(1963); 9, 175 (1964).
45. G.A.Dobren'kov, "Soobshchenie na 5-m Soveshchanii po Organicheskoi Elektrokhimii" (Communication at the Fifth Conference on Organic Electrochemistry), Moscow, 1965.
46. G.A.Dobren'kov and R.K.Bankovskii, Izv.Vys.Ucheb. Zaved., Khim.i Khim.Tekhnol., 5, 75 (1962).
47. R.Parsons, J.Electroanalyt.Chem., 7, 136 (1964); 8, 93 (1964).
48. A.N.Frumkin, J.Electroanalyt.Chem., 7, 152 (1964).
49. B.B.Damaskin, J.Electroanalyt.Chem., 7, 155 (1964).
50. R.Parsons, Trans.Faraday Soc., 55, 999 (1959).
51. A.N.Frumkin, B.B.Damaskin, V.M.Gerovich, and R.I.Kaganovich, Dokl.Akad.Nauk SSSR, 158, 706 (1964).
52. J.H.de Boer, "The Dynamical Character of Adsorption" (Translated into Russian), Inostr.Lit., Moscow, 1962.
53. B.B.Damaskin, Elektrokhimiya, 1, 63 (1965).
54. G.A.Tedoradze, Dokl.Akad.Nauk SSSR, 155, 1423 (1964).
55. B.B.Damaskin, Dokl.Akad.Nauk SSSR, 156, 128 (1964).
56. G.A.Dobren'kov and V.A.Golovin, "Soobshchenie na 5-m Soveshchanii po Organicheskoi Elektrokhimii" (Communication at the Fifth Conference on Organic Electrochemistry), Moscow, 1965.
57. H.M.Cassel and F.Salditt, Z.phys.Chem., A 155, 321 (1931).
58. B.P.Bering and K.A.Ioileva, Izv.Akad.Nauk SSSR, Otd. Khim.Nauk, 9 (1955).
59. M.E.Nicolas, P.A.Joyner, B.M.Tessem, and M.D.Olson, J.Phys.Chem., 65, 1373 (1961).
60. M.A.V.Devanathan, Proc.Roy.Soc., A 263, 133 (1961); A 267, 256 (1962).
61. J.O'M.Bockris, M.A.V.Devanathan, and K.Müller, Proc, Roy.Soc., A 274, 55 (1963).
62. A.N.Frumkin and B.B.Damaskin, "Modern Aspects of Electrochemistry, No.3" (Edited by J.O'M.Bockris and B.E.Conway), Butterworth, London, 1964, p.149.
63. B.B.Damaskin and N.B.Grigor'ev, Dokl.Akad.Nauk SSSR, 147, 135 (1962).
64. B.B.Damaskin, Zhur.Fiz.Khim., 37, 2483 (1963) [Russ.J. Phys.Chem., 1341 (1963)].
65. B.B.Damaskin, Electrochim.Acta, 9, 231 (1964).
66. R.Lerkkh and B.B.Damaskin, Zhur.Fiz.Khim., 38, 1154 (1964); 39, 211 (1965) [Russ.J.Phys.Chem., 631 (1964); 112 (1965)].
67. B.B.Damaskin and R.Lerkkh, Zhur.Fiz.Khim., 39, 495 (1965) [Russ.J.Phys.Chem., 265 (1965)].
68. V.K.Venkatesyan, B.B.Damaskin, and N.V.Nikolaeva--Fedorovich, Zhur.Fiz.Khim., 39, 129 (1965) [Russ.J. Phys.Chem., 63 (1965)].
69. B.B.Damaskin, I.P.Mishutushkina, V.M.Gerovich, and R.I.Kaganovich, Zhur.Fiz.Khim., 38, 1797 (1964) [Russ.J. Phys.Chem., 976 (1964)].
70. L.D.Klyukina and B.B.Damaskin, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1022 (1963).
71. B.B.Damaskin, V.M.Gerovich, I.P.Gladkikh, and R.I.Kaganovich, Zhur.Fiz.Khim., 38, 2495 (1964) [Russ.J. Phys.Chem., 1351 (1964)].
72. B.B.Damaskin, Dokl.Akad.Nauk SSSR, 144, 1073 (1962).
73. B.B.Damaskin and G.A.Tedoradze, Dokl.Akad.Nauk SSSR, 152, 1151 (1963).
74. B.B.Damaskin and G.A.Tedoradze, Electrochim.Acta, 10, 529 (1965).
75. G.A.Tedoradze and Ya.M.Zolotovitskii, Elektrokhimiya, 1, 201 (1965).
76. B.B.Damaskin, Elektrokhimiya, 1, 255 (1965).

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THEORY OF HOMOGENEOUS AND HETEROGENEOUS ELECTRONIC PROCESSES IN LIQUIDS

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I. INTRODUCTION

The theory of electronic processes in liquids occupies a very specific place in the general theory of chemical kinetics. A comparison of various electronic processes occurring in the liquid phase and in solids reveals a great similarity of physical mechanisms. Yet, no such analogy is normally found between gas-phase and liquid-phase reactions. For example, we may consider the electron exchange reaction between ions of the same sign. If we compare the rate of charge transfer between ions in gases with the rate of analogous oxidation–reduction reactions in water, we find that charge transfer in gases not only occurs significantly faster than in solutions, but also, and this is less trivial, that the phenomenon of resonance charge transfer is in general absent in solutions. It is well known that charge transfer between similar ions differing only in valence state proceeds much faster in the gas phase than reactions between unlike ions[1]. At the same time, the reaction $Fe^{2+} + Fe^{*3+} \rightarrow Fe^{3+} + Fe^{*2+}$ is much slower, in solutions, than a reaction like $Fe^{2+} + FeOH^{2+} \rightarrow \rightarrow Fe^{3+} + FeOH^{+}$. On the other hand, it has been possible[2-7] to apply the theory of F-centres and polarons, which was developed for crystals[4], in the study of the absorption spectra and of the conductivity of solutions of metals in liquid ammonia.

The lack of similarity between gas-phase reactions and electronic processes in liquids makes it very difficult to apply the transition state theory effectively to the latter processes. Indeed, this is easily verified by noting that the potential energy surfaces for electronic reactions in a condensed phase must be multidimensional, since we assume that the electron interacts strongly with a very large number of solvent molecules. This does not mean, of course, that the rate of the process will not show activational features: the situation involves, on the one hand, the Franck–Condon principle (i.e. the quasi-classical motion of heavy atoms), and, on the other hand, fluctuation theory (the Boltzmann formula). We are only considering the actual calculation of activation energies by means of the transition state theory. Furthermore, in the case of non-adiabatic reactions with multidimensional electronic energy levels (i.e. potential energy surfaces) there is no method of calculating the pre-exponential factor (the so-called transmission coefficient) similar to the Landau–Zener method for one-dimensional levels, used to calculate the rates of gas reactions. In this sense, the transition state theory hardly justifies its name of theory of absolute reaction rates.

Lastly, we have one further reason for renouncing the formal use of the transition state theory: it is the absence of any criterion whatsoever for its applicability, which has the effect of creating the illusion that the method is of universal applicability. Yet, we know from the most general considerations that such criteria must exist. We shall show below, using a concrete example (see Sections II, 2 and II, 3), that the absolute reaction rate theory is applicable only at high enough temperatures. Formally, this shortcoming stems from the absence of a sufficiently rigorous method of deriving the formulae of the transition state theory. We are not only concerned with the need for a quantitative criterion of the exactness of a theoretical discussion: such a criterion, in conjunction with experimental data, would also throw light on the mechanism of various reactions.

The physical analogy between various electronic processes in liquids and in solids suggests the possibility of applying to electronic processes in liquids the mathematical formalism which has been developed to deal with kinetic phenomena in solids (polar crystals, impurity semiconductors, alloys, etc.). A very wide range of contemporary problems in chemistry, electrochemistry, and biochemistry could be solved by the application of some of the techniques of the quantum theory of irreversible processes. There are a number of problems, however, in which the difference between a liquid and an ordered crystal can prove to be a fundamental one (see, for example, Section II, 5). This is especially true of the calculation of mobilities. In an ideal crystal, the electrical conductivity is infinitely high in the absence of thermal vibrations, whereas in liquids (as in any disordered system) the electronic electrical conductivity remains finite even if the thermal motion of the atoms is ignored. We shall show in Section II, 5 that in this case it is possible to apply (in a slightly modified form) the quantum statistics used to describe disordered solids (alloys, or impurity semiconductors).

In compiling the present article, we have relied mainly on our earlier theoretical results, which we have compared with the results of other workers. This restriction is due to the fact that the method presented here differs very considerably from the theoretical approach of other workers, so that an attempt at unification would not be expedient. However, the list of references includes a selection of reviews[5-8] and original papers by both experimental and theoretical workers.

II. THEORY OF HOMOGENEOUS REACTIONS

1. Model of a Liquid

Since the present review will be concerned mostly with polar liquids, this Section is devoted exclusively to liquids of this type. Non-polar liquids will be discussed to some extent in Section II, 5 in connection with the study of electronic spectra.

