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THEORY OF HYDROGEN-ION DISCHARGE ON METALS: CASE OF HIGH OVERVOLTAGES*

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Abstract—A detailed quantum-mechanical theory for hydrogen discharge on metals showing high hydrogen overvoltage is given, for the case where the discharge reaction is the rate-determining step.

Résumé—Théorie quanto-mécanique détaillée du processus de décharge de l'ion hydrogène sur les métaux. Elle dénote une surtension élevée dans de cas où la réaction de décharge est l'étape régulatrice.

Zusammenfassung—Man entwickelt eine detaillierte quantenmechanische Theorie über die Wasserstoffentladung an Metallen mit hoher Wasserstoffüberspannung für den Fall, wo die Entladungsreaktion den geschwindigkeitsbestimmenden Schritt darstellt.

ELECTRODE reactions are a special case of charge-transfer processes in a condensed system. At present there exists a quantum-mechanical and statistical theory of redox reactions in condensed phases involving electron-transfer. This theory has been extended to the case of electrode reactions.[1–15] An essential assumption of the theory is that the rate-determining step of the charge-transfer elementary act should not involve the breaking or formation of any chemical bonds between the reagents. This narrows down considerably the class of electrode reactions to which the theory in question is applicable. In particular, it is impossible to consider the hydrogen-ion discharge reaction within its framework.

The present paper gives a quantum-mechanical theory of hydrogen-ion discharge on metals showing high overvoltage. This case is considered only for definiteness: the theory can be directly extended to other proton-transfer processes in polar media. Moreover the availability of a theory of proton-transfer reactions may prove to be helpful in understanding the physical picture of other electrochemical processes and in the development of their theory.

We shall consider hydrogen-ion discharge to be the rate-determining step,[16]

$$H_3O^+ + e \rightarrow H_a + H_2O,$$

and we shall assume the removal of adsorbed hydrogen atoms to proceed by the electrochemical mechanism

$$H_a + H_3O^+ + e \rightarrow H_2 + H_2O.$$

1. MODEL OF THE SYSTEM

In concrete quantum-mechanical calculations we shall make use of a definite model to describe the state of individual components of the total system consisting of proton, electron, solvent and electrode.

1. *Proton*

Both in the initial and final states, the proton forms strong enough chemical bonds with the water molecule and with the metal. Analysis of the experimental

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data shows that the frequencies of vibrations in these states are $\omega_i \simeq 5 \times 10^{14}$ sec^{-1}, $\omega_a \simeq 2 \times 10^{14}$ s^{-1}, corresponding to the motion of the proton along the H^+—H_2O or Me—H bonds. There exist also other kinds of vibrations in a real system (*eg* bending of the bonds). Taking these vibrations into consideration, as will appear, does not present any fundamental difficulties. The estimates show, however, that these vibrations do not influence the transition probability to any great extent. Taking them into consideration may result only in the appearance in the formula for the transition probability of a pre-exponential factor of the order of unity. The physical reason for this is that the proton transfer results in its equilibrium co-ordinate significantly changing only in the direction of the chemical bond. In the lateral direction the proton co-ordinates remain practically unchanged. Therefore, as a rule, the overlapping of the proton wave-functions characterizing its motion in the lateral direction is quite large and the corresponding integral of overlapping is close to unity.

Owing to this peculiarity of the behaviour of the wave-functions, in calculating the transition probability of a proton located closest to the electrode, it is possible to make no allowance for the presence of other protons in the hydroxonium ion. At the frequencies given above the inequality

$$\omega_i, \omega_a > \frac{kT}{\hbar} \quad (\approx 4 \cdot 10^{13}\ \mathrm{s}^{-1}) \tag{1.1}$$

is always valid. Its physical significance is that there is the greatest probability of the proton being in the ground vibrational state both in the initial and final states. This is very important for further treatment.

2. *Electron*

In accordance with common practice, in calculating the current, we shall make use of the one-electron approximation. The energy distribution function of the electrons (Fermi distribution) is of the form

$$n(\varepsilon_f) = \left\{\exp\left[\frac{\varepsilon_f - \varepsilon_F}{kT}\right] + 1\right\}^{-1}. \tag{1.2}$$

The electron energy-level density $\rho(\varepsilon_f)$ in the metal is a smooth function of ε_f. The regular character of $\rho(\varepsilon_f)$ is quite evident, for example, in the quasi-free electron model, $\rho \approx \sqrt{|\varepsilon_f - U_0|}$, U_0 being the depth of the potential well in the metal or the edge of the band in a semiconductor.

For simplicity, we shall consider the electron that holds the proton in the adsorbed state to be at the local level ε_a. This means that the number of adsorbed hydrogen atoms is small and no surface band is formed in the electron spectrum in the process of adsorbtion.

3. *Solvent*

A quantitative description of the solvent presents great difficulties, because there is no physical model available to describe equally well the behaviour of the water molecules lying closest to the ion (the so-called inner sphere) and that of more remote solvent molecules (the outer sphere).

The simplest case is when the interaction of the ion with the more remote solvent molecules is of essential importance. Such a situation may arise in the presence of a strong bond between the molecules of the inner sphere and the ion. Then, the molecules of the inner sphere can be combined with the heavy residue of the discharging ion. Such an approach was first suggested for the treatment of electron-transfer reactions by Marcus,[12] and is known as the rigid conducting sphere model. It has been successfully used in the development of the theory of homogeneous and heterogeneous redox reactions involving no breaking of chemical bonds. If the interaction with the nearest molecules of the medium is not negligible, a discrete description should be used for this part of the solvent. At present it is impossible to obtain quantitative results with a discrete model. The difficulties arising are well known from the attempts to develop the theory of liquids.

Therefore, we shall adopt the following model of the solvent: the molecules of the inner sphere are considered as dipoles performing small vibrations; the molecules of the outer sphere are described by a continuous model. In the case of a model of harmonically vibrating oscillators, it is possible to use a quantum-mechanical description. With our model, all the liquid can be described as a system of oscillators vibrating harmonically with different frequencies. The Hamiltonian of the system of oscillators is of the form

$$\mathrm{H}_s = \frac{1}{2}\sum_{k} \hbar\, \omega_k \left(q_k^{2} - \frac{\partial^2}{\partial q_k^{2}}\right), \tag{1.3}$$

where q_k and ω_k are the normal co-ordinates and the frequencies of oscillators, respectively. Just as in the case of redox reactions involving electron transfer, we shall assume that the interaction of the discharging particle with the librations of the dipoles of the medium (*ie* with the vibrations of the water molecules as a whole). Taking into consideration the high frequency vibrations of the inner sphere (if such vibrations were to exist) would not introduce any qualitative changes into the general picture of the phenomenon (nor would making an allowance for the intramolecular vibrations of the H_3O^+ ion, in addition to the proton vibrations along the breaking bond). If the fluctuations of macroscopic polarization $\mathbf{P}(\mathbf{r}, t)$ in time are also considered to be due to the libration of the dipoles of the medium, all the normal frequencies to this approximation can be regarded as being the same, $\omega_k \approx \omega_0$. In order of magnitude, $\omega_0 \approx 10^{11}\ \mathrm{s}^{-1}$. As shown by calculation, the presence of a small dispersion of the vibration frequencies of the dipoles of the medium,

$$\omega_k = \omega_0 + \Delta\Omega_k, \tag{1.4}$$

does not introduce any significant correction into the quantitative picture of the discharge process, since for the librations the following inequality can be always considered to be valid,

$$\omega_k \approx \omega_0 \approx 10^{11}\ \mathrm{s}^{-1} < \frac{kT}{\hbar} \approx 4 \times 10^{13}\ \mathrm{s}^{-1} \tag{1.5}$$

As will be shown later, condition (1.5) permits us to ignore the quantum effects in the treatment of the solvent.

