of the absolute reaction rate theory equivalent to it

$$W = \frac{kT}{h}\kappa \,.\, \mathrm{e}^{-F_a/kT} = \frac{kT}{h}\kappa \,.\, \mathrm{e}^{S_a/k} \,.\, \mathrm{e}^{-E_a/kT} \tag{12}$$

where $\kappa$ is transmission coefficient, $E_a$, $F_a$, and $S_a$ are the energy, free energy and entropy of activation respectively. Naturally, the question of the validity of eqns (11) and (12) for semi-phenomenological theory remains unsolved, since an expression for the transition probability can be obtained only from a quantum-mechanical treatment of the problem based on the use of a certain model for the whole system participating in the reaction. Unfortunately, the derivation of eqn (12) which is usually given in the theory of absolute reaction rates, is quite unsatisfactory. This is due not only to the absence of a rigorous quantum-mechanical calculation, but even to a larger degree to the lack of substantiation for the basic assumptions of the theory. The absence of a criterion of applicability of the theory of absolute reaction rates makes this method appear universal, which is not the case. This accounts for the appearance of a number of papers in which the theory of absolute reaction rates was used in calculation of such processes that cannot lead to equations of the type of (11) or (12). In particular, we shall show in Section IV that if the coordinate of the proton itself is chosen as the reaction coordinate in proton transfer processes in liquids, the transition probability is not described by eqn (12).

At present a rigorous quantum-mechanical derivation of eqn (12) is available only for charge transfer processes in condensed systems of the polar type if the system terms are assumed to have the form of parabolas (harmonic approximation). For radiationless processes in crystals this was demonstrated in References 6 and 8, and for homogeneous electron transfer reactions in polar liquids in References 24–29. The main criterion of applicability of eqn (12) for the reactions considered above can be written as

$$\hbar\omega_0 < kT \tag{13}$$

where $\omega_0$ is the frequency of polarization fluctuations in liquids. If condition eqn (13) is fulfilled, the transition of the system from the initial electron term to the final state term will occur at the intersection point of the potential energy curves, which corresponds to the classical path of transition of the system over the potential barrier. Initially in the theory developed in References 24–29 the intramolecular degrees of freedom of reacting ions were assumed to be 'frozen', i.e. that in a dynamical sense the total system consisted only of electron and solvent. With a view to subsequent calculations for more complex homogeneous and heterogeneous charge transfer processes in polar liquids, we have estimated the quantum-statistical transition probability for one-dimensional terms of a rather general form. The main result obtained by us can be formulated as a criterion of applicability of the classical approach to the motion of a particle:

$$\Delta E < kT \tag{14}$$

where $\Delta E$ is the difference between the first excited state and the ground state of the system.[30] Since the equally-spaced energy levels of an oscillator differ by the quantity $\hbar\omega_0$, we see that condition eqn (13) is a particular case of condition eqn (14).

On this basis, the equation for the transition probability eqn (12) can be interpreted as follows: the classical part of the total system is responsible for the appearance of a factor exponentially dependent on the reciprocal temperature (activation factor), whereas the quantum part of the total system contributes to the transfer coefficient $\kappa$, thus establishing the adiabatic or non-adiabatic nature of the reaction course. Naturally, in this case the activation energy value will depend on the parameters of the quantum subsystem. It is important, however, that the quantum part in itself cannot lead to the activation equation. The parameters of the classical subsystem, in turn, will be contained in the transfer coefficient. Thus, the separation of the roles of classical and quantum subsystems is physical rather than mathematical. In the transfer processes of charge strongly interacting with the polar medium which are of interest to us, there must exist at least one classical component, the solvent, since eqn (13) seems to be valid for all polar solvents. For example, for water at room temperature, we have:

$$\omega_0 \simeq 10^{11}\ \mathrm{sec}^{-1} < \frac{kT}{\hbar} \simeq 4\cdot 10^{13}\ \mathrm{sec}^{-1} \tag{15}$$

On this statement is actually based the most important assumption of the semi-phenomenological theory regarding the applicability of eqn (12) for calculation of electrode processes. In a sense, our assumption is experimentally verified by the exponential dependence of the current on the reciprocal temperature in the Tafel equation.

In addition to the classical part, the total system must contain at least one quantum subsystem—the electron. The kind of motion of other components (the intramolecular degrees of freedom of the reagents) is determined by means of the criterion eqn (14): if the corresponding degrees of freedom are 'frozen' ($\Delta E > kT$), they should be included in the quantum subsystem, whereas the degrees of freedom excited at room temperature ($\Delta E < kT$) should be considered by a classical approach. If in addition to the electron, the reacting system contains other quantum subsystems, in calculating the transition probability $W$ it is necessary to write along with the electron states, the quantum number of these subsystems in the initial and final states, giving corresponding subscripts to the transmission coefficient and the activation free energy. As the quantum subsystem is only weakly excited at room temperature ($\Delta E > kT$), the unexcited ground state is of primary importance for electrochemical kinetics. We shall see later, however, that in certain overvoltage regions these excited states can still make a contribution.

It should be pointed out that the treatment in this section refers only to reactions in condensed phases. In the general case, it may prove inapplicable to reactions in the gas phase. To explain the essential difference between these two types of reactions, it should be recalled that the free translational motion of particles characteristic of gas reaction is practically absent in condensed phases and that in liquids particles move only by jumps (the only exception being very large ions moving almost in a classical manner, i.e. those which have shallow potential wells). Characteristic potential energy profiles for reactions in gas and condensed phases are given in Figs. 3 and 4. It should be noted that some authors sometimes use electron terms of the type shown in Fig. 3 for the treatment of reactions in liquids. In view of the foregoing consideration, such an approach to the problem is incorrect.

In estimating the total transition probability $W$ in condensed systems, the quantum-mechanical expression for the probability is statistically averaged over the initial energies of the system, including only intrinsic degrees of freedom (vibrational and rotational). For gas reactions an analogue of $W$ is the scattering cross section $\sigma(K_{0i}; K_{0f}; T)$, statistically averaged over initial energies of the intrinsic degrees of freedom of scattering particles. ($K_{0i}$ and $K_{0f}$ are kinetic energies of particles before and after scattering.) In order to obtain the rate constant of a gas reaction, the cross section must be statistically averaged over initial velocities of colliding particles by means of Maxwellian distribution and integrated over final velocities

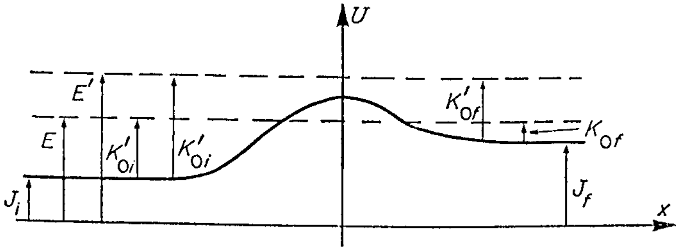

Fig. 3. Characteristic shape of the potential energy profile for reactions in the gas phase. $J_i$, $J_f$ are internal energies of particles before and after reaction, $E, E'$ are total energies of reacting particles.

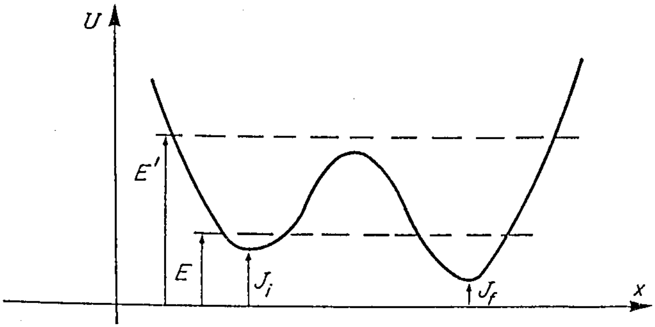

Fig. 4. Characteristic shape of the potential energy profile for reactions in the condensed phase.

$$K \sim \int \sigma(K_{0i}; K_{0f}; T)\, e^{-K_{0i}/kT}\, dK_{0i}\, dK_{0f} \qquad (16)$$

It is specific to gas reactions that the Arrhenius shape of the rate constant can be due not only to the dependence of the cross section on temperature, but also to the Maxwellian averaging over velocities. This becomes evident if we consider cross sections of two types:

(1) $\sigma = 0$ at $K_{0i} < E_a$ and $\sigma =$ constant at $K_{0i} > E_a$ (threshold reaction).

(2) $\sigma \sim \delta(K_{0i} - E_a)$ (resonance reaction), where $\delta(K_{0i} - E_a)$ is the Dirac delta function and $E_a$ is the activation energy.

Thus, in gas reactions even at 'frozen' intrinsic degrees of freedom of molecules the translational motion of particles can act as a classical subsystem.

For a general consideration of reactions on the basis of a semi-phenomenological theory, the type of dependence of the transition probability on the free electron energy in the electrode $\varepsilon_f$ is of great importance. We shall assume everywhere in this article that the transmission coefficient in the energy range of interest to us, which is determined by eqn (5), changes very slightly. In particular, if we use a free electron model for the metal, we can write the wave function as a plane wave

$$\psi_f(X) = \frac{1}{\sqrt{(V_e)}} e^{iK_f X} \tag{17}$$

where the wave number $K_f$ is determined by the equality

$$K_f = \frac{1}{\hbar} \sqrt{(2m_e(\varepsilon_f - U_0))} \tag{18}$$

The transmission coefficient is determined by the square of the exchange integral, which contains the overlap of the function $\psi_f$ and the wave function of the electron in the final state. The latter function, in virtue of our assumption about the local character of the electron state in the ion or adsorbed particle differs from zero only in a small length $a_0$ ($a_0$ is equal to one or several Angstroms). Thus, the criterion of validity of our assumption is of the form

$$|\Delta K_f \,.\, a_0|^2 \simeq \frac{m_e a_0^2 kT}{2\hbar^2} \cdot \frac{kT}{|\varepsilon_F - U_0|} < 1 \tag{19}$$

As the actual values of $(\varepsilon_F - U_0)$ are several electron-volts, we see that at room temperature this condition is satisfied fairly well. Therefore, henceforth the transmission coefficient will be assumed to be independent of $\varepsilon_f$:

$$\kappa(\varepsilon_f) \simeq \kappa(\varepsilon_F) \equiv \kappa_F$$

In order to study the dependence of the free energy of activation on $\varepsilon_f$, let us consider a number of quasithermodynamic characteristics of the system, assuming the electron to be the only quantum particle in the whole system. Let us introduce the concept of the free energy of the system at a fixed quantum state of the electron localized in the electrode at level $\varepsilon_f$. Here and henceforth we denote by $F$ the so called 'standard' free energy, i.e. the free energy calculated for one ion. In calculating $F(\varepsilon_f)$ we should remember that according to the standard procedure for quantum-mechanical calculation of the transition probability, the initial and final states of the system are determined without taking into consideration the perturbation energy, i.e. the interaction of the electron with the discharging ion. The presence of the perturbation leads only to transitions between 'pure' states of the system at the beginning and the end. Hence it follows that the electron energy, equal to $\varepsilon_f - e\varphi_m$ (where $\varphi_m$ is the Galvani potential difference between metal electrode and solution), makes an additive contribution to the free energy:

$$F(\varepsilon_f) = \varepsilon_f - e\varphi_m + \text{constant} \tag{20}$$

Henceforth it will be more convenient for us to use an expression for $F(\varepsilon_f)$ written in a somewhat different form. The free energy of activation of the system in the state when $\varepsilon_f = \varepsilon_F$ and the electrode potential has an equilibrium value $\varphi_0$, can be calculated by means of a familiar equation of statistical physics:

$$\begin{aligned} F_{0F} &= -kT \ln \sum_n \exp\left\{-\frac{1}{kT}(\varepsilon_F - e\varphi_0 + Ze\varphi_{0S} + E^{(1)}_{00} + E^{(1)}_{0n})\right\} \\ &= \varepsilon_F - e\varphi_0 + Ze\varphi_{0S} + E^{(1)}_{00} - kT \ln \sum_n \exp\left(-\frac{E^{(1)}_{0n}}{kT}\right) \equiv J^{(1)}_{0F} + \mathscr{F}^{(1)}_0 \end{aligned} \tag{21}$$

where $\varphi^{(1)}_{0S}$ is the potential at the point from which the discharge occurs; $E^{(1)}_{0n}$ represents the energy levels of the classical subsystem in the initial state reckoned from the ground level $E^{(1)}_{00}$. The symbol $\mathscr{F}$ here and below stands for the free energy of the classical subsystem calculated assuming the energy to be reckoned from the least value of $E_0$. In the literature $E_0$ and $J_{0F}$ sometimes refer to the energy of the system at the temperature $T \to 0$. For chemical reactions however, occurring in the liquid phase this definition is incorrect, since at $T \to 0$ all liquids (except quantum liquids) undergo a phase transition. It is clear that the energy spectrum, as well as the thermodynamic characteristics of a liquid differs essentially from the corresponding quantities for the same substance in the solid phase. The quantity $J_{0F}$ has a particularly simple interpretation if an electron term concept is introduced for the classical subsystem. As is clear from Fig. 5 (curve a) $J_{0F}$ practically coincides with the potential energy minimum since for the classical subsystem $\Delta E < kT$.

Along with the true thermodynamic quantity $F_{0F}$, we can also consider the nonequilibrium quasithermodynamic free energy of the initial state, when the electron is at an arbitrary level $\varepsilon_f$ and the electrode potential is equal to $\varphi_m \neq \varphi_0$:

$$\begin{aligned} F^{(1)}(\varepsilon_f) &= \varepsilon_f - e\varphi_m + Ze\varphi_{0S} \\ &\qquad + E_0^{(1)} - kT \ln \sum_n \exp\left(-\frac{E_n^{(1)}}{kT}\right) \equiv J_f^{(1)} + \mathscr{F}^{(1)} \\ &= (\varepsilon_f - \varepsilon_F) - e\eta + Ze\eta_S + E_0^{(1)} - E_{00}^{(1)} + \mathscr{F}^{(1)} - \mathscr{F}_0^{(1)} + F_{0F} \qquad (22) \end{aligned}$$

where $\eta = \varphi_m - \varphi_0$ and $\eta_S = \varphi_S - \varphi_{0S}$ are the overvoltages on the electrode and at the point from which discharge occurs. The first three terms in the right hand side of the second equation correspond to the changes in the energies of electron and discharging ion on applying an overvoltage and excitation of the electron from level $\varepsilon_F$ to level $\varepsilon_f$. The next two terms in this equation describe the change in the energy spectrum of the classical subsystem with changing potential. With reference to electron terms this means that the first three terms in $F(\varepsilon_f)$ lead to a parallel displacement of the equilibrium term vertically upwards (curve b in Fig. 5); the fourth and the fifth term $F(\varepsilon_f)$ reflect the potential energy change in the classical subsystem with changing electrode potential, $E_0^{(1)} - E_{00}^{(1)}$ corresponding to the vertical displacement of the term minimum point and $\mathscr{F}^{(1)} - \mathscr{F}_0^{(1)}$ characterizing the change in the electron term shape. In order to understand the physical nature of the changes in the classical subsystem caused by overvoltage, let us consider the behaviour of the terms in the vicinity of the minimum point, assuming the deviation of normal coordinates of the classical subsystem $q_K$ from the equilibrium values to be small. Then, the potential energy of the classical

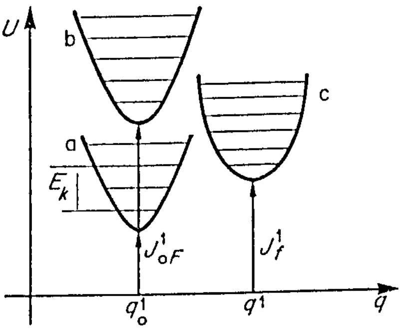

Fig. 5. Qualitative picture of the electronic terms of the classical subsystem: (a) at the equilibrium potential and $\varepsilon_f = \varepsilon_F$; (b) in the presence of overvoltage and $\varepsilon_f \neq \varepsilon_F$ (without allowing for the interaction with the electrode field); (c) at $n \neq 0$ and $\varepsilon_f \neq \varepsilon_F$ (allowing for the interaction with the electrode field).

subsystem, in the absence of the electrode potential, can be roughly shown as a parabola:

$$U(q) = U(0) + \tfrac{1}{2}\sum_k \hbar\omega_K q_K^2 \tag{23}$$

where $\omega_K$ are the normal frequencies of the classical subsystem (solvent and intramolecular vibrations of discharging ion). The interaction of the classical subsystem with the electric field $V(q, \varphi_m)$ can be expanded as a power series in the small deviations of $q_K$ from $q_{K0}(\varphi_m)$, where $q_{K0}(\varphi_m)$ are the coordinates of the electron term minimum point at the electrode potential value $\varphi_m$:

$$V(q, \varphi_m) = V(q_0(\varphi_m), \varphi_m) + \sum_k \frac{\partial V(q_0(\varphi_m), \varphi_m)}{\partial q_K}(q_K - q_{K0}(\varphi_m))$$
$$+ \tfrac{1}{2}\sum_{k,k'} \frac{\partial^2 V(q_0(\varphi_m), \varphi_m)}{\partial q_K \partial q_{K'}}(q_K - q_{K0}(\varphi_m))(q_{K'} - q_{K'0}(\varphi_m)) + \ldots \tag{24}$$

If we take only the first two terms in eqn (24) the electron term can be written as

$$U(q, \varphi_m) = U(q) + V(q, \varphi_m) \simeq U(0) + V(q_0(\varphi_m), \varphi_m)$$
$$+ \tfrac{1}{2}\sum_k \hbar\omega_K[q_{K0}(\varphi_m)]^2 + \tfrac{1}{2}\sum_k \hbar\omega_K[q_K - q_{K0}(\varphi_m)]^2 \tag{25}$$

where the displacement of the coordinates of the term minimum point is determined from the equation

$$q_{K0}(\varphi_m) = -\frac{1}{\hbar\omega_K} \cdot \frac{\partial V(q_0(\varphi_m), \varphi_m)}{\partial q_K} \tag{26}$$

According to eqn (25) the change of the term only amounts to the displacement of the minimum point potential energy by the quantity $q_0(\varphi_m)$, the decrease of minimum potential energy by the value of reorganization energy of the classical subsystem $\tfrac{1}{2}\sum_k \hbar\omega_K[q_{K0}(\varphi_m)]^2$ plus the energy of interaction of the field with the classical subsystem in the new equilibrium state $V(q_0(\varphi_m), \varphi_m)$:

$$E_0^{(1)} = U(q_0(\varphi_m)) + V(q_0(\varphi_m), \varphi_m)$$
$$\simeq U(0) + V(q_0(\varphi_m), \varphi_m) + \tfrac{1}{2}\sum_k \hbar\omega_K[q_{0K}(\varphi_m)]^2 \tag{27}$$

It is important that to the first approximation the vibration frequencies (i.e. the term shape) are not affected by the field. Then the free energy of the system of classical oscillators ($\hbar\omega_K < kT$) can be written as

$$\mathscr{F}^{(1)} \simeq -kT\sum_k \ln \tfrac{1}{2} \operatorname{csch}\frac{\hbar\omega_K}{2kT} \simeq -kT\sum_k \ln\frac{kT}{\hbar\omega_K} \tag{28}$$

The shape of the potential energy surface is changed if we take into consideration the third and the subsequent terms in the energy of interaction of the classical subsystem with the electric field (see eqn (24)). In particular to the second approximation (with account taken of the third term in eqn (24)), it can be shown by means of some simple linear algebraic transformations that the displacement of the term minimum point is accompanied by a change in the frequencies of normal vibrations. The physical sense of this is that to the second approximation the elastic constants of intramolecular degrees of freedom of the classical subsystem change under the action of the electric field. The new frequencies, naturally, will depend on the field. The change of free energy and minimum potential energy upon application of overvoltage can be written as

$$\mathcal{F}^{(1)} - \mathcal{F}_0^{(1)} \simeq kT \sum_k \ln \frac{\Omega_K(\varphi_m)}{\Omega_K(\varphi_0)}, \tag{29}$$

where $\Omega_K(\varphi)$ are the normal frequencies at Galvani potential $\varphi$. In addition, we have:

$$E_0^{(1)} - E_{00}^{(1)} = [U(q_0(\varphi_m)) - U(q_0(\varphi_0))] \\ + [V(q_0(\varphi_m), \varphi_m) - V(q_0(\varphi_0), \varphi_0)] \tag{30}$$

The difficulty of calculating these quantities for particular systems is due not only to the difficulty of determining the shape of the term $U(q)$ and the form of the interaction $V(q, \varphi_m)$, but possibly even to a larger degree to the need to know the distribution of electrical potential in the electrolyte. Therefore, to simplify the calculations we shall assume the whole potential drop to occur within the Helmholtz layer, i.e. the absence of the $\psi_1$-effect. As will be shown later, the basic results of the theory are all formally generalized also for the case of the presence of the $\psi_1$-effect. But in that case concrete expressions become very cumbersome and make quantitative estimates of the results more difficult.

In the absence of the $\psi_1$-effect, the quasithermodynamic nonequilibrium free energy of the initial state is

$$F^{(1)}(\varepsilon_f) = \varepsilon_f - e\varphi_m + E^{(1)} + \mathcal{F}^{(1)} \\ = J_f^{(1)} + \mathcal{F}^{(1)} = (\varepsilon_f - \varepsilon_F) - e\eta + F_{0F} \tag{31}$$

since in this case the electric field in that part of the space where the classical subsystem (solvent and discharging ion) is located is equal to zero. Since we have assumed that the adsorbed particle is neutral it follows that in the general case the free energy of the final state will be a constant, independent of the electrode potential:

$$F^{(2)} = \varepsilon_a + E^{(2)} + \mathcal{F}^{(2)} \equiv J^{(2)} + \mathcal{F}^{(2)} \tag{32}$$

where $\varepsilon_a$ is the electron energy in the final state (in the adsorbed particle or reaction product ion); $E^{(2)}$ and $\mathscr{F}^{(2)}$ are the minimum potential energy and the free energy of the classical subsystem at the end of the reaction, respectively. Accordingly, the change of free energy in the course of reaction is

$$\begin{aligned} \Delta F(\varepsilon_f) &= F^{(1)}(\varepsilon_f) - F^{(2)} \\ &= \Delta J_f + \Delta\mathscr{F} \\ &= -e\eta + (\varepsilon_f - \varepsilon_F) + (F_{0F} - F^{(2)}) \\ &= (\varepsilon_f - \varepsilon_F) - e\eta + \Delta F_{0F} \end{aligned} \tag{33}$$

It can be readily seen that the term which is of real thermodynamic significance is $\Delta F_{0F}$, which determines the equilibrium constant

$$K_0 = \frac{C_0^{(1)}}{C_0^{(2)}} = \exp\left(-\frac{\Delta F_{0F}}{kT}\right) \tag{34}$$

where $C_0^{(1)}$ and $C_0^{(2)}$ are surface concentrations of ions before and after discharge at the equilibrium potential. If we introduce in a strictly formal manner an equilibrium constant for the reaction involving only the electron localized at the level $\varepsilon_f$ and leaving after the reaction a 'hole' at the same level we shall obtain for this quantity

$$K_0(\varepsilon_f) = \frac{C_0^{(1)} \,.\, n(\varepsilon_f)}{C_0^{(2)}[1 - n(\varepsilon_f)]} = \exp\left(-\frac{\Delta F_0(\varepsilon_f)}{kT}\right) \tag{35}$$

where $n(\varepsilon_f)$—the Fermi distribution—appears as the electron concentration at level $\varepsilon_f$; similarly, $1 - n(\varepsilon_f)$ is the 'hole' concentration. Thus, each electron level in the electrode acts as an independent redox system in electrochemical kinetics, it being very important, however, that the equilibrium potential for each level has the same value. In fact, the equilibrium potential value is determined from the equation

$$\Delta F_0(\varepsilon_f) + kT \ln \frac{C_0^{(1)} \,.\, n(\varepsilon_f)}{C_0^{(2)}[1 - n(\varepsilon_f)]} = 0 \tag{36}$$

After substituting for the Fermi distribution, this becomes:

$$\Delta F_0(\varepsilon_f) - (\varepsilon_f - \varepsilon_F) + kT \ln \frac{C_0^{(1)}}{C_0^{(2)}} = 0$$

which according to eqn (33) is equivalent to an equation independent of $\varepsilon_f$, i.e.:

$$\Delta F_{0F} + kT \ln \frac{C_0^{(1)}}{C_0^{(2)}} = 0 \tag{37}$$

In order to obtain an expression for the equilibrium potential eqns (31) and (32) should be substituted into eqn (37):

$$
\begin{aligned}
e\varphi_0 &= (\varepsilon_F - \varepsilon_a) + (E_0^{(1)} - E^{(2)}) + (\mathscr{F}_0^{(1)} - \mathscr{F}^{(2)}) + kT \ln \frac{C_0^{(1)}}{C_0^{(2)}} \\
&= \Delta F(\varepsilon_F, \varphi_m = 0) + kT \ln \frac{C_0^{(1)}}{C_0^{(2)}} \qquad (38)
\end{aligned}
$$

where $\Delta F(\varepsilon_F, \varphi_m = 0)$ is the difference of the free energies of initial and final states at $\varphi_m = 0$. Essentially eqns (36) and (37) correspond to the equilibrium condition of a chemical reaction written as an equality of overall chemical potentials, the quantity $\Delta F(\varepsilon_F, \varphi_m = 0)$ being the change of the chemical potential of the reacting system. Naturally, an expression for the equilibrium potential eqn (38) can be obtained from a consideration of standard thermodynamic cycles.

One of the most important assumptions of the semi-phenomenological theory, as well as of any other microscopic theory now available, is the assumption of the quasiequilibrium nature of the occupation of energy levels of the systems in the case of small deviations from equilibrium. Speaking more generally, this means that we shall use the Gibbs distribution for slightly nonequilibrium systems. Determination of the nonequilibrium distribution function involves a most complicated problem of solving a kinetic equation. However, according to rough estimates, for electrochemical processes under the conditions when the charge transfer is the slow step, our assumption is usually adequate. As will be shown in the next section, the quasiequilibrium Gibbs distribution was actually implicitly used by us when we chose for the transition probability the absolute reaction rate eqn (12). From the condition of quasiequilibrium in conjunction with the principle of balancing, we can find a simple relationship between the forward ($W_{12}$), and back ($W_{21}$) transition probabilities. In the general case, the forward transition probability is of the form:

$$W_{12} = \sum_{i,l} W_{12}(\varepsilon_i^{(1)} \varepsilon_l^{(2)}) g_1(\varepsilon_i^{(1)}) \, \mathrm{e}^{-\varepsilon_i^{(1)}/kT} \left[ \sum_n g_1(\varepsilon_n^{(1)}) \, \mathrm{e}^{-\varepsilon_n^{(1)}/kT} \right]^{-1} \qquad (39)$$

where $\varepsilon^{(1)}$, $\varepsilon^{(2)}$ are the energy levels of initial and final states and $g_1(\varepsilon^{(1)})$ is the statistical weight of an initial state level. The denominator in eqn (39) is a statistical sum for the initial state and can be expressed in terms of the free energy as:

$$\sum_i g_1(\varepsilon_i^{(1)}) \, \mathrm{e}^{-\varepsilon_i^{(1)}/kT} = Q_1 = \exp\left(-\frac{F^{(1)}}{kT}\right) \qquad (40)$$

In accordance with quantum mechanics, when the system passes from level $\varepsilon_i^{(1)}$ to level $\varepsilon_l^{(2)}$ under steady-state conditions, the law of conservation of energy is obeyed, i.e. $\varepsilon_i^{(1)} = \varepsilon_l^{(2)}$. Therefore, using the principle of detailed balancing:

$$W_{12}(\varepsilon_i^{(1)}, \varepsilon_l^{(2)})g_1(\varepsilon_i^{(1)}) = W_{21}(\varepsilon_l^{(2)}, \varepsilon_i^{(1)})g_2(\varepsilon_l^{(2)}) \tag{41}$$

and from eqn (39) we obtain:

$$W_{12} = [\sum_{i,l} W_{21}(\varepsilon_l^{(2)}, \varepsilon_i^{(1)})g_2(\varepsilon_l^{(2)})\, e^{-\varepsilon_l^{(2)}/kT}]\, e^{F^{(1)}/kT}$$

After multiplying and dividing the right hand side by the statistical sum of final state, we finally obtain

$$W_{12} = W_{21}\, e^{\Delta F/kT} \tag{42}$$

Equation (42) obtained above is of a completely general nature and applicable to any kinetic process if the condition of quasiequilibrium of initial and final states is obeyed (generalization for the case of non-steady state processes, i.e. for perturbations dependent on time is a trivial modification, see e.g.[31]). If into eqn (42) we substitute eqn (33) for $\Delta F(\varepsilon_f)$ and use eqns (34) and (35) we obtain the following relations between the forward and back electron transition probabilities in electrochemical kinetics:

$$\frac{W_{21}(\varepsilon_f)}{W_{12}(\varepsilon_f)} = \exp\left(\frac{e\eta - (\varepsilon_f - \varepsilon_F) - \Delta F_{0F}}{kT}\right) = K_0(\varepsilon_f)\, e^{e\eta/kT} \tag{43}$$

Having carried out these preliminary steps we can then pass to direct estimation of the current density. For definiteness, we shall assume a cathodic process to occur on the electrode and introduce the cathodic overvoltage

$$\eta_c = \varphi_0 - \varphi_m = -\eta \tag{44}$$

The expression for the total cathodic current can be written as

$$i_c = \overrightarrow{i_c} - \overleftarrow{i_c} = eC_0^{(1)}\int np W_{12}\, d\varepsilon_f - eC^{(2)}\int(1 - n)pW_{21}\, d\varepsilon_f \tag{45}$$

where integration is performed over the whole electron energy spectrum in the electrode. In writing eqn (45) we have made use of the assumption about the absence of the $\psi_1$-effect and substituted the equilibrium concentration of discharging ions $C_0^{(1)}$. If the potential drop extends beyond the Helmholtz layer to the diffuse part of the double layer, nonequilibrium values should be written for the concentration. In this case, we are faced with the problem of choosing the distance at which the ion discharge occurs. Moreover, in the general case, we should take into consideration the possibility of an ion discharge at any distance from the electrode, i.e. calculate the integral of the type

$$\int_{\delta}^{\infty} C^{(1)}(x) W(x)\,\mathrm{d}x \tag{46}$$

where $\delta$ is the least distance of approach of discharging ion to the electrode. However, in view of the fact, that as a rule the quantum mechanical transition probability $W(x)$ diminishes sharply at atomic distances, whereas $C^{(1)}(x)$ changes fairly smoothly, the integrand in eqn (46) has a very sharp maximum near the point $x = \delta$. This means that in the presence of the $\psi_1$-effect, $C_0^{(1)}$ can be substituted by the nonequilibrium ion concentration at the point $x \approx \delta$, i.e. by $C^{(1)}(\delta, \varphi_m)$.