A polar liquid can be completely described by specifying the coordinates of all the dipoles in the medium. To simplify the discussion, we shall adopt the following scheme: let the position of the dipole be characterised by the coordinate of the centre of gravity $R_i(t)$ and by the angle $\theta_i(t)$ which defines the orientation of the dipole. The subscript i denotes the number of the dipole, and t indicates that both R_i and θ_i are time-dependent. In accordance with modern ideas on the liquid state, the variation of R_i and θ_i with time can be visualised as follows: the dipole resides in a certain temporary equilibrium position R_i^0, θ_i^0, about which it executes small oscillations. The average time interval between sudden changes of R_i^0 and θ_i^0, τ_g, can be calculated from diffusion data. Thus, for water $\tau_g \simeq 10^{-9}$ s, whereas the libration frequency of the dipole (describing changes of the angle θ_i in the neighbourhood of θ_i^0) is of the order of 10^{11} s^{-1}. One of the most important postulates of the theory states that the most fundamental dynamic role is played by the librational oscillations of the dipole, and not by its diffusional jumps. This assumption can be explained as follows. A fairly accurate description would be obtained if the desired physical quantity (say, the probability of electron transfer) could be calculated for fixed values of R_i^0 and θ_i^0, and the result averaged over all R_i^0 and θ_i^0. Unfortunately, this procedure is far from being generally possible. For example, in the presence of strong interaction between the electron and the solution the distribution function of R_i^0 and θ_i^0, i.e. the probability of finding the dipole in the position R_i^0, θ_i^0, is itself, obviously, a function of the distribution of the electronic charge density or of the quantum state of the electron. In practice, this means that if we are interested only in the probability of an electronic transition from some initial state to a final state, we should first calculate the probability for the conditions $R_i^0 = (R_i^0)_{\text{init}}$ at the beginning of the transition and $R_i^0 = (R_i^0)_{\text{fin}}$ at the end of the transition, and we should then sum the probabilities over all possible $(R_i^0)_{\text{fin}}$ and average over $(R_i^0)_{\text{init}}$. We shall assume that the transition from an arbitrary state R_i^0 to a state of thermodynamic equilibrium occurs faster than the time τ_e between electronic transitions. In this case it is no longer necessary to average over R_i^0. Thus, for $\tau_e \gg \tau_g$ we can ignore the effect of discontinuous changes in the coordinates R_i^0 and θ_i^0, and consider only the librational oscillations of the dipole as the total or intramolecular vibrations of the liquid. Lastly, we shall make one further observation, of which we shall make use in what follows. If the static dielectric constant ϵ_s is calculated for a system of oscillating dipoles, it is found to be independent of temperature. Thus, yet another criterion for the applicability of our model is that ϵ_s should be an insensitive function of temperature. In particular, for water $\epsilon_s = a/T$, so that the relative change

of ϵ_s, $\left(\left|\frac{\Delta\epsilon_s}{\epsilon_s}\right| = \left|\frac{\Delta T}{T}\right|\right)$, is not large at ordinary temperatures. As for our fundamental criterion $\tau_e \gg \tau_g$, we shall merely state at this point that it is always satisfied in practice by the systems of interest, and that a more detailed discussion (from a somewhat different viewpoint) will be given in Section II, 3.

Strictly speaking, the oscillations of dipoles in a liquid are not of the harmonic type. However, the problem of electronic processes is susceptible to fully quantitative treatment and can be solved quantum-mechanically only in the harmonic approximation. In this approximation the model of the liquid takes the form of an assembly of harmonic oscillators (phonons) whose Hamiltonian expressed in normal coordinates is

$$H_s = \frac{1}{2}\sum_k \hbar\omega_k \left(q_k^2 - \frac{\partial^2}{\partial q_k^2}\right). \qquad (2.1)$$

In this formula the normal frequencies ω_k should be treated as empirical. In general, the electron can interact both with optical and with acoustic phonons, but in polar systems only longitudinal phonons of the optical type[4] of low dispersion (i.e. $\omega_k \simeq \omega_0$) play a really important role. Physically, either intramolecular vibrations of the dipoles or librational oscillations can correspond to these types. For example, for water we have the vibrations of the O–H bond or of the H–H hydrogen bond, and also the librational oscillations of the molecule as a whole. As will be evident from what follows, it is most rational to choose the latter (librational) type of oscillation for water, with $\omega_0 \simeq \simeq 10^{11}\ s^{-1}$. If complex or hydrated ions are relevant to the problem, it becomes necessary to consider several optical vibration types. The presence of a small dispersion in the optical type does not affect the final results in any way, but for purely computational reasons[9] it is convenient to introduce a finite dispersion at an intermediate stage and make this tend to zero in the final result.

The theory becomes particularly revealing if the model used to describe the liquid is a continuum with macroscopic specific polarisation $\vec{P}$. Strictly speaking, such a model can describe a real system satisfactorily only some distance away from the electron (or ion), but the formulae obtained from this model offer some valuable though approximate numerical results. The Hamiltonian for this system was first obtained by Pekar[4] and Fröhlich[10], and we shall not derive it here (see also Ref. 6). We shall only point out that it is of the same form as Eqn. (2.1), but we must set $\omega_k = \omega_0$, and the normal coordinates q are found to be related to the Fourier amplitudes of $\vec{P}$ by the expression

$$\vec{P}(\vec{r}) = \left(\frac{c\hbar\omega_0}{4\pi V}\right)^{1/2} \sum_k \vec{Q}_k e^{i\vec{k}\vec{r}}; \quad q_k = \frac{1}{2}\begin{cases} i(Q_k - Q_k^*), & k > 0; \\ Q_k + Q_k^*, & k \leqslant 0, \end{cases} \qquad (2.2)$$

where $V(\to\infty)$ is the volume of the fundamental region of periodicity of $\vec{P}$, and

$$c = \frac{1}{\epsilon_0} - \frac{1}{\epsilon_s}. \qquad (2.3)$$

ϵ_0 denotes the optical dielectric constant (equal, for example, to 1.78 for water). The parameter c plays a fundamental role in the polarisation model. Its function can be illustrated as follows. When expressing the potential energy of a liquid, one should consider only that part which concerns the motion of heavy particles, since the electronic part of the polarisation follows their motion without inertia and contributes a constant term to the energy. On the other hand, the interaction between a slow electron in homogeneous reactions and the electronic part of the polarisation can also be assumed constant if one considers that the electrons of the liquid molecule are moving immeasurably faster than the outer electron which is taking part in the reaction. Therefore, this term also can be omitted if the electron does not leave the liquid. The case of heterogeneous reactions, when the electron passes from the liquid into the electrode, will be considered separately (see Section III, 1). The notion of calculating the potential energy of the inertial part of the non-equilibrium polarisation, $\vec{P}_{\text{inert}}$, amounts to a calculation of the work needed to form $\vec{P}_{\text{inert}}$ by slowly applying a fictitious electrical induction $\vec{D}$ and then removing it instantaneously:

$$U_{P_{\text{inert}}} = -\frac{1}{4\pi}\int_0^D DdE - \frac{1}{4\pi}\int_D^0 DdE = -\frac{1}{4\pi\epsilon_s}\int_0^D DdD - \frac{1}{4\pi\epsilon_0}\int_D^0 DdD = \frac{c}{8\pi}D^2. \qquad (2.4)$$

The value of D must, of course, be chosen so that the polarisation in the final state is equal to P_{inert}. Since the first stage (application of the induction) was carried out slowly, we can use the equilibrium formula

$$\vec{P}_{\text{inert}} = \vec{P} - \vec{P}_{\text{electr}} = \frac{\epsilon_s - 1}{4\pi\epsilon_s}\vec{D} - \frac{\epsilon_0 - 1}{4\pi\epsilon_0}\vec{D} = \frac{c}{4\pi}\vec{D}. \qquad (2.5)$$

On inserting formula (2.5) into (2.4), we find

$$U_{P_{\text{inert}}} = \frac{2\pi}{c}P^2_{\text{inert}}. \qquad (2.6)$$

This expression was first obtained by Pekar[4], and also by Marcus[11], who used an independent and somewhat more complicated method. This deduction, based on non-equilibrium thermodynamics, has one major shortcoming: the quantum-mechanical Hamiltonian is found to depend on temperature through $\epsilon_s(T)$. In practice, this means that, instead of a single statistical averaging of the final results, we have performed a partial averaging at the Hamiltonian stage. This procedure can be justified by using the concepts expressed at the beginning of this Section. Indeed, the condition that D should be applied slowly implies that a preliminary averaging with respect to R_i^0 and θ_i^0 is permissible. Hence it is evident that formula (2.6) is also correct only if the condition $\tau_e \gg \tau_g$ is satisfied. In other words, in all formal thermodynamic calculations ϵ_s is to be treated as a parameter which does not depend on temperature.

2. Adiabatic Perturbation Theory

As was pointed out above, the characteristic feature of a polar medium is that the interaction between an electron and the medium (i.e. the phonons) is not a weak one. Therefore, the familiar methods of the theory of small perturbations are not suitable in this case for calculating the probability of electron transfer, if the solution is wanted in the form of a power series of the electron–phonon interaction constant. Physically, this means that several phonons are emitted during the electron transfer process rather than a single phonon. One of the methods of calculation used in problems of this type relies on the so-called adiabatic perturbation theory. We shall now describe the physical concepts underlying this theory.