4. *ion distribution*

Finding the space distribution of ions in the solution near the electrode (in the double layer) is a complex statistical problem. This problem has been solved only in the simplest cases.[17–18] Below we shall assume the H_3O^+ ion discharge to occur directly from the outer Helmholtz plane. Therefore, instead of the space distribution of the discharging ions, it is necessary to know only their concentration at the surface C_S'. This assumption is physically justified since the transition probability decreases sharply with increasing distance from the electrode.

Actually, the ion distribution of an indifferent electrolyte affects only the potential distribution in the solution, *ie* it influences only the value of the initial energy of the system and the value of C_S. As will be evident below, the statistical problem can be separated from the quantum-mechanical calculation and the current can be formally calculated and presented in closed form. However, for definiteness, we shall consider the concentration of the indifferent electrolyte to be large enough and the total potential drop to occur in the inner region of the double layer. In that case, the value of C_S will be close to that of the bulk concentration and the electrostatic energy of the discharging ion will be zero. It should be emphasized that in some cases our assumptions, in particular, the model of harmonic vibrations of the water dipoles, will be insufficiently accurate. Thus, the deviation from the harmonic approximation can be due to a partial dielectric saturation of the inner sphere or to effects associated with the structure of liquid water. In principle, making an allowance for the deviation from harmonic approximation can lead to a quantitative change in the parameters of the theory. Nevertheless, to obtain estimates we shall make use of the dielectric continuum model. Comparison of theory with experimental data shows this model to give good enough quantitative results. As regards the qualitative results, it will be seen later that actually they account almost for all the experimental data available at present.

2. TERMS OF THE SYSTEM

Since hydroxonium-ion discharge results in a proton transfer from the water molecule contained in the hydroxonium ion to the electrode, the complete quantum-mechanical Hamiltonian of the system can be conveniently written as

$$\begin{aligned} H(x_w, x_m, R, q) &= H_i^{\circ}(x_w, x_m, R, q) + V_{pm}(x_m, R) \qquad (2.1) \\ &= H_a^{\circ}(x_m, x_w, R, q) + V_{pw}(x_w, R), \end{aligned}$$

where x_w, x_m, R are the co-ordinates of the electrons binding the proton in the hydroxonium ion, of the electron forming with the proton an adsorbed state and of the proton, respectively; q is a set of normal co-ordinates of the solvent $\{q_k\}$; V_{pw} and V_{pm} are the energies of the interaction of the proton with the water molecule in the hydroxonium ion and with the electrode, respectively. H_i° and H_a° are the unperturbed values of the Hamiltonian of the system in the initial and final states of the system, respectively.

The electron terms of the initial and final states should be obtained using the adiabatic approximation. We shall consider the electrons to be the fast sub-system and the proton and the solvent the slow sub-system. The physical significance of this approximation is that in determining the wave-function of the electron sub-system it is possible to ignore the kinetic energy of the slow sub-system, the proton and the solvent, owing to the slowness of their motion. In other words, the electron state can be determined accurately enough if the proton and the solvent are considered to be almost at rest. Naturally, the electron energy in the initial $\varepsilon_f(R, q)$ and final ε_a (R, q) states depend on the co-ordinates of the slow sub-system as on parameters.

The use of the adiabatic approximation for the slow sub-system means that the proton and the solvent interact with a cloud of fast moving electron charge rather than with a point electron. In this case $\varepsilon_f(R, q)$ and $\varepsilon_a(R, q)$ act as the potential energy of interaction between the heavy particles and the electron cloud.

In an adiabatic approximation, the wave-function of the total system in the initial and final states can be represented as

$$\Psi^0_{f,a}(x, R, q) = \Psi_{f,a}(x)\theta_{f,a}(R, q), \tag{2.2}$$

where $\Psi_{f,a}(x)$ are the wave-functions of the electrons and $\theta_{f,a}(R, q)$ the wave-function of the proton and the solvent, which are determined from

$$\left\{-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial R^2} - \frac{1}{2}\hbar\omega_0\sum_k \frac{\partial^2}{\partial {q_k}^2} + U^e_{f,a}(R, q)\right\}\theta_{f,a}(R, q) = E^0_{f,a}\theta_{f,a}(R, q) \tag{2.3}$$

Here M is the proton mass and, $U^e_{f,a}(R, q)$ incorporates both $\varepsilon_{f,a}(R, q)$ and the energy of direct interaction between the heavy particles. It is evident from (2.3) that the quantities $U^e_{f,a}(R, q)$ act as complete potential energy for the slow sub-system; they are called electron terms.

In addition to the electron terms, the electron–proton terms can be introduced, owing to the existence of the relationship between the proton and polarization frequencies,

$$\omega_i, \omega_a \gg \omega_0. \tag{2.4}$$

When condition (2.4) is fulfilled, it is possible to use adiabatic perturbation theory, assuming the proton to be the fast sub-system and the solvent the slow one. Thus a complete physical picture is based on the use of a double adiabatic approximation (1) the electron is considered as being fast compared to the proton and the solvent, (2) the proton is considered fast compared to the solvent.

In the double adiabatic approximation, the wave-functions of the system in the initial and final states can be written

$$\Psi^0_{f,a}(x, R, q) = \Psi_{f,a}(x)\chi_{f,a}(R, q)\phi_{f,a}(q) \tag{2.5}$$

where Ψ and χ are the wave-functions of the electrons and the proton.

The wave-functions of the solvent ϕ are determined from

$$\left\{-\frac{1}{2}\hbar\omega_0\sum_k \frac{\partial^2}{\partial {q_k}^2} + U^{ep}_{f,a}(q)\right\}\phi_{f,a}(q) = E^0_{f,a}\phi_{f,a}(q), \tag{2.6}$$

where $U^{ep}_{f,a}$ is the potential energy of the solvent, *ie* the electron–proton term.

By expanding the electron term of the initial state in power series in terms of small deviations from the equilibrium values of the co-ordinates of the proton and the solvent, we obtain

$$U_f^e = J_f^e + \tfrac{1}{2}\hbar\omega_0\sum_k {Q_k}^2 + \tfrac{1}{2}\hbar\omega_i\xi^2 + \sum_k \gamma_k Q_k\xi_k, \tag{2.7}$$

where $\xi = \sqrt{M\omega_i/\hbar}(R - R_{0i})$ is the deviation of the dimensionless co-ordinate of the proton from the equilibrium value corresponding to the initial state; $Q_k = q_k - q_{k0}$ is the deviation of the normal co-ordinates of the solvent from the equilibrium values. The minimal value of the potential energy in the initial state can be written

$$J_f^e = \varepsilon_f - e\varphi + E_{0i}, \tag{2.8}$$

where φ is the potential of the metal and E_{0i} the minimal potential energy of the proton in the hydrated H_3O^+ ion, comprising both the electrostatic energy of hydration and the chemical binding energy.