So far we have discussed only the concentration of discharging ions. If we wish to consider the concentration of discharged ions, we have to distinguish between two cases:

(1) when these ions are not adsorbed; and
(2) when these ions are adsorbed.

In the former case, $C^{(2)}$ can be substituted by the equilibrium value $C_0^{(2)}$. In the latter case, it is necessary to consider the particular desorption mechanism in the given system and to write the steady-state condition for the electrochemical process, i.e. to equate the numbers of adsorbed and desorbed particles per unit time. The supplementary equation thus obtained allows us to express the nonequilibrium concentration of adsorbed particles in terms of the concentrations of initial and final reaction products, which in the absence of the $\psi_1$-effect have equilibrium values. In order not to complicate the description of general methods of semi-phenomenological theory, we shall not consider here the desorption current and shall retain the formally nonequilibrium concentration $C^{(2)}$ in the ionization current $\overleftarrow{i}_c$. An example of the procedure of taking into consideration the desorption processes in electrochemical kinetics will be given in Section IV in the treatment of the hydrogen overvoltage theory.

Using eqns (35) and (42) let us rewrite the expression for the total current in the form

$$\begin{aligned} i_c &= eC_0^{(1)} \int n\rho W_{12} \left(1 - \frac{C^{(2)}}{C_0^{(2)}} \cdot \frac{C_0^{(2)}}{C_0^{(1)}} \cdot \frac{1-n}{n} \cdot \frac{W_{21}}{W_{12}}\right) \mathrm{d}\varepsilon_f \\ &= eC_0^{(1)} \int n\rho W_{12} \left(1 - \frac{C^{(2)}}{C_0^{(2)}}\, \mathrm{e}^{-e\eta_c/kT}\right) \mathrm{d}\varepsilon_f \end{aligned} \tag{47}$$

The relation between forward and back currents is then:

$$\overleftarrow{i}_c = \overrightarrow{i}_c \cdot \frac{C^{(2)}}{C_0^{(2)}} \mathrm{e}^{-e\eta_c/kT}; \quad i_c = \overrightarrow{i}_c \left(1 - \frac{C^{(2)}}{C_0^{(2)}} \mathrm{e}^{-e\eta_c/kT}\right) \tag{48}$$

Thus the treatment can be confined to the calculation of the discharge current $\overrightarrow{i}_c$, which by means of eqn (12) can be rewritten for metal electrodes as

$$\overrightarrow{i}_c = eC_0^{(1)} \frac{kT}{h} \kappa_F \rho_F \int n(\varepsilon_f)\, \mathrm{e}^{-F_a(\varepsilon_f)/kT}\, \mathrm{d}\varepsilon_f = \int \mathrm{d}\overrightarrow{i}_c(\varepsilon_f) \tag{49}$$

For further treatment we have to determine more accurately the nature of the dependence of the free energy of activation on $\varepsilon_f$ and on overvoltage $\eta_c$. It will be shown in Section IV on the basis of a rigorously quantum-mechanical treatment without any assumptions about the model that the free energy of activation can contain as an argument the difference of energies of the quantum subsystem in initial and final states only in terms of the quantity $\Delta J$. As shown above, this is the difference of the total energies of the system in initial and final states, assuming the classical subsystem to be in the ground (unexcited) energy state. If the behaviour of the classical subsystem is described by means of a potential energy surface, $\Delta J$ is the difference of minimum potential energies of initial and final states (see Fig. 4). Evidently, the above statement does not mean that $\Delta J$ is the only argument of the free activation energy $F_a$. Moreover, an expression for $F_a$ will certainly contain the parameters characterizing the energy spectrum and wave functions of the classical subsystem, or in terms of the potential energy surface the parameters characterizing the geometric shape and relative positions of the terms.

In the absence of the $\psi_1$-effect, according to eqns (31)–(33) we have:

$$F_a = F_a(\Delta J_f, \gamma) = F_a(\varepsilon_f - e\varphi_m + E^{(1)} - \varepsilon_a - E^{(2)}, \gamma) \tag{50}$$

where $\gamma$ stands for the set of all parameters characterizing the geometric shape and relative position of the terms of initial and final states. Since in the absence of the $\psi_1$-effect, the quantities $\gamma$, $E^{(1)}$, $E^{(2)}$, and $\varepsilon_a$ do not depend on $\varphi_m$, the whole dependence of the free energy of activation on the electrode potential $\varphi_m$ is contained in the combination $\varepsilon_f - e\varphi_m$, i.e.

$$F_a = F_a(\varepsilon_f - e\varphi_m, \gamma) \tag{51}$$

However in what follows it will be sometimes more convenient to write the argument of the free energy of activation not as $\Delta J_f$ or $\varepsilon_f - e\varphi_m$, but as $\Delta F(\varepsilon_f)$. This possibility results from the independence of $\Delta\mathscr{F}$ on $\varepsilon_f$ and $\varphi_m$ or ultimately from the constancy of the shape of the terms of initial and final states. Thus, according to eqns (33) and (44) we have

$$\begin{aligned} F_a &= F_a(\Delta F(\varepsilon_f), \gamma) = F_a(\Delta J_f + \Delta\mathscr{F}, \gamma) \\ &= F_a(\varepsilon_f - \varepsilon_F + e\eta_c + \Delta F_{0F}, \gamma) \end{aligned} \tag{52}$$

It should be stressed that eqn (52) (as well as eqn (51)) is valid only in the case of the absence of the $\psi_1$-effect, or to be more precise, in the case when the coefficients determining the geometric shape of the potential energy surfaces and their relative position do not depend on the electrode potential. If this condition is not obeyed, we can use only eqn (50), taking into consideration, however, that parameters $E^{(1,2)}$ and $\gamma$ may depend on the electrode potential $\varphi_m$ and that change of electrostatic energy of the ion upon discharge should be added to the quantity $\Delta J_f$.

The problem of the dependence of the parameters on the electrode potential is of interest not only in connection with quantitative calculation of electrochemical kinetics, but has a fundamental physical significance. In fact, if $\gamma$ does not depend on $\varphi_m$, from eqn (52) we can write the microscopic analogue of the Brönsted equation relating the change of the activation free energy to that of the quasithermodynamic reaction free energy $\Delta F(\varepsilon_f)$, for the elementary electrochemical discharge current involving the electron localized at an arbitrary quantum level $\varepsilon_f$:

$$\alpha(\varepsilon_f) = -\frac{\partial F_a(\Delta F(\varepsilon_f))}{\partial \Delta F(\varepsilon_f)} \tag{53}$$

The microscopic nature of this relation is due to its containing a parameter of a thermodynamically non-averaged subsystem, i.e. the electrode electrons. Below, however, we shall show from eqn (53) that it is possible to introduce the concept of the transfer coefficient $\alpha$ having a macroscopic sense. If, however, the coefficients $\gamma$ depend on $\varphi_m$, eqn (50) should be used in place of eqn (52) which permits us to relate the change of the activation free energy to change of $\Delta J_f$:

$$\alpha(\varepsilon_f) = -\frac{\partial F_a(\Delta J_f)}{\partial \Delta J_f} \tag{54}$$

The advantage of the Brönsted equation (53) over eqn (54) is that at a known transfer coefficient $\alpha(\varepsilon_f)$ it is possible to relate the kinetic characteristic $F_a$ directly to the quasi-thermodynamic quantity for the reaction free energy $\Delta F(\varepsilon_f)$, whereas from eqn (54) we can only relate $F_a$ to the quantity $\Delta J_f$, which is not of a directly thermodynamic nature. This advantage is particularly apparent in considering the dependence of free energy of activation and the current on overvoltage. In the absence of the $\psi_1$-effect, it follows from eqns (52) and (60) that

$$\alpha(\varepsilon_f) = -\frac{\partial F_a(\Delta F(\varepsilon_f))}{\partial e\eta_c} = -\frac{\partial F_a(\Delta F(\varepsilon_f))}{\partial \varepsilon_f} \tag{55}$$

By means of this equation it is possible to make a rather general qualitative analysis of the form of the current-voltage dependence. For this purpose, let us consider the experimentally measured transfer coefficient, which according to eqn (49) we shall write in the form:

$$\alpha_{\mathrm{exp}} = kT\frac{\mathrm{d}\ln \vec{i}_c}{\mathrm{d}e\eta_c} = \frac{kT}{\vec{i}_c}\, eC_0^{(1)}\frac{kT}{h}\kappa_F\rho_F\int n\,\frac{\mathrm{d}}{\mathrm{d}e\eta_c}\,\mathrm{e}^{-F_a/kT}\,\mathrm{d}\varepsilon_f \tag{56}$$

If now we use eqn (55) we shall have:

$$\alpha_{\mathrm{exp}} = \frac{\int\alpha(\varepsilon_f)\,\mathrm{d}\vec{i}_c(\varepsilon_f)}{\vec{i}_c} = \langle\alpha(\varepsilon_f)\rangle_{av} \tag{57}$$

Thus, in the absence of the $\psi_1$-effect, the experimental value of the transfer coefficient coincides with the mean value of the microscopic transfer coefficient calculated for an individual value of $\varepsilon_f$. The weight of $\alpha(\varepsilon_f)$ should be equal to the contribution of the current from an individual level $\varepsilon_f$ to the total discharge current. If we assume the main contribution to the total current to be made by a small group of electron levels in a metal electrode localized in the vicinity of a certain level $\varepsilon^*$ dependent on overvoltage, the mean value of the transfer coefficient can be approximately substituted by

$$\alpha_{\mathrm{exp}} \simeq \alpha(\varepsilon^*) \equiv \alpha^*(e\eta_c) \tag{58}$$

Taking into consideration the physical significance of $\varepsilon^*$, it is possible to relate the macroscopic values of the free activation energy

$$F_a^* = F_a(\varepsilon^* + e\eta_c)$$

to the change of the nonequilibrium free energy of the electrode reaction at given overvoltage $\Delta F^* = \Delta F(\varepsilon_f^*)$:

$$\begin{aligned}\frac{\partial F_a^*}{\partial\Delta F^*} &= \frac{\partial F_a^*}{[1 + (\partial\varepsilon^*/\partial e\eta_c)]\,\partial e\eta_c}\\ &= \frac{1}{1 + (\partial\varepsilon^*/\partial e\eta_c)}\left(\frac{\partial F_a(\varepsilon_f + e\eta_c)}{\partial\varepsilon_f}\right)_{\varepsilon^*}\left(1 + \frac{\partial\varepsilon^*}{\partial e\eta_c}\right)\end{aligned}$$

whence we obtain a macroscopic generalization of the Bronsted equation for eqn (53):

$$\alpha^* = -\frac{\partial F_a^*}{\partial \Delta F^*} \tag{59}$$

Another very important relation for $\alpha_{\mathrm{exp}}$ can be obtained from eqn (55) if in the integral we substitute differentiation with respect to $e\eta_c$ by the derivative with respect to $\varepsilon_f$ (see eqn (55)) and then integrate by parts. After simple transformations, we obtain:

$$\alpha_{\mathrm{exp}} = \frac{1}{\vec{i}_c} \int [1 - n(\varepsilon_f)]\, \mathrm{d}\vec{i}_c(\varepsilon_f) = 1 - \langle n(\varepsilon_f) \rangle_{av} \tag{60}$$

where averaging has the same significance as in eqn (57). Comparing eqns (57) and (60) we see that the mean value of the occupation of electron levels in a metal electrode is given by an accurate formula

$$\alpha_{\mathrm{exp}} = \langle \alpha(\varepsilon_f) \rangle_{av} = 1 - \langle n(\varepsilon_f) \rangle_{av} \tag{61}$$

which can be written approximately as:

$$\alpha_{\mathrm{exp}} \simeq \alpha(\varepsilon^*) \simeq 1 - n(\varepsilon^*) \tag{62}$$

In spite of the fact that eqns (61) and (62) are strictly phenomenological, we can draw from these equations some important conclusions about the nature of electrochemical kinetics for the processes under consideration. First of all, it should be pointed out that since the electron level occupation numbers in the metal $n(\varepsilon_f)$ are less than unity, according to eqn (61) we have

$$0 \leqslant \langle \alpha(\varepsilon_f) \rangle_{av} \simeq \alpha(\varepsilon^*) \leqslant 1 \tag{63}$$

The nontriviality of this assertion follows from the fact that the microscopic transfer coefficient for individual electrons $\alpha(\varepsilon_f)$ localized at arbitrary levels $\varepsilon_f$ on the whole does not satisfy eqn (63), i.e. $\alpha(\varepsilon_f)$ can be less than zero or greater than 1. To prove this, let us make another important assumption: let us consider the entropy of activation to be practically independent of $\varepsilon_f$. Then in the Brönsted equation (53) (or eqn (59)) the free energy of activation can be substituted by the activation energy $E_a(\varepsilon_f)$ (or $E_a(\varepsilon^*) = E_a^*$)

$$\alpha(\varepsilon_f) = -\frac{\partial E_a(\Delta F(\varepsilon_f))}{\partial \Delta F(\varepsilon_f)} \tag{64}$$

or

$$\alpha^* = -\frac{\partial E_a^*}{\partial \Delta F^*} \tag{64a}$$

Now let us consider the three possible cases of the positions of initial terms (1) with respect to the fixed term of final state (2) shown in Fig. 6(a). As follows from a simple mathematical analysis, if the minimum of the initial term is located inside the final term (with the subscript $\varepsilon_{f1}$ in Fig. 6(a)), the transfer coefficient is negative ($\alpha(\varepsilon_{f1}) < 0$); if the final term minimum is inside the initial term, the transfer coefficient is greater than unity ($\alpha(\varepsilon_{f3}) > 1$ in Fig. 6(a)). In all the remaining cases (see e.g. the term with subscript $\varepsilon_{f2}$) we have $0 < \alpha < 1$. To formulate this result quantitatively, let us introduce some definitions. We shall say that the transition is of a barrierless nature if the initial state term passes through the minimum of the final term (see the term with subscript $\varepsilon_{bl}$ in Fig. 6(b)). If at the beginning the system was at the term $U_1(q)$, the quantity

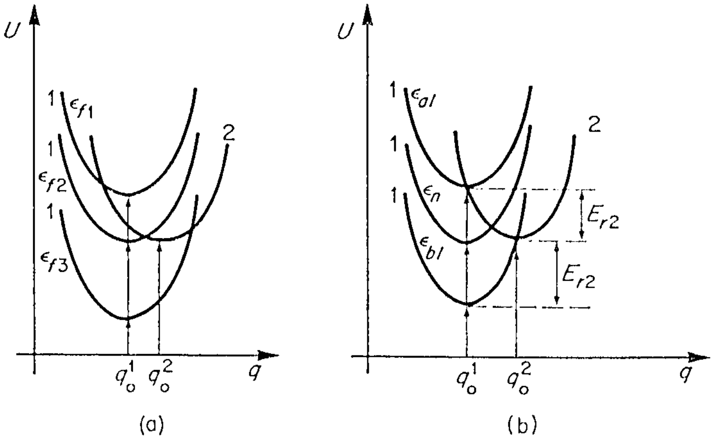

Fig. 6. Qualitative picture of the terms for electrons localized at different levels in the electrode.

$$U_1(q_{02}) - U_1(q_{01}) = E_{r1} \tag{65}$$

will be called the reorganization energy for a forward process ($q_{01}$ and $q_{02}$ are the coordinates of the initial and final terms minima, respectively, see Fig. 6(b)). We are justified in giving this name to the quantity in question, because the quantity $E_{r1}$ is equal to the work to be performed for the initial equilibrium configuration of the classical subsystem to be reorganized into the equilibrium final configuration at a fixed electron state. The reorganization energy for a back process is determined in a similar manner:

$$U_2(q_{01}) - U_2(q_{02}) = E_{r2} \tag{66}$$

where $U_2(q)$ is the final state term (see Fig. 6(b)). In the general case, the quantities $E_{r1}$ and $E_{r2}$ may not coincide, but if the terms of initial and final states have the same shape, i.e.

$$U_2(q - q_{02}) = U_1(q_{01} - q), \quad E_{r1} = E_{r2}$$

The process of a barrierless transition of the system from initial to final terms can be treated as follows. First, the classical subsystem becomes activated: from the equilibrium value $q_{01}$ it passes to the intersection point $q^*$. Then at fixed coordinates of the classical subsystem the quantum transition of the electron from the first to the second term occurs. In this case, since for a barrierless process $q^*$ coincides with the equilibrium configuration of the final state $q_{02}$, there is no need for the relaxation of the classical subsystem after the electron transition. The value of the activation energy for a barrierless process is determined by the relation (see eqn (33):

$$E_a(\varepsilon_{bl}) = \Delta J(\varepsilon_{bl}) = (\varepsilon_{bl} - \varepsilon_F) + e\eta_c + \Delta J_{0F} \tag{67}$$

The so-called activationless transition is treated in a similar manner (see the term with subscript $\varepsilon_{al}$ in Fig. 6(b)). Here the activation energy is zero and the electron transition from initial to final terms occurs directly at the equilibrium point $q_{01}$, whereupon the classical subsystem relaxes to the final equilibrium configuration. A transition will be called normal if the initial state term is located between the barrierless and activationless terms (see, e.g. the term with subscript $\varepsilon_n$ in Fig. 6(b)). In the case of a normal transition, the classical subsystem is at first activated from the equilibrium configuration $q_{01}$ into the configuration $q^*$, whereupon the quantum electron transition occurs, i.e. the system passes from initial to final term, which is followed by the relaxation of the configuration of the classical subsystem from $q^*$ to $q_{02}$. In terms of the reorganization energy, it is easy to formulate the criteria determining the possible values of the microscopic transfer coefficient:

$$\alpha(\varepsilon_f) \geqslant 1, \quad \Delta J = (\varepsilon_f - \varepsilon_F) + e\eta_c + \Delta J_{0F} \leqslant -E_{r1} \tag{68a}$$

$$\alpha(\varepsilon_f) \leqslant 0, \quad \Delta J = (\varepsilon_f - \varepsilon_F) + e\eta_c + \Delta J_{0F} \geqslant E_{r2} \tag{68b}$$

$$0 \leqslant \alpha(\varepsilon_f) \leqslant 1, \quad -E_{r1} \leqslant \Delta J = (\varepsilon_f - \varepsilon_F) + e\eta_c + \Delta J_{0F} \leqslant E_{r2} \tag{68c}$$

Comparing eqns (63) and (68c) we can conclude that the electron term corresponding to the level $\varepsilon^*(\eta_c)$, which makes the main contribution to the resulting discharge current is always located between the barrierless and activationless terms. For instance, if at some overvoltage $\eta_c^{(1)}$ the main contribution to the current is made by the level $\varepsilon_f^{(1)} = \varepsilon^*(\eta_c^{(1)})$ with a sufficient increase of overvoltage the term corresponding to this level can rise so high that $\Delta J(\varepsilon_f^{(1)})$ will be larger than $E_{r2}$. According to eqns (63) and (68), at the new value of overvoltage $\eta_c$ level $\varepsilon_f^{(1)}$ will practically make no contribution to the current. Now the main contribution to the current will be made by another level $\varepsilon_f$ situated below $\varepsilon_f^{(1)}$ so that condition eqn (68c) should be satisfied. A decrease of overvoltage, when $\Delta J(\varepsilon_f^{(1)})$ becomes less than $(-E_{r1})$, can be treated in a similar manner. In this case, the current will be determined by level $\varepsilon_f$ situated above $\varepsilon_f^{(1)}$, so that condition eqn (68c) should be satisfied as before. Thus condition eqn (63) can be treated in a similar manner. In this case, the current will be determined by level $\varepsilon_f$ situated above $\varepsilon_f^{(1)}$, so that condition eqn (68c) should be satisfied as before. Thus condition eqn (63) can be rewritten according to eqn (68c) in the form:

$$-E_{r1} \leqslant (\varepsilon^*(\eta_c) - \varepsilon_F) + e\eta_c + \Delta J_{0F} \leqslant E_{r2} \tag{69}$$

For a more detailed analysis of the discharge current-overvoltage curve let us introduce conditionally three regions of overvoltages:

*Barrierless Region* (low overvoltages). Let us consider the region of low overvoltages in which the following condition is obeyed:

$$0 < e\eta_c < -(\Delta J_{0F} + E_{r1}) \tag{70}$$

It should be noted that this overvoltage region cannot exist for all systems, since the necessary condition for eqn (70) to be valid is that

$$-\Delta J_{0F} > E_{r1} \tag{71}$$

or, since

$$\Delta J_{0F} = \Delta F_{0F} - \Delta\mathscr{F} = kT \ln \frac{C_0^{(1)}}{C_0^{(2)}}$$

that

$$kT \ln \frac{C_0^{(1)}}{C_0^{(2)}} > E_{r1} + \Delta\mathscr{F} \simeq E_{r1} \tag{72}$$

Here we make use of the fact that $\Delta\mathscr{F} \lll E_{r1}$, which can be readily shown to a harmonic approximation, for example, when $\Delta\mathscr{F} \simeq kT \ln(\omega_1/\omega_2)$, where $\omega_1$ and $\omega_2$ are the characteristic frequencies of initial and final terms (see derivation of eqn (28)).

The reorganization energy being as a rule much larger than $kT$, condition eqn (72) can be satisfied at very small concentrations of discharged ions. For example, if we take $E_{r1} \simeq 1$ eV, at room temperature condition eqn (72) gives $C_0^{(2)} \simeq 10^{-18} C_0^{(1)}$. Evidently, condition eqn (72) is never satisfied for redox systems and therefore the barrierless region can be observed only in the case of adsorption of discharged ions on the electrode and only if the adsorption energy is small enough (or the bond energy of the discharging ion in solution is very large). In other words, the barrierless discharge region can be observed only for metals with very high overvoltage. Comparing eqns (68a) and (71) we can formulate the condition of the appearance of the barrierless discharge on the electrode as the requirement that the electron localized at the Fermi level at the equilibrium potential ($\eta_c = 0$) should be characterized by a microscopic transfer coefficient greater than unity

$$\alpha(\varepsilon_F, \varphi_m = \varphi_0) > 1 \tag{73}$$

As has been already stated above, in this case, the main contribution to the current will be made by level $\varepsilon^* > \varepsilon_F$ so that

$$\alpha^* = \alpha(\varepsilon^*(\eta_c)) \lesssim 1 \tag{74}$$

or according to eqn (61)

$$n^* = n(\varepsilon^*(\eta_c)) \gtrsim 0 \tag{75}$$

It should be pointed out that the electron term corresponding to level $\varepsilon^*$ is not exactly barrierless, for this would require $\alpha^* = 1$ and $n^* = 0$. Using the form of the Fermi distribution eqn (7) we can readily see that $n^* \rightarrow 0$ only at $(\varepsilon^* - \varepsilon_F) \rightarrow +\infty$, i.e. at $\eta_c \rightarrow -\infty$, which has no physical sense. However, $\alpha^*$ practically reaches the value 1 even at small deviations of $\varepsilon^*$ from $\varepsilon_F$. In fact, already at $(\varepsilon^* - \varepsilon_F) \simeq 5kT$ the value of $n^*$ is 0·007 and the transfer coefficient $\alpha^* = 0{\cdot}993$, which cannot be experimentally distinguished from unity. Thus, we arrive at a very important conclusion that even at a significant decrease of overvoltage the level making the main contribution to the current $\varepsilon^*$ deviates insignificantly from the Fermi level. Thereby, we actually prove eqn (5) for the low overvoltage region.

In the barrierless discharge region, the value of the activation energy $E_a^*$ practically coincides with the reorganization energy of the direct process $E_{r1}$ (see Fig. 6(b)) and has a nearly constant value independent of overvoltage:

$$(E_a^*)_{bl} \simeq E_{r1} = \text{constant} \tag{76}$$

On the other hand, by definition, this quantity is equal to the difference of minimum potential energies of the final term and the initial term corresponding to the electron level $\varepsilon^*$:

$$(E_a^*)_{bl} \simeq E_{r1} \simeq -\Delta J(\varepsilon^*) = (\varepsilon^* - \varepsilon_F) + e\eta_c + \Delta J_{0F} \tag{77}$$

or

$$\varepsilon^*(\eta_c) - \varepsilon_F \simeq -e\eta_c - (E_{r1} + \Delta J_{0F}) \tag{78}$$

Hence, according to eqn (78) in the barrierless discharge region $\varepsilon^*$ decreases linearly with increasing overvoltage. This result has a simple physical sense. If at an overvoltage $\eta_c^0$, the current was determined by level $\varepsilon^*(\eta_c^0)$, over the whole overvoltage range under consideration the corresponding term occupies a barrierless configuration (see Fig. 7, the term with subscript zero). When the overvoltage is increased by a small quantity $\Delta\eta_c$, so that the system does not go out of the barrierless discharge region ($\alpha^*(\eta_c^0 + \Delta\eta_c) \simeq 1$), the initial term $\varepsilon^*(\eta_c^0)$ rises by the quantity $\Delta\eta_c$ and the barrierless configuration is now occupied by a different term $\varepsilon^*(\eta_c^0 + \Delta\eta_c)$, which was located lower than the term $\varepsilon^*(\eta_c^0)$ by the quantity $\Delta\eta_c$ (see Fig. 7).

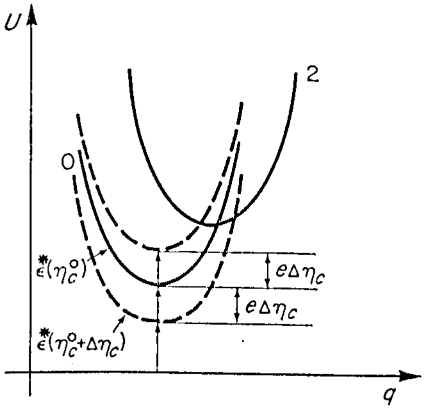

Fig. 7. Schematic representation of the terms determining the current in the barrierless region.