It is convenient to set up the Hamiltonian for the total system in the form

$$H(x, q) = H_e(x) + H_s(q) + V(x, q) + H'(x, q) = H(x, q) + H'(x, q). \qquad (2.7)$$

Here $H_e(x)$ is the total energy of an electron interacting with a given external field (for example, with ions, with

light, etc.); $H_S(q)$ is the total energy of the liquid (in the phonon model assumed here); $V(x,q)$ is the electron–phonon interaction energy. To make the treatment more general, we have introduced the term $H'(x,q)$, which is small in comparison with $H(x,q)$, as required by perturbation theory. In a sense, this term can describe the effect of, for example, neighbouring ions on an electron situated close to some specific ion. Since the calculation of $H'(x,q)$ does not present particular difficulty, we shall consider for the time being the Hamiltonian $H(x,q)$. The basic concept which we intend to use is that the rate of motion of the electron is very much higher than that of the heavy atoms of the liquid, i.e. of the phonons. Hence, as "seen from" the fast electron, the atoms of the liquid can be treated as immobile, and the problem becomes that of an electron in a given field:

$$\{H_e(x)+V(x,q)\}\psi_\alpha(x,q)=\varepsilon_\alpha(q)\psi_\alpha(x,q), \qquad (2.8)$$

where α is the number of the electronic level, and the energy $\epsilon_\alpha(q)$ and the electron function ψ depend on q as a parameter. If $H_S(q)$ were to vanish, i.e. if the atoms of the liquid were immobile, $\psi_\alpha(x,q)$ would be an exact solution of the problem. However, allowance for the slow motion of the atoms introduces the possibility of electron transfer from one state α to another state α'. Therefore, the exact solution of the problem takes the form of a superposition of all states $\psi_\alpha(x,q)$, with some "weighting" factors $\chi_\alpha(q)$ which are, of course, a function of q. Mathematically speaking, we have expanded an exact ψ-function into a series as a full set of orthogonalised functions $\psi_\alpha(x,q)$:

$$\psi(x,q)=\sum_\alpha \chi_\alpha(q)\psi_\alpha(x,q). \qquad (2.9)$$

On substituting this expression into the wave equation for $H(x,q)$, after multiplying the left-hand side by $\psi^*_\beta(x,q)$ and integrating with respect to x, we obtain the following equation for $\chi_\alpha(q)$:

$$\{H_s(q)+\varepsilon_\beta(q)-E\}\chi_\beta(q)=\sum_\alpha L_{\beta\alpha}(q)\chi_\alpha(q), \qquad (2.10)$$

where

$$L_{\beta\alpha}(q)=\frac{1}{2}\sum_k \hbar\omega_k\left\{\int\psi^*_\beta\frac{\partial\psi_\alpha}{\partial q_k}dx\cdot\frac{\partial}{\partial q_k}+\int\psi^*_\beta\frac{\partial^2\psi_\alpha}{\partial q_k^2}dx\right\}. \qquad (2.11)$$

Since $\frac{\hbar}{i}\frac{\partial}{\partial q_k}$ is an operator for the rate of motion of heavy particles, the first term in (2.11) can be interpreted, in a sense, as a mean velocity, and the second term as a mean square velocity. Therefore, the operator L must be treated as small in the adiabatic approximation (this operator is sometimes called the non-adiabaticity operator). If we use the quasi-classical approximation for the electron, we can show that $L\simeq\sqrt{m/M}$, where m is the mass of the electron and M the mass of the heavy particles. In the zeroth approximation, assuming $L=0$, we obtain

$$\left\{-\frac{1}{2}\sum_k\hbar\omega_k\frac{\partial^2}{\partial q_k^2}+\frac{1}{2}\sum_k\hbar\omega_k q_k^2+\varepsilon_\beta(q)\right\}\chi_{\beta n}(q)=E_n\chi_{\beta n}(q), \qquad (2.12)$$

where the subscript n identifies the various quantum levels of the slow subsystem. If the electron is initially in the state α, $\chi_{\beta n}(q)\simeq\delta_{\beta\alpha}$, i.e. the electronic state α with $L=H'=0$ will not suffer any changes. The quantity

$$U_\beta(q)=\frac{1}{2}\sum_k\hbar\omega_k q_k^2+\varepsilon_\beta(q) \qquad (2.13)$$

plays the role of potential energy for the heavy subsystem, and admits of the following simple interpretation: the first term represents the direct interaction of the heavy particles; the second term represents the interaction of the heavy particles with the blurred electron cloud (i.e. the heavy particles "perceive" the fast-moving electron only in a smeared out form). Therefore, the latter must evidently depend on the electronic state β. $U_\beta(q)$ is called the electronic energy level, or the potential energy surface.

If L or H' is finite, transitions can occur between the different states $\Psi_{\alpha,n}=\psi_\alpha\chi_{\alpha n}$ and $\Psi_{\alpha' n'}$ with probability $w_{\alpha n\to\alpha' n'}$. Therefore, if we are interested only in the change of electronic state, $w_{\alpha n\to\alpha' n'}$ must be summed over n' and statistically averaged over n (we assume that the heavy subsystem is initially in statistical equilibrium):

$$w_{\alpha\to\alpha'}=\sum_{n'}\langle w_{\alpha n\to\alpha' n'}\rangle_n. \qquad (2.14)$$

To calculate w it is necessary to know $\chi_{\alpha n}$, i.e. to be able to solve Eqn. (2.12). An approximate solution can be obtained by expanding $\epsilon_\alpha(q)$ in a power series of q around the equilibrium value q_0^α and retaining only the first two terms:

$$\varepsilon_\alpha(q)\simeq\varepsilon_\alpha(q_0^\alpha)+\sum_k u^\alpha(q_k-q_{k0}^\alpha). \qquad (2.15)$$

The electronic energy level then has the form

$$U_\alpha(q)=\varepsilon_\alpha(q_0^\alpha)-\sum_k u_k^\alpha\left(q_{k0}^\alpha+\frac{u_k^\alpha}{2\hbar\omega_k}\right)+\frac{1}{2}\sum_k\hbar\omega_k\left(q_k+\frac{u_k^\alpha}{\hbar\omega_k}\right)^2.$$

Since by definition q_0^α corresponds to a minimum value of $U_\alpha(q)$, it follows that $q_{k0}^\alpha=-\frac{u_k^\alpha}{\hbar\omega_k}$ and

$$U_\alpha(q)=\varepsilon_\alpha(q_0^\alpha)+\frac{1}{2}\sum_k\hbar\omega_k q_{k0}^2+\frac{1}{2}\sum_k\hbar\omega_k(q_k-q_{k0}^\alpha)^2=J_\alpha+$$
$$+\frac{1}{2}\sum_k\hbar\omega_k(q_k-q_{k0}^\alpha)^2. \qquad (2.16)$$

This expression allows a simple physical interpretation: before the electron is introduced, the liquid executes small oscillations close to the unpolarised state $q=0$ (see curve a of Fig. 1); after introduction of an electron into the state α, the liquid becomes polarised to the value q_0^α, and the total potential energy of the system is made up of the polarisation energy of the liquid $-\frac{1}{2}\sum_k\hbar\omega_k q_{k0}^2$, the energy of the electron in the polarised liquid $\epsilon_\alpha(q_0^\alpha)$, and the energy of the oscillatory motion of the liquid close to its equilibrium state $\frac{1}{2}\sum_k\hbar\omega_k(q_k-q_{k0}^\alpha)^2$. It is evident from this picture that the approximation (2.15) adopted here corresponds to the case where it is permissible to ignore the changes in vibrational frequency of the dipoles caused by the interaction between the electron and the liquid.

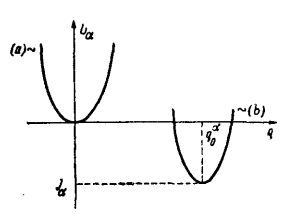


Fig. 1.

In order to apply the perturbation theory to the continuous spectrum, we shall assume that $\omega_k = p_k\Omega_0$, where p_k are integers and $\Omega_0 \to 0$. Without reproducing the lengthy calculations[12-14], we shall quote the expression for the probability of electronic transition per unit time:

$$w_{\alpha\to\alpha'} = \frac{2\pi}{\hbar}|V_{\alpha'\alpha}|^2 e^{\frac{J_\alpha - J_{\alpha'}}{2kT} - \sum_k z_k \coth\frac{\hbar\omega_k}{2kT}} \sum_{m=-\infty}^{+\infty} \frac{\sin m\Omega_0 t}{\pi\hbar m\Omega_0} e^{-\frac{m\hbar\Omega_0}{2kT}} \sum_{l_k}' \prod_k I_{l_k}(z_k). \tag{2.17}$$