The surface described by (2.7) is a paraboloid in $(N + 1)$ dimensional space (N is the number of oscillators). The presence of the last term in (2.7), which corresponds to the interaction between the proton vibrations and the water oscillators, leads to the turning of the main axes of the paraboloid about the axes of the co-ordinates in the $(N + 1)$ dimensional space. The angle of rotation is determined by

$$\gamma_k = \left(\frac{\partial^2 U_f^e}{\partial \xi \partial Q_k}\right)_{\zeta = Q_k = 0}. \tag{2.9}$$

Although further calculations can be carried out taking into consideration the last term in (2.7) it is possible to simplify the formulae by taking advantage of the fact that the frequency of vibrations of the proton differs greatly from that of the solvent. An accurate calculation shows that the parameter determining the value of the interaction of these vibrations is

$$\frac{16 \sum_k \gamma_k^2}{\hbar^2(\omega_i^2 - \omega_0^2)} \approx 16 \frac{\omega_0}{\omega_i} \cdot \frac{\int (\mathbf{P}_0 - \mathbf{P}_0^\circ)^2 \, dv}{\int \mathbf{P}_0(\mathbf{P}_0 - \mathbf{P}_0^\circ) \, dv}. \tag{2.10}$$

The significance of the quantities $\mathbf{P}_0^\circ$ and $\mathbf{P}_0$ can be explained as follows. Let us denote by R_{0i}° the co-ordinate of the equilibrium position of the proton in the H_3O^+ ion in the gaseous phase. When the H_3O^+ ion is placed into the solvent, its equilibrium position alters due to polarization. Let us denote the new value of the co-ordinate of the equilibrium point by R_{0i}. The quantities $\mathbf{P}_0^\circ$ and $\mathbf{P}_0$ are equal to the equilibrium values of polarization due to the H_3O^+ ion, in which the equilibrium co-ordinate of the proton is R_{0i}° and R_{0i}, respectively. The estimation of the parameter (2.10) with a dielectric continuum approximation gives

$$\frac{16 \sum_k \gamma_k^2}{\hbar^2(\omega_i^2 - \omega_0^2)} \approx \frac{\omega_0}{\omega_i} \cdot \frac{|R_{0i} - R^\circ_{0i}|}{\tau_0} \ll 1, \tag{2.11}$$

where τ_0 is the radius of the H_3O^+ ion.

The inequality (2.11) shows that the last term in (2.7) can be dropped. Finally U_f^e can be written as

$$U_f^e = J_f^e + \frac{1}{2} \hbar\omega_0 \sum_k (q_k - q_{k0})^2 + \frac{M\omega_i^2}{2} (R - R_{0i})^2. \tag{2.12}$$

Similarly, for the term of the final state U_a^e we have

$$U_a^e = J_a^e + \frac{1}{2} \hbar\omega_0 \sum_k q_k^2 + \frac{M\omega_a^2}{2} (R - R_{0a})^2, \tag{2.13}$$

where J_a^e is the minimal potential energy corresponding to the adsorbed state of the hydrogen atom. R_{0a} is the equilibrium coordinate of the proton in the adsorbed state.

The theoretical analysis of our problem can be greatly simplified if the system of coordinates is turned in $(N + 1)$ dimensional space $\{q_k\}$ in such a way that in the new coordinates, η_k, the minimum of the initial state term, lies on one of the new axes η. Then the proton transfer will correspond to the change in the equilibrium co-ordinate of only one oscillator.[2] Finally the electron terms of the system can be written in the form

$$U_i^e = J_i^e + \tfrac{1}{2}\hbar\omega_0(\eta - \eta_0)^2 + \tfrac{1}{2}M\omega_i^2(R - R_{0i})^2, \tag{2.14}$$

$$U_a^e = J_a^e + \tfrac{1}{2}\hbar\omega_0\eta^2 + \tfrac{1}{2}M\omega_a^2(R - R_{0a})^2, \tag{2.15}$$

$$(\eta_0 = \sum_k q_{k0}^2).$$

Thus, in the variables η and R the electron terms prove to be two-dimensional (Fig. 1). This greatly simplifies the graphic analysis of the transition.

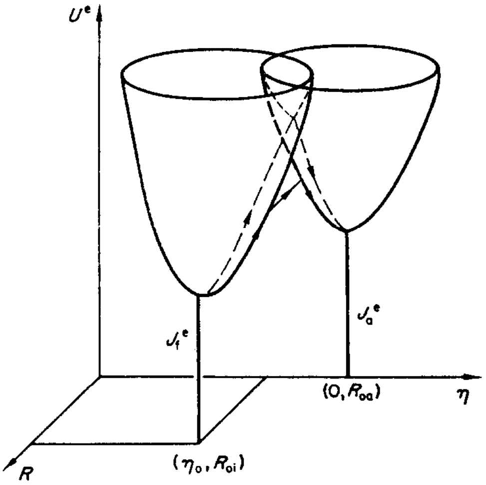

FIG. 1

The electron–proton terms are obtained in a similar way,

$$U_{i,n}^{ep} = J_{in} + \tfrac{1}{2}\hbar\omega_0(\eta - \eta_0)^2, \tag{2.16}$$

$$U_{a,n'}^{ep} = J_{an'} + \tfrac{1}{2}\hbar\omega_0\eta^2, \tag{2.17}$$

where

$$J_{in} = J_i^e + \hbar\omega_i(n + \tfrac{1}{2}), \tag{2.18}$$

$$J_{an'} = J_a^e + \hbar\omega_a(n' + \tfrac{1}{2}). \tag{2.19}$$

3. TRANSITION PROBABILITY

The solutions of Schrödinger's equations of unperturbed Hamiltonians H_i° and H_a° have been considered above. The dropped terms V_{pm} and V_{pw} cause transitions between the unperturbed states to occur (proton discharge and hydrogen ionization respectively). According to the general principles of quantum mechanics, the transition probability per unit time is determined by

$$W_{\mathrm{ia}} = \frac{2\pi}{\hbar} \mathrm{Av} \sum |\langle \Psi_{\mathrm{a}}{}^{\circ} | \, V_{\mathrm{pm}} \, | \Psi_{\mathrm{i}}{}^{\circ} \rangle|^2 \, \delta(E_{\mathrm{i}}{}^{\circ} - E_{\mathrm{a}}{}^{\circ}), \tag{3.1}$$

where Av is the averaging over initial states of the system, summation being made over all the final states. This formula is a general one and describes any possible reaction mechanisms. Concrete results depend on the manner of the choice of the wave functions of the initial and final states as well as on the approximations in further calculations.