The experimental value of the transfer coefficient $\alpha_{\text{exp}} \simeq \alpha^*$ in the region under consideration being unity, the logarithm of the current for a barrierless discharge should depend linearly on overvoltage. On the other hand, according to eqn (76) the activation energy, and thus the transition probability does not depend on overvoltage. Hence it follows that the current-over-voltage dependence in the barrierless region should be controlled by a factor other than the transition probability. To establish this mechanism it should be pointed out that according to eqn (49) the discharge current is determined not only by the activation factor $\exp(-E_a^*/kT)$, but also by the electron 'concentration' factor $n^* = n(\varepsilon^*)$ (this statement will be proved more rigorously below, see eqn (85)):

$$\vec{i}_c \sim n^* \, \mathrm{e}^{-E_a^*/kT} \simeq \mathrm{e}^{-\varepsilon^* - \varepsilon_F/kT} \, \mathrm{e}^{-E_{r1}/kT} = \mathrm{e}^{e\eta_c/kT} \, \mathrm{e}^{\Delta J_{0F}/kT} \tag{79}$$

where we used eqns (76) and (78). The equation obtained above shows that the experimental value of the discharge current activation energy in the barrierless region is determined not only by the transition probability $E_a^*$, but also by the occupation of the levels contributing to the current

$$\begin{aligned} \varepsilon^* - \varepsilon_F = E_a^{\text{exp}}(\eta_c) &= -kT \ln n^* + E_a^* \\ &\simeq [\varepsilon^*(\eta_c) - \varepsilon_F] + E_a^* \simeq e\eta_c + \Delta J_{0F} \end{aligned} \tag{80}$$

Extrapolating this value of the experimental activation energy at $e\eta_c \rightarrow 0$, we obtain

$$E_a^{\exp}(\eta_c \rightarrow 0) = \Delta J_{0F} \tag{81}$$

Equation (81) is very important since it allows us to determine experimentally one of the most essential parameters of the theory, $\Delta J_{0F}$.

The barrierless discharge region was first experimentally observed by Krishtalik, who investigated the kinetics of the hydrogen ion discharge on a mercury electrode (see, e.g. References 32–36).

*Normal Region* (medium overvoltages). Now we shall consider the overvoltage region determined by the relation:

$$-(\Delta J_{0F} + E_{r1}) < e\eta_c < E_{r2} - \Delta J_{0F} \tag{82}$$

To establish the nature of the current-voltage dependence in the range eqn (82), let us analyse the integrand in eqn (49) for the discharge current. In Fig. 8 the solid curve shows the qualitative form of the dependence of the integrand on the electron energy. Of great importance in this case is the assumption made by us that the dashed curve corresponding to the activation factor is bell-shaped. This assumption is readily justified in the treatment of arbitrary electron terms of initial and final terms with a sufficiently plausible shape. The activation factor reaches its maximum value at

$$\varepsilon_{al} = \varepsilon_F - e\eta_c - \Delta J_{0F} + E_{r2}$$

i.e. when the initial term has an activationless configuration (see the term with subscript $\varepsilon_{al}$ in Fig. 6(b)). As is clear from Fig. 6, with deviations from $\varepsilon_f = \varepsilon_{al}$ in both directions ($\varepsilon_f > \varepsilon_{al}$ or $\varepsilon_f < \varepsilon_{al}$) the activation energy increases smoothly, which accounts for the bell-shape of the factor $\exp(-E_a/kT)$. Naturally, in this treatment we proceed from the assumption made by us earlier that the activation entropy depends only slightly on $\varepsilon_f$. Since $\varepsilon_{al}$ depends linearly on $e\eta_c$ with changing overvoltage the dashed curve in Fig. 8

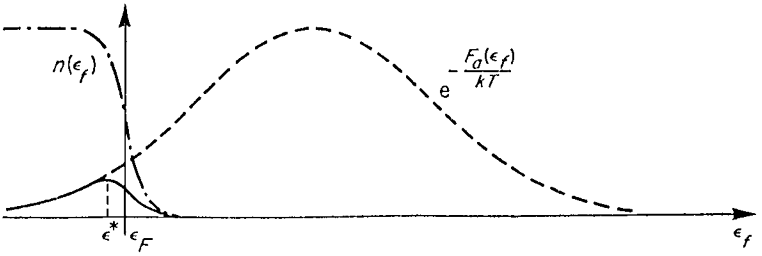

Fig. 8. Qualitative picture of the Fermi distribution function $n(\varepsilon_f)$, activation factor $\exp[-F_a(\varepsilon_f)/kT]$ and their product (solid curve).

without changing its form will shift to the right (with decreasing $e\eta_c$) or to the left (with increasing $e\eta_c$). The maximum of the whole integrand will shift in the same direction. It can readily be seen that the level at which the integrand maximum is reached coincides in its sense with the quantity $\varepsilon^*$ introduced earlier, i.e. with the level making the main contribution to the total discharge current. This can be also directly proved mathematically if the derivative of the integrand is equated to zero,

$$\frac{\mathrm{d}}{\mathrm{d}\varepsilon_f}(n\,\mathrm{e}^{-E_a/kT}) = 0 \tag{83}$$

After simple transformations we obtain the equation for determination of $\varepsilon^*$:

$$1 - n(\varepsilon_f) = \alpha(\varepsilon_f) \tag{84}$$

Comparing this equation with formula eqn (62), we see that at $\varepsilon_f = \varepsilon^*$ they coincide absolutely. If now we use the Laplace method (analogue of the method of steepest descent for functions of real variables), we can find an approximate expression for the discharge current

$$\vec{i}_c = eC_0^{(1)}\frac{kT}{h}\,\kappa_F\rho_F n(\varepsilon^*)\exp\left[-\frac{F_a^*}{kT}\right]\Delta\varepsilon^* \tag{85}$$

where

$$\Delta\varepsilon^* = \sqrt{(2\pi)}kT[n^*(1-n^*) + kTF_a''(\varepsilon^*)]^{-1/2} \tag{86}$$

has the significance of the width of levels located near $\varepsilon^*$ and contributing to the discharge current. In calculating the integral eqn (49) by the Laplace method, the quantity $F_a''(\varepsilon^*)$ is assumed to be practically independent of $\varepsilon^*$, i.e. of overvoltage. Taking this into consideration and assuming the reorganization energies of forward and back processes to be of the same order of magnitude ($E_{r1} \simeq E_{r2} = E_r$), we can estimate the second derivative of the free activation energy

$$F_a''(\varepsilon^*) \simeq \frac{1}{2E_r} = \text{constant} \tag{87}$$

This formula will be rigorously proved in the next section in the model quantum-mechanical treatment of the problem. For the present, however, we shall consider it as a relation which is sufficiently valid. An expression for the width of levels $\Delta\varepsilon^*$ can be written in a somewhat more convenient form if we make use of the identity

$$\frac{\mathrm{d}\varepsilon^*}{\mathrm{d}e\eta_c} = -\left[1 + \frac{n^*(1-n^*)}{kTF_a''(\varepsilon^*)}\right]^{-1} \simeq \left[1 + \frac{2E_r}{kT}n^*(1-n^*)\right]^{-1} \tag{88}$$

Substituting eqn (88) into eqn (86) we obtain

$$\Delta\varepsilon^* = \left\{\frac{2\pi kT}{F''_a(\varepsilon^*)}\left|\frac{d\varepsilon^*}{de\eta_c}\right|\right\}^{1/2} \simeq \left\{4\pi kTE_r\left|\frac{d\varepsilon^*}{de\eta_c}\right|\right\}^{1/2} \tag{89}$$

The estimates obtained at real values of $E_r$ (of the order of some electron-volts) show that the halfwidth of the levels ($\frac{1}{2}\Delta\varepsilon^*$) depends slightly on $n^*$, i.e. on potential, and amounts to several $kT$. For example, for $E_r = 2$ eV in the normal region ($n^* \simeq 0{\cdot}5$) we have $\frac{1}{2}\Delta\varepsilon^* \simeq 2{\cdot}5kT$, and in the barrierless ($n^* \simeq 0{\cdot}01$) and activationless ($n^* \simeq 0{\cdot}99$) regions $\frac{1}{2}\Delta\varepsilon^* \simeq 5{\cdot}4kT$. Hence in calculating the transfer coefficient, the quantity $\Delta\varepsilon^*$ can be assumed to be constant; the correction for $\alpha_{\text{exp}}$ appearing in this case being no greater than several hundredths. Thus, the experimental activation energy will appear as the quantity (see eqn (85))

$$E_a^{\text{exp}} = -kT\ln n^* + E_a(\varepsilon^*) \tag{90}$$

whence for the experimental transfer coefficient we obtain the relation eqn (58)

$$\alpha_{\text{exp}} = \frac{d\ln \vec{i}_c}{de\eta_c/kT} = -\alpha^*\frac{d\varepsilon^*}{de\eta_c} + \alpha^*\left(1 + \frac{d\varepsilon^*}{de\eta_c}\right) = \alpha^* \tag{91}$$

It is characteristic of the normal region that at a certain overvoltage $\eta_c = \eta_c^F$ the discharge current is determined mainly by the electron localized at the Fermi level: $\varepsilon^*(\eta_c^F) = \varepsilon_F$. At small deviations of overvoltage from $\eta_c^F$, the discharge current can be written as

$$\begin{aligned}\vec{i}_c &\simeq eC_0^{(1)}\frac{kT}{h}\kappa_F\rho_F\tfrac{1}{2}\Delta\varepsilon^* \\ &\qquad \exp\left\{-\frac{F_a(\varepsilon_F + e\eta_c^F)}{kT} + \frac{e\eta_c - e\eta_c^F}{2kT}\left(1 - \frac{e\eta_c - e\eta_c^F}{4kT + 1/F''_a}\right)\right\} \\ &\simeq eC_0^{(1)}\frac{kT}{h}\kappa_F\rho_F\tfrac{1}{2}\Delta\varepsilon^* \\ &\qquad \exp\left\{-\frac{F_a(\varepsilon_F + e\eta_c^F)}{kT} + \frac{e\eta_c - e\eta_c^F}{2kT}\left(1 - \frac{e\eta_c - e\eta_c^F}{2E_r}\right)\right\}\end{aligned} \tag{92}$$

Accordingly, for the transfer coefficient we have

$$\alpha_{\text{exp}} \simeq \tfrac{1}{2}\left(1 - \frac{e\eta_c - e\eta_c^F}{2kT + 1/F''_a}\right) \simeq \tfrac{1}{2} - \frac{e\eta_c - e\eta_c^F}{2E_r} \tag{93}$$

The reorganization energy being a sufficiently large quantity, we can conclude on the basis of formula eqn (93) that in the normal region over a wide enough overvoltage range the transfer coefficient is equal to $\frac{1}{2}$. For example, if $E_r = 2$ eV the transfer coefficient is $0{\cdot}5 \pm 0{\cdot}1$ at $\Delta e\eta_c \simeq 0{\cdot}8$ eV.

*Activationless Region* (high overvoltages). With further increase of overvoltage, when the condition

$$e\eta_c > E_{r2} - \Delta J_{0F} \tag{94}$$

is valid, electrochemical kinetics is determined by the activationless discharge. Comparing eqns (94) and (68b) we see that the activationless region begins at overvoltages such that the microscopic transfer coefficient for the electron localized at the Fermi level becomes negative:

$$\alpha(\varepsilon_F + e\eta_c) < 0 \tag{95}$$

On the other hand, it follows from formula eqn (69) that the electron level $\varepsilon^*$ determining the discharge current in the activationless region is located below the Fermi level, i.e. $n(\varepsilon^*) \simeq 1$ and $\alpha(\varepsilon^*) \simeq 0$. Just as in the barrierless region actual deviation of $\varepsilon^*$ from $\varepsilon_F$ is not large. For example, at $\varepsilon^* \simeq \varepsilon_F - 5kT$ $n^*$ is equal to $0{\cdot}993$ and the transfer coefficient is practically zero: $\alpha^* = 0{\cdot}007$. Thus, with overvoltage changing over an extremely large range

$$\Delta e\eta_c \simeq E_{r1} + E_{r2}$$

covering the three regions of electrochemical kinetics, the level $\varepsilon^*$, making the chief contribution to the current, varies over a small range of energies near the Fermi level ($\pm 5kT$).

As has been already stated earlier, in the activationless region the activation energy is zero and $\Delta J(\varepsilon^*) \simeq E_{r2}$, whence we find directly the dependence of $\varepsilon^*$ on overvoltage:

$$\varepsilon^* \simeq \varepsilon_F - e\eta_c - (\Delta J_{0F} - E_{r2}) \tag{96}$$

The linear dependence of $\varepsilon^*$ on $e\eta_c$ in the activationless region has the same physical nature as in the barrierless region (see explanation for formula eqn (78)). Since in the overvoltage range under consideration $n^* \simeq 1$, not only $E_a^*$ but also the experimental activation energy is zero (see eqn (90)), which results in the current having a constant value:

$$\vec{i}_c = eC_0^{(1)} \frac{kT}{h} \kappa_F \rho_F \, e^{S_a/kT} \Delta\varepsilon^* = \text{constant} \tag{97}$$

A practical realization of an activationless mechanism presents certain experimental difficulties, since increase of discharge current may lead to the violation of condition eqn (1) the physical significance of which is that diffusion control starts to operate.[46,47] In considering experimental conditions for establishing activationless or barrierless mechanisms for an electrochemical reaction, one should bear in mind that both these processes always occur simultaneously, viz. if the forward process is barrierless, the back process will be an activationless process, and vice versa.[36] This can readily be seen if according to formula eqn (47) we write the relation between direct and reverse currents for an individual electron level $\varepsilon_f$:

$$\mathrm{d}\overrightarrow{i_c}(\varepsilon_f) = \mathrm{d}\overleftarrow{i_c}(\varepsilon_f)\, \mathrm{e}^{e\eta_c/kT} \frac{C_0^{(2)}}{C^{(2)}} \tag{98}$$

This formula shows that for each fixed overvoltage $e\eta_c$ the maximum contribution both to direct and reverse currents is made by the same level $\varepsilon^*$ determined by eqn (84). In considering the ionization current, the transfer coefficient $\beta$ can be conveniently determined using the formula

$$\beta_{\mathrm{exp}} = -kT \frac{\mathrm{d}}{\mathrm{d}e\eta_c} \ln \frac{C_0^{(2)}}{C^{(2)}} \overleftarrow{i_c} \tag{99}$$

to isolate the dependence of the adsorbed particles concentration on overvoltage. If now we use formula eqn (48) we obtain from eqn (99) the usual relation between the transfer coefficients of forward and back processes:

$$\beta_{\mathrm{exp}} = 1 - \alpha_{\mathrm{exp}} \tag{100}$$

We have described qualitatively the whole discharge current-overvoltage curve and shown that, generally speaking three asymptotic overvoltage regions are possible: barrierless ($\alpha_{\mathrm{exp}} \simeq 1$), normal ($\alpha_{\mathrm{exp}} \simeq 0{\cdot}5$) and activationless ($\alpha_{\mathrm{exp}} \simeq 0$). These three asymptotic curves are shown in logarithmic scale in Fig. 9. The smooth curve is only qualitative in nature, since strictly

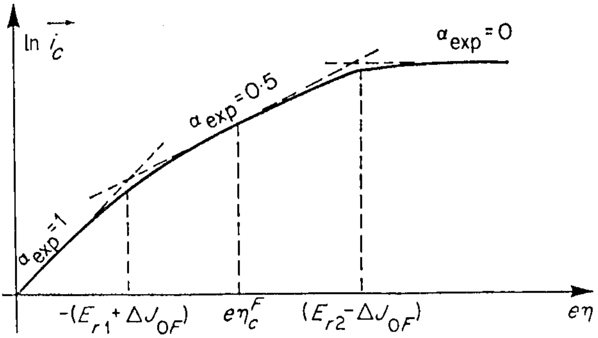

Fig. 9. Schematic representation of the dependence of the logarithm of current on overvoltage.

within the framework of the semi-phenomenological theory it is impossible to investigate the shape of the transition region, i.e. the overvoltage range near $e\eta_c = -\Delta J_{0F} \pm E_{r1,2}$. Further quantitative elaboration of the theory depends essentially on the concrete form of the dependence of the free energy of activation on $\varepsilon_f$. The quantity $F_a(\varepsilon_f)$ can be calculated only for a definite model; this calculation is made in subsequent sections. An attempt can be made, however, to approach the problem from a semiempirical point of view. The first approach is to try to reconstruct on the basis of the experimental data the shape of the $F_a - \varepsilon_f$ dependence. For this purpose, we shall write the $\alpha(\varepsilon_f)$ dependence as the inverse function

$$e\eta_c + kT \ln \frac{1 - n(\varepsilon_f)}{n(\varepsilon_f)} = \varepsilon_f - \varepsilon_F + e\eta_c = F(\alpha) \tag{101}$$

where $F(\alpha)$ is the unknown function. Let us substitute in this formula $\varepsilon^*(\eta_c)$ for $\varepsilon_f$ and replace $\alpha$ by $\alpha^* = 1 - n^* = \alpha_{\mathrm{exp}}$

$$e\eta_c = F(\alpha_{\mathrm{exp}}) + kT \ln \frac{1 - \alpha_{\mathrm{exp}}}{\alpha_{\mathrm{exp}}} \tag{102}$$

The obtained relation actually solves the problem posed since it gives the form of the function $F$ if the dependence of the transfer coefficient on overvoltage is experimentally known. With $\alpha(\varepsilon_f)$ known, it is possible to find the activation energy using formula eqn (64)

$$E_a(\varepsilon_f) = -\int \alpha(\varepsilon_f)\, d\varepsilon_f \tag{103}$$

For practical use of the method described above, it is necessary to bear in mind that in order to find the detailed form of the functional dependence $E_a(\varepsilon_f)$ one should have at one's disposal experimental data on the dependence of $\alpha_{\mathrm{exp}}$ on $e\eta_c$ over a wide enough overvoltage range, the overvoltage range in which the transfer coefficient shows a marked variation being of most importance.

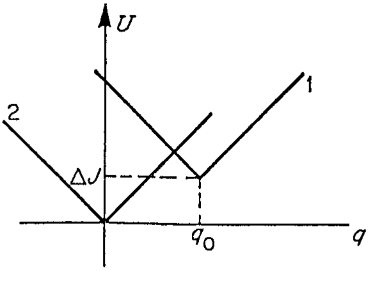

Fig. 10. Model linear terms.

Another semi-empirical approach to the problem consists in assuming the form of the dependence $E_a(\varepsilon_f)$ or the form of the electronic terms and determining the theoretical parameters from comparison with experiment. Below we shall give as an example a calculation of the current for symmetrical linear terms (see Fig. 10) which are seldom used in electrochemical literature:[37]

$$\begin{aligned} U_1(q) &= (\varepsilon_f - \varepsilon_F) + e\eta_c + \Delta J_{0F} + \frac{E_r}{q_0}|q - q_0| \\ &= \Delta J(\varepsilon_f) + \frac{E_r}{q_0}|q - q_0|, \\ U_2(q) &= \frac{E_r}{q_0}|q| \end{aligned} \tag{104}$$

The activation energy for linear terms is found from simple geometric considerations and is of the form

$$E_a(\varepsilon_f) = \tfrac{1}{4}(E_r - \Delta J(\varepsilon_f)), \quad |\Delta J(\varepsilon_f)| \leqslant E_r \tag{105}$$

In the case when $|\Delta J(\varepsilon_f)| > E_r$ the terms do not intersect and the activation energy can be formally considered to be equal to infinity. Accordingly, the discharge current can be written as (see eqn (49)):

$$\vec{i}_c = eC_0^{(1)} \frac{kT}{h} \kappa_F \rho_F \, e^{S_a/kT} \int_{\varepsilon_F - e\eta_c - \Delta J_{0F} - E_r}^{\varepsilon_F - e\eta_c - \Delta J_{0F} + E_r} n(\varepsilon_f) \exp\left(-\frac{E_a(\varepsilon_f)}{kT}\right) d\varepsilon_f$$

The integral in the right hand side can be calculated accurately, and finally for the discharge current we obtain the expression

$$\vec{i}_c = eC_0^{(1)} \frac{kT}{h} \kappa_F \rho_F \, e^{S_a/kT} 2kT \, e^{e\eta_c + \Delta J_{0F} - E_r/2kT} \operatorname{arctg} \frac{sh(E_r/2kT)}{ch(e\eta_c + \Delta J_{0F}/2kT)} \tag{106}$$

which can be asymptotically represented for the three regions as follows:

(*a*) for the barrierless region:

$$\ln \vec{i}_c = \ln \Delta\varepsilon_{bl}^* A + \frac{e\eta_c + \Delta J_{0F}}{kT}; \quad \Delta\varepsilon_{bl}^* = 2kT; \quad 0 < e\eta_c < -(\Delta J_{0F} + E_r) \tag{107a}$$

(*b*) for normal region:

$$\ln \vec{i}_c = \ln \Delta\varepsilon_n^* A + \tfrac{1}{2}\frac{e\eta_c + \Delta J_{0F} - E_r}{kT}; \quad \Delta\varepsilon_n^* = \pi kT;$$

$$-(\Delta J_{0F} + E_r) < e\eta_c < E_r - \Delta J_{0F} \tag{107b}$$

(*c*) for the activationless region:

$$\ln \vec{i}_c = \ln \Delta\varepsilon^*_{al} A; \quad \Delta\varepsilon^*_{al} = 2kT; \quad e\eta_c > E_r - \Delta J_{0F} \tag{107c}$$

where the constant $A$ is determined from the formula

$$A = eC_0^{(1)} \frac{kT}{h} \kappa_F \rho_F \, e^{S_a/kT} \tag{108}$$

and the quantity $\Delta\varepsilon^*$ as before has the significance of the range of levels making the chief contribution to the current. The overvoltage dependence of the discharge current, corresponding to eqn (106), is plotted in Fig. 11,

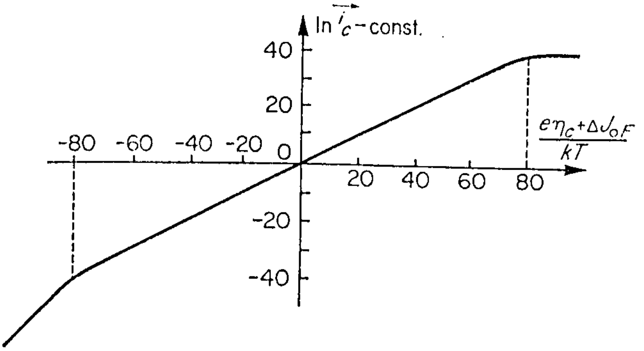

Fig. 11. Dependence of the logarithm of current on overvoltage for model linear terms; $E_r = 2$ eV, $kT = 0{\cdot}025$ eV, constant $= \ln \pi A_K T - E_r/2kT$.

where the value 2 eV is chosen for the parameter $E_r$ (reorganization energy). It can be seen from the plot that practically over the whole normal region $\alpha = 0{\cdot}5$. According to the general semi-phenomenological theory, in the barrierless region $\alpha = 1$ and in the activationless region $\alpha = 0$. The transition between these three regions occurs in a very narrow overvoltage range: $\Delta e\eta \simeq 6kT \simeq 0{\cdot}15$ eV. Here the transition region is that part of the curve where $\alpha$ varies within 0·05–0·45 (near the activationless region) or within 0·55–0·95 (near the barrierless region).

In the present section we have proceeded practically everywhere from the assumption of the electron being the only quantum subsystem in the problem. But in considering some other particular systems, we find other particles to possess quantum spectra along with the electron. The condition of a quantum treatment of the particle was formulated by us already at the beginning of this section and amounted to the requirement that the excitation energy $\Delta E$

should be greater than the thermal energy $kT$. As we shall see in what follows, this is the case for example, in the treatment of the proton transfer processes. Below we shall give a method for taking into consideration other than electron quantum subsystems.

If during the ion discharge the quantum subsystem located at an initial moment at an arbitrary excited level $\varepsilon_r^{(1)}$ passes to any other excited level of the final state $\varepsilon_{r'}^{(2)}$, we can use for the current corresponding to this process formula eqn (85), taking into consideration, however, that now the transmission coefficient $\kappa_F$ will depend on $r$ and $r'$, since in this case the exchange integral will contain the overlapping of the wave functions of the quantum subsystem in initial and final states. Moreover, the position of the electron level $\varepsilon^*$, making the chief contribution to the discharge current, will depend on the subscripts $r$ and $r'$. Now the difference of minimum potential energies of the classical subsystem can be conveniently written as

$$\Delta J^{rr'}(\varepsilon_f) = (\varepsilon_f - \varepsilon_F) + e\eta_c + \Delta J_{0F} + (\varepsilon_r^{(1)} - \varepsilon_{r'}^{(2)}) \tag{109}$$

where $\Delta J_{0F}$ comprises the difference of zero energies of the quantum subsystem, and $\varepsilon_r^{(1)}$ and $\varepsilon_r^{(2)}$ are reckoned from the energies of unexcited states. If the parameters $\gamma$ determining the geometric shape and relative horizontal arrangement of the terms are assumed to be unchanged when the quantum subsystem is excited, the values $\varepsilon^*$ for various $r$ and $r'$ can be readily interrelated. In fact, under this assumption, the excitation of the quantum subsystem amounts only to a vertical displacement of corresponding term, which is equivalent to a change of overvoltage by the quantity $(\varepsilon_r^{(1)} - \varepsilon_{r'}^{(2)})$. Therefore, if by $\varepsilon_0^*(\eta_c)$ we designate the electron level making the chief contribution to the current upon transition of the quantum subsystem from the ground level of the initial state to the ground level of the final state, we have

$$\varepsilon_{rr'}^*(e\eta_c) = \varepsilon_0^*(e\eta_c + \varepsilon_r^{(1)} - \varepsilon_{r'}^{(2)}) \tag{110}$$

Now the total discharge current averaged over the initial states and summed over the final states of the quantum subsystem can be written as

$$\vec{i}_c = \sum_{r,r'} \frac{\kappa_{rr'}}{\kappa_0} \vec{i}_{c0}(e\eta_c + \varepsilon_r^{(1)} - \varepsilon_{r'}^{(2)})\, \mathrm{e}^{-\varepsilon_r^{(1)}/kT} \left[\sum_r \mathrm{e}^{-\varepsilon_r^{(1)}/kT}\right]^{-1} \tag{111}$$

where $\vec{i}_{c0}$ corresponds to the discharge current calculated assuming the quantum subsystem to be passing from the unexcited initial state to the unexcited final state.

It follows from the derivation of formula eqn (111) itself that the method described above permits us to take into account also an excited state of the electron in the ion and in the adsorbed particle, for which purpose $\varepsilon_r^{(1)}$ and $\varepsilon_r^{(2)}$ should also signify excited electron levels.

## III. EFFECT OF THE SOLVENT ON ELECTRODE PROCESSES

### 1. Solvent Model

The course of most electrochemical reactions is strongly affected by the polar solvent. Physically, this can be explained by the fact that the charge transfer process usually involves strong reorganization of polar medium. For example, if the discharge of a charged particle results in the formation of a neutral particle, the solvent near the discharging particle will be completely depolarized in the course of electrochemical reaction. Accordingly, the heat of such a reaction will comprise the ion hydration energy. In view of the strong interaction of the charge with the polar medium, in electrochemical kinetics it is impossible to neglect the effect of the solvent on the reaction course; moreover, as a rule, this effect cannot be taken into account by introducing a small correction for some basic physical effects. The mathematical sense of this is that the contribution of the polar medium cannot be estimated by the perturbation theory method and that the interaction of the charge with the solvent should be taken into consideration already in the zero approximation. There is one more reason which makes it necessary for us to exercise particular care in analysing the role of the medium in kinetics. As has been already pointed out in the previous section, according to condition eqn (15) the dynamical behaviour of the solvent is classical and therefore the activation energy of electrochemical processes should depend to a considerable extent on the properties of the polar medium.

From a theoretical point of view, in electrochemical and homogeneous kinetics it seems to be impossible at present to take into consideration accurately the properties of a polar liquid. It should be recalled that one of the vital problems of modern physics—the determination of the energy spectrum and correlation functions (space distribution of liquid atoms) has not been solved theoretically as yet. We can only hope to be able to use a polar liquid model which would be adequate enough for the problem posed. In the present and subsequent sections we shall always assume as being possible the use of the dielectric continuum model for an approximate description of the medium. As the charge interacts mainly with the dipole moments of the solvent molecules, it is sufficient to know the specific polarization for the description of the medium in a continuum model. We have already said that of essential importance in electrochemical kinetics is the dynamical behaviour of the solvent, i.e. the dependence of polarization on time. In other words, to describe the medium it is necessary to know not only the polarization value $\vec{P}(\vec{r})$ at any point of space but also the rate of the change of polarization $\dot{\vec{P}}(\vec{r})$. We shall consider the solvent state to be completely known if we know two independent function: $\vec{P}(\vec{r})$ and $\dot{\vec{P}}(\vec{r})$. Thus, $\vec{P}(\vec{r})$ and $\dot{\vec{P}}(\vec{r})$ in the continuum model play the same part as canonically conjugate variables: coordinates and velocities of particles in mechanics. From what we have just said, it is possible to draw very important physical conclusions. First of all, due to the dynamic nature of polarization, the relations of macroscopic electrodynamics, being valid only for averaged quantities, are not valid for $\vec{P}(\vec{r})$. For example, even in the absence of an external field, dynamic polarization of the solvent differs from zero. In terms of statistical physics, dynamic polarization is equivalent to polarization fluctuation. In the presence of a constant external electric field characterized by electric induction $\vec{D}$, this field is proportional only to the mean statistical (i.e. averaged over a long time interval) value of dynamic polarization:

$$\langle\vec{P}\rangle = \frac{\varepsilon_S - 1}{4\pi\varepsilon_S}\vec{D} \tag{112}$$

where $\varepsilon_S$ is the static dielectric constant, and $\langle. . .\rangle$ denotes statistical averaging. In this case, dynamic polarization corresponds to fluctuations of $\vec{P}$ about the mean value of $\langle\vec{P}\rangle$. Physically the fluctuation nature of dynamic polarization is due to thermal vibrations of solvent atoms and molecules. Since we are interested only in polar liquids, we have to take into consideration that the solvent molecules have their own dipole moment in the absence of an external electric field. As the result, the polarization fluctuations will be caused both by the vibrations, due to the change in the relative positions of atoms inside the solvent molecule and by the orientation (libration) vibrations of the whole molecule. For example, in water vibrations of the atomic type can include those of the O—H or H—H bonds, whereas the orientation motion results from the vibration of the whole molecule about the axis of symmetry (so-called hindered rotation). The frequencies of orientation vibrations being considerably lower than the frequencies of atomic vibrations, at room temperature the orientation vibrations, are the most highly excited, and they will make the maximum contribution to the polarization fluctuation. The characteristic values of the vibration frequencies are as follows: $\omega_0 \simeq 10^{11}$ sec$^{-1}$ for orientation vibrations and $\omega_a \simeq 10^{13} - 10^{14}$ sec$^{-1}$ for atomic vibrations. The dynamic behaviour of polarization being chiefly due to the orientation motion of dipoles of the medium, we shall henceforth use everywhere for the frequencies of polarization vibrations the quantity $\omega_0$ assuming atomic vibrations to be practically 'frozen'.