We have introduced the following terminology: $V_{\alpha'\alpha}$ is a matrix element of the perturbation, i.e. either $L_{\alpha'\alpha}$ or $H_{\alpha'\alpha}$, according to which of the two is the most significant; $z_k = \frac{1}{2}(q_{k0}^{\alpha} - q_{k0}^{\alpha'})^2 \operatorname{cosech}\frac{\hbar\omega_k}{2kT}$; $I_l(z)$ is a Bessel function of imaginary argument of order l; lastly, the prime in the summation denotes the choice of values of l_k among all possible integral values such that $\sum_k \hbar\omega_k l_k = J_{\alpha'} - J_\alpha + m\hbar\Omega_0$. The only assumption made in the derivation of this formula was $t < \frac{1}{\Omega_0} \to \infty$. The physical significance of this condition is that the times considered are small enough to make (according to the uncertainty principle) $\Delta E \sim \frac{\hbar}{t} \gg \hbar\Omega_0$, i.e. such that there is no noticeable dispersion of the energy spectrum. From the exact formula (2.17) we can obtain an asymptotic expression for the case of very small dispersion of the frequency spectrum ($p_k \simeq p_0 = \frac{\omega_k}{\Omega_0} \to \infty$). Since we are assuming that the type of dispersion plays no part, we shall choose $p_{k_1} = p_0$ and $p_{k_2} = p_0 + 1$ ($k_1 \neq k_2$). Under these conditions, division of all k by k_1 and k_2 is arbitrary. Using the asymptotic properties of $I_m(z)$, it is possible to show that

$$w'_{\alpha\to\alpha'} \simeq \frac{2\pi|V_{\alpha'\alpha}|^2}{\hbar^2\omega_0} e^{\frac{J_\alpha - J_{\alpha'}}{2kT} - \frac{E_s}{\hbar\omega_e}\coth\frac{\hbar\omega_e}{2kT}} I_{m_0}\left(\frac{E_s}{\hbar\omega_0}\operatorname{cosech}\frac{\hbar\omega_0}{2kT}\right); \quad \hbar\omega_e \ll \sqrt{kTE_s}. \tag{2.18}$$

The parameter $E_S = \frac{1}{2}\sum_k \hbar\omega_0(q_{k0}^{\alpha} - q_{k0}^{\alpha'})^2$ has the significance of a "reorganisation" energy (or "transpolarisation" energy) for the liquid as a result of the electronic transition and $m_0 = \frac{J_\alpha - J_{\alpha'}}{\hbar\omega_0}$.

This formula assumes a particularly simple form at high temperatures, when $\hbar\omega_0 < kT$:

$$w_{\alpha\to\alpha'} = \left(\frac{\pi}{\hbar^2 kTE_s}\right)^{1/2}|V_{\alpha'\alpha}|^2 e^{-\frac{E_a}{kT}}; \quad kT > \hbar\omega_0, \tag{2.19}$$

where the activation energy E_a is given by

$$E_a = \frac{(J_{\alpha'} - J_\alpha + E_s)^2}{4E_s}. \tag{2.20}$$

Thus, we have in fact arrived at a formula of the same type as that of the transition state theory, but only in the particular case of $kT > \hbar\omega_0$.

The advantage of the $\omega_k = \omega_0$ model, i.e. the model in which the motion of the dipoles can be characterised by a single frequency, is that a single effective coordinate q can be introduced in place of the many coordinates q_k. (One of us[15] has given a strict mathematical proof of this.) In this case we are in fact dealing with one-dimensional potential curves $U_\alpha(q)$, and we can therefore use the Landau–Zener theory of adiabatic electronic transitions if the motion of heavy particles (dipoles) is described classically. Omitting the straightforward mathematical derivations, we shall describe the physical results obtained in the case of interest. The broken lines in Fig. 2 denote two electronic energy levels, corresponding to two electronic states α and α', between which the transition occurs. At the intersection (q^*) of the two levels the electronic state is doubly degenerate, i.e. the same energy $\epsilon_\alpha(q^*) = \epsilon_{\alpha'}(q^*)$ corresponds to two distinct states α and α' [this follows from Eqn. (2.13)]. However, when allowance is made for the perturbation $V_{\alpha'\alpha}$, this degeneracy is removed and resonance splitting of the levels arises at the point q^*. (See the solid line in Fig. 2.) If the perturbation $|V_{\alpha'\alpha}|^2$ is smaller than some critical value $|V_{cr}|^2 = \hbar\omega_0\left(\frac{kTE_s}{\pi^3}\right)^{1/2}$, we can suppose that the system, initially at the level U_α, jumps non-adiabatically to the level $U_{\alpha'}$, but only after several passages through the intersection point. If, however, $|V_{\alpha'\alpha}| \gg |V_{cr}|$, the separation of the levels at the point q^* will be large, and transitions from the level U_α to the level $U_{\alpha'}$ will occur in such a way that the system remains always at the lowest level: these transitions are called adiabatic transitions. Calculations of the probability of transition per unit time by the quasi-classical Landau–Zener method lead to the high-temperature approximation formula (2.19) for non-adiabatic transitions; in the case of adiabatic transitions we obtain the formula

$$w_{\alpha\to\alpha'} = \frac{\omega_0}{2\pi} e^{-\frac{E_a}{kT}}, \tag{2.21}$$

where the activation energy E_a is approximately the same as in Eqn. (2.20), i.e. it equals the distance from the point of "intersection" of the levels to the minimum of the initial level (Fig. 2).

In the discussion which follows we shall make use of the above theory to investigate various concrete problems.

3. Theory of Oxidation–Reduction Reactions

This section deals with oxidation–reduction reactions occurring in a liquid by an electronic mechanism, i.e. a mechanism whose fundamental step does not involve either breaking or forming chemical bonds. Such a reaction can be represented schematically in the form

$$A^{z_1} + B^{z_2} \to A^{z_1+1} + B^{z_2-1}. \tag{2.22}$$

We shall classify all reactions into fast and slow. To clarify the meaning of this classification, we shall consider two ions taking part in a reaction of the type of (2.22).

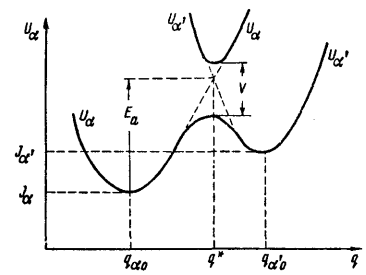


Fig. 2.

First of all, we introduce the concept of a reaction volume, this being the region within which the ions A^{z_1} and B^{z_2} must be to enable electron transfer to proceed from A^{z_1} to B^{z_2}. If the residence time of the ions in the reaction volume (τ_g) is much greater than the time between electronic transitions (τ_e), the reaction should be called fast or proceeding by a diffusion mechanism. Since electronic equilibrium between the ions can be established at each "collision" (i.e. each time the ions fall into the reaction volume), diffusion must be the rate-determining step. We are assuming that the reaction volume is so small that the residence time of the ions in this volume is of the same order as the time between diffusional jumps (τ_g).

In this review we shall be concerned only with slow reactions, i.e. with the case $\tau_e \gg \tau_g$. These reactions are characterised by the fact that electron transfer occurs only after several "collisions" between the ions. On the other hand, this is just the case where we can apply the formulae of perturbation theory, which are correct at times $t \ll \frac{1}{w_{\alpha\alpha'}} = \tau_e$. Indeed, since the ions remain in the reaction volume for a time $\tau_g \ll \tau_e$, it can be assumed that the probability of an electronic transition is directly proportional to time, which is equivalent to ignoring reverse transitions during the interval τ_g. It can be shown[16] that the specific rate constant of the bimolecular reaction (2.22) is of the form

$$K_{AB} = \int w_e(R)\, w_{AB}(R)\, dv, \qquad (2.23)$$

where $w_{AB}(R)$ is the probability of finding the ions A^{z_1} and B^{z_2} at a distance R apart, $w_e(R)$ is the probability of an electronic transition from A^{z_1} to B^{z_2}. In view of the assumption that $\tau_g \ll \tau_e$, we can use the equilibrium distribution function of the ions (which at small distances has the form $e^{-\frac{z_1 z_2 e^2}{\varepsilon_s kTR}}$) in place of w_{AB}. It is surprising to find that the condition for a slow reaction obtained here corresponds to the assumption $\tau_g \ll \tau_e$, which was made in Section II.1, if the diffusion coefficients of the ions A^{z_1} and B^{z_2} are of the same order of magnitude as the self-diffusion coefficients of the liquid molecules.

All slow reactions can be divided into two classes: adiabatic and non-adiabatic. For the former, the quantity w_e should be expressed by formula (2.21), when the resulting rate constant takes the form

$$K_{AB} = \frac{kT}{h} e^{-\frac{\Delta F^{\neq}}{kT}} v_r, \qquad (2.24)$$

where v_r is the volume of the reaction region, and $\Delta F^{\neq}$ is the free energy of activation, which is related to the activation energy by the expression

$$\Delta F^{\neq} = \Delta E^{\neq} - T\Delta S^{\neq}, \qquad (2.25)$$

$$\Delta E^{\neq} = E_a + \frac{z_1 z_2 e^2}{\varepsilon_s R_r}, \qquad (2.26)$$

$$\Delta S^{\neq} = k \ln \frac{\hbar\omega_0}{kT}. \qquad (2.27)$$

Here E_a is given by formula (2.20), and R_r is the mean distance between the ions in the reaction region.