First of all, using the general formula (3.1) it is possible to obtain the results of Horiuti and Polanyi's theory.[19] According to the physical ideas of this theory, the solvent has no effect on the transition and its state remains unchanged, *ie* the overlapping of the wave-functions of the solvent is equal to unity, $\langle \phi_{\mathrm{e}} | \phi_{\mathrm{e}'} \rangle = \delta_{\mathrm{e,e}'}$. Therefore, in (3.1) it is necessary to calculate the exchange integral connected with the electron wave-functions and the overlappings of the proton wave-functions. The first quantity corresponds physically to the transmission coefficient and in Horiutu and Polanyi's theory should be substituted for unity. Thus, in Horiuti and Polanyi's approximation, the transition probability should be written as

$$w_{\mathrm{ia}} = C_1 \, . \, \mathrm{Av}_n \sum_{n'} |\langle \chi_{n'} \, | \, \chi_n \rangle|^2 \, \delta(E_{\mathrm{i}}{}^{\circ} - E_{\mathrm{a}}{}^{\circ}).$$

With a harmonic approximation, *ie* substituting the oscillator wave functions for χ, this expression can be accurately calculated and is equal to

$$w_{\mathrm{ia}} = C_2 \exp\left\{\frac{\Delta J}{2kT} - \frac{E_{\mathrm{p}}}{\hbar\omega_{\mathrm{p}}} \coth \frac{\hbar\omega_{\mathrm{p}}}{2kT}\right\} . \, I_{\Delta J/\hbar\omega_{\mathrm{p}}} \left(\frac{E_{\mathrm{p}}}{\hbar\omega_{\mathrm{p}}} \operatorname{cosech} \frac{\hbar\omega_{\mathrm{p}}}{2kT}\right), \tag{3.2}$$

where ΔJ is the reaction heat, E_{p} the proton state reorganization energy, ω_{p} the proton frequency and $I_{\mathrm{m}}(z)$ the Bessel function. In order to obtain the result of Horiuti and Polanyi, who used the activated complex method, it is necessary in (3.2) to assume $\hbar\omega_{\mathrm{p}} \ll kT$. Then we obtain the activation formula

$$w_{\mathrm{ia}} = C_3 \exp\left\{-\frac{E_{\mathrm{a}}}{kT}\right\}, \qquad \hbar\omega_{\mathrm{p}} \ll kT, \tag{3.3}$$

where E_{a} is the activation energy (Fig. 2). In actual fact, a reverse relation to that

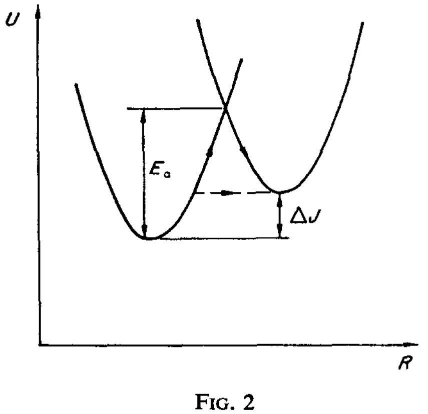

FIG. 2

used by Horiuti and Polanyi is valid, *viz* $\hbar\omega_p \ll kT$. In this case (3.2) gives

$$w_{ia} = C_4 \exp\left\{-\frac{\Delta J}{kT}\right\}, \qquad \hbar\omega_p \ll kT. \tag{3.4}$$

(3.4) has a quite obvious physical sense and shows that in the case of the higher vibrational levels being weakly excited ($\hbar\omega_p \gg kT$) a quantum sub-barrier transition takes place instead of the classical one, which is described by (3.3) (see Fig. 2). Thus, assuming the solvent to take no part in the discharge process, we inevitably arrive at formula (3.4), which can be easily seen to be in contradiction with the experimental data. In fact, according to (3.4) the activation energy should be equal to the reaction heat, *ie* the transfer coefficient α in Brönsted equation should be unity. Thus, it follows necessarily from the analysis of Horiuti and Polanyi's theory that the re-organization of the solvent in the discharge process should be taken into consideration.

We have dwelt at some length on the analysis of Horiuti and Polanyi's theory for the reason that the main physical ideas of this theory have been used in one form or another in many later studies.[20–24]

It follows from the above analysis that, just as in the case of redox reactions, the solvent plays an essential role in the process of hydrogen-ion discharge. Therefore, in calculations it is important to separate the overlapping of the solvent wave-functions. If an adiabatic approximation is used only for the electron, (2.2) should be used as the wave-function. In this case, the solvent wave-function can be separated using a harmonic approximation for the solvent and proton wave-functions. Then, as has been shown above, owing to a large difference in the frequencies, the Hamiltonian takes the form of a sum of non-interacting oscillators and the wave-function of the slow sub-system can be represented as $\chi_{i,a}(R)\phi_{ia}(\eta)$. If, however, the harmonic approximation for the proton is not accurate enough, a double adiabatic approximation can be used, which is applicable, provided the condition $\Delta E \gg \hbar\omega_0$ is fulfilled (where ΔE is the distance between the proton levels). Naturally, the calculations made by the two methods give the same result in a harmonic approximation.

Below will be given the results obtained using a double adiabatic approximation, since they are more general. The transition probability per unit time from the initial (the electron is at the level ε_f, the proton in the H_3O^+ ion at the level E_n) to the final states (the electron is at the local level ε_a, the proton in the adsorbed state at the level $E_{n'}$) is of the form

$$W_{nn'}(\varepsilon_f) = \frac{2\pi}{\hbar}\,|L_{nn'}(\varepsilon_f)|^2\,\mathrm{Av}_l \sum_{l'} |\langle\phi_{l'}|\phi_l\rangle^2 \times \delta(J_{an'} - J_{fn} + \hbar\omega_0(l' - l)), \tag{3.5}$$

where averaging and summation are made over the solvent states. Using the results obtained by us earlier for redox reactions, we shall write

$$W_{nn'}(\varepsilon_f) = \kappa_{nn'} \cdot \frac{\omega_0}{2\pi} \cdot \exp\left\{-\frac{(J_{an'} - J_{fn} + E_s)^2}{4E_s kT}\right\}. \tag{3.6}$$

Formally this expression is of the same form as the corresponding formula for the electron-transfer probability obtained for redox reactions. However, essentially, there are considerable differences between these formulae, *viz* the transmission coefficient in (3.6) depends not only on the electron wave-functions, but also on the proton wave-functions

$$\kappa_{nn'} = |L_{nn'}(\varepsilon_f)|^2/L_c^2, \qquad \text{(nonadiab)} \tag{3.7}$$

$$\kappa_{nn'} = 1. \qquad \text{(adiab)} \tag{3.8}$$

The conditions for non-adiabaticity and adiabaticity are

$$|L_{nn'}{}^2| < L_c{}^2 = \hbar\omega_0\sqrt{\frac{kTE_s}{4\pi^3}} \text{ and } (|L_{nn'}| > L_c) \tag{3.9}$$

respectively.

The exchange integral $L_{nn'}$ can be calculated if the electron–proton wave-functions are known,

$$L_{nn'} = \int\psi_a{}^*(x)\chi_{n'}{}^*(R)V_{pm}(x, R)\psi_f(x)\chi_n(R)\,d^3x\,dR. \tag{3.10}$$

The usual adiabatic approximation has been used here (Condon approximation), according to which the wave-functions of the fast sub-system depend on q slightly and can be taken at the point corresponding to the activated state of the solvent.