Naturally, along with the atomic-orientational part, polarization of the electron clouds of the atoms also makes a contribution to total polarization of the medium. In our treatment of electronic polarization we shall make use of the fact that with fixed positions of the solvent atomic nuclei and in the absence of an external field, electronic polarization cannot fluctuate at room temperature, since the characteristic frequencies for the electron are too high: $\omega_e \simeq 10^{15} - 10^{16}\,\text{sec}^{-1} \gg kT/\hbar$. In other words, electronic polarization adjusts itself instantaneously to the change in the coordinates of the solvent atomic nuclei. If we designate electronic polarization caused by the interaction of the solvent nuclei with electron clouds of atoms as $\vec{P}_{en}$, and polarization due to the dipole moment of nuclei as $\vec{P}_n$, in virtue of what has been said above, we can relate these two quantities by an equilibrium formula of macroscopic electrodynamics:

$$\vec{P}_{en} = \frac{1 - \varepsilon_0}{\varepsilon_0}\vec{P}_n \tag{113}$$

where $\varepsilon_0$ is the optical (electronic) dielectric constant. It should be stressed that, although electronic polarization itself does not fluctuate, according to formula eqn (113) fluctuation of the nuclei ($\vec{P}_n$) involves a change in the quantity $\vec{P}_{en}$ so that both $\vec{P}_n$ and $\vec{P}_{en}$ contribute to dynamic polarization. The polarization made up of these two polarizations is usually termed inertial (according to Pekar[4]) or infrared (according to Fröhlich) polarization:

$$\vec{P}_{tr} = \vec{P}_n + \vec{P}_{en} = \frac{1}{\varepsilon_0}\vec{P}_n \tag{114}$$

In the presence of an external electric field varying with frequency $\omega \ll \omega_e$, electronic polarization of the atoms of the medium follows instantaneously the change of external field

$$\vec{P}_{op} = \frac{\varepsilon_0 - 1}{4\pi\varepsilon_0}\vec{D} \tag{115}$$

where $\vec{D}$ is the electric induction of the external field and $\vec{P}_{op}$ is the electronic polarization of the medium due to this field. The quantity $\vec{P}_{op}$ is usually called inertialess (according to Pekar) or optical (according to Fröhlich) polarization. Thus, total polarization of the medium is made up of $\vec{P}_{tr}$ and $\vec{P}_{op}$:

$$\vec{P}(r) = \vec{P}_{tr}(\vec{r}) + \vec{P}_{op}(\vec{r}) \tag{116}$$

Since optical polarization does not undergo fluctuations and contribute to dynamic polarization, in what follows we shall consider only the inertial part of the total polarization $\vec{P}_{ir}$, omitting everywhere for brevity the subscript *ir*, $\vec{P}(\vec{r})$ being understood to mean only the infrared component.

In a theoretical treatment of polar systems it is convenient to represent specific polarization as a set of sinusoidal waves

$$\vec{P}(\vec{r}) = \frac{1}{\sqrt{V_S}} \sum_{\vec{k}} \vec{P}_{\vec{k}}\, e^{i\vec{k}\vec{r}} \tag{117}$$

where $\vec{P}_{\vec{k}}$—the Fourier amplitudes—figure as normal coordinates for the solvent and a complete set of them unambiguously describes the polarization state of the medium at any point in the space: the wave vector $\vec{k}$ determines the length of the wave and the direction of the corresponding sinusoid (harmonic); $V_S$ is the volume of the polar medium ($V_S \rightarrow \infty$). The interaction of the charges introduced into the solvent from outside with the polar liquid can be represented as an ordinary coulombic interaction with the charges of the medium the density of which in the continuum model is of the form:

$$\rho = -\mathrm{div}\vec{P} = -i\sum_{\vec{k}} (\vec{P}_{\vec{k}}\vec{k})\, e^{i\vec{k}\vec{r}} \tag{118}$$

If polarization is divided into longitudinal ($\vec{P}_{\vec{k}}$ parallel to $\vec{k}$) and transverse ($\vec{P}_{\vec{k}}$ perpendicular to $\vec{k}$) components, it can be seen from eqn (118) that only the longitudinal polarization interacts with the external charges:

$$\vec{P}_{11}(\vec{r}) = \frac{1}{\sqrt{V_S}} \sum_{\vec{k}} \frac{\vec{k}}{k^2} (\vec{P}_{\vec{k}}\vec{k})\, e^{i\vec{k}\vec{r}} \equiv \frac{1}{\sqrt{V_S}} \sum_{\vec{k}} \frac{\vec{k}}{k} P_{\vec{k}}\, e^{i\vec{k}\vec{r}} \tag{119}$$

With certain assumptions, it is possible to show that longitudinal and transverse components do not interact; therefore we shall deal only with the longitudinal component of inertialess polarization, which for simplicity we shall write as $\vec{P}(\vec{r})$ instead of $\vec{P}_{11}(\vec{r})$.

For a quantum-mechanical treatment of the dynamic behaviour of the polar solvent, it is necessary to find first the form of the classical Hamiltonian, i.e. the energy of the medium, which depends on the functions $\vec{P}(\vec{r})$ and $\dot{\vec{P}}(\vec{r})$.

For a pure solvent, in the absence of an external field, the energy can be written as a functional expansion in small polarization fluctuations:

$$E = \tfrac{1}{2}\int\sum_{\alpha,\beta} F_{\alpha\beta}(\vec r - \vec r\,')\dot P_{\alpha}(\vec r)\dot P_{\beta}(\vec r\,')\,d\vec r\,d\vec r\,' + \tfrac{1}{2}\int\sum_{\alpha\,\beta}\phi_{\alpha\beta}(\vec r - \vec r\,')P_{\alpha}(\vec r)P_{\beta}(\vec r\,')\,d\vec r\,d\vec r\,' \quad (120)$$

where subscripts $\alpha$, $\beta = x, y, z$ determine the projections on Cartesian coordinates, the functions $F$ and $\phi$, in virtue of homogeneity of the medium, depend only on the distance between points $\vec r$ and $\vec r\,'$ and are basic characteristics of the polar medium in the continuum model. The physical significance of $F$ and $\phi$ we shall establish later; here we shall only point out that the linear term with respect to $\vec P(\vec r)$ is absent in the functional expansion owing to isotropy of the medium. The expression for the energy in eqn (120) has a standard form of the sum of kinetic (the first term) and potential (the second term) energies. In the potential energy, we have restricted ourselves to the quadratic term with respect to polarization, which is equivalent to a harmonic approximation.

Expanding the functions $F_{\alpha\beta}(\vec r)$ and $\phi_{\alpha\beta}(\vec r)$ into the Fourier series and substituting them into formula eqn (120) we can write for the energy

$$E = \tfrac{1}{2}\sum_{\vec k}\{F_{\vec k}|\dot P_{\vec k}|^2 + \phi_{\vec k}|P_{\vec k}|^2\} \quad (121)$$

where $F_{\vec k}$ and $\phi_{\vec k}$ are related to the Fourier applitudes $F_{\alpha\beta}(\vec k)$ and $\phi_{\alpha\beta}(\vec k)$ by the formulae

$$\sum_{\alpha,\beta} F_{\alpha\beta}(\vec k)\frac{k_\alpha k_\beta}{k^2} = F_{\vec k}; \quad \sum_{\alpha,\beta}\phi_{\alpha\beta}(\vec k)\frac{k_\alpha k_\beta}{k^2} = \phi_{\vec k} \quad (122)$$

If we introduce the frequencies for normal vibrations of longitudinal polarization according to:

$$\omega_{\vec k}^2 = \frac{\phi_{\vec k}}{F_{\vec k}} \quad (123)$$

the classical Hamiltonian for the solvent assumes the same form as for a set of oscillators:

$$E = \tfrac{1}{2}\sum_{\vec k}\{|\dot P_{\vec k}|^2 + \omega_{\vec k}^2|P_{\vec k}|^2\}F_{\vec k} \quad (124)$$

Now let us consider in more detail the structure of the solvent energy in formula eqn (120). Let us divide conditionally the function $\phi_{\alpha\beta}(\vec r - \vec r\,')$ into local and nonlocal components:

$$\phi_{\alpha\beta}(\vec r - \vec r\,') = \phi_0\delta_{\alpha\beta}\delta(\vec r - \vec r\,') + \phi_0\varphi_{\alpha\beta}(\vec r - \vec r\,'); \quad \phi_0 = \text{constant} \quad (125)$$

where the first term describes the part of potential energy that is chiefly due to elastic forces of a single dipole performing orientational vibrations at a limiting long-wave frequency $\omega_0$. The second term in formula eqn (125) characterizes the interaction of polarizations at different points of the space and can be qualitatively described by the interaction of two dipoles located at points $\vec{r}$ and $\vec{r}'$. Similarly, the kinetic energy can be divided into local and nonlocal components:

$$F_{\alpha\beta}(\vec{r} - \vec{r}') = F_0 \delta_{\alpha\beta} \delta(\vec{r} - \vec{r}') + F_0 f_{\alpha\beta}(\vec{r} - \vec{r}'); \quad F_0 = \text{constant} \qquad (126)$$

where the first term is the kinetic energy of the dipole and the second term corresponds to the interaction of the polarization currents arising at points $\vec{r}$ and $\vec{r}'$ with the time-dependent dipole moments. According to qualitative estimates for the problems of interest to us, the second term in formula eqn (126) is insignificant and in zero approximation can be ignored. Moreover, if in the potential energy we retain only the local interaction, we shall have for the energy an approximate expression:

$$E_{\text{loc}} = \frac{\phi_0}{2} \int \left[ \frac{F_0}{\phi_0} \dot{\vec{P}}^2(\vec{r}) + \vec{P}^2(\vec{r}) \right] \mathrm{d}\vec{r} = \frac{2\pi}{c} \int \left[ \frac{1}{\omega_0^2} \dot{\vec{P}}^2(\vec{r}) + \vec{P}^2(\vec{r}) \right] \mathrm{d}\vec{r} \qquad (127)$$

which coincides exactly with Pekar's formula for the classical Hamiltonian of the polar medium.[4,27] From eqn (127) we obtain the values of the constants $F_0$ and $\phi_0$ contained in eqns (125) and (126)

$$F_0 = \frac{4\pi}{c\omega_0^2}; \quad \phi_0 = \frac{4\pi}{c}; \quad c = \frac{1}{\varepsilon_0} - \frac{1}{\varepsilon_S} \qquad (128)$$

The analysis carried out above gives physical premises of Pekar's theory, which are rigorously valid only in the absence of nonlocal interaction of dipole moments of the medium, or according to eqn (123) in the absence of dispersion of vibration frequencies ($\omega_{\vec{k}} = \omega_0$), when only the limiting long-wave dipole vibration frequency $\omega_0$ is of importance. As follows from estimates, as well as from the comparison of theory with experimental data, Pekar's Hamiltonian eqn (127) describes correctly the order of magnitude of the energy of the system. It is of interest, however, to take into account the nonlocal interaction of dipoles. This introduces into the theory, in addition to the quantities $c$ and $\omega_0$, some new characteristics of the medium, which enable us to investigate the effect of the substitution of one solvent for another. Below we shall show that the most important parameters of Pekar's theory (e.g. reorganization energy) of all the solvent characteristics contain only the quantity $c$, which changes but slightly upon substitution of one solvent for another. Assuming that in first approximation we have to take into account only the nonlocal interaction in the potential energy (i.e. $F_{\vec{k}} = F_0$) we can rewrite the frequency dispersion law eqn (123) as

$$\omega_{\vec{k}}^2 = \omega_0^2(1 + \varphi_{\vec{k}}) \tag{129}$$

where the quantity $\varphi_{\vec{k}}$ is related to the Fourier-component function $\varphi_{\alpha\beta}(\vec{r})$ by the formula

$$\varphi_{\vec{k}} = \sum_{\alpha,\beta} \frac{k_\alpha k_\beta}{k^2} \varphi_{\alpha\beta}(\vec{k}) \tag{130}$$

To relate $\varphi_{\vec{k}}$ to physically observed quantities, we shall introduce the function

$$S(\vec{r} - \vec{r}) = \langle \vec{P}(\vec{r})\vec{P}(\vec{r}\,')\rangle_{av} \tag{131}$$

which characterizes the space correlation of dipole moments of the particles located at points $\vec{r}$ and $\vec{r}\,'$ (symbol *av* here denotes averaging over a large time interval). The Fourier component of the correlation function is found after substitution of eqn (117) into eqn (131):

$$S_{\vec{k}} = \langle |P_{\vec{k}}|^2 \rangle_{av} \tag{132}$$

Now the quantity $S_{\vec{k}}$ can be related to the mean potential energy of the oscillator with the wave vector $\vec{k}$ (see eqn (124)). Considering that according to the virial theorem for an oscillator, the mean potential energy is equal to the mean kinetic energy, we obtain

$$S_{\vec{k}} = \frac{\langle \varepsilon_{\vec{k}} \rangle_{av}}{\phi_{\vec{k}}} = \frac{\hbar\omega_{\vec{k}}(n_{\vec{k}} + \frac{1}{2})}{\phi_0(1 + \varphi_{\vec{k}})} \simeq \frac{c}{4\pi} \cdot \frac{kT}{1 + \varphi_{\vec{k}}} \tag{133}$$

where the mean oscillator energy is expressed in terms of Bose-Einstein distribution:

$$\langle \varepsilon_{\vec{k}} \rangle_{av} = \hbar\omega_{\vec{k}}[(e^{\hbar\omega_{\vec{k}}/kT} - 1)^{-1} + \tfrac{1}{2}] = \frac{\hbar\omega_{\vec{k}}}{2} \operatorname{cth} \frac{\hbar\omega_{\vec{k}}}{2kT} \simeq kT \tag{134}$$

and the classical nature of the motion of the medium dipoles ($\hbar\omega_{\vec{k}} \ll kT$) is taken into consideration. Equation (133) establishes direct relationship between the basic characteristic of the medium $\phi_{\vec{k}}$ (or $\varphi_{\vec{k}}$) and the correlation of the dipole moments observed experimentally $S_{\vec{k}}$. In particular, it follows from eqn (133) that Pekar's approximation ($\phi_{\vec{k}} = \phi_0 = 4\pi/c$) points to the absence of space correlation between dipole moments:

$$S_{\vec{k}}^{(0)} \simeq \frac{kT}{\phi_0} = \frac{c}{4\pi} kT \equiv S_0 \tag{135}$$

or passing from the Fourier components to the functions of the coordinates

$$S^{(0)}(\vec{r}-\vec{r}\,') = S_0\delta(\vec{r}-\vec{r}\,') = \frac{c}{4\pi}kT\delta(\vec{r}-\vec{r}\,') \tag{136}$$

It also follows from eqn (133) that if the correlation function is known, it is possible to determine the frequency dispersion law

$$\omega_{\vec{k}}^2 = \frac{\langle \varepsilon_{\vec{k}} \rangle_{av}}{F_0 S_{\vec{k}}} \simeq \omega_0^2 \cdot \frac{c}{4\pi} \cdot \frac{kT}{S_{\vec{k}}} = \omega_0^2 \cdot \frac{S_0}{S_{\vec{k}}} \tag{137}$$

For practical purposes, the correlation function can be conveniently approximated by the Gaussian distribution:

$$S(\vec{r}) = S_0 \sqrt{\left(\frac{2}{\pi r_0^2}\right)} \frac{1}{4\pi r^2} \cdot \exp\left(-\frac{r^2}{2r_0^2}\right) \tag{138}$$

where the parameter $r_0$ figures as the correlation radius of the solvent dipole moments. Calculation shows that the choice of other tentative correlation functions does not affect the qualitative results given below. The Fourier components for function eqn (138) are of the form:

$$S_{\vec{k}} = S_0 \sqrt{\left(\frac{\pi}{2}\right)} \frac{1}{kr_0} Erf\left(\frac{kr_0}{\sqrt{(2)}}\right) \tag{139}$$

where *Erf* is the probability function. According to eqn (137) the correlation function of the form eqn (138) corresponds to the following frequency dispersion law

$$\omega_{\vec{k}}^2 = \omega_0^2 \sqrt{\left(\frac{2}{\pi}\right)} \frac{kr_0}{Erf(kr_0/\sqrt{(2)})} \simeq \omega_0^2\left(1 + \frac{k^2r_0^2}{6}\right) \tag{140}$$

The dependence of normal vibration frequencies on the wave number $k$, determined by eqn (140) is shown in Fig. 12 by a solid curve. Equation (140) obtained by us for the dispersion law is valid only for small $k$ (large wavelengths). In order to obtain a correct dependence of the frequencies on the wave vector at large $k$ (small wavelengths) it is necessary to take into consideration also the correlation of polarization currents, which is important at short distances. If the correlation can be approximated by a Gaussian distribution in this case as well, the dispersion law valid for any wavelengths, can be written as

$$\omega_{\vec{k}}^2 = \omega_0^2 \cdot \frac{r_0}{l_0} \cdot \frac{Erf(kl_0/\sqrt{(2)})}{Erf(kr_0/\sqrt{(2)})}; \quad \omega_\infty^2 = \omega_0^2 \cdot \frac{r_0}{l_0} \tag{141}$$

where $l_0$ is the correlation radius of polarization currents (derivatives of dipole moments with respect to time). The dispersion law, corresponding to eqn (141) is shown on the plot (Fig. 12) by a dashed line. Later we shall show that only long polarization waves (small $k$), are of essential importance in the transfer process, the minimum wavelength coinciding in order of magnitude with the distance $R_0$, to which the charge is transferred (in the case of homogeneous reactions), or with the discharging ion radius (in heterogeneous reactions). Pekar's approximation, which was actually used also by Marcus, is valid only in the case when the correlation radius of the dipole moments $r_0$ is less than the distance $R_0$. This is just the case, when according to eqn (140) we can neglect the frequency dispersion and use the Hamiltonian eqn (127). This approximation is the more accurate the larger is the ion radius. In the literature the charge together with the fluctuating polarization 'cloud' surrounding it, is usually called a polaron. If the condition

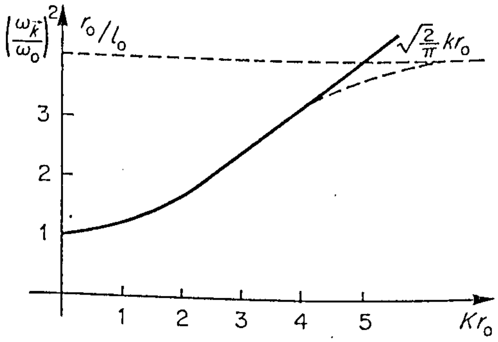

Fig. 12. Vibration frequencies dispersion law of polarization waves.

$$r_0 k_{\max} \simeq \frac{r_0}{R_0} < 1 \tag{142}$$

is valid, we have a large radius polaron. In the case when the correlation radius of the dipole moments $r_0$ is less or of the order of magnitude of the distance to which charge is transferred, i.e. when the condition

$$r_0 k_{\max} \simeq \frac{r_0}{R_0} \gtrsim 1 \tag{143}$$

is valid, we say that we have a small radius polaron. At present the theory of the small radius polaron is fairly thoroughly elaborated (see, e.g. References 38–41), frequency dispersion having been shown to be of importance in quantitative calculations of kinetic parameters (such as activation energy). However, in the case of a small radius polaron as well, the activation energy can be estimated in order of magnitude using Pekar's theory, assuming $\omega_{\vec{k}} \simeq \omega_0$. In this case, the activation energy thus calculated will be only several times higher, as we shall show later. This qualitative coincidence can be physically accounted for by a rather large number of the medium dipoles participating in the establishment of the activated state of the solvent. In fact, since the contribution of each dipole to the activation energy in order of magnitude must be equal to $\hbar\omega_0$ (vibrational energy quantum), the number of dipoles participating in the activation process can be estimated from the formula

$$N_a \simeq \frac{E_a}{\hbar\omega_0} \tag{144}$$

where $E_a$ is the activation energy due to solvent fluctuation. For example, if we assume that $E_a \simeq 0{\cdot}5$ eV, about $1{\cdot}3 \times 10^3$ dipoles of the medium will participate in activation. By means of eqn (144) we can estimate the maximum extent of the solvent region, which is of importance in the charge transfer process:

$$R_{\text{max}} \simeq \left(\frac{3m_0N_a}{4\pi\gamma}\right)^{1/3} \tag{145}$$

where $m_0$ is the dipole mass and $\gamma$ is the solvent density. In particular, for water at $E_a \simeq 0{\cdot}5$ eV we have $R_{\text{max}} \simeq 20$ Å.

It follows from the above that the wave numbers of most importance lie within the range

$$k_{\text{min}} \simeq \frac{1}{R_{\text{max}}} < k < k_{\text{max}} \simeq \frac{1}{R_0} \tag{146}$$

In other words, the charge transfer process is significantly affected by the portion of solvent located outside the ion in the region

$$r_0 \simeq R_0 < r < R_{\text{max}} \tag{147}$$

As regards theoretical calculations, the treatment of the first solvation shell of the ion (small $r$, i.e. large $k$) is the most difficult, since in this region the notion of specific polarization itself has only a qualitative significance. Strictly speaking, in this case one should use a discrete description of the solvent particles and take into consideration both vibrational motion and diffusion jumps of dipoles (jumpwise change of the coordinates of the centre of gravity of dipoles or of the dipole axis directions). The mean interval between jumps ($\tau_d \simeq 10^{-9}$ sec) being much larger, however, than the period of libration motions of a dipole ($\tau_0 = 2\pi/\omega_0 \simeq 2\pi \,.\, 10^{-11}$ sec) we can ignore the effect of diffusional motion of solvent particles on the dynamic behaviour of the medium. Considering the libration motion of dipoles as a harmonic motion, we can approximately write for the energy of the particles in the first solvation shell

$$E = \tfrac{1}{2}\sum_{l} \hbar\omega_l (q_l^2 + g_l^2) \tag{148}$$

where $q_l$ and $g_l$ are the normal coordinates and momenta of dipoles, the normal frequencies $\omega_l$ coincide in order of magnitude with normal frequencies of libration vibrations $\omega_0$, their dispersion being due to the interaction of dipoles.

The classical Hamiltonian eqn (124) in the continuum model can be also written in the form eqn (148) if we pass from $P_{\vec{k}}$, and $\dot{P}_{\vec{k}}$ to real canonically conjugate variables

$$\left.\begin{aligned} g_{\vec{k}} &= \left(\frac{F_0}{2\hbar\omega_{\vec{k}}}\right)^{1/2} \cdot \begin{cases} i(\dot{P}_{\vec{k}} - \dot{P}^*_{\vec{k}}), & k_x > 0 \\ \dot{P}_{\vec{k}} + \dot{P}^*_{\vec{k}}\,, & k_x \leqslant 0 \end{cases} \\ q_{\vec{k}} &= \left(\frac{F_0\omega_{\vec{k}}}{2\hbar}\right)^{1/2} \cdot \begin{cases} i(P_{\vec{k}} - P^*_{\vec{k}}), & k_x > 0 \\ P_{\vec{k}} + P^*_{\vec{k}}\,, & k_x \leqslant 0 \end{cases} \end{aligned}\right\} \tag{149}$$

In these variables, eqn (124) can be written as

$$E = \tfrac{1}{2}\sum_{\vec{k}} \hbar\omega_{\vec{k}} (q^2_{\vec{k}} + g^2_{\vec{k}}) \tag{150}$$

From the similarity of eqns (148) and (150) it is to be hoped that the use of a continuum model will enable us to take into account qualitatively also the solvent particles located near the discharging ion.[48,49]

It is known that we can pass from the classical Hamiltonian eqn (150) to the quantum Hamiltonian by formal substitution of the generalized momentum $g_{\vec{k}} \to -i(\partial/\partial q_{\vec{k}})$:

$$H_S(q) = \tfrac{1}{2}\sum_{\vec{k}} \hbar\omega_{\vec{k}} \left(q^2_{\vec{k}} - \frac{\partial^2}{\partial q^2_{\vec{k}}}\right) \tag{151}$$

Finally it should be pointed out that below in statistical averaging of the solvent state, we shall substitute in the Gibbs distribution function the Hamiltonian eqn (151), which depends itself on the temperature in virtue of our model approximations. For instance, in Pekar's Hamiltonian eqn (127) the temperature dependence of the parameter $c$ is due to the dielectric constant $\varepsilon_S(T)$ and in the presence of dispersion, the parameters $r_0$ and $l_0$, determining the correlation radii of dipole moments and their derivatives with respect to time, can be also temperature dependent (see eqn (141)). As an indirect criterion of the validity of our model, we can use the requirement that the Hamiltonian should depend slightly on temperature. As follows from estimates for the polar media of interest to us, this condition is always fulfilled quite well in practice. For instance, for water the relative variation of the energy value in eqn (127) does not exceed 1 per cent practically at any reasonable temperature values (see Reference 42).

## 2. Calculation of the Transition Probability

A detailed picture of an elementary act of ion discharge or ionization on the electrode is extremely complicated. In the general case, ion and electrode electrons, solvent and heavy particles (nuclei) forming part of a discharging ion participate in the process. More or less, all these components undergo changes in the discharge process. As we consider only the reactions in which electrochemical kinetics is determined by the charge transfer process, it is always necessary to take into account the change in the solvent state. Moreover, all processes of interest to us necessarily involve a change in the electron state in the electrode. As regards the remaining components of the system (inner electrons and heavy particles forming part of discharging ion), their role in the process can be determined only by considering a particular case of a discharging ion. For instance, for redox processes occurring without breaking or formation of chemical bonds, it is necessary to take into consideration only the electron participating in the process and the solvent, whereas in the hydrogen ions discharge, we should take into account not only the change in the proton state, but also the change in the state of the electrons holding the proton in the hydroxonium ion.

According to the quantum-mechanical perturbation theory the probability of one elementary electrochemical act occurring per unit time can be written as

$$W_{if} = \frac{2\pi}{\hbar} Av \sum |\langle \Psi_f(x, q, R)| V_{if} |\Psi_i(x, q, R)\rangle|^2 \delta(E_i - E_f) \qquad (152)$$

where $\Psi_i$ and $\Psi_f$ are the wave functions of initial and final states; $(x, q, R)$ is the coordinates of the electrons, solvent and heavy particles, respectively; $V_{if}$ is the perturbation responsible for the transitions. Summation is performed over all possible final states of the system, taking into consideration the conservation of energy law between the initial and final states, which is accomplished by introducing the $\delta$-function into eqn (152); the symbol *Av* stands for statistical averaging over initial system states. The possibility of applying perturbation theory to our problem follows directly from the condition eqn (1) assumed by us earlier. In fact, eqn (152) is valid only for a small time interval $t < \tau_e$, where $\tau_e = W_{if}^{-1}$ is the mean time interval between transitions. However, since the ion resides in the reaction zone on the average during the time $\tau_d < \tau_e$, during the time of the 'impingement' of the ion on the electrode $\tau_d$ we can use eqn (152).