For non-adiabatic reactions, expression (2.19) must be used in place of w_e, and $V_{\alpha'\alpha}$ should be interpreted as an exchange integral[13]. The result is the following formula for K_{AB}:

$$K_{AB} = \varkappa \frac{kT}{h} e^{-\frac{\Delta F^{\neq}}{kT}} V_r, \qquad (2.28)$$

where the transmission coefficient $\varkappa$ is of the form

$$\varkappa = |V_{\alpha'\alpha}|^2 \left(\frac{4\pi^3}{\hbar^3 \omega_0^3 kTE_s}\right)^{1/2} = \frac{|V_{\alpha'\alpha}|^2}{|V_{cr}|^2}. \qquad (2.29)$$

Experimental data for the specific rate constants of different reactions, computed by means of formula (2.28), are given in the Table together with calculated values of the corresponding transmission coefficients $\varkappa$. The Table shows that most of the reactions are non-adiabatic, with $\varkappa \sim 10^{-3}$. Only four of the reactions are exceptional, and proceed by an adiabatic mechanism.

We have recently attempted[15] a numerical evaluation of K_{AB} for the Fe^{2+}/Fe^{3+} system. For R_r we used the value[17] 6.8 Å, and ω_0 was assumed to be 10^{11} s^{-1}, whilst E_s was calculated from the Born model. On the assumption that the reaction is adiabatic, we obtained K_{AB} = = 50 litre $mole^{-1}$ s^{-1}, $\Delta F^{\neq}$ = 15.1 kcal $mole^{-1}$, and $\Delta E^{\neq}$ = = 11.5 kcal $mole^{-1}$. By comparing these with the experimental results, we find that the values obtained are in reasonable agreement with experiment, despite the coarseness of the approximation.

To conclude this Section, we shall give the quantitative formulation of the criterion for a slow reaction. From (2.23) and (2.28), the rate constant can be related to $\tau_e = 1/w_e$:

$$K_{AB} = \frac{1}{\tau_e} v_r e^{-\frac{z_1 z_2 e^2}{\varepsilon_s R_r kT}} \qquad (2.30)$$

The condition $\tau_g \ll \tau_e$ leads to the inequality

$$K_{AB} \ll \tau_g^{-1} v_r e^{-\frac{z_1 z_2 e^2}{\varepsilon_s R_r kT}}. \qquad (2.31)$$

Knowing the radius of the reacting ions, the radius v_r of the reaction volume can be readily evaluated. In particular, if we adopt a value of 7 Å for R_r, and insert 10^{-9} s for τ_g in Eqn. (2.31), we obtain $K_{AB} \ll 2 \times 10^6$ litre $\times$ $\times$ $mole^{-1}$ s^{-1}.

4. Absorption of Light by Anions

The theory developed above can be applied to the study of the absorption of light by halide ions. According to the Franck–Condon principle, the light energy absorbed

TABLE.

System	Ratio constant, litre $mole^{-1}$ s^{-1}	Activation energy $E^{\neq}$, kcal $mole^{-1}$	Temperature, °C	Transmission coefficient, $\varkappa$
Fe^{3+}/Fe^{2+}	0.87	9.9	0	$1.3 \cdot 10^{-3}$
Fe^{3+}/Fe^{3+}	8.1	9.9	25	$4.7 \cdot 10^{-3}$
$FeOH^{2+}/Fe^{2+}$	1010	7.4	0	$2.3 \cdot 10^{-2}$
FeF^{2+}/Fe^{2+}	9.7	9.1	0	$5.6 \cdot 10^{-3}$
FeF^{2+}/Fe^{3+}	2.5	9.5	0	$2.9 \cdot 10^{-3}$
$FeCl^{2+}/Fe^{2+}$	9.7	8.8	0	$3.1 \cdot 10^{-3}$
$F(SCN)^{2+}/Fe^{3+}$	41.5	7.9	25	$1.0 \cdot 10^{-2}$
$Fe(SCN)_3^+/Fe^{3+}$	7.6	8.6	25	$0.6 \cdot 10^{-3}$
$EuCl^{2+}/Eu^{2+}$	$6.5 \cdot 10^{11} e^{-\frac{E^{\neq}}{kT}}$	20.8	25	~1
Eu^{2+}/Eu^{3+}	$3.6 \cdot 10^{-4}$	20.8	25	~1
NpO_2^+/NpO_2^{2+}	29	8.3	0	$4.2 \cdot 10^{-3}$
MnO_4^-/MnO_4^{2-}	710	10.5	0	~1
VOH^{2+}/VO^{2+}	$10^8 e^{-\frac{E^{\neq}}{kT}}$	10.7		$7 \cdot 10^{-3}$
Ce^{3+}/Ce^{4+}	$1.9 \cdot 10^{11} e^{-\frac{E^{\neq}}{kT}}$	16.8		~1

$\hbar\omega_a$ is equal to the distance between energy levels at fixed polarisation. To calculate the average value of $\hbar\omega_a$, it is necessary to average out $U_\beta(q) - U_\alpha(q)$ by means of the quantum distribution function for a one-dimensional oscillator[18]:

$$dw(q) = \left(\frac{1}{\pi}\tanh\frac{\hbar\omega_0}{2kT}\right)^{1/2} e^{-q^2\tanh\frac{\hbar\omega_0}{2kT}}\,dq. \qquad (2.32)$$

The result is

$$\hbar\bar{\omega}_\beta = J_\beta - J_\alpha + E_s = \varepsilon_\beta(q_0^\alpha) - \varepsilon_\alpha(q_0^\alpha). \qquad (2.33)$$

Physically this means that, to find $\hbar\bar{\omega}_a$, we must know the ground level and the first excited level of the electron at fixed initial equilibrium polarisation, defined by the coordinate q_0^α. The difference between these energies gives the mean energy of the light absorbed by a halide ion. The mean energy of the emitted light is found by an analogous procedure:

$$\hbar\bar{\omega}_e = J_\beta - J_\alpha - E_s = \varepsilon_\beta(q_0^\beta) - \varepsilon_\alpha(q_0^\beta). \qquad (2.34)$$

In addition to $\hbar\bar{\omega}_a$, it is interesting to calculate also the width of the absorption band, i.e. the standard deviation of the light energy absorbed:

$$D^2 = (\hbar\omega_a)^2 - (\hbar\bar{\omega}_a)^2 = \hbar\omega_0\coth\frac{\hbar\omega_0}{2kT}E_s, \qquad (2.35)$$

or in the high-temperature approximation

$$D^2 = (2kTE_s)^{1/2}. \qquad (2.36)$$

The width of the absorption band varies with temperature as $T^{1/2}$. On changing the temperature from 10° to 50°, the width of the band increases, according to Eqn. (2.36), by 7%, which agrees tolerably well with the experimental value[19] of 5%.

5. Theory of Electron Mobility

The problem of slow electrons in various liquids has attracted considerable attention in recent literature. In particular, the problem has been discussed extensively in radiation chemistry[27] and biological investigations[28]. Some electrochemical papers which consider the possible kinetic role of solvated electrons are beginning to appear. Not surprisingly, systems in which the liquid is water present the greatest interest. We shall therefore consider the case of a polar medium in the first part of the present subsection, and we shall report a number of results for non-polar media in the second part.

The basic problem facing us when considering polar liquids is the calculation of mobility. In order to throw some light on the physical mechanism of electrical conduction in liquids, we shall begin by stating the theory of electron mobility in polar crystals.

There is a large number of semiconductors whose properties cannot be described by the conventional band theory They show a characteristic, activational dependence of mobility upon temperature:

$$u \sim e^{-\frac{E_a}{kT}}.$$

This phenomenon cannot be explained within the framework of the normal band theory, since the thermal motion of the crystal lattice increases the probability of scattering of carriers, and should therefore lower the mobility. A mobility which increases with temperature is observed in substances with very small mobility values. For example, for Fe_2O_3 and NiO, $u \simeq 4\times10^{-3}$ cm^2 V^{-1} s^{-1}, and the mean free path λ of current carriers is found to be much smaller than the lattice constant. Contrary to the band theory, according to which the electrical conductivity depends on the changes in the velocity of the free electron as a result of scattering by lattice vibrations, Ioffe suggested[20] that the transport process in semiconductors of this type should be treated as the transition of an electron from a given cell of the crystal to a neighbouring one. Since we know that the theory developed in Section II, 2 is applicable in this case, it is obvious that the desired temperature dependence can be obtained from formula (2.19) at high enough temperatures. The difficulty, however, is that "band" solutions are found because of the translational symmetry of the crystal, which persists even in the semiconductors under discussion. A great deal of work[9,21-26] has been devoted to the problem of the change in the mechanism of electrical conduction, i.e. to the manner in which electrons in bands (or delocalised) can be correctly assigned to localised states. Unfortunately, lack of space prevents us from giving rigorous derivation of the results of the theory: we shall only point out that the criteria for the applicability of the band and of the transfer mechanism of conduction have been obtained from the above work. Calculation shows that at low enough temperatures the mobility decreases with increase of temperature, but begins to rise again exponentially with further increase of temperature: we know that this corresponds to a change from the band mechanism to the barrier (or "jump") mechanism. The model we have described is correct only for the case of strong binding, when the electron interacts strongly just with the atom in whose neighbourhood it happens to be at a given moment. In other words, the exchange integral for two nearest-neighbour atoms is fairly small. This is why the overall theory has been called the theory of small polarons. (We are using the term polaron in its usual meaning of an electron surrounded by a "coat" due to the polarisation of the dipoles.) However, in the case of weak interaction between the electrons and all the atoms of the crystal (but strong interaction with the polarisation) we must apply the theory of large polarons, developed by Pekar[4].