The exchange integral (3.10) is determined by the overlapping both of the electron and the proton wave-functions. It should be noted that in the case of hydrogen-ion discharge, the smallness of the exchange integral is not due to a weak overlapping of the electron wave-function as in redox reactions, but is caused by a weak overlapping of the proton wave-functions. Since the proton wave-functions change more sharply than the other functions under the integral, the latter can be taken at an intermediate point R^*, in which the overlapping of the proton functions is maximal. Finally $L_{nn'}$ can be written as

$$L_{nn'} = L^e \,.\, S_{nn'}, \tag{3.11}$$

where

$$L^e = \int\Psi_a{}^*(x, R^*, q^*)V_{pm}(x, R^*)\Psi_f(x, R^*, q^*)\,d^3x, \tag{3.12}$$

$$S_{nn'} = \int\chi_{n'}{}^*(R, q^*)\chi_n(R, q^*)\,dR. \tag{3.13}$$

The transition probability with an allowance made for any initial and final states is of the form

$$W_{ia}(\varepsilon_f) = \text{Av}_n \sum_{n'} W_{nn'}(\varepsilon_f). \tag{3.14}$$

As has been shown in the investigations on the theory of redox reactions,[10] the transition of the solvent from the initial to the final state follows the classical path (through the intersection point of the electron terms). Naturally, the situation is the same in the case of a proton discharge the only difference being that here the classical transition occurs on the electron–proton terms. The proton transition must be assumed to occur from a given level n to a definite level n'. The transition probability obtained above permits us to interpret the reaction path by means of the electron terms. For definiteness, the transition of the system at $n = n' = 0$ is shown in Fig. 3. It is clear from the figure that at first activation of the solvent occurs at a fixed position of the proton. At the point q^*, at fixed co-ordinates of the solvent, occurs a quantum proton transition.

It should be stressed that in considering a quantum proton transition at the point q^*, it is impossible to calculate the transition probability using the Gamov formula,

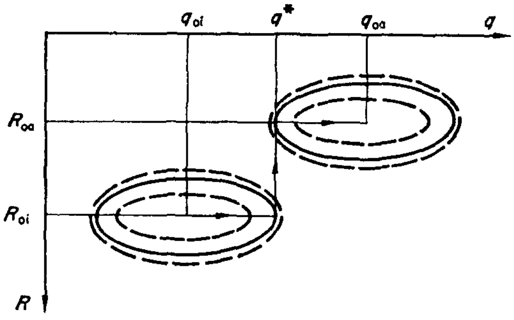

FIG. 3

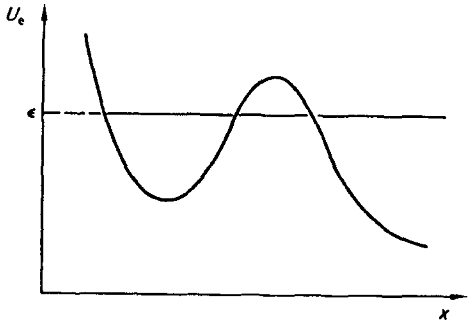

FIG. 4

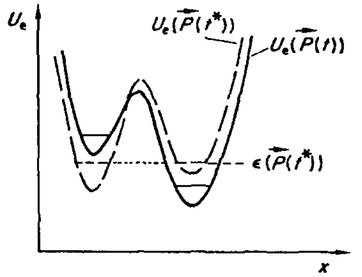

FIG. 5

which gives a transition probability in a given potential field (Fig. 4). Here the potential field is determined by all the particles in the system, so that the removal of one of them (*eg* an α-particle from the heavy neucleus) practically does not affect the field configuration. The energy of a tunnelling particle does not change with time. In the tunnel transitions occurring in chemical reactions of interest to us, which usually involve a transition from one term to another, the situation is quite different.

For simplicity we shall explain this by considering as an example the case of the tunnel transition of one particle, *eg* an electron, occurring in a redox reaction. This must be described in terms of the electron potential energy $U_e(x)$ as a function of its co-ordinate x (Fig. 5).

The electron potential energy depends on the fluctuating polarization $\mathbf{P}(\mathbf{r}, t)$ of the surrounding solvent, *ie* it is time-dependent. Fig. 5 shows the electron potential energies at two moments of time (solid and dashed curves). The total electron energy also proves to be time-dependent. At a random moment of time the electron energies in the left hand and right hand wells do not coincide and tunnelling is impossible.

The possibility of tunnelling arises at the moment of time t^* when the energies $\varepsilon(\mathbf{P}^*)$ become equal. This polarization value $\mathbf{P}^*$ corresponds to the intersexion point of the electron terms. Evidently, the transition probability depends not only on the probability of attaining the state $\mathbf{P}^*$, but also on the velocity of passing through this state $\dot{\mathbf{P}}^*$ by the system. In the limiting case of infinitely slow passing ($\dot{\mathbf{P}}^* \to 0$) of the polarization value $\mathbf{P}^*$, the transition probability is $\frac{1}{2}$ (the so-called adiabatic transition). In the reverse limiting case, the transition probability tends to zero. In an intermediate case of a finite velocity of passing, the transition probability is given by Landau–Zener formula. To be sure, all what has just been said is valid for the processes of a tunnel transition involving the participation of two particles: proton and electron, in the presence of a solvent.

The transitions at n and n' other than zero can be interpreted in a similar way. In this case the position of the activation point q^* depends on n and n'. The activation point q^* is determined by the condition that for the terms $U_{\mathrm{f}}^{\mathrm{e}}(R, q^*)$ and $U_{\mathrm{a}}^{\mathrm{e}}(R, q^*)$ the energies E_n and $E_{n'}$ should be equal. Then first, proton excitation to the level E_n will occur (the probability of this process is taken into consideration in the averaging over the initial states in the formula (3.14)), which can be followed by a quantum proton transfer.

The above interpretation of the transition probabilities is based on the assumption that the quantum proton states n and n' are fixed. We are interested, however, in the total transition probability. Therefore, formula (3.14) for the total transition probability should be considered. Since for calculating the sum (3.14) it is necessary to know the explicit forms of the quantities $\kappa_{nn'}$, $J_{\mathrm{f}n}$ and $J_{\mathrm{a}n'}$ we shall give below the quantitative results for a harmonic approximation. Most of the results are qualitatively valid in the general case as well, when the approximation of small proton and solvent vibrations is not sufficiently accurate.