Actually, the calculation of $W_{if}$ we shall perform within the framework of the adiabatic perturbation theory. The adiabatic theory is known to be used in the treatment of systems containing particles differing sharply in the velocities of their motion. Sometimes, adiabatic treatment is associated with the difference in the particle masses (as in the theory of molecules). However, this is true only in the case when mean kinetic energies of these particles are approximately equal:

$$\frac{mv^2}{2} \simeq \frac{MV^2}{2}; \quad \frac{V}{v} \simeq \left(\frac{m}{M}\right)^{1/2} \ll 1 \tag{153}$$

where $m$ and $M$ are the masses and $v$ and $V$ the velocities of light and heavy particles, respectively. It should be stressed that in the general case, we have to deal with the difference between mean particle velocities and therefore adiabatic approximation can be used even for a system containing slow and fast electrons. This is the case in solid state theory, when slow conduction electrons become separated from fast valence electrons. In the problem under consideration we can say beforehand that the electrons in ion and electrode constitute a fast subsystem with respect to the slow moving dipoles of the medium. An analysis of intramolecular vibrational motion of heavy particles forming part of the discharging ion is more complicated. If we assume the states of electrons and solvent to be fixed and calculate the energy levels of these heavy particles, from the appearance of the spectrum we can say what place is occupied by these particles in the adiabatic theory. If the characteristic interval between levels (e.g. the excitation energy) $\Delta E$ is greater than that between the solvent levels $\hbar\omega_0$, these particles, just as electrons, can be included in the fast subsystem. This is the case, for instance, in the consideration of the proton contained in the hydroxonium ion, or adsorbed on the electrode. In a harmonic approximation, the vibration frequency of the proton in hydroxonium ion is $\omega_i \simeq 5 \times 10^{14}$ sec$^{-1}$ and $\omega_a \simeq 2 \times 10^{14}$ sec$^{-1}$ for mercury electrode, which corresponds to the excitation energies

$$\Delta E_i \simeq \hbar\omega_i \simeq 0{\cdot}3 \text{ eV} \quad \text{and} \quad \Delta E_a \simeq \hbar\omega_a \simeq 0{\cdot}1 \text{ eV}$$

Thus, in both cases

$$\Delta E_{i,a} > \hbar\omega_0 \simeq 2{\cdot}5 \times 10^{-3} \text{ eV}$$

If the excitation energy of internal degrees of freedom of ion or adsorbed particle is less than or of the order of $\hbar\omega_0$ only electrons should be included in the fast subsystem, whereas the solvent, together with heavy particles, forms a slow subsystem.

First we shall consider a theoretically more simple case, when $\Delta E > \hbar\omega_0$, i.e. when the slow subsystem consists only of the solvent. The Hamiltonian of the system in the initial state before discharge can be schematically written as:

$$\mathscr{H}_i^0(x, q, R) = H_e^0(x, R) + H_S(q) + V_{eS}(x, R; q) \tag{154}$$

where the first term in the right hand side corresponds to the energy of the fast subsystem (electrons and ionic internal degrees of freedom); the second term is given by eqn (151) and the last term describes the interaction of the solvent with the fast subsystem and can be written as

$$V_{eS}(x, R; q) = \sum_{\vec{k}} v_{\vec{k}}(x, R) q_{\vec{k}}$$

The form $v_{\vec{k}}$ depends on the concrete choice of an electrochemical system. If, for instance, the fast subsystem contains only one electron, we obtain for $v_{\vec{k}}(x)$ the following expression

$$v_{\vec{k}}(x) = \mathrm{e}\left(\frac{8\pi c\hbar\omega_0^2}{k^2\omega_{\vec{k}} V_S}\right)^{1/2} \begin{Bmatrix} -\cos \vec{k}\,\vec{x}, & k_x > 0 \\ \sin \vec{k}\,\vec{x}, & k_x \leqslant 0 \end{Bmatrix} \tag{155}$$

Using this formula, we can find the interaction energy for each concrete case. Within the framework of the adiabatic theory, owing to the slow change of the solvent polarization (i.e. of coordinates $q$) with time, the state of the fast subsystem can be approximately determined with fixed values of the solvent coordinates (i.e. with fixed polarization of the medium):

$$\{H_e^0(x, R) + V_{eS}(x, R; q)\}\psi_\alpha(x, R; q) = \varepsilon_\alpha(q)\psi_\alpha(x, R; q) \tag{156}$$

The physical sense of this equation is that the fast subsystem can instantaneously adjust itself in an 'equilibrium' manner to the slowly changing polarization of the medium. The slow fluctuation change of polarization involving a change in the interaction energy of the fast subsystem (e.g. electron) with the solvent, i.e. in the potential energy of the fast subsystem, the total energy of the fast subsystem $\varepsilon_\alpha(q)$ is a function of polarization of the medium (of coordinates $q$). In other words, the energy of the fast subsystem $\varepsilon_\alpha(q)$ will fluctuate with polarization. Figure 13 shows schematically the 'fluctuating' curves of potential energy with different solvent polarizations. In particular, curve (a) corresponds to the absence of polarization $q = 0$), i.e. to the ion in the gas phase. Curves (b) and (c) show various differences from zero polarizations of the medium. The subscript $\alpha$ for the energy of the

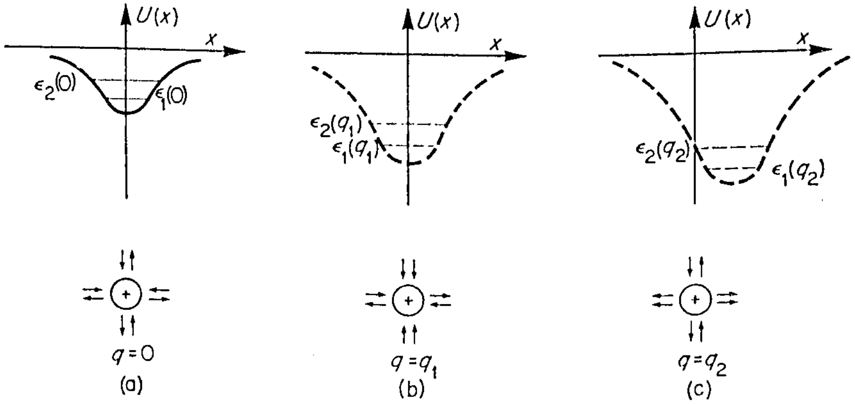

Fig. 13. Qualitative picture of the potential energy of fast subsystem for various solvent polarization values. Arrows show schematically the orientations of the solvent medium dipoles around the ion.

fast subsystem indicates that several quantum levels can exist in a given potential well.

With a given quantum state α of the fast subsystem, the state of the solvent (the slow subsystem) according to the adiabatic theory, is determined from the equation

$$\{H_S(q) + \varepsilon_\alpha(q)\}\chi_{\alpha n}(q) = E_{\alpha n}\chi_{\alpha n}(q) \qquad (157)$$

where $n$ is the number of the quantum state of the slow subsystem and $E_{\alpha n}$ is the total energy of the whole system in initial state. For physical interpretation of eqn (157), we shall write the Hamiltonian appearing in this equation and determining the total energy of the system as kinetic and potential energies:

$$H_S(q) + \varepsilon_\alpha(q) = -\tfrac{1}{2}\sum_{\vec{k}} \hbar\omega_{\vec{k}} \frac{\partial^2}{\partial q_{\vec{k}}} + U_\alpha(q) \qquad (158)$$

where the potential energy is of the form

$$U_\alpha(q) = \tfrac{1}{2}\sum_{\vec{k}} \hbar\omega_{\vec{k}} q_{\vec{k}}^2 + \varepsilon_\alpha(q) \qquad (159)$$

Thus, the total energy of the whole system can be found from the solution of the Schrodinger equation only for the slow subsystem if we include formally $\varepsilon_\alpha(q)$ in the potential energy of the solvent. Physically it means that along with the potential energy of dipoles (the first term in eqn (159)), we take into account the interaction of the solvent with the 'diffuse' cloud of the fast subsystem (the second term in eqn (159)). For this reason, in the adiabatic theory the function $U_\alpha(q)$ is usually called the potential energy surface. The interpretation for $U_\alpha(q)$ will prove to be somewhat different if the kinetic energy of the slow subsystem is assumed to be negligible. In this case $U_\alpha(q)$, will correspond to the total energy of the whole system with a given solvent polarization. Hence, another name for $U_\alpha(q)$ is the term of the system. If the fast subsystem contains only electrons, $U_\alpha(q)$ is called the electronic term. By analogy, if proton as well is included in the fast subsystem $U_\alpha(q)$ will be called the electron-protonic term, or simply, the term of the system.

Given the law of interaction of the slow and fast subsystems in the form eqn (155) we can write the expression for the term $U_\alpha(q)$ in a more convenient form:

$$\begin{aligned} U_\alpha(q) &= \tfrac{1}{2}\sum_{\vec{k}} \hbar\omega_{\vec{k}} q_{\vec{k}}^2 + \varepsilon_\alpha(q_\alpha) + \sum_{\vec{k}} v_{\vec{k}\alpha}(q_{\vec{k}} - q_{\vec{k}\alpha}) \\ &= \varepsilon_\alpha(q_\alpha) + \tfrac{1}{2}\sum_{\vec{k}} \hbar\omega_{\vec{k}} q_{\vec{k}\alpha}^2 + \tfrac{1}{2}\sum_{\vec{k}} \hbar\omega_{\vec{k}}(q_{\vec{k}} - q_{\vec{k}\alpha})^2 \end{aligned} \qquad (160)$$

where

$$q_{\vec{k}\alpha} = -\frac{v_{\vec{k}\alpha}}{\hbar\omega_{\vec{k}}} = -\frac{1}{\hbar\omega_{\vec{k}}} \int v_{\vec{k}}(x, R)|\psi_\alpha(x, R; q_\alpha)|^2 \, \mathrm{d}\vec{x}\, \mathrm{d}\vec{R} \qquad (161)$$

To explain the physical significance of the result obtained let us consider Fig. 14, where the dashed curve shows schematically the term of the pure solvent in the absence of ion, when polarization perform harmonic fluctuation vibrations near the nonpolarized state $\vec{P}(\vec{r}) = 0$ (i.e. $q_{\vec{k}} = 0$). After the introduction of ion into the solvent, the interaction of the charge with the medium gives rise to a different from zero mean polarization $\vec{P}_\alpha(\vec{r})$, near

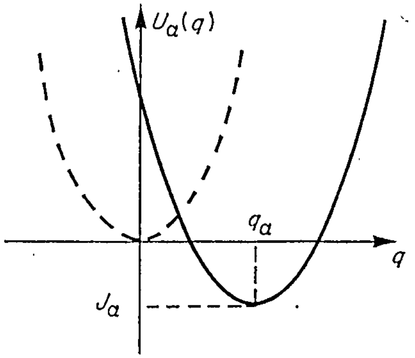

Fig. 14. Qualitative picture of the terms for the solvent, in the absence of ions (dashed curve) and in the presence of an ion (solid curve).

which harmonic fluctuations will now occur. Normal coordinates, corresponding to mean polarization, we shall denote by $q_{\vec{k}\alpha}$ (see eqn (161); in Fig. 14 $q_\alpha$). The third term in the right hand side of eqn (160) corresponds to purely vibrational potential energy. The second term corresponds to the work expended in producing mean polarization $\vec{P}_\alpha(\vec{r})$ and, finally, the first term corresponds to the energy of the fast subsystem, calculated with equilibrium polarization $\vec{P}_\alpha(\vec{r})$. Using the symbols of the preceding section, we can rewrite eqn (160) in the form:

$$U_\alpha(q) = J_\alpha + \tfrac{1}{2}\sum_{\vec{k}} \hbar\omega_{\vec{k}}(q_{\vec{k}} - q_{\vec{k}\alpha})^2 \tag{162}$$

where the minimum potential energy $J_\alpha$ for the initial state in the model under consideration can be written as:

$$J_\alpha = \varepsilon_f - e\varphi_m + \varepsilon_\alpha^0 + Z_\alpha e\psi_1 - \frac{\varepsilon_s - 1}{8\pi\varepsilon_s}\int D_\alpha^2\, \mathrm{d}\vec{r} \tag{163}$$

Here $\varepsilon_\alpha^0$ is the energy of ion in the gas phase, $Z_\alpha$ is the ion charge and the last term is the ion solvation energy ($\vec{D}_\alpha$ is electrostatic induction set up by the ion).

The term of the final state can be considered in much the same way as the term of the initial state (see above)

$$U_{\alpha'}(q) = J_{\alpha'} + \tfrac{1}{2}\sum_{\vec{k}} \hbar\omega_{\vec{k}}(q_{\vec{k}} - q_{\vec{k}\alpha'})^2 \tag{164}$$

where $q_{\vec{k}\alpha'}$ are normal coordinates corresponding to mean polarization $\vec{P}_{\alpha'}(\vec{r})$ in the final state, and the form of the minimum potential energy is readily found for each particular electrochemical system. For instance, for a reaction occurring via an adsorption step, $J_{\alpha'}$ is equal to the adsorption energy, and for a redox reaction

$$J_{\alpha'} = \varepsilon_{\alpha'}^0 + Z_{\alpha'} e\psi_1 - \frac{\varepsilon_s - 1}{8\pi\varepsilon_s}\int D_{\alpha'}^2\, \mathrm{d}\vec{r} \tag{165}$$

Like the initial state term, in the final state the term is in the form of a parabola in $(N + 1)$-dimensional space, where $N$ is the number of excited libration vibrational degrees of freedom of the solvent, i.e. the number of oscillators ($N \to \infty$). Figure 15 shows schematically in the form of one-dimensional parabolas the terms for initial and final states.

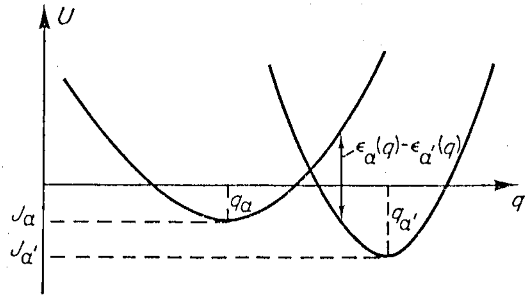

Fig. 15. Qualitative picture of the terms of initial and final states.

The unperturbed Hamiltonians of the solvent in initial and final states reducing to the sum of oscillator Hamiltonians, the corresponding energies are of the form:

$$E_{\alpha n} = J_{\alpha} + \sum_{\vec{k}} \hbar\omega_{\vec{k}}(n_{\vec{k}} + \tfrac{1}{2}); \quad E_{\alpha' n} = J_{\alpha'} + \sum_{\vec{k}} \hbar\omega_{\vec{k}}(n'_{\vec{k}} + \tfrac{1}{2});$$

$$n_{\vec{k}}, n'_{\vec{k}} = 0, 1, 2, \ldots \tag{166}$$

where $n_{\vec{k}}$ and $n'_{\vec{k}}$ are the occupation numbers of oscillators with the wave vector $\vec{k}$ in initial and final states. Similarly, in an adiabatic approximation the unperturbed wave function reduce to the product of the wave functions of the fast and slow subsystems:

$$\Psi_{\alpha,n} = \psi_{\alpha}\prod_{\vec{k}}\chi_{n_{\vec{k}}}(q_{\vec{k}} - q_{\vec{k}\alpha}); \quad \Psi_{\alpha',n'} = \psi_{\alpha'}\prod_{\vec{k}}\chi_{n'_{\vec{k}}}(q_{\vec{k}} - q_{\vec{k}\alpha'}) \tag{167}$$

where $\chi$ are the ordinary oscillator wave functions, and $\psi$ are determined as solutions of eqn (156). Naturally, the expressions given above for energies eqn (166) and wave functions eqn (167) are not accurate solutions of the total Hamiltonian of the system. In seeking for $E_{\alpha n}$ and $\Psi_{\alpha n}$, we ignored the interaction of the discharging particle with the electrode. For instance, in order to determine the unperturbed (approximate) initial state in a redox reactions we have to ignore the interaction with the electrode of the electron, localized at first in the reducing ion. This interaction causes the electron transfer from the ion to the electrode. Likewise, in considering the unperturbed final state, we do not take into account the energy of the interaction of the electron localized in the electrode with the oxidizing ion. Taking account of this interaction leads only to the electron transfer from the electrode to the ion. When considering hydrogen ion discharge, we ignore the interaction of proton first with the electrode, then with the water molecule, in order to determine approximate initial and final states of the system. To determine the discharge probability per unit time, it is possible to use eqn (152). But, in compliance with the general semi-phenomenological theory, we have to establish first the quantum states $\alpha,\alpha'$ of the fast subsystem before and after the transition. Averaging over all initial states $\alpha$ and summation over final states $\alpha'$ can be performed in the final expression for the discharge current, as in the previous section (see eqn (111)). For redox reactions the quantum number $\alpha$ corresponds to excited states of the electron in the reducing ion and the quantum number $\alpha'$ to different electron levels in the electrode. In hydrogen ion discharge $\alpha$ corresponds first to the vibrational quantum number of the proton in hydroxonium ion and, second, to the number of the energy level $\varepsilon_f$, on which the electron of the metal was localized before the discharge. Similarly, $\alpha'$ contains the vibrational quantum number of the adsorbed hydrogen atom and the quantum number of the electron in the adsorbed particle. In the approximation of adiabatic perturbation theory the transition probability per unit time is determined by the formula

$$W_{\alpha\alpha'} = \frac{2\pi}{\hbar} |\langle\psi_{\alpha'}|V|\psi_\alpha\rangle|^2 Av_n \sum_{n'} |\langle\chi_{n'}|\chi_n\rangle|^2 \delta(J_{\alpha'} - J_\alpha + \varepsilon_n - \varepsilon_{n'}) \quad (168)$$

where $\varepsilon_n$ and $\varepsilon_{n'}$ are excitation energies of the slow subsystem (solvent). If we use the wave functions eqn (167) and energies eqn (166) for oscillators, the probability $W_{\alpha\alpha'}$ can be calculated quite rigorously both in the absence of frequency dispersion[27,43,44] and for an arbitrary frequency dispersion.[51] In the general case, $W_{\alpha\alpha'}$ has a rather complex form and is expressed in terms of the Bessel function of imaginary argument (or the product of the Bessel functions of imaginary argument in the presence of frequency dispersion), the formula being much simpler, however, in two limiting cases, which we shall consider below.

(*a*) *Classical Oscillators*:

$$\hbar\omega_{\vec{k}} < kT \quad (169)$$

If the slow subsystem is classical, i.e. the condition eqn (169) is fulfilled, the transition probability assumes the form:

$$W_{\alpha\alpha'} = |V_{\alpha'\alpha}|^2 \left(\frac{\pi}{\hbar^2 kTE_r}\right)^{1/2} e^{-E_a/kT} \quad (170)$$

where the quantity

$$E_a = \frac{1}{4E_r}(J_{\alpha'} - J_\alpha + E_r)^2 \quad (171)$$

figures as the activation energy.

$E_r$ is the reorganization energy of the solvent:

$$E_r = \tfrac{1}{2}\sum_{\vec{k}} \hbar\omega_{\vec{k}}(q_{\vec{k}\alpha'} - q_{\vec{k}\alpha})^2 \tag{172}$$

Thus the assumption of the classical nature of motion of the medium dipoles leads to the Arrhenius equation for the transition probability. Moreover, as a simple mathematical analysis shows, the quantity $E_a$ determined by eqn (171) coincides geometrically with the difference of energies at the saddle point on the intersection surface of the terms and at the minimum point of the initial term (see Fig. 16(a)). This fact allows us to make use of the analogy with the particle transition from one potential well to another in classical physics. The fluctuation motion of the medium dipoles produces an activated state $q^*$, i.e. the system rises to the top of the potential barrier. At the moment when the activated state $q^*$ is established, the fast subsystem is able to accomplish a quantum ('tunnel') transition from initial to final terms, whereupon the classical subsystem 'falls' into the final well. In Fig. 16(a) this reaction path is shown by a line with arrows. At this point, we have to make a very important reservation. Although by tradition we have used the words 'tunnel' transition, it does not mean that in calculating the probability of a jump of the fast subsystem from term to term in the activated state we can use Gamov's equation[45]

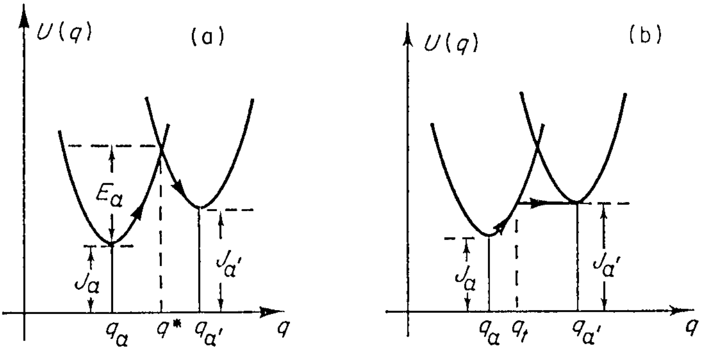

Fig. 16. Interpretation of the classical (a) and quantum (b) transitions of the system from initial to final state.

$$W = \exp\left(-\frac{2}{\hbar}\int_a^l |p|\,\mathrm{d}x\right) \tag{173}$$

as some authors do (see e.g. Reference 46). This becomes evident if we consider the form of potential energy of the fast subsystem, since the 'tunnel' transition must occur just in this field. As we have already said in discussing Fig. 13, the potential energy of the fast subsystem fluctuates (i.e. varies in time) with the motion of dipoles of the medium. Figure 17 shows qualitatively the forms of potential energy at two polarization values: $q^*$ is corresponding to the activated state of the solvent polarization (solid curve) and $q_\alpha$ is corresponding to the initial equilibrium polarization (dashed curve). In the case of equilibrium polarization $q_\alpha$ the energy levels of the fast subsystem do not coincide (see also Fig. 15) and therefore the quantum transition is not favoured. In the case of activated polarization, the levels of the fast subsystem become equal ($\varepsilon_\alpha(q^*) = \varepsilon_{\alpha'}(q^*)$) and the transition probability is maximal. Here the probability is determined not only by the shape of the potential hump (shaded area in Fig. 17), but mainly by the time interval during which the levels $\varepsilon_\alpha(q^*)$ and $\varepsilon_{\alpha'}(q^*)$ are close enough to each other, i.e. by the rate of change of polarization with time. For instance, if the polarization changes very quickly ($\dot{\vec{P}} \to \infty$), practically no transition occurs and vice versa, with a very slow change of polarization ($\dot{\vec{P}} \to 0$) the transition will occur with a large probability. The problem of particle transition with the potential varying with time is known as the Landau-Zener problem.[45] As regards eqn (173) it is used only for the particle motion with the potential constant in time (e.g. the problem of nuclear $\alpha$-decay). To avoid misunderstanding, in what follows we shall use the term quantum transition instead of 'tunnel' transition.

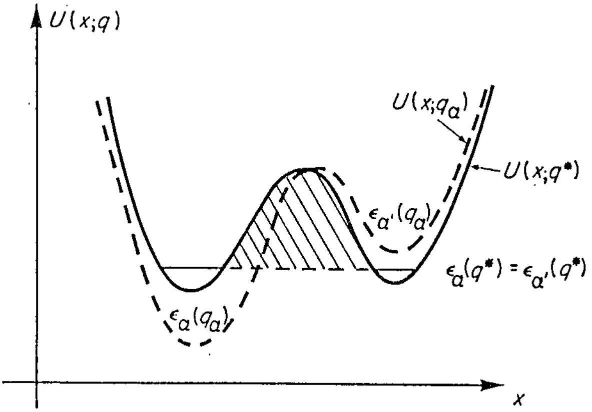

Fig. 17. Qualitative picture of the potential energy of fast subsystem with equilibrium polarization (dashed curve) and with polarization corresponding to the activation state (solid curve).

It is clear from eqns (170) and (171) that the basic parameter of the theory is the reorganization energy $E_r$, for an accurate calculation of which it is necessary to know the wave functions of the subsystem and the law of the interaction of the charge with the solvent (see eqn (161)). For instance, for redox reactions we can use eqn (155) and write for $E_r$:

$$E_r = \frac{2\pi c e^2}{V_S} \sum_{\vec{k}} \left| \int \{ |\psi_\alpha|^2 - |\psi_{\alpha'}|^2 \} \, e^{i\vec{k}\vec{r}} \, d\vec{r} \right|^2 \cdot \frac{\omega_0^2}{k^2 \omega_{\vec{k}}^2} \tag{174}$$

In the case of homogeneous reactions $|\psi_\alpha|^2$ and $|\psi_{\alpha'}|^2$ are localized in the ions of the reducing and oxidizing agents separated by the distance $R_0$. By means of the Fourier theory, it can be shown that the integral contained in eqn (174) has its largest value at $k \lesssim R_0^{-1}$ (see eqn (142)). In the case of heterogeneous reactions, the electron in the electrode is delocalized and $|\psi_{\alpha'}|^2 \sim 1/V_e \to 0$, therefore

$$E_r = \frac{2\pi c e^2}{V_S} \sum_{\vec{k}} \left| \int |\psi_\alpha|^2 \, e^{i\vec{k}\vec{r}} \, d\vec{r} \right|^2 \cdot \frac{\omega_0^2}{k^2 \omega_{\vec{k}}^2} \tag{175}$$

Since $|\psi_\alpha|^2$ varies significantly over the dimensions of the discharging ion $R_0$, the maximum value of the integral in eqn (175) will be reached at $k \lesssim R_0^{-1}$. By a vector analysis it is possible to transform eqn (174) identically to the form

$$E_r = \frac{c}{8\pi} \cdot \sum_{\vec{k}} \frac{\omega_0^2}{\omega_{\vec{k}}^2} |\vec{D}_{\vec{k}\alpha} - \vec{D}_{\vec{k}\alpha'}|^2 = \frac{2\pi}{c} \cdot \sum_{\vec{k}} \frac{\omega_0^2}{\omega_{\vec{k}}^2} |\vec{P}_{\vec{k}\alpha} - \vec{P}_{\vec{k}\alpha'}|^2 \tag{176}$$

where $\vec{P}_{\vec{k}\alpha}$ and $\vec{P}_{\vec{k}\alpha'}$ are the Fourier components of equilibrium polarizations, and $\vec{D}_{\vec{k}\alpha}$ and $\vec{D}_{\vec{k}\alpha'}$ the inductions related to $\vec{P}_{\vec{k}\alpha}$ and $\vec{P}_{\vec{k}\alpha'}$ by the formula

$$\vec{D}_{\vec{k}\alpha(\alpha')} = \frac{4\pi}{c} \vec{P}_{\vec{k}\alpha(\alpha')} \tag{177}$$

In particular, it is evident from eqn (176) that in the absence of frequency dispersion, the reorganization energy coincides with the expression obtained by Marcus[11] and by the author of this article[24] earlier:

$$E_r^{\text{loc}} = \frac{2\pi}{c} \int \{ \vec{P}_\alpha(\vec{r}) - \vec{P}_{\alpha'}(\vec{r}) \}^2 \, d\vec{r} \tag{178}$$

As shown above (see eqns (140) and (141)), in the presence of dispersion $\omega_0$ corresponds to minimum frequency in the oscillator spectrum ($\omega_{\vec{k}} \geqslant \omega_0$) and hence eqn (178) gives the upper limit of the reorganization energy. Using eqn (141) it is possible to find the lower limit of $E_r$:

$$\frac{l_0}{r_0} E_r^{\text{loc}} \leqslant E_r \leqslant E_r^{\text{loc}} \qquad (179)$$

Since the correlation radius of dipole moments $r_0$ can exceed the correlation radius of the rates of change of dipole moments $l_0$ only several times, the substitution of $E_r^{\text{loc}}$ for $E_r$ might be approximately justified. If, however, we know experimentally the correlation radii of dipole moments of different solvents, using eqns (176) and (140) it is possible to calculate the change in the reorganization energy in various media. It can be pointed out qualitatively that in media with a strong correlation of dipole moments $E_r$ must decrease.[50]

(*b*) *Quantum Oscillators*:

$$\hbar\omega_{\vec{k}} > kT \qquad (180)$$

When the slow subsystem is a quantum system we have for $W_{\alpha\alpha'}$

$$W_{\alpha\alpha'} = \text{constant} \begin{Bmatrix} \exp\,(J_\alpha - J_{\alpha'}/kT), & J_{\alpha'} > J_\alpha \\ 1, & J_{\alpha'} < J_\alpha \end{Bmatrix} \qquad (181)$$

where we have not written an expression for the constant (see e.g. Reference 27). This formula also has a simple physical sense. If $J_{\alpha'} > J_\alpha$ the slow subsystem first fluctuates from the initial equilibrium state $q_\alpha$ to the point $q_t$ (see Fig. 16(b)), which makes it possible for the quantum subbarrier transition of the slow subsystem to occur. Thus, both the slow and the fast subsystems perform a quantum transition. In Fig. 16(b) the reaction path described above is shown by a heavy line with arrows. Evidently, when $J_{\alpha'} < J_\alpha$ a subbarrier ('tunnel') transition is possible directly from the initial equilibrium state $q_\alpha$. Although in the description of the solvent the criterion of the classical behaviour eqn (169) is always fulfilled, an analysis of case (*b*) is of fundamental importance to us. Since for oscillators $\hbar\omega_{\vec{k}}$ is the distance between the levels, it can be assumed from the above consideration that the criterion of the classical behaviour of one or the other of the subsystems is the condition (see eqn (14)):

$$\Delta E < kT \qquad (182)$$

where $\Delta E$ is the characteristic distance between the levels of the respective subsystem. To verify this assumption we considered first the linear terms shown in Fig. 10, which permit of a quantum calculation. It proved that the criterion eqn (182) is valid in this case as well, if $\Delta E$ is understood to mean the distance from the first excited level to the ground level. Finally, by means of the quasi-classical wave functions we calculated the transition probability for one-dimensional terms of a rather general form. It was shown in this case as well that when condition eqn (182) is valid, a transition of the system over the barrier occurs, whereas with the reverse condition a sub-barrier ('tunnel') transition of the system takes place. A very important conclusion can be drawn from what has been just said, which we shall give as a prescription. In considering the internal degrees of freedom of the particles participating in the reaction (before and after reaction), they should be divided into classical and quantum according to criterion eqn (182). Then, in an adiabatic treatment, all the quantum degrees of freedom should be included in the fast subsystem and all the classical degrees of freedom in the slow subsystem:

$$\Delta E_{\text{quant}} > kT > \Delta E_{\text{cl}} \tag{183}$$

Thus, condition eqn (183) allows us to divide the whole system into only two subsystems: a slow and a fast subsystem. This is due to the fact that the condition $\Delta E_{\text{quant}} > \Delta E_{\text{cl}}$ in terms of an adiabatic approximation means at the same time that the quantum subsystem is faster than the classical subsystem. With such an approach, the potential energy surfaces should be automatically introduced only in the case of a classical subsystem, whereas the quantum subsystem will contribute to the minimum potential energy $J_{\alpha,\alpha'}$. Here we have to make a reservation. Above we assumed for simplicity that a particle which was 'classical' before the reaction remains so after it as well. The case when a 'classical' particle becomes a 'quantum' one as the result of the reaction (or vice versa) permits of a theoretical calculation, but here we shall not give the results of such a treatment. It should be noted, however, that in spite of the appearance of some interesting effects, the general picture described above remains valid.[51,52]

In order to calculate the transition probability it is possible to use eqn (168), where the exchange integral (the first factor) is completely determined by the quantum subsystem, and the rest of the formula gives the Arrhenius activation factor. In this case $\chi_{n,n'}$ and $\varepsilon_{n,n'}$ should be understood to mean respectively the wave functions and excitation energies of the whole classical subsystem. It is clearly evident from eqn (168) that the transition probability $W_{\alpha\alpha'}$ depends on $\Delta J$ (the last factor in eqn (168)) and on the parameters determining the shape of the term (through $\varepsilon_{n,n'}$ and $\chi_{n,n'}$) as was assumed in the previous section.