In polar liquids the situation is much more complex; the following cases are possible.

1. The mobility arises by the large polaron mechanism, i.e. the electron has a weak interaction with one solvent molecule. Since the radius of the large polaron is much greater than the average distance between neighbouring liquid molecules, we can apply the continuum model of the liquid, so that Pekar's original theory can be used without any modification.

2. The mobility is determined by a band polaron of small radius. This situation can arise when the correlation length between liquid molecules (i.e. the distance of short-range order) is greater than the mean free path of the polaron.

3. Lastly, one more variant is possible, in which the jump mechanism applies to polarons of small radius. In this case the difference between liquids and crystals disappears. To simplify the discussion, we shall quote the expression for the mobility:

$$u = \frac{ea^2|V|^2}{\hbar kT}\left(\frac{\pi}{kTE_s}\right)^{1/2} e^{-\frac{E_s}{4kT}}, \qquad (2.37)$$

where a is the average distance between liquid molecules,

V is the exchange integral, and as before E_S denotes the energy of "transpolarisation". If the electron jump takes place adiabatically, we can write

$$u = \frac{ea^2}{kT}\frac{\omega_0}{2\pi}e^{-\frac{E_s}{4kT}}. \quad (2.38)$$

Formulae (2.37) and (2.38) are readily integrated using the Einstein relation $u = eD/kT$ if we introduce the diffusion coefficient of the electron:

$$D_{\text{adiab}} = \frac{a_2}{\tau_e}; \quad D_{\text{non-adiab}} = \varkappa\frac{a^2}{\tau_e}. \quad (2.39)$$

It is interesting to note that oxidation–reduction reactions in liquids can give rise to an electronic contribution to the electrical conductivity (in parallel with the ionic component). This was first pointed out by Frumkin. Since we have considered only slow reactions ($\tau_e \ll \tau_g$) in Section II,3, it is obvious that the contribution of the electronic component to the total electrical conductivity will be small. Simple calculation shows that the electrical conductivity is given by

$$\sigma_e = \frac{e^2c^2R_i^2K_{AB}}{6kT}. \quad (2.40)$$

To conclude this Section, we shall discuss the behaviour of electrons in non-polar liquids. The calculation of mobility in this system presents considerable difficulty, and we shall therefore confine ourselves to a study of the energy spectrum of the electron. As will be shown below, a knowledge of the spectrum offers also a qualitative understanding of the mechanism of electrical conduction in non-polar liquids.

To simplify the calculation, we shall examine the one-dimensional model of a liquid[29], i.e. a chain of identical atoms distributed in a practically random fashion. Since the concentration of electrons is assumed to be very small, the calculation can be made by the one-electron approximation. The Hamiltonian for this problem is of the form

$$H(x) = -\frac{\hbar^2}{2m}\Delta_x + \sum_i u(x - R_i), \quad (2.41)$$

where the first term is the kinetic energy of the electron, and $u(x - R_i)$ is the interaction energy between the electron and the ith atom of the liquid. The values of R_i can be treated as random, but determined by a known distribution function $\Phi(R_1, \ldots, R_N)$. In practice, of course, the form of Φ is not known, since there is no theory of the liquid state at present. We shall therefore, in what follows, confine ourselves to a consideration of some plausible models of the liquid state which offer a basis for discussion. Thus, our problem is to determine the spectrum of the Hamiltonian (2.41), averaged with respect to Φ, with arbitrary values of the parameter R. The most convenient mathematical approach to this problem is the method of Green functions, well known in quantum field theory and in statistics. The mean density of levels is related to a Green function by the expression[30]

$$\left\langle\frac{dn}{dE}\right\rangle = \frac{1}{\pi}JmSp\langle G\rangle. \quad (2.42)$$

Here Jm denotes the imaginary part of the spur of $\langle G\rangle$, where the angular brackets are used to indicate averaging with respect to random values of R_i. The Hamiltonian (2.41) is conveniently written in the form $H = \langle H\rangle + V$, where $V = H - \langle H\rangle$ is the departure of H from the value $\langle H\rangle$. Under certain conditions V can be assumed to be small, so that the problem can be solved by perturbation theory. The zeroth approximation for V gives the usual spectrum of a one-dimensional crystal in the strong binding approximation:

$$E_0(p) = \varepsilon_0 + 2\langle J\rangle\cos p, \quad (2.43)$$

where ϵ_0 is the energy of the electron in an isolated atom of the liquid, $\langle J\rangle$ is the mean value of the exchange integral, and p is the quasi-momentum of the electron. The function $E_0(p)$ is shown in Fig. 3 as a broken line. Allowance for the perturbation V produces two effects in the first approximation. First, it alters the form of the spectrum within the previous band (see Fig. 3, full line):

$$E(p) \simeq \varepsilon_0 + 2\langle J\rangle\left(1 - \frac{\langle I^2\rangle}{2\langle J\rangle^2}\right)\cos p, \quad (2.44)$$

where $\langle I^2\rangle = \langle(J - \langle J\rangle)^2\rangle$ is the dispersion of the exchange integral. Secondly, the state of quasi-momentum p begins to relax in time, the relaxation time τ being given by the formula

$$\tau_p^{-1} = \gamma_p = \frac{\langle I^2\rangle}{|\langle J\rangle\sin p|}(1 + \cos^2 p). \quad (2.45)$$

Analysis of formula (2.45) shows that the results obtained from the perturbation theory are correct at sufficiently low dispersions:

$$\langle I^2\rangle \ll \langle J\rangle^2. \quad (2.46)$$

To give more real significance to the condition (2.46), we can attempt a calculation, assuming that $J(R) \sim e^{-R/R_0}$. We shall also assume that correlation operates only between the positions of the two nearest atoms in the liquid. Without explicitly stating the form of $\Phi(R)$, we shall assume that the deviation of R from its average value is small and of the order of l. Condition (2.46) then reduces to the requirement that

$$l \ll R_0. \quad (2.47)$$

In practice, the following condition must also be satisfied:

$$p^3 \gg \frac{\langle I^2\rangle}{\langle J\rangle^2}. \quad (2.48)$$

The inequality (2.48) follows directly from (2.43) and (2.45). This condition means that the theory of perturbations is not applicable near the band edge[30]. Using an improved form of the perturbation theory, it can be shown that a shift of the old band edge in the direction of expansion does in fact occur, and that the form of the spectrum in the region of the new band edge is as shown in Fig. 3 (dotted line close to the new band edge):

$$E(p) \simeq \varepsilon_0 + 2\langle J\rangle\left\{1 + \left(\frac{\langle I^2\rangle}{\sqrt{2}\langle J\rangle^2}\right)^{2/3} - \frac{p^2}{3}\right\}, \quad p^3 \ll \frac{\langle I^2\rangle}{\langle J\rangle^2}. \quad (2.49)$$

It follows from this formula that the average width of the band increases, due to the presence of dispersion, by an amount of the order of $(\langle I^2\rangle/\langle J\rangle^2)^{2/3}$, and that the

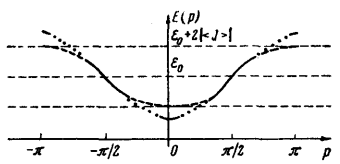


Fig. 3.

effective mass in the new band differs from the mass calculated for the old band by formula (2.43):

$$m_{\text{eff}} = \frac{3}{2} m^0_{\text{eff}}. \qquad (2.50)$$

The factor 3/2 in this formula appears because of the non-analytical variation of $E(p)$ with the small parameter $\epsilon = \langle I^2\rangle/\langle J\rangle^2$ [$E(p) \sim \epsilon^{2/3}$].

The most interesting case is, of course, that of large dispersion of the exchange integral [see Eqn. (2.47)]:

$$l \gg R_0. \qquad (2.51)$$

In this case perturbation theory is already inapplicable, but it has been possible to carry out a partial summation in the expression for the Green function. Retaining the most significant terms, the following equation for the electron spectrum was obtained:

$$E(p) - \varepsilon_0 = 2(E(p) - \varepsilon_0)\left\langle \frac{J^2(R)}{(E(p)-\varepsilon_0)^2 - J^2(R)} \right\rangle + 2(E(p)-\varepsilon_0)^2 \left\langle \frac{J(R)}{(E(p)-\varepsilon_0)^2 - J^2(R)} \right\rangle \cos p. \qquad (2.52)$$

This equation also was derived on the assumption that all the exchange integrals are uncorrelated, but the parameter $\epsilon = \langle I^2\rangle/\langle J\rangle^2$ was treated as much larger than unity. Eqn. (2.52) can be solved only if the binary distribution function of the atoms of the liquid is known. To arrive at the final expressions, we have used the simple model

$$\Phi(R) = \begin{cases} 0, & |R-a| > l, \\ \dfrac{1}{2l}, & |R-a| < l, \end{cases}$$

where a is the average distance between the atoms of the liquid. The result was the following formula for the spectrum:

$$E_u(p) = \varepsilon_0 + |J_m|\left(1 \pm e^{-\frac{R_0}{2l(1-\cos p)}}\right),$$
$$E_l(p) = \varepsilon_0 - |J_m|\left(1 \pm e^{-\frac{R_0}{2l(1+\cos p)}}\right), \qquad (2.53)$$

where E_u and E_l apply to the upper and the lower band (see full line in Fig. 4), and J_m denotes the maximum value of the exchange integral, corresponding to the minimum distance between the atoms, $R_{\min} = a - l$. In the derivation of (2.53) it was assumed that $J(R) \sim e^{-R/R_0}$.