In a harmonic approximation, the sum over n and n' in (3.14) can be calculated accurately. Then the total transition probability is

$$w_{\mathrm{ia}} = |L^{\mathrm{e}}|^2/L_{\mathrm{c}}^2 \cdot \frac{\omega_0}{2\pi} \cdot \sum_{m=-\infty}^{+\infty} I_{\mathrm{m}}(z_{\mathrm{p}}) \, . \exp\left\{- z_{\mathrm{p}} \operatorname{ch} \frac{\hbar\omega_{\mathrm{p}}}{2kT} - \frac{m\hbar\omega_{\mathrm{p}}}{2kT}\right\} \times \exp\left\{- \frac{(J_{\mathrm{a}}^{\mathrm{e}} - J_{\mathrm{f}}^{\mathrm{e}} - m\hbar\omega_{\mathrm{p}} + E_{\mathrm{s}})^2}{4E_{\mathrm{s}}kT}\right\}, \quad (3.15)$$

where $z_{\mathrm{p}} = E_{\mathrm{p}}/\hbar\omega_{\mathrm{p}} \operatorname{cosech} \hbar\omega_{\mathrm{p}}/2kT$, and $I_{\mathrm{m}}(z_{\mathrm{p}})$ is the Bessel function of the imaginary argument; it being assumed to simplify the formulae that $\omega_{\mathrm{i}} \approx \omega_{\mathrm{a}} \approx \omega_{\mathrm{p}}$.

(3.15) can be simplified for a number of limiting cases. It should be noted that not all those cases can be realized in a proton discharge. Their consideration, however, can be of interest for the investigation of other electrode reactions.

We shall analyse the limiting cases for all the possible transition mechanisms in electrode reactions in a harmonic approximation. It is to be hoped that this approximation could be used for a qualitative description of all transitions at electrodes.

Only one of the limiting cases of (3.15) is for a proton-discharge process.

1. Let us consider a high-temperature approximation for the proton

$$\hbar\omega_p \ll kT, \qquad z_p \gg 1. \tag{3.16}$$

Then for Bessel functions it is necessary to take their asymptotic representation and the expression (3.15) will assume the simple form

$$W_{ia} = |L^e|^2/L_c^2 \cdot \frac{\omega_0}{2\pi} \cdot \exp\left\{-\frac{(J_a^e - J_f^e + E_s + E_p)^2}{4(E_s + E_p)kT}\right\}, \tag{3.17}$$

where E_p is the re-organization energy of the proton state. If the transition probability is interpreted by means of electron terms, (3.17) corresponds to a classical transition, the reaction path passing through the saddle point of the intersection line of the terms, as is evident from the activation energy (Fig. 1). This case is not realized for proton transitions, but is possible, however, for heavy particle transfers.

2. When

$$\hbar\omega_p \ll kT, \qquad z_p \ll 1, \tag{3.18}$$

ie in the case of a high-temperature approximation and a narrow barrier, an expression is obtained for the transition probability which corresponds to the proton transfer following the one-phonon mechanism (a weak interaction with the medium). In this case the formula is of a non-activation (with respect to temperature) character.

3. Let us consider a low-temperature approximation for the proton and the case of a narrow barrier,

$$\hbar\omega_p \gg kT, \qquad z_p \ll 1. \tag{3.19}$$

In this case the expression is for the transition probability that corresponds to the condition that, in the sum (3.14) over n and n', only one term with $n = n' = 0$ should be retained. The corresponding transition path as expressed by means of electron terms is shown in Figs. 1 and 3. This result is most evident from (3.15) at $J_a^e = J_f^e = 0$. In this case the sum over m is of the form

$$\sum_{m=-\infty}^{+\infty} \frac{1}{|m|!}\left(\frac{z_p}{2}\right)^{|m|} \exp\left\{-\frac{m^2(\hbar\omega_p)^2}{4E_s kT}\right\}. \tag{3.20}$$

It is clear from (3.20) that the largest term in the sum is the term with $m = 0$, which corresponds to $n = n' = 0$. It is just this situation which is mostly present in the case of a proton discharge. At $J_a^e \neq J_f^e$ a small number of excited levels can contribute to the probability, the proton transition being of a sub-barrier nature in all cases.

4. Finally, when

$$\hbar\omega_p \gg kT, \qquad z_p \gg 1, \qquad \text{(wide barrier)} \tag{3.21}$$

the transition occurs from a group of intermediate levels. The expressions obtained are as before of the form $w = \text{const} \,.\, \exp(-E_a/kT)$, but it is evident from the expression for the activation energy E_a that in this case the transition does not correspond to the classical path through the saddle point. The proton transition is again sub-barrier and in the simple case, when $J_a^e = J_f^e$, for the activation energy determined by

$$E_a = -\frac{\mathrm{d}\ln w}{\mathrm{d}(1/kT)},$$

$$E_a = \frac{E_s}{4} + \frac{E_p}{4}\exp\left(-\frac{\hbar\omega_p}{2kT}\right). \tag{3.22}$$

Thus, for the reaction to follow the classical path it is necessary for both the conditions (3.17) to be fulfilled. This conclusion, as well as the results obtained for the cases 1–3, were substantiated by calculation made for non-parabolic terms as well. Thus the qualitative results obtained for the limiting cases 1–3 remain valid practically for any arbitrary terms. The result obtained for case 4 shows some specific features of a harmonic approximation. In actual practice processes with wide barriers are more complicated and will not be considered here.

4. CURRENT DENSITY

Knowing the transition probability it is possible to determine the cathodic cd by means of the general formula

$$i = 2eC_s \int w_{ia}(\varepsilon_f) n(\varepsilon_f) \rho(\varepsilon_f) \, d\varepsilon_f, \tag{4.1}$$

where C_s is the surface concentration of hydroxonium ions (on the outer side of the double layer). $n(\varepsilon_f)$ is the Fermi distribution,

$$n(\varepsilon_f) = \left\{ \exp\left[\frac{\varepsilon_f - \varepsilon_F}{kT}\right] + 1 \right\}^{-1}, \tag{1.2}$$

$\rho(\varepsilon_f)$ the electron-level density in the metal and $w_{ia}(\varepsilon_f)$- the H_3O^+-ion discharge probability per unit time. The factor 2 is introduced since under steady state conditions there is one act of electrochemical desorbtion per one act of the H_3O^+ discharge.

In accordance with the general formula for the transition probability, all possible excited states of the proton both in the initial and the final states should be taken into consideration,

$$i = \mathrm{Av}_n \sum_{n'} i(n, n'), \tag{4.2}$$

where $i(n, n')$ is the current calculated assuming that in the initial state the proton is at the level E_n, and in the final state at $E_{n'}$. In the harmonic approximation,

$$E_n = \hbar\omega_i(n + \tfrac{1}{2}), \qquad E_{n'} = \hbar\omega_a(n' + \tfrac{1}{2}), \tag{4.3}$$

where the quantum numbers $n, n' = 0, 1, 2, \ldots$. First we shall calculate $i(n, n')$, and then find the expression for the mean current i.