The transition of the classical subsystem occurring above the potential barrier, the value of $W_{\alpha\alpha'}$ can be calculated by a method which is a generalized version of the Landau-Zener method developed for one-dimensional terms. Below we shall give only the basic steps of the derivation of this formula for

$W_{\alpha\alpha'}$. First of all, we shall write in a very general form the expressions for the energies corresponding to initial and final states of the classical subsystems:

$$E_{\alpha,\alpha'} = \sum_{i=1}^{N} \frac{M_i V_i^2}{2} + J_{\alpha,\alpha'} + U_{\alpha,\alpha'}(X_i) \tag{184}$$

where $M_i$, $V_i$, $X_i$ are the mass, velocity and coordinate of the $i$th particle of the classical subsystem, respectively. Now let us pass to dimensionless coordinates and momenta

$$q_i = X_i \left(\frac{M_i kT}{h^2}\right)^{1/2}; \quad P_i = V_i \left(\frac{M_i}{kT}\right)^{1/2} \tag{185}$$

In these canonically conjugate variables, the energies assume the form

$$E_{\alpha,\alpha'}(P, q) = kT \sum_{i=1}^{N} \frac{P_i^2}{2} + J_{\alpha,\alpha'} + U_{\alpha,\alpha'}(q_i) \tag{186}$$

and the quantities

$$\dot{q}_i = \frac{kT}{h} P \tag{187}$$

appear as the particle velocities.

In the $N$-dimensional space $\{q_i\}$ the activated state corresponds to the points $\{q_i^*\}$, lying on the surface $S^*$; the equation for this surface is found from the condition of the intersection of the terms:

$$U_\alpha(q_i^*) = U_{\alpha'}(q_i^*) + J_{\alpha'} - J_\alpha; \quad \phi(q^*) = 0 \tag{188}$$

For clarity, the surface $S^*$ is shown in Fig. 18 as a curve $\phi(q_1^*, q_2^*) = 0$ for the case when $N = 2$. Now we have to find the probability of the system located at the term $U_\alpha(q_i)$ passing in the time $\mathrm{d}t$ to the term of the final state $U_{\alpha'}(q_i)$:

$$\mathrm{d}W_{\alpha\alpha'} = W_{\alpha\alpha'}\,\mathrm{d}t \tag{189}$$

where $W_{\alpha\alpha'}$ is the transition probability in unit time sought for. With arbitrary (but fixed) velocities of the motion of particles $\dot{q}_i = (kT/h)P_i$ the system can pass through the intersection surface of the terms $S^*$ in the time $\mathrm{d}t$, if the particles of the classical subsystem are contained in the volume element

$$\mathrm{d}V_q^* = \prod_{i=1}^{N} \mathrm{d}q_i^* = \mathrm{d}S^* \vec{\dot{q}}_{n*}\,\mathrm{d}t = \frac{kT}{h}\,\mathrm{d}S^* \vec{P}_{n*}\,\mathrm{d}t \tag{190}$$

where $\vec{P}$ is the $N$-dimensional momentum vector of the system with the components $(P_1, \ldots, P_N)$, the subscript $n^*$ indicates that we have a projection of vector $\vec{P}$ onto a direction normal to the surface $S^*$ at the point $(q_1^*, \ldots, q_N^*)$ $\mathrm{d}S^*$ is an element of the activated surface $S^*$ near the point $(q_1^*, \ldots, q_N^*)$. Figure 18 shows for a two-dimensional case the vector $\vec{P}$ and its normal and tangential components, the region $\mathrm{d}V_q^*$ eqn (190) is shaded. The probability of the system initially located at the term $U_\alpha(q)$ being localized in the space

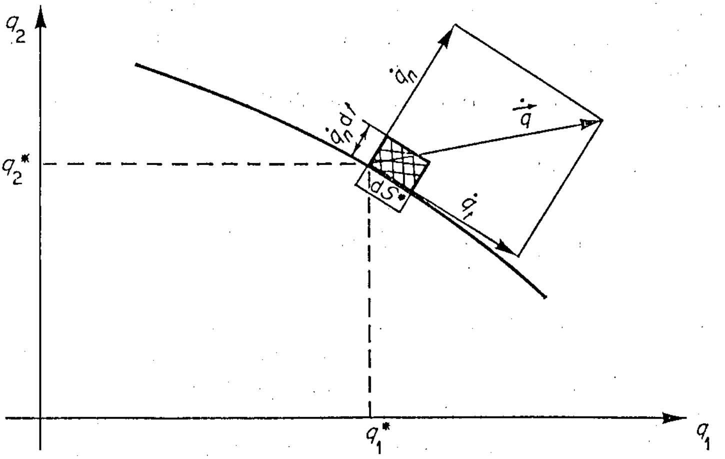

Fig. 18. Schematic picture of the intersection line of two-dimensional terms ($N = 2$). $\dot{q}_n$ and $\dot{q}_t$ are normal and tangential components of the two-dimensional vector $\dot{\vec{q}}$, $\mathrm{d}V_q^* = \dot{q}_n\,\mathrm{d}t\,\mathrm{d}S^*$ (shaded area).

$\mathrm{d}V_q^*$ (see eqn (190)) and of the particles having given momenta $(P_1 \ldots P_N)$ can be found from the Gibbs distribution:

$$W(P, q^*)\,\mathrm{d}V_q^*\,\mathrm{d}\vec{P} = \mathrm{e}^{-E_\alpha(p,q^*)/kT} \cdot \frac{kT}{h}\,\mathrm{d}S^* P_{n^*}\,\mathrm{d}t\,\mathrm{d}\vec{P}\left[\int \mathrm{e}^{-E_\alpha(p,q)/kT}\,\mathrm{d}\vec{q}\,\mathrm{d}\vec{p}\right]^{-1} \tag{191}$$

The probability that upon transition through an activated state at the point $(q_1^*, \ldots, q_N^*)$ at the velocity $(P_1, \ldots, P_N)$ the system will pass to the term of the final state can be found by a method similar to that of Landau-Zener

$$W_{LZ}(q^*, P) = 1 - \exp\left\{-\frac{4\pi^2|V_{\alpha'\alpha}|^2}{kT|P_{n^*}\nabla_{n^*}(U_\alpha - U_{\alpha'})|}\right\} \tag{192}$$

where $V_{\alpha'\alpha}$ is the exchange integral of the quantum subsystem (see eqns (168) and (170)) and the gradient $\nabla_n^*$ is taken at the point $(q_1^*, \ldots, q_N^*)$ in the direction normal to the surface $S^*$. Now the expression for $W_{\alpha\alpha'}$ can be written as

$$W_{\alpha\alpha'}\,\mathrm{d}t = \underset{(N)}{\int \ldots \int} \mathrm{d}\vec{P} \underset{(N-1)}{\int \ldots \int} \mathrm{d}S^* \frac{kT}{h} P_{n*}\,\mathrm{d}t\,W(P, q^*)W_{LZ}(q^*, P) \tag{193}$$

where integration is performed over momenta and $S^*$ because the transition from one term to another may occur at any intersection point of the terms with particles moving at any velocities directed normal to the surface $S^*$.

To reduce the expression, eqn (193), to a form similar to the equation of the theory of absolute reaction rates, we shall consider below two limiting cases:

(*a*) Adiabatic reactions:

$$|V_{\alpha\alpha'}|^2 \gg \frac{kT}{4\pi^2}\,|P_{n*}\nabla_{n*}(U_\alpha - U_{\alpha'})| \equiv |V_{cr}|^2 \tag{194}$$

This criterion is physically valid in the case when the resonance splitting of the terms at the 'intersection point' is so large that the system, when passing over the potential hump, cannot jump to the upper excited term and falls into the final potential well, remaining all the time at the lower term. On the other hand, it is clear from eqn (194) that for practically any $|V_{\alpha'\alpha}|$, the transition can be of an adiabatic nature if the mean velocity of motion of the particles of the classical subsystem is small enough ($P_{n*} \to 0$). If eqn (194) is fulfilled $W_{LZ}$ in eqn (192) can be substituted by 1. As has been said earlier, the activation energy for a classical subsystem (in terms of the Arrhenius dependence of the transition probability on temperature) appears as the quantity

$$E_a = U_\alpha(q_S^*) \tag{195}$$

where $q_S^*$ is the saddle point on the activation surface $S^*$. If the potential energy in the activated state is reckoned from the minimum value

$$U_a(q^*) = U_\alpha(q^*) - U_\alpha(q_S^*) \tag{196}$$

eqn (193) can be rewritten as

$$W_{\alpha\alpha'} = \frac{kT}{h}\,\frac{\mathrm{e}^{-Ea/kT} \int \mathrm{d}\vec{P}\mathrm{d}S^* P_{n*}\ \mathrm{e}^{-\frac{1}{2}\Sigma P_i{}^2 - (1/kT)U_a(q^*)}}{\int \mathrm{d}\vec{P}\,\mathrm{d}\vec{q}\ \mathrm{e}^{-\frac{1}{2}\Sigma P^2 - (1/kT)U_\alpha(q)}} \tag{197}$$

For this expression to be written in the form of the equation of the absolute reaction rates theory, the last factor in it should be identified formally with the entropy factor:[53]

$$e^{Sa/k} = \frac{\displaystyle\int_{(P_{n*}>0)} d\vec{P}\, dS^* P_{n*}\, e^{-\frac{1}{2}\vec{P}^2-(1/kT)U_a(q^*)}}{\int d\vec{P}\, d\vec{q}\, e^{-\frac{1}{2}\vec{P}^2-(1/kT)U_\alpha(q)}} \tag{198}$$

It should be stressed that in eqn (197) only the Arrhenius factor containing the activation energy is of real physical significance, whereas in the general case the origin of the entropy factor is only of a formal mathematical nature. This is accounted for by the fact that in eqn (198) the momenta and coordinates of particles in the activated state are not separated due to the presence of the factor $P_n^*$ and hence it is impossible to determine the state of the system for which the entropy could be calculated by means of general thermodynamic formulae. In a sense, the distortion of the activation surface $S^*$ gives rise to noninertial (centrifugal) forces operating in the activated state. The problem is greatly simplified if the intersection surface of the terms is plane (in Fig. 18 the curve $\phi = 0$ in this case is a straight line). It can be readily seen that in the general case, this can be true only of parabolic terms, when the terms of initial and final states have an identical shape and are shifted with respect to one another (without turning). The approximation of $S^*$ by a plane can be used, however, also in the case of a slight distortion, or if only a small region near the saddle point contributes to the integral, eqn (198). Of a particularly simple form is the entropy of activation for parabolic terms in the absence of frequency dispersion $\omega_i = \omega_0$:

$$S_a = k \ln \frac{\hbar\omega_0}{kT} \tag{199}$$

This result, obtained by us from eqn (198) can be also derived by a strictly thermodynamic method, if we take into consideration that the activated state differs from the initial state by the absence of one vibrational degree of freedom:

$$S_a = -k \ln \int_{-\infty}^{+\infty} e^{-\frac{1}{2}P^2}\, dP \int_{-\infty}^{+\infty} e^{-(\hbar^2\omega_0{}^2q^2/2k^2T^2)}\, dq = k \ln \frac{\hbar\omega_0}{kT} \tag{200}$$

In the presence of an arbitrary frequency dispersion, the activation entropy is of the form similar to eqn (199), where $\omega_0$ is substituted by some effective frequency:[27]

$$S_a = k \ln \frac{\hbar\omega_{\text{eff}}}{kT}; \quad \omega_{\text{eff}}^2 = \sum_i \omega_i^2 \frac{E_{ri}}{E_r} \tag{201}$$

where $E_{ri}$ is the reorganization energy of the $i$th oscillator, and $E_r$ is the total reorganization energy.

(*b*) Nonadiabatic reactions:

$$|V_{\alpha'\alpha}|^2 \ll |V_{cr}|^2 \tag{202}$$

In the case of the resonance splitting of the terms being slight there is a large probability that when the system passes the 'intersection point' it can remain at the initial term. Physically, this effect is due either to a small overlapping the wave functions of the quantum subsystem ($V_{\alpha'\alpha} \rightarrow 0$), or to a large mean velocity of motion of classical particles ($P \rightarrow \infty$). Thus, the transition from term to term occurs only after a repeated passing through the 'intersection point'. For a nonadiabatic transition eqn (193) can be written as

$$W_{\alpha\alpha'} = \frac{kT}{h}\kappa_{\alpha\alpha'}\,\mathrm{e}^{-(E_a/kT)}\,\mathrm{e}^{S_a/k} \tag{203}$$

where $E_a$ is the activation energy (as understood above). $S_a$ as before is determined by eqn (198) and the transmission coefficient is determined from the relation:

$$\begin{aligned}\kappa_{\alpha\alpha'} &= \frac{\sqrt{(2\pi)}4\pi^2|V_{\alpha'\alpha}|^2}{kT}\int\frac{\exp\,[-(1/kT)U_a(q^*)]}{|\nabla_{n*}(U_\alpha - U_{\alpha'})|}\,\mathrm{d}S^* \Big/ \int \mathrm{e}^{-(1/kT)U_a(q^*)}\,\mathrm{d}S^* \\ &= \frac{\sqrt{(2\pi)}4\pi^2|V_{\alpha'\alpha}|^2}{kT}\left\langle\frac{1}{|\nabla_{n*}(U_\alpha - U_{\alpha'})|}\right\rangle_{av}\end{aligned} \tag{204}$$

In the general case, in order to calculate $\kappa_{\alpha\alpha'}$ it is necessary to know the concrete form of the terms. But if the intersection surface of the terms is approximated by a plane, the transmission coefficient can be readily estimated. In particular, we obtain from eqn (204) the following expression:

$$\kappa_{\alpha\alpha'} = |V_{\alpha'\alpha}|^2\left(\frac{4\pi^3}{\hbar^2\omega_{\mathrm{eff}}^2 kTE_r}\right)^{1/2} \tag{205}$$

where $\omega_{\mathrm{eff}}$ is determined in eqn (201). Comparing eqn (204) with the determination of the critical value of the exchange integral $V_{cr}$ (see eqn (194)), we see that if $P_{n*}$ is replaced by the mean momentum $\langle|P|\rangle_{av} = \sqrt{(2/\pi)}$, we obtain for $\kappa_{\alpha\alpha'}$ for nonadiabatic transitions the condition:

$$\kappa_{\alpha\alpha'} = \frac{2|V_{\alpha'\alpha}|^2}{\langle|V_{cr}|^2\rangle_{av}} \ll 1 \tag{206}$$

Thus, we can consider the transition probability to be always determined by eqn (203) but for adiabatic reactions $\kappa_{\alpha\alpha'}$ should be replaced by 1.

It can be readily seen that upon substitution of eqns (201) and (205) into eqn (203) we obtain exactly the same expression as we derived from a rigorous quantum-mechanical treatment, eqn (170). Thus, the application of the quantum-mechanical perturbation theory gives an expression for the transition probability only in nonadiabatic processes. The advantage of the semi-classical treatment developed above is that it permits us to advance further than the perturbation theory and, on the whole, to obtain an expression for the probability of adiabatic transitions. Unfortunately, at present this fact can be made use of only in the calculation of homogeneous reactions. In the investigation of electrochemical processes we used essentially the one-electron approximation. In this case, due to the delocalization of the electron in the electrode, the one-electron exchange integral is in inverse proportion to the electrode volume (see eqn (17)) and hence the condition of a nonadiabatic transition, eqn (202) is valid. We obtain a final expression for the current, since the electron level density is directly proportional to the electrode volume (see eqn (4)). In the treatment of adiabatic electrochemical reactions, the reorganization of the many-electron state, is of great importance even if the metal electrons can be assumed to be noninteracting. This problem requires a serious theoretical investigation.[54] At present we can readily formulate only a prescription for order-of-magnitude estimation of the current: in adiabatic processes unity should be substituted for the product of the one-electron transmission coefficient $\kappa_F$ the level density $\rho_F$ (see eqn (4)) and the range of levels contributing to the current:

$$\kappa_F \rho_F kT \rightarrow 1 \tag{207}$$

## IV. QUANTUM THEORY OF ELECTROCHEMICAL PROCESSES

In this section we shall consider some electrochemical systems for which the current will be calculated on the basis of the general semi-phenomenological theory presented in Section III. We shall use the continuum model for the solvent and eqn (170) for the transition probability.

### 1. Redox Reactions at the Metal Electrode

Redox reactions occurring without breaking or formation of any chemical bonds of reactants are the simplest case as regards theoretical calculations. Calculation of the current for these systems is described at length by many authors (see, e.g. References 42–44, 47–49). Therefore, we shall dwell here only on some fundamental points.

According to the theory presented in the previous section, redox reactions involve electron (quantum subsystem) and solvent (classical subsystem). Therefore, in calculating the electron transfer probability, we should proceed from consideration of the electronic terms of the solvent, eqns (162) and (164). For the process of electron transfer from the electrode to the oxidizing ion, the difference of minimum potential energies at the beginning and at the end of the reaction can be written as (see eqns (163) and (165))

$$\begin{aligned}\Delta J(\varepsilon_f) &= (\varepsilon_f - e\varphi_m - E^{0}_{\mathrm{solv}}) - (-\varepsilon_i - E^{R}_{\mathrm{solv}})\\ &= (\varepsilon_f - \varepsilon_F) - e\eta + \Delta J_{0F}\\ &= (\varepsilon_f - \varepsilon_F) - e\eta + kT \ln \frac{C_R}{C_0} \qquad (208)\end{aligned}$$

where $\varepsilon_i$ is the electron binding energy in the reducing ion; $E^{0,R}_{\mathrm{solv}}$ is the solvation energy of the oxidizing and reducing ions and $C_0$, $C_R$ are the surface concentrations of ions (for simplicity we assume the $\psi_1$-effect to be absent). Due to the symmetry of parabolic terms of the solvent, the reorganization energies for forward and reverse processes coincide and are determined from eqn (172).

For all redox systems at reasonable values of ion concentrations, the quantity $\Delta J_{0F}$ is much less than $E_r$. Therefore, over a very wide overvoltage range the eqn (82) is valid. This means that electrochemical kinetics of all redox reactions is confined to the normal region. According to eqns (171) and (208) the activation energy for redox systems can be written as

$$E_a = \frac{(\varepsilon_F - \varepsilon_f + e\eta - kT \ln (C_R/C_0) + E_r)^2}{4E_r} \qquad (209)$$

The level $\varepsilon^*$ making the chief contribution to the current, according to eqns (53), (84), and (209) is determined from the equation

$$1 - n(\varepsilon_f) = \tfrac{1}{2} + \frac{e\eta}{2E_r} - \frac{kT}{2E_r} \ln \frac{C_R}{C_0} - \frac{\varepsilon_f - \varepsilon_F}{2E_r} \qquad (210)$$

As has been already pointed out above, the third term in the right hand side of this equation for redox systems is very small and can be ignored. Then from eqn (210) we obtain that $\varepsilon^* = \varepsilon_F$ at the equilibrium potential ($\eta = 0$), i.e. $\eta^F = 0$. According to eqn (93) the transfer coefficient for redox reactions can be written as

$$\alpha^* = \tfrac{1}{2} + \frac{e\eta}{2E_r}, \quad |e\eta| < E_r \qquad (211)$$

In order to calculate the current by means of eqn (92) it is necessary only to find the free energy for the Fermi electron at the equilibrium potential ($\eta^F = 0$). According to eqns (201) and (209) we have

$$F_a(\varepsilon_F - e\eta^F) = \frac{1}{4E_r}\left(E_r - kT\ln\frac{C_R}{C_0}\right)^2 - kT\ln\frac{\hbar\omega_{\text{eff}}}{kT}$$

$$\simeq \frac{E_r}{4} - \frac{kT}{2}\ln\frac{C_R}{C_0} - kT\ln\frac{\hbar\omega_{\text{eff}}}{kT} \tag{212}$$

The final expression for the current density is obtained if we substitute into eqn (92) the transmission coefficient $\kappa$, eqn (205), the width of the levels contributing to the current $\Delta\varepsilon^* \simeq \sqrt{(8\pi)}kT$ eqn (86) and the free activation energy eqn (212):

$$\vec{i} = \frac{\pi e\rho_F}{\hbar}\sqrt{(C_R C_0)}\left(\frac{2kT}{E_r}\right)^{1/2}|V_{iF}|^2\,\mathrm{e}^{-[(E_r+e\eta)^2/4E_r kT]}$$

$$= i_0\,\mathrm{e}^{-(e\eta/2kT)-[(e\eta)^2/4E_r kT]} \tag{213}$$

where $i_0$ is the exchange current and $V_{iF}$ the electron exchange integral. The total current density with an allowance made for the back reaction can be found by means of eqn (48)

$$i = \overleftarrow{i} - \vec{i} = i_0(\mathrm{e}^{e\eta/2kT} - \mathrm{e}^{-(e\eta/2kT)})\,\mathrm{e}^{-[(e\eta)^2/4E_r kT]} \tag{214}$$

According to eqn (207) the exchange current for adiabatic reactions can be calculated in order of magnitude from the relation:

$$i_0^{ad} \simeq \frac{e\omega_{\text{eff}}}{2\pi}\sqrt{(C_R C_0)}\,\mathrm{e}^{-(E_r/kT)} \tag{215}$$

The deviation of the transfer coefficient from the constant value 0·5 is of fundamental importance, since in an experimental verification of eqn (211) we can say with great certainty that in electrochemical kinetics the solvent plays the main dynamic part. Moreover, eqn (211) shows that in redox reactions the electron transfers from the Fermi level are of essential importance only with a strictly equilibrium potential ($\eta = 0$), whereas when overvoltage is applied the chief contribution to the current is made by the levels located near $\varepsilon_F$. To verify eqns (211) and (213) we have analysed the data obtained by Frumkin and collaborators,[50] who investigated the electroreduction of $Fe(CN)_6^{3-}$ anions on a mercury electrode. The comparison of the theoretical and experimental curves (see Fig. 19) shows qualitative agreement of theory with experiment. The greatest discrepancy is observed in the range of the potentials at which other effects can come into play[50] (such as the formation

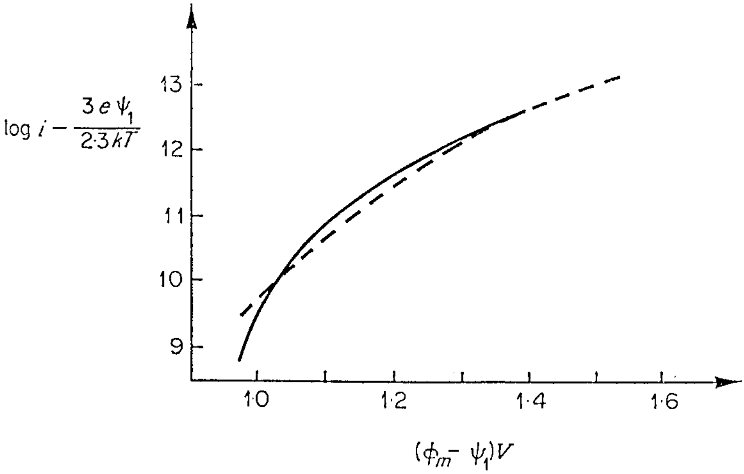

Fig. 19. Theoretical (dashed curve) and experimental (solid curve) polarization curves for the electroreduction reaction of $Fe(CN)_6^{3-}$ anions on mercury electrode.

of ion pairs). A specific feature of this reaction is that the $Fe(CN)_6^{3-}$ ion is rather large and the quantity $E_r$ relatively small. Therefore, according to the predictions of the theory, already with not very large overvoltages a deviation from the linear Tafel equation should be observed, which is actually the case in experiment. Later Parsons and Passeron[51] carried out measurements on the $Cr^{3+}/Cr^{2+}$ system at a mercury electrode to test relations, eqn (211), which showed theory to agree with experiment within experimental error.

We have considered above redox systems in which an elementary electrochemical act involves transfer of only one electron. In more complex redox systems, along with the one electron process, reactions involving the transfer of two or more electrons can occur. Below we shall give for illustration a calculation of the current due to the transfer of two electrons from the electrode to the oxidizing ion. In this case, as before, we shall assume that in an elementary act the chemical bonds of the discharging ion are unchanged. Then, similarly to eqn (49) the direct current can be written as

$$\vec{i}_2 = 2eC_0 \frac{kT}{h} \kappa\, e^{S_a/k} \rho_F^2 \int d\varepsilon_1\, d\varepsilon_2 n(\varepsilon_1) n(\varepsilon_2)\, e^{-[E_a(\varepsilon_1, \varepsilon_2)/kT]} \qquad (216)$$

where the activation energy $E_a$ depends on the difference of minimum potential energies at the beginning and end of the reaction

$$\Delta J(\varepsilon_1, \varepsilon_2) = (\varepsilon_1 - \varepsilon_F) + (\varepsilon_2 - \varepsilon_F) - 2e\eta + \Delta J_{0F} \qquad (217)$$

In the treatment of two electron processes it is possible to use the general ideas of the semi-phenomenological theory presented in Section II. In particular, the microscopic transfer coefficient should be determined according to the following relation (see eqn (55)):

$$\alpha(\varepsilon_1, \varepsilon_2) = \frac{\partial E_a}{\partial 2e\eta} = -\frac{\partial E_a}{\partial \varepsilon_{1,2}} = -\frac{\partial E_a}{\partial \varepsilon} \tag{218}$$

where $\varepsilon = \varepsilon_1 + \varepsilon_2$ is the energy of two electrons in the electrode. Similarly to eqn (56) the following quantity will appear as the experimental transfer coefficient

$$\alpha_{\mathrm{exp}} = -kT\frac{\partial \ln \vec{i}_2}{\partial 2e\eta} \tag{219}$$

for which as can be readily shown in the general form, the following relation is valid (see derivation of eqns (57) and (60)):

$$\alpha_{\mathrm{exp}} = \langle \alpha(\varepsilon_1, \varepsilon_2) \rangle_{av} = 1 - \langle n(\varepsilon_1) \rangle_{av} = 1 - \langle n(\varepsilon_2) \rangle_{av} \tag{220}$$

Here averaging is understood to mean that the corresponding quantity is taken with the weight factor proportional to the elementary current associated with the electron transfer from the levels $\varepsilon_1$ and $\varepsilon_2$. For instance,

$$\langle \alpha(\varepsilon_1, \varepsilon_2) \rangle_{av} = \iint \alpha(\varepsilon_1, \varepsilon_2) \frac{\mathrm{d}\vec{i}_2(\varepsilon_1, \varepsilon_2)}{\vec{i}_2} \tag{221}$$

It follows from eqn (221) that the transfer coefficient determined by means of eqn (219) always lies within the range from zero to 1.