It follows from (2.53) that the distance between the centres of the upper and the lower band is $2|J_m|$, and the width of both bands is $2|J(a)|$, i.e. the value of the exchange integral calculated for an average distance a. To make clear the physical significance of the result, we can compare formulae (2.53) with the spectrum calculated for the periodic chain shown in Fig. 5. This problem can be solved exactly, and the resulting form of the spectrum is (see broken curve in Fig. 4):

$$E^0_u = \varepsilon_0 + \sqrt{(J_1+J_0)^2 - 4J_1J_0\cos^2 p},$$
$$E^0 = \varepsilon_0 - \sqrt{(J_1+J_0)^2 - 4J_1J_0\cos^2 p}. \qquad (2.54)$$

Here J_1 is the exchange integral for particles 1 and 2, J_0 for particles 2 and 3 (see Fig. 5). The distance between the centres of the bands E^0_u and E^0_l is $2\sqrt{J_1^2 + J_0^2} \simeq 2|J_1|$, since $|J_1| \gg |J_0|$, and the width of each of the bands is $2|J_0|$. We see by inspection of formulae (2.53) and (2.54) that the major contribution to the average spectrum of the electron at high dispersions is given by the

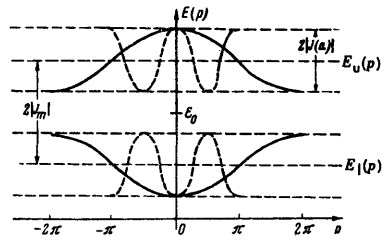


Fig. 4.



Fig. 5.

configurations of the atoms in which the closest approach of two atoms of the liquid occurs. This situation is reminiscent of the fact that in the calculation of mobility it is just these configurations which are the most important. This somehow corresponds to an electronic jump between two atoms. It is not hard to see that the temperature dependence of the mobility is also in qualitative agreement with the case of small polarons, discussed earlier in this Section. Thus (2.45) requires that a low temperatures the dispersion increases with increase of temperature, whilst τ_p decreases; consequently, the mobility $u \sim e\tau_p/m_{\text{eff}}$ also decreases. On the other hand, at high dispersions an increase in temperature must obviously increase the frequency of the jumps, and therefore the mobility.

III. THEORY OF OXIDATION-REDUCTION REACTIONS

The simplest electrode reactions from the point of view of a theoretical study are of the form

$$A^z + e\,(\text{in the electrode}) \rightarrow A^{z-1}, \qquad (*)$$

where A^z and A^{z-1} are ions of charge z and z - 1 respectively

An electrode process involves several steps. In what follows, we shall be concerned exclusively with processes in which the slow (and therefore the rate-determining) step is discharge of the ion at the electrode. The phenomenological theory of slow discharge for reactions of the type (*) at a metal electrode was developed by Frumkin[31].

In the work of Levich, Vdovin, and Myamlin[32,33], the phenomenological slow discharge theory is extended to cover reactions at semiconductor electrodes. The earliest attempts at deriving a microscopic theory of oxidation-reduction reactions of the type (*) are due to Randles[35] and Hush[36]. Gerischer[37] had discussed heterogeneous reactions involving negligible changes in the inner coordination sphere of the ion. In his studies of oxidation-reduction reactions at metal and semiconductor electrodes, Gerischer has suggested that the activation energy arises mainly from the displacement of the atoms in the first coordination sphere of the ion. This approach gives the correct physical picture, but it failed to provide quantitative results.

Many more quantitative results were obtained by examining heterogeneous oxidation–reduction reactions not involving adsorption of reagents, formation or breaking of chemical bonds, and proceeding without any changes in the first coordination sphere of the ion. This review will deal exclusively with reactions of this type. The theory of these reactions has been developed in papers by Marcus[38-40], and Dogonadze, Chizmadzhev, and Kuznetsov[41-49]. As was stated at the beginning of this article, Marcus used the thermodynamic method, which offers several advantages coupled with the disadvantage of not allowing calculation of the exchange current.

In our previous papers[41-49] we have used the approach followed in the discussion of homogeneous reactions (see Section II). The main results of this work will now be described.

1. Calculation of the Fundamental Ion-Discharge Step at an Electrode and General Kinetic Relations

We shall consider a system consisting of an electrode, a polar solvent, an ion A^z, and an electron which can be associated either with the electrode or with the ion. The probability of electron transfer in this problem is determined by formula (2.19), in which V is to be intepreted as an exchange integral and J_s and J_f are given by the following expressions

$$J_s = \varepsilon_{z-1} - e\varphi(R) - \frac{\varepsilon_s - 1}{8\pi\varepsilon_s}\int D^2_{0z-1}\,dv, \tag{3.1}$$

$$J_f = \varepsilon_f - e\varphi_e - U_0 - \frac{\varepsilon_s - 1}{8\pi\varepsilon_s}\int D^2_{0z}\,dv, \tag{3.2}$$

where ϵ_{z-1} is the energy of the electron in the isolated ion A^{z-1}, $\varphi(R)$ is the potential at the point where the ion undergoing discharge is located, φ_e is the potential of the electrode, U_0 is the depth of the potential well for the electron in the electrode (see Fig. 6), J_f is the level of the electron in the electrode, and D_{0z} (D_{0z-1}) are the inductions of the ions A^z (A^{z-1}). The quantities ϵ_s and J_f have the same meaning as in the case of homogeneous reactions (Section II), but when dealing with heterogeneous reactions we must include in J_s the energy of the interaction of the electron with the electronic polarisation of the solvent, since this is not included in J_f and is not retained in the electron transfer process. In Eqns. (3.1) and (3.2) the subscript s indicates that the electron is in the solution

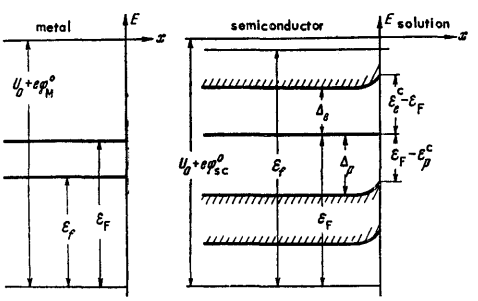


Fig. 6.

whilst f indicates that the electron is in the electrode at the energy level ϵ_f.

These expressions for the probability of electron transfer allow us to calculate the current flowing in the electrode–solution system. The current density can be expressed in the form

$$i = i_a - i_c,$$

where i_a is the anodic current, generated by the passage of the electron from the solution into the electrode, and i_c is the cathodic current. We shall invariably assume that all the ions are discharged at the electrode independently of each other. This implies that an expression for (say) the anodic current can be obtained as follows. The probability of electron transfer from the solution to the energy level ϵ_f of the electrode is multiplied by the concentration of the appropriate ions, $c_{z-1}(x)$, at the particular point in the solution, and by the probability of finding the energy level of the electrode unoccupied, $1 - n(\epsilon_f)$. The resulting expression must then be integrated over all possible states of the electron in the electrode and with respect to all the coordinates of the ion in the solution. An expression for i_c can be obtained by a similar procedure:

$$i_a = e\int_0^\infty c_{z-1}(x)\,dx \int w_{sf}(x)\,[1 - n(\varepsilon_f)]\,\rho_f\,d\varepsilon_f, \tag{3.3}$$

$$i_c = e\int_0^\infty c_z(x)\,dx \int w_{fs}\,n(\varepsilon_f)\,\rho_f d\varepsilon_f, \tag{3.4}$$

where $n(\epsilon_f)$ is the distribution function of the electrons over the energy levels in the electrode, and ρ_f is the density of energy states in the electrode. It must be noted that the problem of calculating the current really consists of two separate problems: the first problem is to find the probability of an ion being at a distance x from the electrode, i.e. to evaluate $c_z(x)$ and $c_{z-1}(x)$; the second problem is to find w_{sf} (w_{fs}). The solution of the second problem has been discussed in the previous paragraph. To find the probability that an ion approaches to a given distance from the electrode is a complex statistical problem which is still not finally solved. We shall therefore have to resort to one of the approximate theories, such as the Gouy–Stern theory. Within the framework of the theory developed in Section II, 2 it can be shown that the probability of the forward transition is related to the probability of the reverse transition by the expression $w_{sf} = w_{fs}\exp[(J_s - J_f)/kT]$. By using this expression, the resulting current can be written in the form[44]

$$i = e\int_0^\infty dx \int d\varepsilon_f \rho_f n(\varepsilon_f)\, c_z w_{fs}(x)\left\{\frac{c_{z-1}(x)}{c_z(x)}\,\frac{1-n(\varepsilon_f)}{n(\varepsilon_f)}\,e^{\frac{J_s-J_f}{kT}} - 1\right\} \tag{3.5}$$

To simplify the subsequent calculations, we shall assume that the currents are not large, so that the Boltzmann equilibrium distribution can be used to express c_{z-1} and c_z. For the same reason, we shall ignore departures from equilibrium within the electrode and use the normal Fermi distribution function for $n(\epsilon_f)$. This procedure is always justifiable for metals and intrinsic semiconductors at low current densities, and it can also be applied to impurity semiconductors if the current of minority carriers through the semiconductor interface is smaller than the limiting diffusion current of minority carriers. The formulae can be easily generalised to allow for departures from equilibrium in a semiconductor[45,49], which can be quite large at high currents and especially if

the semiconductor is illuminated (see also III, 5). In the light of these assumptions, Eqn. (3.5) can be rewritten

$$i = i_c\left(\exp\left\{\frac{e\varphi_e - (\alpha_{z-1}-\alpha_z) + \varepsilon_{z-1} - (\varepsilon_F - U_0) - kT\ln\frac{c_z}{c_{z-1}}}{kT}\right\} - 1\right), \quad (3.6)$$

where ϵ_F is the Fermi level in the electrode and c_z and c_{z-1} are the concentrations of the ions A^z and A^{z-1} respectively in the bulk of the solution at $x \to \infty$; the potential of the solution is taken to be zero. The quantity $\alpha_{z,z-1} = \frac{\epsilon_S - 1}{8\pi\epsilon_S}\int D^2_{0z,z-1}dv$ is the hydration energy of the ions $A^{z,z-1}$ in the Born approximation[50].