Using the formula for the transition probability and the Fermi distribution, we write $i(n, n')$ as

$$i(n, n') = 2ec_s\rho^* \frac{\omega_0}{2\pi} \cdot \kappa(n,n') \int \frac{\exp\left\{-\dfrac{(\varepsilon_f - \varepsilon^0_{nn'})^2}{4E_s kT}\right\}}{\exp\left[\dfrac{\varepsilon_f - \varepsilon_F}{kT}\right] + 1} \, d\varepsilon_f, \tag{4.4}$$

where

$$\varepsilon^0_{nn'} = \varepsilon_F + E_s + (J_{an'} - J_{Fn}{}^0) - e\eta \tag{4.5}$$

In this case we consider the density of the levels to be a smooth function of ε_f and therefore take it out of the integration sign. It is convenient to calculate this integral by the Laplace method (*ie* by the steepest descent method for the function of a real variable). For this purpose we equate to zero the derivative of the index of the exponent of the whole expression under the integral,

$$\frac{\mathrm{d}}{\mathrm{d}\,\varepsilon_f}\left(\ln n(\varepsilon_f) - \frac{E_a}{kT}\right) = 0. \tag{4.6}$$

The quantity

$$\alpha(\varepsilon_f) = -\frac{\mathrm{d}\,E_a}{\mathrm{d}\,\varepsilon_f} = \frac{\mathrm{d}\,E_a}{\mathrm{d}\,(J_{an'} - J_{fn})}, \tag{4.7}$$

is readily seen to be the analogue of the transfer coefficient in the Brönsted equation for electrode reactions. These quantities are not identical since the Brönsted equation relates the changes in the process activation energy to that in the reaction heat, which is a thermodynamic quantity. In our case however, the quantity $(J_{an'} - J_{fn})$ has different values for electrons at different levels ε_f and has no thermodynamic significance. It will be shown below that for the electrochemical process the Brönsted equation can be generalized as

$$\alpha^* = \left.\frac{\mathrm{d}\,E_a}{\mathrm{d}\,(J_{an'} - J_{fn})}\right|_{\varepsilon_f=\varepsilon^*}, \tag{4.8}$$

where ε^* corresponds to the electron level at which the expression under the integral for the current has a maximum. In other words, ε^* is the energy level from which the actual transfer of the electron participating in the electrode reaction is realized. ε^*, as pointed out above, is found from (4.6), which can be re-written

$$n(\varepsilon_f) = 1 - \alpha(\varepsilon_f) \tag{4.9}$$

$$n(\varepsilon_f) = \frac{1}{2} - \frac{J_{an'} - J_{fn}^{\circ}}{2E_s} + \frac{e\eta}{2E_s} + \frac{\varepsilon_f - \varepsilon_F}{2E_s}. \tag{4.10}$$

If the values of the parameters E_s and $(J_{an'} - J_{fn}^{\circ})$ are known, the solution of this equation, ε^*, can be found numerically. However we now give a method for the solution of this transcendental equation. We shall consider three regions of overvoltage

1. *Low overvoltage*

$$e\eta < (J_{an'} - J_{fn}^{\circ}) - E_s. \tag{4.11}$$

It is clear from Fig. 6 that the straight line, for which the corresponding equation coincides with the right hand side of (4.10) intersects the function $n(\varepsilon_f)$ at such value of ε_1^* that $n^* \equiv n(\varepsilon_1^*) \ll 1$. From (4.10) it is easy to find ε_1^*, n^*, α^* and E_a,

$$\varepsilon_1^* \approx \varepsilon_F - E_s + (J_{an'} - J_{fn}^{\circ}) - e\eta, \tag{4.12}$$

$$n^* \approx \exp\left\{\frac{E_s - (J_{an'} - J_{fn}^{\circ})}{kT}\right\} . \exp\left(\frac{e\eta}{kT}\right), \tag{4.13}$$

$$E_a \approx E_s, \tag{4.14}$$

$$\alpha^* \approx 1 - n^*. \tag{4.15}$$

The value of the activation energy thus found corresponds to the arrangement of the terms shown in Fig. 7, *ie* in this region of overvoltage the transition process is of a barrierless nature. For the current we have

$$i(n, n') = 2ec_s\rho^*\omega_0\kappa(n, n')\left(\frac{kTE_s}{\pi}\right)^{1/2} \exp\left\{\frac{J_{fn}^{\circ} - J_{an'}}{kT}\right\} \exp\left(\frac{e\eta}{kT}\right). \tag{4.16}$$

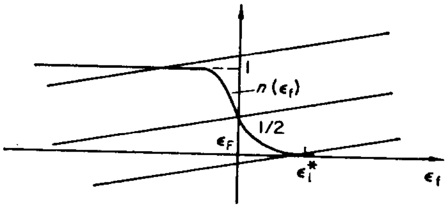

FIG. 6

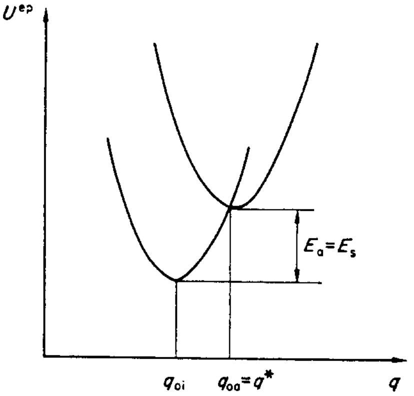

FIG. 7

In the region of barrierless transitions the adsorption bond between hydrogen and the electrode is realized by an electron which before the transition had been strongly excited state ($\varepsilon_1{}^* - \varepsilon_F > kT$). Since the number of these electrons is very small ($n^* \ll 1$), the current is small too. The slope of the polarization curve in this region in semi-logarithmic scale is 1,

$$\frac{\mathrm{d} \ln i(n, n')}{\mathrm{d}\left(\dfrac{e\eta}{kT}\right)} \approx \alpha^* \approx 1 \tag{4.17}$$

2. "*Normal*" *overvoltage*

$$|e\eta - (J_{an'} - J_{fn}{}^{\circ})| < E_s. \tag{4.18}$$

In this region the intersection takes place near the Fermi level and it can be readily shown that

$$\varepsilon^* \approx \varepsilon_F + \frac{2kT}{E_s}(J_{an'} - J_{fn}{}^{\circ} - e\eta) \approx \varepsilon_F, \tag{4.19}$$

$$n^* \approx \frac{1}{2} - \frac{J_{an'} - J_{fn}{}^{\circ} - e\eta}{2E_s} \approx \frac{1}{2}, \tag{4.20}$$

$$E_a \approx \frac{E_s}{4} + \frac{J_{an'} - J_{fn}{}^{\circ} - e\eta}{2} \approx \frac{E_s}{4}, \tag{4.21}$$

$$\alpha^* \approx \frac{1}{2} + \frac{J_{an'} - J_{fn}{}^{\circ}}{2E_s} - \frac{e\eta}{2E_s} \approx \frac{1}{2}. \tag{4.22}$$

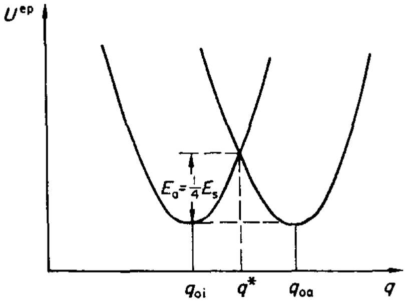

FIG. 8

In this region the activation energy corresponds to the arrangement of the terms shown in Fig. 8. Accordingly, the current is of the form

$$i(n, n') = ec_s\rho^*\omega_0\kappa(n, n')kT\exp\left\{-\frac{E_s}{4kT} - \frac{J_{an'} - J_{fn}{}^{\circ}}{2kT} + \frac{e\eta}{2kT}\right\}. \tag{4.23}$$

We see that the transfer coefficient α^* is close to the value $\frac{1}{2}$. The exact value $\alpha^* = \frac{1}{2}$ is obtained at $e\eta_{1/2} = J_{an'} - J_{fn}{}^{\circ}$. However at large enough E_s, the transfer coefficient α^* is equal to $\frac{1}{2}$ in a considerable region of overvoltages. As we have emphasized before, the theory is based on the assumption that the re-organization energy is large, a quantity of the order of several eV.