In calculating the current $\vec{i}_2$ it is convenient in eqn (216) to pass to new variables

$$\varepsilon = \varepsilon_1 + \varepsilon_2; \quad \varepsilon' = \varepsilon_1 - \varepsilon_2 \tag{222}$$

and to perform accurate integration with respect to $\varepsilon'$. As a result, we obtain the formula

$$\vec{i}_2 = 2eC_0 \frac{kT}{h} \kappa_F \, \mathrm{e}^{S_a/k} \rho_F^2 kT \int \mathrm{d}\varepsilon \mu(\varepsilon) \, \mathrm{e}^{-[E_a(\varepsilon)/kT]} \tag{223}$$

where

$$\mu(\varepsilon) = \frac{\varepsilon - 2\varepsilon_F}{kT} \left[ \exp\left( \frac{\varepsilon - 2\varepsilon_F}{kT} \right) - 1 \right]^{-1} \tag{224}$$

Now the integral contained in eqn (223) can be calculated by the Laplace method:

$$\vec{i}_2 = 2eC_0 \frac{kT}{h} \kappa_F \, e^{S_a/k} \rho_F^2 kT \mu(\varepsilon^*) \, e^{-[E_a(\varepsilon^*)/kT]} \, \Delta\varepsilon^* \qquad (225)$$

where $\varepsilon^*$ corresponds to the optimum energy of two electrons making the maximum contribution to the current and is determined as the solution of the equation

$$\alpha(\varepsilon) = 1 - \nu(\varepsilon) \qquad (226)$$

where

$$\nu(\varepsilon) = \frac{kT}{\varepsilon - 2\varepsilon_F} [1 - \mu(\varepsilon)] \qquad (227)$$

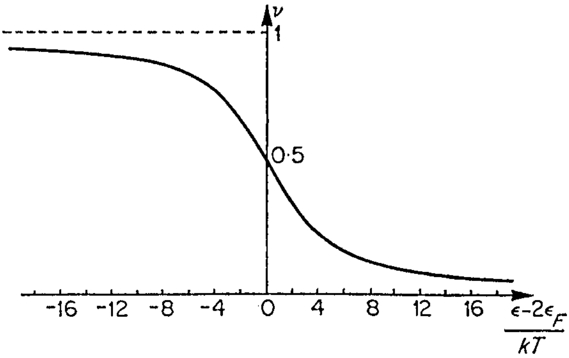

Fig. 20. Plot of the function $\nu(\varepsilon)$.

The function $\nu(\varepsilon)$ shown graphically in Fig. 20 is formally very similar to the Fermi distribution function $n(\varepsilon_f)$ (see Fig. 8) and differs from it only by a more smooth behaviour. Therefore, from the comparison of eqns (84) and (226), we can speak of there being an analogy between one-electron and two-electron processes, if we understand $\varepsilon$ to mean the energy of both electrons and take into consideration that the chemical potential of such system is equal to $2\varepsilon_F$. Strictly speaking, the above analogy was contained in eqns (223) (cf. eqn (49)) and (225) (cf. eqn (85)). In particular in two electron processes the quantity (cf. eqn (90))

$$E_a^{\text{exp}} = -kT \ln \mu(\varepsilon^*) + E_a(\varepsilon^*) \qquad (228)$$

appears as the experimental activation energy and the transfer coefficient $\alpha_{\text{exp}}$ is given by the relation (see derivation of eqn (91)):

$$\alpha_{\text{exp}} = \frac{\partial E_a^{\text{exp}}}{\partial 2e\eta} = \alpha(\varepsilon^*) = 1 - \nu(\varepsilon^*) \tag{229}$$

The treatment given above was based on the general semi-phenomenological theory and did not contain any model assumptions. If we use now the model of the solvent described in Section III and the expression for the quantum-mechanical transition probability eqn (170), eqn (226) can be rewritten as (cf. eqn (210)):

$$1 - \nu(\varepsilon) = \tfrac{1}{2} + \frac{2e\eta}{2E_r} - \frac{kT}{2E_r}\ln\frac{C_R}{C_0} - \frac{\varepsilon - 2\varepsilon_F}{2E_r} \tag{230}$$

Assuming as before the one before the last term in the right hand side of this equation to be very small and that, in addition $\varepsilon^*$, differs little from $2\varepsilon_F$ (this is valid at low overvoltages $|2e\eta| < E_r$), we can solve eqn (230)

$$\alpha_{\text{exp}} = \alpha(\varepsilon^*) \simeq \tfrac{1}{2} + \frac{2e\eta}{2E_r}; \quad |2e\eta| < E_r \tag{231}$$

Knowing $\alpha_{\text{exp}}$ we can find by the method described in Section II (see eqns (101)–(103)) the experimental activation energy

$$E_a^{\text{exp}} = \frac{(E_r + 2e\eta)^2}{4E_r} - \frac{kT}{2}\ln\frac{C_R}{C_0} \tag{232}$$

In this case we made use of the fact that, just as in the one-electron processes, the kinetics of the two-electron discharge is confined to the normal region, since according to eqn (230) at the equilibrium potential ($\eta = 0$) the transitions occur mainly from the level $\varepsilon_F(\varepsilon^* = 2\varepsilon_F)$. We obtain a final expression for the current density, if we substitute into eqn (225) the activation entropy (see eqn (201)) and

$$\mu(\varepsilon^*) \simeq 1; \quad \Delta\varepsilon^* \simeq 2\sqrt{(6\pi)}kT \tag{233}$$

As the result we have

$$i_2 = \overleftarrow{i_2} - \overrightarrow{i_2} = i_0(\mathrm{e}^{2e\eta/2kT} - \mathrm{e}^{-(2e\eta/2kT)})\,\mathrm{e}^{-[(2e\eta)^2/4E_r kT]} \tag{234}$$

where the exchange current is determined by the formula:

$$i_0 = \frac{2\pi}{\hbar}\cdot 2e\rho_F^2\sqrt{(3)}kT\sqrt{(C_R C_0)}\left(\frac{2kT}{E_r}\right)^{1/2}|V_{iF}|^2\,\mathrm{e}^{-(E_r/4kT)} \tag{235}$$

To estimate the exchange current in the case of an adiabatic process we have to make in eqn (235) the following substitution

$$\tfrac{1}{4}\,\kappa_F\rho_F^2\left[\sqrt[4]{\left(\frac{3\pi}{2}\right)}\,kT\right]^2 \rightarrow 1 \tag{236}$$

whereupon we obtain

$$i_0^{ad} \simeq \frac{2e\omega_{\text{eff}}}{2\pi}\,\sqrt{(C_R C_0)}\;\mathrm{e}^{-(E_r/4kT)} \tag{237}$$

A formal similarity in the expressions for the current in one electron and two electron processes (upon substitution of 2e for e) is accounted for by the fact that in the scheme calculated above the transitions of two electrons were considered as being simultaneous and independent of each other. Nevertheless, the values of the current in one electron and two electron transitions can differ essentially since the reorganization energies of the solvent in these processes are also essentially different. For instance, if we assume the quantity $E_r$ to be proportional to the charge being transferred squared, in two electron processes $E_r$ will be four times as large as in one electron transitions. If redox reactions occur by steps, the total current can be found from the formulae obtained above by the methods of formal kinetics only in the case when the one electron and two electron transitions occur independently. The case is much more complicated in the presence of a correlation between the transitions of the first and second electrons from one ion, i.e. when these transitions are separated by a time interval $\Delta t < \tau_d$. In such case, after the transition of the first electron there is not enough time for the ion to diffuse into the solution and thus the transition of the second electron may occur under non-equilibrium conditions. Further theoretical consideration is required for the investigation of such processes.

## 2. Redox Reactions on a Semi-conductor Electrode

The quantum-mechanical theory of redox reactions on a semi-conductor electrode is presented in detail in References 52–58 where electrochemical kinetics was considered both on intrinsic[52,55] and impurity semiconductors.[57] Some steady state processes occurring on a semiconductor electrode were studied[58] (e.g. the steady state photoeffect). In addition, in Reference 53, the kinetics of redox reactions was studied on a metal electrode coated with a thin semiconductor film. In the present article we shall not give in detail the results of the above mentioned studies (see also reviews[42–44]) but will only consider briefly the general physical picture and the statement of the problem within the framework of the general semi-phenomenological theory developed in Section II.

The physical difference in the mechanism of the passage of electrochemical current at the metal and semiconductor electrodes is due to the fact that in the latter case the Fermi level lies in the forbidden band and the occupation of the energy levels by electrons depends strongly on the temperature and potential distribution in the system. Figure 21 shows schematically the structure of the electron energy spectrum in the case of anodic polarization. Below for definiteness we shall consider practically the most important case of the non-degenerate semiconductor surface, i.e. the case when the Fermi level does not intersect with the bent bands

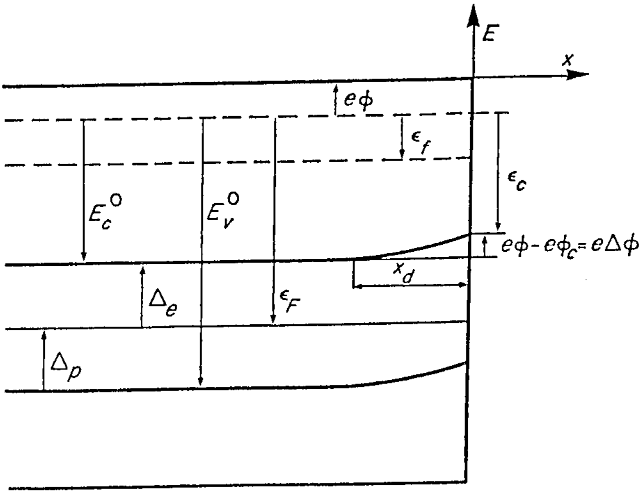

Fig. 21. Schematic picture of the electron energy spectrum in semiconductor in the presence of a contact with electrolyte solution. $\psi$ and $\psi_c$ are the potential in the bulk of semiconductor and at the contact, $\Delta_{e,p}$—the distance from the bottom of the conduction band and the top of the valence band to the Fermi level $\varepsilon_F$. $X_d$—the Debye screening distance.

$$|e\Delta\varphi| < \Delta_{e,p} \tag{238}$$

(for designations see Fig. 21). In this case the electron concentration in the conduction band and the hole concentration in the valence band are very small, so that the main potential drop between solution and semiconductor will occur on the electrode at a sufficiently large distance (e.g. the Debye screening distance $X_d$ for Ge is of the order of $10^{-4}$–$10^{-5}$ cm). Because of this fact, not all electrons and holes can participate in electrochemical kinetics. For example, in the case of anodic polarization from the conduction band only the electrons with energies greater than $\varepsilon_c = E_c^0 + e\Delta\varphi$ participate in the kinetics, since the other electrons would have to travel 'tunnelwise' to a large distance of the order of $X_d$. Thus, the electron component of the total discharge current, which is due only to transitions from the conduction band, can be written as

$$\vec{i}^{e} = eC_0 \frac{kT}{h} \kappa_e \, \mathrm{e}^{S_a/k} \int_{\varepsilon_c}^{\infty} \mathrm{d}\varepsilon_f \rho_e(\varepsilon_f - e\Delta\varphi) n(\varepsilon_f) \, \mathrm{e}^{-[E_a(\Delta J(\varepsilon_f))/kT]} \tag{239}$$

where, unlike the metal electrode, the level density cannot be considered as being a slow function and taken out of the integral (see eqn (9)). In much the same way as was done in the general semi-phenomenological theory (see eqns (57) and (60)), it is possible to obtain from eqn (239) a number of accurate relations for an experimental transfer coefficient $\alpha^e_{\text{exp}}$, the mean value of the microscopic transfer coefficient $\langle \alpha^e(\varepsilon_f) \rangle_{av}$ and the mean occupation of the levels $\langle n(\varepsilon_f) \rangle_{av}$

$$\alpha^e_{\text{exp}} = \langle \alpha^e(\varepsilon_f) \rangle_{av} + \left\langle \frac{kT}{2(\varepsilon_f - \varepsilon_c)} \right\rangle_{av} \left( 1 - \frac{\mathrm{d}\eta_c}{\mathrm{d}\eta} \right) \tag{240}$$

$$\alpha^e_{\text{exp}} = 1 - \langle n(\varepsilon_f) \rangle_{av} - \left\langle \frac{kT}{2(\varepsilon_f - \varepsilon_c)} \right\rangle_{av} \cdot \frac{\mathrm{d}\eta_c}{\mathrm{d}\eta} \tag{241}$$

where $\eta = \varphi - \varphi_0$ is the overvoltage in the bulk of the semiconductor, $\eta_c = \varphi_c - \varphi_c^0$ is the overvoltage at the interface and for the level density use was made of the eqn (9). Equations (240) and (241) we obtain a relation similar to eqn (60)

$$\langle \alpha^e(\varepsilon_f) \rangle_{av} = 1 - \langle n(\varepsilon_f) \rangle_{av} - \left\langle \frac{kT}{2(\varepsilon_f - \varepsilon_c)} \right\rangle_{av} \tag{242}$$

Comparing eqns (61) and (242) we see that the difference in the metal and semiconductor spectra leads to the appearance of one more term in eqn (242). To understand this result it should be recalled that eqn (61) reflects physically the competition of two tendencies in the case of a reaction at a metal electrode. On one hand, the transitions from high electron energy levels for which the activation energy is small are favoured. On the other hand, the occupation of these levels is very small. In the case of semiconductor electrodes, a third factor enters into competition, i.e. the level density $\rho_e$, which is zero in the forbidden band and increases rather sharply near the bottom of the conduction band. To analyse this question it is convenient to use the expression for the electron discharge current obtained in the calculation of the integral in eqn (239) by the Laplace method:

$$\vec{i}^{e} = eC_0 \frac{kT}{h} \kappa_e \, \mathrm{e}^{S_a/k} \rho_e(\varepsilon^*) n(\varepsilon^*) \, \mathrm{e}^{-[E_a(\varepsilon^*)/kT]} \, \Delta\varepsilon^* \tag{243}$$

where $\varepsilon^*$ is the level making the main contribution to the current and $\Delta\varepsilon^*$ is the width of the energy levels near $\varepsilon^*$ participating in the reaction. It can be readily shown by a direct calculation that the accurate relations obtained above, eqns (240)–(242) are now valid for the level $\varepsilon^*$. For instance from eqn (242) we obtain an equation for the determination of $\varepsilon^*$:

$$\alpha^e(\varepsilon^*) = 1 - n(\varepsilon^*) - \frac{kT}{2(\varepsilon^* - \varepsilon_c)} \tag{244}$$

It is physically evident that the main contribution to the current will be made by the levels located in the immediate vicinity of $\varepsilon_c$. Therefore, if we assume the potential at the interface to depend very slightly on overvoltage (this is valid at not too large surface state densities of semiconductors) we shall obtain from eqn (241)

$$\alpha^e_{\text{exp}} \simeq 1 \tag{245}$$

This result is due to the fact that at $\varepsilon^* \simeq \varepsilon_c$ and $\mathrm{d}\eta_c/\mathrm{d}\eta \rightarrow 0$ the activation energy and hence $\alpha^e(\varepsilon^*)$ practically do not depend on overvoltage

$$\begin{aligned} E_a(\Delta J(\varepsilon^*)) &\simeq E_a(\Delta J(\varepsilon_c)) = E_a(\varepsilon_c - \varepsilon_F - e\eta + \Delta J_{0F}) \\ &= E_a(\Delta_e + e\Delta\varphi_0 - e\eta_c + \Delta J_{0F}) \simeq \text{constant} \end{aligned} \tag{246}$$

On the other hand, according to eqn (244) the level density will not depend on overvoltage either

$$\rho_e(\varepsilon^*) \sim \sqrt{(\varepsilon^* - \varepsilon_c)} = \left[\frac{kT}{2(1 - \alpha^e(\varepsilon^*))}\right]^{1/2} \simeq \text{constant} \tag{247}$$

Thus, the total dependence of the current on overvoltage will be determined by the electron concentration at the contact:

$$n(\varepsilon^*) \simeq \mathrm{e}^{-(\varepsilon^* - \varepsilon_F/kT)} \simeq \mathrm{e}^{-(\varepsilon_c - \varepsilon_F/kT)} \simeq \mathrm{e}^{-(e\eta + \Delta_e + e\Delta\varphi_0/kT)} \tag{248}$$

which gives directly relation eqn (245).

It is clear from the above consideration that unlike the metal electrode, the experimental transfer coefficient for semiconductors can differ essentially from the mean microscopic transfer coefficient in the Brønsted relation. In order to calculate $\alpha^e(\varepsilon^*)$ it is possible to use the model described in the previous section. As shown by calculation, in this case

$$\alpha^e(\varepsilon^*) = \frac{\frac{1}{2} - (\Delta_e + e\Delta\varphi_0 - e\eta_c + kT\ln C_R/C_O)}{2E_r} \tag{249}$$

and for the redox systems in which the reorganization energy is larger than the halfwidth of the forbidden band $\Delta_e$ and the equilibrium bending of the band $e\Delta\varphi_0$, the discharge will occur in the normal region ($\alpha^e(\varepsilon^*) \simeq 0, 5$). An interesting situation may arise in the opposite case of small $E_r$, when $\alpha^e(\varepsilon^*) < 0$. If the surface state density is large enough, the overvoltage at the interface will vary considerably[42,59] and according to eqn (240)

$$\alpha^e_{\text{exp}} \simeq \alpha^e(\varepsilon^*) < 0 \tag{250}$$

i.e. the polarization curve for the electron current may have a descending branch (for the discussion of this problem see also Gerischer's article[60]).

Up to the present we have considered only one component of the total current. The reverse current can be found by means of eqn (48), which is of a general nature. The hole current $\overrightarrow{i}^p$ associated with the electron transfers from the valence band to the solution can be calculated using simple physical considerations, which are confirmed by direct calculations. In fact, the quantity $\overrightarrow{i}^p$ is equivalent to the reverse current of positive holes when the oxidizing ion is replaced by the reducing ion. Therefore, $\overrightarrow{i}^p$ can be obtained from $\overrightarrow{i}^e$ by multiplying it by $e^{e\eta/kT}$ (see eqn (48)), taking into consideration the plus sign of the hole) and with the substitutions:

$$C_R \rightleftarrows C_0; \quad \Delta_e \rightleftarrows \Delta_p; \quad \kappa_e \rightleftarrows \kappa_p; \quad \eta \rightleftarrows -\eta \tag{251}$$

### 3. Hydrogen Overvoltage

The quantum-mechanical theory of electrode reactions developed in the previous section permits us to calculate practically any process of proton transfer in polar liquids. As an illustration we shall consider below, hydrogen ion discharge on electrodes with a high overvoltage value. Let us assume that the slowest process is proton transition from the hydroxonium ion to the electrode

$$H_3O^+ + e_f \rightarrow H_{ads} + H_2O \tag{252}$$

In addition, let us assume hydrogen atom desorption to follow the electrochemical mechanism:

$$H_{ads} + H_3O^+ + e_f \rightarrow H_2 + H_2O \tag{253}$$

(Other possible mechanisms of hydrogen discharge and desorption are given in the book[61].) The most representative case satisfying the above conditions seems to be hydrogen ion discharge on the mercury electrode.

Both in initial and final states, the proton forms a sufficiently strong chemical bond with the water molecule and electrode respectively. As shown by the analysis of experimental data, the proton vibration frequencies in these states are

$$\omega_i \simeq 5 \times 10^{14}\,\text{sec}^{-1} > \frac{kT}{\hbar}; \quad \omega_a \simeq 2 \times 10^{14}\,\text{sec}^{-1} > \frac{kT}{\hbar} \tag{254}$$

where the quantity $\omega_a$ is taken for the mercury electrode.[36] The frequencies in eqn (254) correspond to proton motion along an axis normal to the electrode. There exist also other forms of vibrations in a real system (such as bending of bonds). Taking account of these vibrations does not present any fundamental difficulties, but, as shown by estimates, they do not affect to any considerable degree the transition probability. The physical reason for this is that as a result of transfer of the proton its equilibrium coordinate changes significantly only in the direction normal to the electrode. Therefore, overlap of the proton wave functions characterizing its transverse motion is very large and the corresponding overlap integral is close to unity. Owing to this peculiarity of the behaviour of the wave functions, it is possible in the case of $H_3O^+$ ion discharge to take into account only the proton nearest to the electrode. A somewhat different approach will give the same result, if we take into consideration eqn (1), according to which the $H_3O^+$ ion has an opportunity to 'impinge' upon the electrode several times before the discharge occurs. Thus, the hydroxonium ion will frequently happen to be near the electrode in a position 'convenient' for the reaction. To make an allowance for this situation, it is sufficient to introduce into the expression for the current a steric factor of the order of 1. However, if the following condition is fulfilled

$$\tau_e \gg \tau_d \gg \tau_r \tag{255}$$

where $\tau_r$ is the mean time of turning of $H_3O^+$ ions, the steric factor will be exactly equal to 1.

According to the preceding section (see eqn (183)), eqn (254) means that proton should be included in the quantum subsystem along with electron. A physical interpretation of the reaction path for the case of the proton discharge is given in Section III (see Fig. 16(a)) if $U(q)$ is understood to mean the electron-protonic term and $q$—the solvent coordinates. However, since the problem of proton transfers has been discussed more than once in the literature[62] in terms of the electron term, in Fig. 22(a) we show the 'reaction path' corresponding to the theory developed in the previous section. Here, unlike earlier theories (see e.g. Reference 62) which did not take into account the dynamic role of the solvent, the electronic terms in Fig. 22(a) are plotted against the coordinates of proton $R$ and solvent $q$. In addition, for illustration a case is considered when the proton in initial and final states performs harmonic motion with the same frequency. This approximation is particularly helpful in that it permits of a rigorous analytical calculation supporting the interpretation given below.[63-64] In virtue of the quantum nature of the proton behaviour, only the medium dipoles can perform classical fluctuations. Therefore, we can assume the proton coordinate in the initial state to be rigidly fixed ($R = R_{i0}$) and the motion along the electron term to occur only towards $q$. When due to fluctuation the solvent coordinate assumes the value $q^*$, the system will have the energy $J_i + \frac{1}{2}\hbar\omega_0(q^* - q_{i0})^2$ (Section 01 in Fig. 22(a)); if the proton in initial state was at the excited state with the

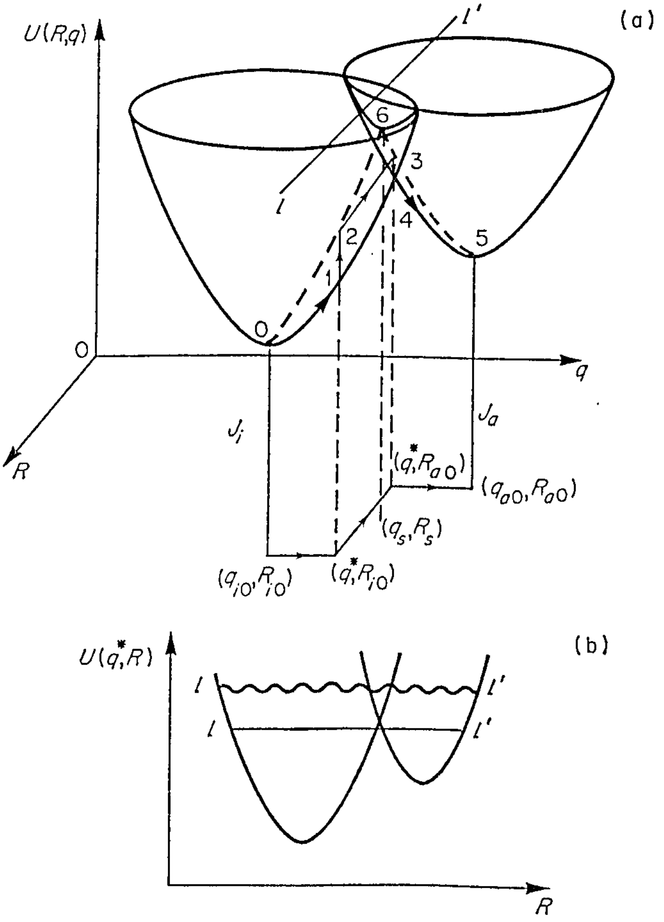

Fig. 22. Schematic diagram of the 'reaction path' for a proton transition: (1) according to the theory of absolute reaction rates (dashed curve); (2) the true reaction path (solid curve).

energy $\varepsilon_e^{(i)} = \hbar\omega_p(l + \frac{1}{2})$ (Section 12 in Fig. 22(a)) the total energy of the system in the activated state $q^*$ will be

$$U_i(q^*, R_{i0}) + \varepsilon_e^{(i)} = J_i + \tfrac{1}{2}\hbar\omega_0(q^* - q_{i0})^2 + \tfrac{1}{2}\hbar\omega_p(2l + 1) \qquad (256)$$

The solvent being a slow subsystem with respect both to electron and proton, the transition from term to term occurs with a fixed coordinate $q^*$ (the Franck-Condon principle). The transition from the initial to final terms involves, in addition to the change in the electronic state, a change in the proton coordinate (Section 23 in Fig. 22(a)). To illustrate this stage Fig. 22(b) shows the intersection of the electron terms with the plane $ll'$ parallel to the plane $UOR$ and passing the point $(q^*, R_{i0})$. Since $U(q^*; R)$ is the proton potential energy the nature of the proton transition should be explained on this plot (Fig. 22(b)). The proton transition can be both subbarrier (solid line in Fig. 22(b)) above the barrier (wiggly line in Fig. 22(b)). It should be stressed that in both cases we have to deal with a purely quantum proton transfer. Moreover, as has been already stated in the previous section, even in the case of a subbarrier transition, the probability is not determined by the Gamow factor, but is calculated from the Landau-Zener equation. At the final term, the proton has the excitation energy $\varepsilon_{e'}^{(a)} = \hbar\omega_p(l' + \frac{1}{2})$ (Section 34 in Fig. 22(a)) and the total energy of the system is determined by the formula:

$$U_a(q^*; R_{a0}) + \varepsilon_{e'}^{(a)} = J_a + \tfrac{1}{2}\hbar\omega_0(q^* - q_{a0})^2 + \tfrac{1}{2}\hbar\omega_p(2l' + 1) \qquad (257)$$

After the transition from term to term, the system relaxes classically from the point $(q^*, R_{a0})$ to the equilibrium point of final state $(q_{a0}, R_{a0})$. By conservation of energy, the quantum transition in Section 23 of Fig. 22(a) can occur only if the energies of the system before and after the reaction coincide (see also Fig. 22(b))

$$J_i + \tfrac{1}{2}\hbar\omega_0(q^* - q_{i0})^2 + \varepsilon_e^{(i)} = J_a + \tfrac{1}{2}\hbar\omega_0(q^* - q_{a0})^2 + \varepsilon_{e'}^{(a)} \qquad (258)$$

Actually, this relation is the equation for the determination of the activation configuration of the solvent $q^*$. After solution of eqn (258) we obtain for the activation energy the expression:

$$E_a^{ll'} = \frac{(E_S - \Delta J^{ll'})^2}{4E_S} \qquad (259)$$

where $E_S$ is the reorganization energy of the solvent

$$E_S = \tfrac{1}{2}\hbar\omega_0(q_{i0} - q_{a0})^2 \rightarrow \tfrac{1}{2}\sum_{\vec{k}}\hbar\omega_{\vec{k}}(q_{\vec{k}i} - q_{\vec{k}a})^2 \qquad (260)$$

and

$$\Delta J^{ll'} = (J_l + \varepsilon_e^{(l)}) - (J_a + \varepsilon_{e'}^{(a)})$$
$$= (\varepsilon_f - \varepsilon_F) + e\eta_c + \Delta J_{0F} + (\varepsilon_e^{(l)} - \varepsilon_{e'}^{(a)}) \tag{261}$$

($\eta_c$ is the cathodic overvoltage eqn (43)).

In Fig. 22(a) for comparison is shown, by a dashed line, the 'transition path' according to the absolute reaction rate theory, when the reaction coordinate passes through the saddle point ($q_S$, $R_S$). Physically, this path corresponds to the classical fluctuation motion both of solvent and proton, when during the reaction the proton chemical bond stretches. In this case the activation energy differs from eqn (259) and is of the form

$$E_a^* = \frac{(E_S + E_p - J_l + J_a)^2}{4(E_S + E_p)} \tag{262}$$

where $E_p$ is the proton reorganization energy:

$$E_p = \frac{M_p\omega_p^2}{2}(R_{l0} - R_{a0})^2 \tag{263}$$

($M_p$ is the proton mass.) An accurate quantum-mechanical calculation shows this result to be valid only in the case when $\hbar\omega_p < kT$. Since in practice the reverse condition is fulfilled (see eqn (254)), the application of the 'standard' absolute reaction rate theory to the proton transfer processes should be considered as incorrect.

In calculating the discharge current, we shall proceed from the results of the semi-phenomenological theory, into which we shall substitute an expression for the transition probability in eqn (170). Moreover, in accordance with the general theory, we shall first find the discharge current assuming the proton to be at the beginning and at the end of the reaction at the unexcited levels: $\varepsilon_e^{(l)} = \varepsilon_{e'}^{(a)} = 0$. Since in the mechanism under consideration there is for each reaction act, eqn (252), one electrochemical desorption act eqn (253) (condition of steadiness) the total discharge current will be twice as large as the current due only to the process, eqn (252):

$$\vec{i}_c^0 = 2eC_{H^+}^0 \frac{\omega_{\text{eff}}}{2\pi} \kappa_{00}\rho_F \int n(\varepsilon_f) \exp\left[-\frac{(E_S - \Delta J)^2}{4E_S kT}\right] \mathrm{d}\varepsilon_f \tag{264}$$

where $C_{H^+}^0$ is the surface density of the $H_3O^+$ ions on the outer side of the Helmholtz layer (for simplicity, the $\psi_1$-effect is assumed to be absent) and $\kappa_{00}$ is the transmission coefficient calculated using the wave function of the proton in unexcited state. Even for a continuum model of the solvent, the integral in eqn (264) is not calculated accurately, but assuming the parameter

$E_S$ to have a definite value, we can calculate numerically the current as a function of the overvoltage. Such a calculation of the current at $E_S = 2$ eV was carried out by means of a computer, the result obtained having been shown to be practically the same as in the case of an approximate analytical treatment. Therefore, we shall use the Laplace method for the calculation of the integral in eqn (264). According to eqn (84) the level $\varepsilon^*$ making the main contribution to the current is found from the equation

$$\alpha(\varepsilon^*) = 1 - n(\varepsilon^*) = \tfrac{1}{2} - \frac{\Delta J_{0F}}{2E_S} - \frac{e\eta_c}{2E_S} - \frac{\varepsilon_f - \varepsilon_F}{2E_S} \tag{265}$$

With respect to $\varepsilon^*$ this transcendental equation cannot be solved analytically, but the dependence of the transfer coefficient $\alpha^* = \alpha(\varepsilon^*) = \alpha_{\text{exp}}$ on overvoltage can be readily found from it as the inverse function:

$$e\eta_c = E_S - \Delta J_{0F} - 2E_S\alpha^* + kT \ln \frac{1-\alpha^*}{\alpha^*} \tag{266}$$

The dependence of the transfer coefficient on overvoltage corresponding to eqn (266) is shown in Fig. 23, where the parameter $E_S$ was assumed to be 2 eV. It is evident from the plot that $\alpha^*$ in the range $|e\eta_c + \Delta J_{0F}| < E_S$ is approximated quite well by the linear function of overvoltage:

$$\alpha^* \simeq \tfrac{1}{2} - \frac{e\eta_c + \Delta J_{0F}}{2E_S}; \quad |e\eta_c + \Delta J_{0F}| < E_S \tag{267}$$

The overvoltage range in which the transfer coefficient has an approximately constant value depends essentially on the reorganization energy of the solvent $E_S$. For illustration, we can consider two cases: (*a*) $E_S = 2$ eV. Then in the overvoltage range $|e\eta_c + \Delta J_{0F}| < 0{\cdot}4$ eV we have $\alpha^* = 0{\cdot}5 \pm 0{\cdot}1$; (*b*) $E_S = 4$ eV. Here we have $\alpha^* = 0{\cdot}5 \pm 0{\cdot}1$ already in the overvoltage range 1·6 V ($|e\eta_c + \Delta J_{0F}| < 0{\cdot}8$ eV).

From eqn (266) we can readily find the experimental activation energy as the function of the transfer coefficient:

$$\begin{aligned} E_a^{\text{exp}} &= -\textstyle\int \alpha^*(e\eta_c)\, \mathrm{d}e\eta_c = \displaystyle\int_0^{\alpha^*} \alpha^* \left(2E_S + \frac{kT}{\alpha^*(1-\alpha^*)}\right) \mathrm{d}\alpha^* \\ &= \alpha^{*2} E_S - kT \ln(1-\alpha^*) \end{aligned} \tag{268}$$

As the result, the final expression for the discharge current without an allowance for proton excited states assumes the form:

$$\vec{i}_c^{\,0} = 2eC_{H^+}^0 \frac{\omega_{\text{eff}}}{2\pi} \kappa_{00}\rho_F (1-\alpha^*)\, \mathrm{e}^{-\alpha^{*2}(E_S/kT)}\, \Delta\varepsilon^* \tag{269}$$

where the width of the levels $\Delta\varepsilon^*$ making the main contribution to the current is determined by the eqn (86):

$$\Delta\varepsilon^* = \sqrt{(2\pi)}kT\left[\frac{kT}{2E_s} + \alpha^*(1-\alpha^*)\right]^{-1/2} \qquad (270)$$

Equation (269) together with eqn (266) gives the dependence of the discharge current on overvoltage over the whole potential range. Figure 24 shows the

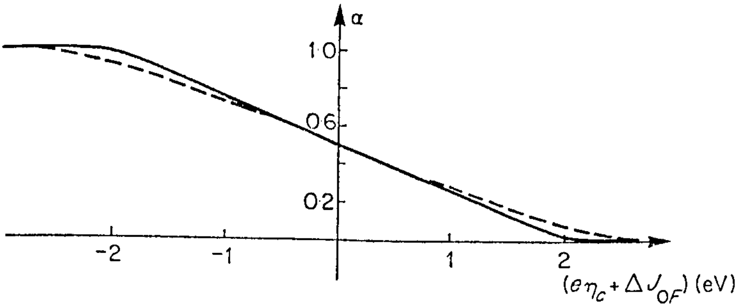

Fig. 23. Theoretical dependence of the transfer coefficient on overvoltage without an allowance (solid curve) and with an allowance (dashed curve) for the proton excited states. $E_r = 2$ eV, $R_{i0} - R_{a0} = 10^{-8}$ cm, $kT = 0{\cdot}025$ eV.

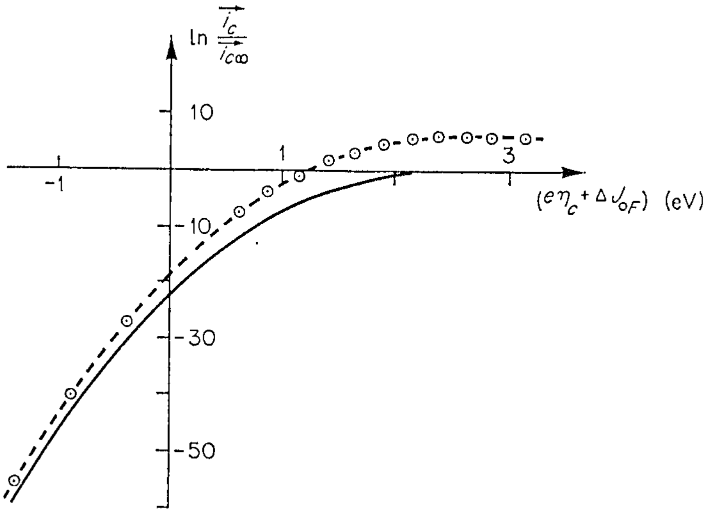

Fig. 24. Theoretical polarization curves for hydrogen ion discharge without allowance (solid curve) and with allowance (dashed curve) for the proton excited states. $E_r = 2$ eV, $R_{i0} - R_{a0} = 10^{-8}$ cm, $kT = 0{\cdot}025$ eV.

polarization curve in a semi-logarithmic scale calculated from eqns (266) and (269) at $E_S = 2$ eV, the logarithm of the ratio of the discharge current to the limiting activationless current being plotted along the ordinate axis

$$\vec{i}^0_\infty = 2eC^0_{H^+} \frac{\omega_{\text{eff}}}{2\pi} \kappa_{00} \rho_F \sqrt{(4\pi kTE_S)} \tag{271}$$

In compliance with the general semi-phenomenological theory, the whole discharge current-overvoltage curve can be divided into three characteristic regions: barrierless ($\alpha^* \simeq 1$), normal ($\alpha^* \simeq 0{\cdot}5$) and activationless ($\alpha^* \simeq 0$). It should be noted that in plotting the theoretical polarization curve, it is possible to calculate the current only for the overvoltage range $e\eta_c + \Delta J_{0F} > 0$, since in the range $e\eta_c + \Delta J_{0F} < 0$, the curve is completed automatically by means of the identity

$$\ln \vec{i}^0_c(-e\eta_c - \Delta J_{0F}) = \ln \vec{i}^0_c(e\eta_c + \Delta J_{0F}) - \frac{e\eta_c + \Delta J_{0F}}{kT} \tag{272}$$

which follows directly from eqns (266) and (269)-(271).

In conclusion, we shall consider the role of the excited states in the kinetics of the proton discharge. According to eqn (111) the total discharge current can be written as:

$$\vec{i}_c = \sum_{ll'} \frac{\kappa_{ll'}}{\kappa_{00}} \cdot \vec{i}^0_c(e\eta_c + \varepsilon^{(l)}_e - \varepsilon^{(a)}_{e'})\, \mathrm{e}^{-(\varepsilon_l{}^{(l)}/kT)} \tag{273}$$

First of all, it can be readily seen from eqn (273) that the excited states should be of most importance in the activationless and barrierless regions. In fact, the ratio of the current $\vec{i}^{ll'}_c$ due to the proton transfer from the excited level $\varepsilon^{(l)}_e$ to the excited level $\varepsilon^{(a)}_{e'}$ can be written as:

$$\frac{\vec{i}^{ll'}_c}{\vec{i}^0_c} \simeq \frac{\kappa_{ll'}}{\kappa_{00}} \begin{cases} \exp\left(-\dfrac{\varepsilon^{(a)}_{e'}}{kT}\right) & \text{(barrierless region)} \\[2ex] \exp\left(-\dfrac{\varepsilon^{(l)}_e + \varepsilon^{(a)}_{e'}}{2kT}\right) & \text{(normal region)} \\[2ex] \exp\left(-\dfrac{\varepsilon^{(l)}_e}{kT}\right) & \text{(activationless region)} \end{cases} \tag{274}$$

For analysis of this formula let us first consider the case when $\kappa_{00} \simeq 1$. Since the overlapping of the proton wave function is larger in excited states than in the ground state, evidently $\kappa_{ll'} \simeq 1$. According to eqn (272) in the barrierless region the contribution of the excited proton levels in the adsorbed state is exponentially small and the transitions can be assumed to occur to the ground level of the final state ($\varepsilon_e^{(a)} = 0$). However, the excited states of the proton in the $H_3O^+$ ion will make the same contribution to the current as the ground state. In the normal region the contribution of all excited levels (both of initial and final states) is exponentially small. Therefore, it is possible to take into consideration only the transitions from one ground level to another ($\varepsilon_e^{(i)} = \varepsilon_e^{(a)} = 0$). Finally, in the activationless region the contribution of the excited proton levels of the proton in the $H_3O^+$ ion is exponentially small and of essential importance are the transitions to the excited levels of the final state.

If the proton transitions for lower levels are of a nonadiabatic nature ($\kappa_{00} < 1$), the relative role of excited states in different kinetic regions is the same as in adiabatic processes considered above. However, for a qualitative analysis, the change of the transmission coefficient for different excited levels becomes of importance now.

In order to evaluate quantitatively the role of the proton excited states, we have calculated the discharge current with the use of a computer taking into account the ground and two excited levels. The Morse potential parameters used are as follows:

$$\left.\begin{aligned} \omega_a &= 10^{14}\ \text{sec}^{-1}; & D_a &= 1{\cdot}3\ \text{eV} \\ \omega_i &= 5{\cdot}10^{14}\ \text{sec}^{-1}; & D_i &= 7{\cdot}8\ \text{eV} \end{aligned}\right\} \qquad (275)$$

The distance of proton transfer was assumed to be 1 Å. The remaining parameters are: $E_S = 2$ eV, $kT = 0{\cdot}025$ eV. The dotted curve on Fig. 24 corresponds to the case when the proton excited states are taken into account, and the solid one—to the case of the proton transfer between the ground vibrational states. The dependence of the transfer coefficient on overvoltage for these two cases is shown on Fig. 23.

The discussion of the results of the present investigation with Professor Levich and Dr Kuznetsov, who have read my manuscript and made a number of valuable comments, has been exceedingly helpful to me. I wish also to thank my colleagues Dr Harkats, Dr German, Vorotyntsev, Kats, Shvets, and Konkina, who helped me in writing this article.

## 4. Further Developments of the Theory

In references 65 and 66 there are further developments of semi-phenomenological theory. The most important new results are described in refs. 67–69, where the dielectric formalism for description of polar solvents is developed. All the parameters of chemical and electrochemical reaction rates connected with the solvent reorganization are expressed in terms of the complex dielectric permittivity $\varepsilon(\kappa,\omega)$, i.e. the time dispersion of $\varepsilon$ is taken into account along with the space dispersion of $\varepsilon$. For example, the reorganization energy can be written as [cf. eqn. (176) above]:

$$E_r = \frac{1}{8\pi}\sum_{\vec{k}}\left|\vec{D}_{\vec{k}\alpha} - \vec{D}_{\vec{k}\alpha'}\right|^2 \cdot \frac{2}{\pi}\int_0^{kT/\hbar\alpha(1-\alpha)} \frac{\mathrm{d}\omega}{\omega}\,\frac{\operatorname{Im}\varepsilon(\kappa,\omega)}{|\varepsilon(\kappa,\omega)|^2}$$

The general expressions for the transition probability in the harmonic approximation are given in ref. 70 for the case of arbitrary change of frequencies and normal coordinates; this includes consideration of the mutual transformations of classical and quantum degrees of freedom in the course of reaction. The effect of deviation of the potential energy from harmonicity on the transition probability is discussed in ref. 71. Further development of the semiclassical method of calculation of transition probabilities is given in ref. 72, where in particular a closed expression for the entropy of activation is obtained, *viz.*:

$$\mathrm{e}^{S_a/k} = \frac{\hbar\omega_{\mathrm{eff}}}{kT}\cdot Z_i^{-1}\left\{\det \|\, G_{kl}\|\right\}^{-1/2}$$

$$\|G_{kl}\| = \|\,(1-\alpha)\Omega_k^{*2}\,\delta_{kl} + \alpha\sum_n \Omega_m'^{*2}\,\tau_{kn}\,\tau_{ln}\|$$

where $Z_i$ is the partition function for intermolecular degrees of freedom, and $\alpha$ is the transfer coefficient. For the calculation of $\Omega_k^*$ and $\Omega_k'^*$ one must approximate the initial and final potential energy surface near the saddle point by quadratic forms, $\tau_{kn}$ is the orthogonal matrix connecting the initial and final normal coordinates. $\Omega_k^*$ and $\Omega_k'^*$ are the 'frequencies' in these quadratic forms.

The theory of adiabatic electrochemical redox reactions is given in ref. 73. The theory of electrochemical isotope effects is developed in ref. 74. This theory has been confirmed by experimental results obtained by Krishtalik and co-workers,[75] which have shown that proton transfer is of a quantum nature.

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## LIST OF SYMBOLS

| | |
|---|---|
| av | Symbol of statistical averaging |
| $a_0$ | Radius of localization of electron in ion or adsorbed particle |
| $c$ | Basic parameter of the continuum model of dielectric in the absence of frequency dispersion, eqn (128) |
| $C^0_{H^+}$ | Surface concentration of $H_3O^+$ ions in the Helmholtz layer |
| $C_R$; $C_0$ | Surface concentration of reducing and oxidizing ions in the Helmholtz layer |
| $C^{1,2}_{0S}$ | Surface concentration of ions in the Helmholtz layer at equilibrium potential before and after discharge |

| | |
|---|---|
| $C_S$ | Concentration of discharging ions in the reaction zone |
| $\vec{D}$ | Vector of electric induction |
| $E$ | Classical Hamiltonian (energy) of polar solvent (eqn (120) and subsequently) |
| $E;\ E'$ | Variables corresponding to total energies of the system during chemical reactions (Fig. 3–4) |
| $E_a$ | Activation energy |
| $E_a^*$ | Macroscopic value of activation energy |
| $E_a^{\mathrm{exp}}$ | Experimental activation energy |
| $E_c^0$ | Energy corresponding to the bottom of the conduction band in semiconductor |
| $\varepsilon_i$ | Ionization energy of ion |
| $E_k$ | Energy levels of classical subsystem reckoned from the ground state |
| $E_0$ | Energy of the ground state of classical subsystem |
| $E_p$ | Reorganization energy of proton |
| $E_r$ | Reorganization energy of classical subsystem |
| $E_{r1};\ E_{r2}$ | Reorganization energies for forward and back reactions |
| $E_{ri}$ | Reorganization energy of the $i$th oscillator |
| $E_r^{\mathrm{loc}}$ | Reorganization energy of solvent in the absence of frequency dispersion |
| $E_S$ | Reorganization energy of solvent |
| $E_{\mathrm{solv}}$ | Solvation energy of ion |
| $E_v^0$ | Top of the valence band in semiconductor |
| $E_{\alpha n}$ | Energy of the total system in the adiabatic perturbation theory |
| $E_\alpha(p,q)$ | Hamiltonian for classical subsystem |
| $\Delta E$ | Difference between energies of the first excited level and the ground state |
| $\mathrm{e}_f$ | Electron localized at the level $\varepsilon_f$ in electrode |
| $e\Delta\varphi$ | Bending of semiconductor bands at interface |
| $e\Delta\varphi_0$ | Equilibrium bending of semiconductor bands at interface |
| $F(\vec{r} - \vec{r}\,')$ | Function characterizing the fluctuation energy of solvent |
| $F(\varepsilon_f)$ | Free energy with fixed state of electron in electrode |
| $F_a$ | Free energy of activation |
| $\Delta F(\varepsilon_f)$ | Free energy of electrode reaction with fixed electron state |
| $\Delta F_{0F}$ | Free energy of reaction at the equilibrium potential of electrode |
| $\Delta F^*$ | Macroscopic value of free energy of electrode reaction |
| $(f\vec{r} - \vec{r}\,')$ | Function characterizing the fluctuation energy of solvent |
| $\mathscr{F}$ | Free energy calculated from the spectrum of classical subsystem reckoned from the ground state |
| $g(\varepsilon)$ | Statistical weight for level |
| $g_i$ | Generalized dipole momentum in ion solvation shell |
| $g_{\vec{k}}$ | Generalized polarization wave momentum in solvent |
| $\mathscr{H}^0$ | Quantum-mechanical unperturbed Hamiltonian of the system |
| $H_e^0$ | Quantum-mechanical Hamiltonian of fast subsystem |
| $H_S(q)$ | Quantum-mechanical Hamiltonian of polar solvent |
| $h(\hbar)$ | Planck's constant (divided by $2\pi$) |
| $\vec{i}^{\,e,p}$ | Electron and hole discharge currents on semiconductor |
| $i_c$ | Total cathodic current |
| $\vec{i}_c;\ \overleftarrow{i}_c$ | Cathodic currents for forward and back processes |

| | |
|---|---|
| $i_0(i_0^{ad})$ | Exchange current (for adiabatic process) |
| $\vec{i}_2$ | Discharge current with transfer of 2 electrons |
| $J$ | Minimum potential energy of classical subsystem |
| $\Delta J(\varepsilon_f)$ | Change of minimum potential energy of classical subsystem during reaction |
| $\Delta J^{rr'}(\varepsilon_f)$ | Change of minimum potential energy of Classical subsystem with fixed states of quantum subsystem before ($r$) and after ($r'$) reaction |
| $K$ | Reaction rate constant in the gas phase |
| $K_0$ | Equilibrium constant of electrode reaction |
| $K_{0i,f}$ | Kinetic energy of particles in the gas phase |
| $k$ | Boltzmann constant |
| $k_f$ | Wave number of electron in electrode |
| $\vec{k}$ | Wave vector of polarization wave |
| $l$; $l'$ | Quantum numbers of excited states of proton in $H_3O^+$ ion and $H_{ads}$. |
| $l_0$ | Correlation radius of polarization currents in solvent |
| $M$; $m$ | Masses of heavy and light particles in the adiabatic perturbation theory |
| $M_i$ | Mass of the $i$th particle of classical subsystem |
| $M_p$ | Mass of proton |
| $m$ | Mass of electron |
| $m_0$ | Mass of dipoles of solvent |
| $m_e^*$, $m_p^*$ | Effective masses of electrons and holes in semiconductor |
| $N_a$ | Number of dipoles contributing to activation energy |
| $n(\varepsilon_f)$ | Fermi–Dirac distribution function |
| $\bar{n}_{\vec{k}}$ | Mean occupation numbers of oscillator levels |
| $Ox$ | Oxidizing ion |
| $\vec{P}$; $\dot{\vec{P}}$ | Specific polarization and polarization current |
| $\vec{P}_{en}$ | Electronic polarization due to atomic nuclei of solvent |
| $\vec{P}_{ir}$ | Infrared (inertial) polarization |
| $\vec{P}_{\vec{k}}$; $\dot{\vec{P}}_{\vec{k}}$ | Fourier amplitudes of polarization waves and polarization current |
| $\vec{P}_n$ | Polarization due to dipole moments of solvent nuclei |
| $\vec{P}_{op}$ | Optical (inertialess) polarization |
| $\vec{P}_{11}$ | Longitudinal polarization |
| $P_i$ | Generalized momentum of the $i$th particle of classical subsystem |
| $Q$ | Statistical sum |
| $q_i$ | Normal coordinate of classical subsystem (also in eqn (148) normal coordinate of dipole in solvation shell) |
| $q_{\vec{k}}$ | Normal coordinate of polarization wave |
| $q_{k0}(\varphi_m)$ | Equilibrium normal coordinate of classical subsystem versus electrode potential |
| $q_{\vec{k}\alpha}$ | Equilibrium normal coordinate of polarization wave |
| $q_s^*$ | Saddle point activated state |
| $q_t$ | Normal coordinate of solvent at which the 'tunnel' transition of quantum subsystem is possible |
| $q^*$ | Normal coordinate of solvent corresponding to activated state |
| $R_{i0}$; $R_{a0}$ | Equilibrium coordinate of proton in $H_3O^+$ ion and in $H_{ads}$ |

| | |
|---|---|
| Red | Reducing ion |
| $r_0$ | Correlation radius of dipole moments of solvent |
| $S(\vec{r})$ | Correlation function of dipole moments of solvent |
| $S_a$ | Entropy of Activation |
| $S^*$ | Intersection surface of terms |
| $T$ | Temperature (degrees Kelvin) |
| $U(q_i\,\varphi_m)$ | Term of classical subsystem versus electrode potential |
| $U_a(q^*)$ | Potential energy of classical subsystem in activated state |
| $U_0$ | Depth of potential well for electrons in metal |
| $U_{\alpha,\alpha'}(q)$ | Terms of classical subsystem corresponding to the states $\alpha$ and $\alpha'$ of quantum subsystem |
| $V$; $v$ | Velocities of heavy and light particles in the adiabatic perturbation theory |
| $V(q;\varphi_m)$ | Energy of interaction of classical subsystem with electric field of electrode |
| $V_e$ | Electrode volume |
| $V_{eS}$ | Energy of interaction of electron with solvent |
| $V_{cr}$ | Critical value of exchange integral separating adiabatic and non-adiabatic reactions |
| $V_S$ | Solvent volume |
| $V_{\alpha'\alpha}$ | Exchange integral |
| $v_{\vec{k}}$ | Function determining the interaction of solvent with quantum subsystem |
| $v_i$ | Velocity of the *i*th particle of classical subsystem |
| $W$ | Transition probability per unit time |
| $W_{LZ}$ | Transition probability from term to term in the Landau-Zener theory |
| $X_d$ | Debye screening distance for semiconductors |
| $X_i$ | Cartesian coordinate of the *i*th classical subsystem |
| $Z_\alpha$ | Ionic charge |
| $\alpha(\varepsilon_f)$ | Microscopic transfer coefficient in the Brønsted equation |
| $\alpha_{\mathrm{exp}}$ | Experimental transfer coefficient |
| $\alpha^e$; $\alpha^e_{\mathrm{exp}}$ | Transfer coefficients for electronic current on semiconductor |
| $\beta_{\mathrm{exp}}$ | Experimental transfer coefficient for reverse current |
| $\gamma$ | Parameters determining the geometric form and relative position of terms |
| $\gamma_0$ | Solvent density |
| $\Delta_{e,p}$ | Distance from the bottom of conduction and the top of valence bands to Fermi level |
| $\delta(x)$ | Dirac delta function |
| $\varepsilon_a$ | Electron energy in adsorbed particle |
| $\varepsilon_{ai}$; $\varepsilon_{bi}$; $\varepsilon_n$ | Electron levels in metals for which the discharge is activationless, barrierless and normal |
| $\varepsilon_c$ | Minimum energy of conduction electron at interface |
| $\varepsilon_f$ | Arbitrary electron level in electrode |
| $\varepsilon_F$ | Fermi level of electron in electrode |
| $\varepsilon_i$ | Quantum levels of electron in ion |
| $\varepsilon_e^{(i)}$; $\varepsilon_{e'}^{(a)}$ | Excitation energies of proton in $H_3O^+$ ion and $H_{ads}$ |
| $\varepsilon_n$ | Excitation energies of slow subsystem |
| $\varepsilon_0$ | Optical dielectric constant of solvent |

| | |
|---|---|
| $\varepsilon_r^{(1)}$; $\varepsilon_{r'}^{(2)}$ | Excited levels of quantum subsystem before ($r$) and after reaction ($r'$) |
| $\varepsilon_s$ | Static dielectric constant of solvent |
| $\varepsilon_\alpha(q)$ | Quantum energy of fast subsystem |
| $\varepsilon^*$ | Electron level in electrode making maximum contribution to current |
| $\Delta\varepsilon^*$ | Range of levels near $\varepsilon^*$ contributing to current |
| $\eta$ | Overvoltage |
| $\eta_c$ | Cathodic overvoltage (also overvoltage at interface for redox reactions on semiconductor) |
| $\eta^F$ | Overvoltage at which main contribution to current is made by electron at Fermi level |
| $\eta_s$ | Overvoltage at the point where discharging ion is localized |
| $\kappa$ | Transmission coefficient |
| $\mu(\varepsilon)$ | Two-electron distribution function for metals, eqn (224) |
| $\nu(\varepsilon)$ | Analogue of occupation number of electrons in metal for 2-electron processes, eqn (227) |
| $\rho$ | Density of bound charges of polar medium |
| $\rho(\varepsilon_f)$ | Density of energy levels of electron in electrode |
| $\sigma$ | Cross-section for gas reactions |
| $\tau_d$ | Mean time interval between diffusion jumps of ion in solution |
| $\tau_e$ | Mean time necessary for discharge of one ion |
| $\tau_r$ | Mean time of ion turning in solution |
| $\phi(\vec{r})$; $\varphi(\vec{r})$ | Functions characterizing fluctuation energy of solvent |
| $\varphi_c(\varphi_c^0)$ | (Equilibrium) potential at semiconductor interface |
| $\varphi_m$ | Galvani potential of metal electrode |
| $\varphi_0$ | Equilibrium Galvani potential of electrode |
| $\varphi_s$ | Potential at the point where discharging (discharged) ion is localized |
| $\chi_{\alpha n}(q)$ | Wave function of slow subsystem in the adiabatic perturbation theory |
| $\Psi'_f(x)$ | Wave function of electron in electrode |
| $\Psi'_1$ | Psi-prime potential |
| $\Omega_k(\varphi_m)$ | Normal frequencies of classical subsystem depending on electrode potential |
| $\omega_a$; $\omega_i$ | Vibration frequencies of proton in $H_{ads}$ and $H_3O^+$ ion |
| $\omega_{eff}$ | Effective frequency of polarization waves in solvent |
| $\omega_{\vec{k}}$ | Normal frequencies of polarization waves in solvent |
| $\omega_0$ | Limiting infrared frequency of polarization waves in solvent |
| $\omega_p$ | Proton vibration frequency |
| $\omega_\infty$ | Maximum frequency of polarization waves in solvent |