In this region all the electrons participating in the reaction can be considered to have the energy which is very close to the Fermi level.

In the normal region the slope of the polarization curve in a semi-logarithmic scale is close to $\frac{1}{2}$ in the range of overvoltage indicated.

In this region, as well as in the barrierless region, the value of α^* determined by means of (4.8) coincides with the determination of α as

$$\alpha = \frac{\mathrm{d}\ln i(n, n')}{\mathrm{d}\dfrac{e\eta}{kT}} \approx \alpha^* \tag{4.24}$$

It should be noted that the theory provides the existence of (4.24) to a good approximation at arbitrary overvoltage values (in the absence of concentration effects).

Since in the metal the number of electrons near the Fermi level is large and the activation energy E_a four times as small as in the barrierless region, the current in the normal region is relatively large.

3. *High overvoltage*

$$e\eta > J_{an'} - J_{Fn}{}^{\circ} + E_s. \tag{4.25}$$

In this region

$$\varepsilon^* \approx \varepsilon_F + E_s + J_{an'} - J_{Fn}{}^{\circ} - e\eta, \tag{4.26}$$

$$n^* \approx 1 - \exp\left\{\frac{E_s + J_{an'} - J_{an}{}^{\circ} - e\eta}{kT}\right\} \approx 1, \tag{4.27}$$

$$E_a \approx 0, \tag{4.28}$$

$$\alpha^* \approx 1 - n^* \approx 0. \tag{4.29}$$

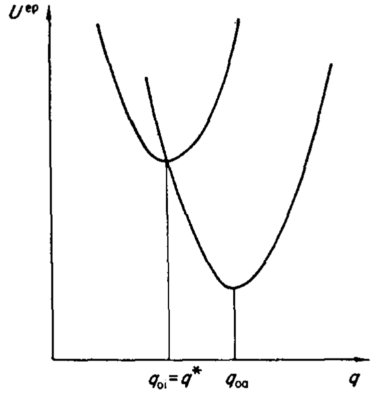

FIG. 9

The activation energy, which is zero, corresponds to the arrangement of the terms shown in Fig. 9. Since $E_a \approx 0$ at high enough overvoltage the discharge process must be of an activationless nature. Then the current is equal to

$$i(n, n') = 2ec_s\rho^*\omega_0\kappa(n, n')\sqrt{\frac{kTE_s}{\pi}}. \tag{4.30}$$

Since in this region of overvoltage the discharge involves the participation of the electrons from practically all the occupied energy levels, ($n^* \approx 1$), *ie* from the levels located below the Fermi level ($\varepsilon^* < \varepsilon_F$), and moreover the activation energy of the transition is zero, the current has a constant and very large value. This condition obviously offers great experimental difficulties in the way of the detection of activationless transitions.

The expressions for the current in three different regions of overvoltage given above can be combined into one formula in which the overvoltage in the explicit form is substituted by the transfer coefficient α^*, which depends on η,

$$i(n, n') = \frac{2ec_s\rho^*\omega_0\kappa(n, n')}{\left(1 + \dfrac{2E_s}{kT}\alpha^*(1 - \alpha^*)\right)^{1/2}} \cdot \left(\frac{kTE_s}{\pi}\right)^{1/2} \cdot (1 - \alpha^*) \exp\left(-(\alpha^*)^2\frac{E_s}{kT}\right). \tag{4.31}$$

The dependence of α^* upon η can be found with good accuracy from

$$\alpha^* = \begin{cases} 1 - \exp\left\{-\dfrac{J_{an'} - J_{fn}^{\circ} - E_s - e\eta}{kT}\right\}; & e\eta < J_{an'} - J_{fn}^{\circ} - E_s; \\ \dfrac{1}{2} + \dfrac{J_{an'} - J_{fn}^{\circ} - e\eta}{2E_s}; & J_{an'} - J_{Fn}^{\circ} - E_s < e\eta < J_{an'} - J_{fn}^{\circ} + E_s; \\ \exp\left\{\dfrac{J_{an'} - J_{fn}^{\circ} + E_s - e\eta}{kT}\right\}; & e\eta > J_{an'} - J_{fn}^{\circ} + E_s. \end{cases} \tag{4.32}$$

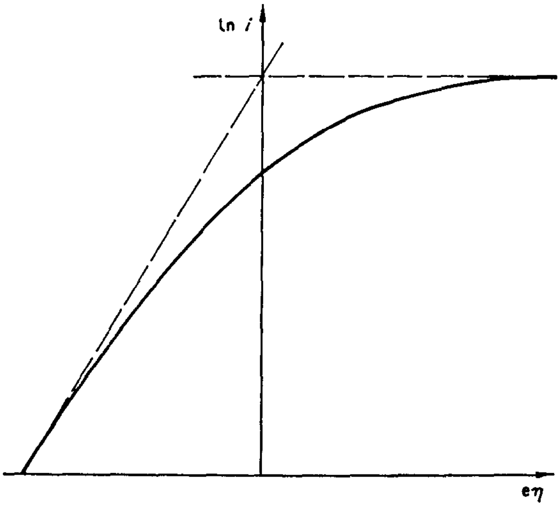

Fig. 10

Fig. 10 shows the polarization curve in a semi-logarithmic plot for $E_s = 2$ eV. The parameters contained in the theory—the pre-exponential factor and $(J_{an'} - J_{fn}{}^0)$ are not defined concretely since, without changing shape, they can shift the curve only along the abcissa and ordinate axes.

According to the formula (4.2) the total cathodic current is

$$i = \sum_{n,n'} \frac{\kappa(n, n')}{\kappa_0} \cdot i_0(e\eta - E_{n'} + E_n) \exp\left(-\frac{E_n - E_0}{kT}\right), \tag{4.33}$$

where i_0 and H_0 are the current and the transmission coefficient calculated for the case when the proton passes from the non-excited initial state to the non-excited final state.

Strictly speaking, the measured current is given by (4.33), rather than by the expressions presented earlier. However, if the current is approximately represented as

$$i \sim \sum_{n,n'} \kappa(n, n') \exp\{-\alpha(E_{n'} - E_0) - (1 - \alpha)(E_n - E_0)\}/kT, \tag{4.34}$$

by a simple analysis we can draw the following conclusions for the region of normal overvoltages. The main contribution to the total current is made by the transition from the ground initial state to the zero level of the final state.

In the regions of low and high overvoltage, the situation may be somewhat different. At low overvoltages $\alpha \approx 1$ and excited initial states can contribute to the current. On the contrary, at high overvoltage, when $\alpha \approx 0$ the transitions to the final excited states can be realized.

It should be stressed, however, that the above effect may change the pre-exponential factor, but cannot alter the qualitative nature of the expression for the current/overvoltage characteristic.

A more detailed analysis can be carried out with the harmonic approximation.

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