Using (3.6), it is easy to derive an expression for the equilibrium Galvani potential difference at the semiconductor–solution interface[44] from the condition that the total current must vanish:

$$e\varphi_e^0 = (\alpha_{z-1}-\alpha_z) - \varepsilon_{z-1} + (\varepsilon_F - U_0) + kT\ln\frac{c_z}{c_{z-1}}. \quad (3.7)$$

It is evident from (3.7) that the equilibrium Galvani potential depends on properties of the electrode ($\epsilon_F - U_0$), on properties of the ions (ϵ_{z-1}, $\Delta\alpha$), on the concentration of the ions, and on the properties of the solvent ($\Delta\alpha$).

An expression for φ_e^0 can be obtained also by using a thermodynamic cycle[42]. The various stages of the cycle are shown in Fig. 7. Under equilibrium conditions the work done in stages 1, 5, and 7 is zero. The work done in stages 2 and 4 is

$$\bar{\mu}_{z-1} = \psi_{z-1} + kT\ln c_{z-1};\quad \bar{\mu}_z = \psi_z + kT\ln c_z, \quad (3.8)$$

where $\psi_{z-1} = kT\ln N + \alpha_{z-1}$; $\psi_z = kT\ln N + \alpha_z$; N is the number of solvent particles.

Denoting by $\alpha_m^e = e_e\varphi_0 + U_0 - \epsilon_F$ the work of extraction of the electron from the electrode, and equating to zero the work expended in the entire cycle, we obtain

$$-\bar{\mu}_{z-1} - \varepsilon_{z-1} + \bar{\mu}_z - e\varphi_V^0 - \alpha_m^e = 0, \quad (3.9)$$

where $_e\varphi_0$ is the potential jump at the electrode–gas boundary and φ_V^0 is the equilibrium Volta potential of the electrode. The equilibrium Galvani potential at the electrode–solution interface is

$$\varphi_e^0 = \varphi_V^0 - {}_e\varphi_0. \quad (3.10)$$

Formulae (3.8), (3.9), and (3.10) lead to the expression (3.7).

We now introduce the overvoltage η defined as

$$\eta = \varphi_e - \varphi_e^0. \quad (3.11)$$

Eqn. (3.6) can therefore be rewritten

$$i = i_c(e^{\frac{e\eta}{kT}} - 1). \quad (3.12)$$

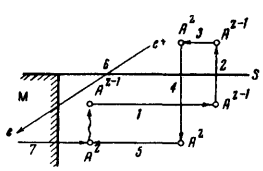


Fig. 7.

Furthermore, it follows from (3.12) that

$$i_a = i_c e^{\frac{e\eta}{kT}}. \quad (3.13)$$

It is obvious from the derivation of formulae (3.7), (3.12), and (3.13) that these expressions are applicable both to metal and to semiconductor electrodes.

The formulae derived here are quite general. To obtain more concrete expressions, we make the following approximation: the transition probability decreases very steeply as the distance from the ion to the electrode increases. The concept of an effective reaction region of thickness l, within which discharge occurs, thus arises quite naturally. The integral with respect to distance in formulae (3.3) and (3.4) can then be approximated by the product of l by the value of the integrand function at some intermediate point $x = \delta$, which can be thought of as the most probable distance over which discharge occurs. In practice, the quantity δ can, of course, be identified with the thickness of the Helmholtz layer.

2. Kinetics at Metal Electrodes

To obtain concrete expressions for the current at a metallic electrode, it is necessary to carry out the integration with respect to the electronic states in the metal in expressions (3.3) and (3.4). Since in a metal all the states lying below the Fermi level are occupied, and all those lying above the Fermi level are empty, the integration in (3.3) must be performed between the limits ϵ_F and U_0, and that in (3.4) between 0 and ϵ_F. Calculation leads[42] to the following expression for the anodic current

$$i_a = \left(\frac{\pi e^2 kT}{\hbar^2 E_s}\right)^{1/2}\cdot \rho_f c_{z-1}(\delta)\, l\, |V|^2 \exp\left\{-\frac{\left(e\varphi(\delta) + kT\ln\frac{c_{z-1}}{c_z} + E_s - e\eta\right)^2}{4E_s kT}\right\}, \quad (3.14)$$

where $\varphi(\delta)$ is the potential in the solution at the point δ (in practice, the ψ_1-potential). A similar calculation gives i_c.

Eqn. (3.14) shows that the variation of $\ln i_a$ with η is not, in general, of the Tafel form. However, if $e\eta$ is small compared with E_S, the squared expression in brackets can be expanded and small terms of the second order can be ignored (the quantity $e\varphi'(\delta) + kT\ln\frac{c_{z-1}}{c_z}$ is usually much smaller than E_S). The expression for the total current then takes the Tafel form (provided that the potential jump $\varphi'(\delta)$ has its equilibrium value):

$$i = i_0(e^{\frac{e\eta}{2kT}} - e^{-\frac{e\eta}{2kT}}), \quad (3.15)$$

where the exchange current is equal to

$$i_0 = \left(\frac{\pi e^2 kT}{\hbar^2 E_s}\right)^{1/2}\rho_f l\,|V|^2\sqrt{c_{z-1}(\infty)\,c_z(\infty)}\,e^{-\frac{E_s}{4kT} - \frac{(2z-1)e\varphi'(\delta)}{2kT}} \quad (3.16)$$

In this case the transfer coefficient α, defined by the expression

$$\alpha = -\frac{kT}{e}\frac{d\ln i_c}{d\eta}, \quad (3.17)$$

equals 1/2.

Brønsted's rule. The Tafel formula is usually derived by invoking a semi-empirical rule due to Brønsted[31], according to which

$$E^{\neq}(\eta) - E^{\neq}(\eta = 0) = -\beta[\Delta J(\eta) - \Delta J(\eta = 0)]$$

where $E^{\neq}$ is the activation energy and ΔJ is the heat of the reaction (in our case ΔJ is the difference between the minima of the potential energy curves of the system in its initial and final states). This expression is the equivalent of Polanyi's rule[34], formulated for gas-phase reactions. In the theory discussed here, Brønsted's rule applies[44,47,49] for $e\eta < \sqrt{4E_S kT}$, the constant β having the value 1/2 for a metallic electrode. It must be noted, however, that Brønsted's rule is obeyed by our system only at low enough overvoltages. When the overvoltage is appreciable, the rule ceases to apply, because the current–voltage characteristic deviates from the Tafel relation.

It is interesting to compare these theoretical results with experimental data obtained relatively recently by Frumkin and his coworkers[63]. Those workers investigated the electrolytic reduction of anions at metallic electrodes, and observed departures from the Tafel relation. Of all the reactions investigated, only the reduction of $Fe(CN)_6^{3-}$ behaves as required by the theory, but the qualitative nature of the agreement is evident from Fig. 8. The theoretical curve is smoother than the experimental curve. The greatest discrepancy between the two curves occurs in the region of potentials where other effects can become appreciable (for example, ion-pair formation). The particular feature of this reaction is that the $Fe(CN)_6^{3-}$ ion is fairly large, whereas E_S is relatively small. Therefore, according to the theoretical predictions, deviations from Tafel's formula should set in at not very high overvoltages, as is indeed found to be the case in practice.

We must stress that the equilibrium potential does not appear in the expressions for the current which have been obtained: only departures from the equilibrium potential. In other words, the formulae for the current do not include quantities depending on the work function of the metal, and therefore the reaction rate in this sense is independent of the work function of the metal. Different electrodes are characterised by their density of states and by the exchange integral V rather than by their work function.

The expressions (3.14)–(3.16) for the current are derived for reactions proceeding non-adiabatically. The study of adiabatic electrode reactions involves a number of difficulties arising from the presence of a continuous spectrum of states in the solid. However, we may suggest (without as yet any real proof) that these formulae will be applicable to the adiabatic case with the usual substitution of V by V_α [see for example Eqn. (2.21)].

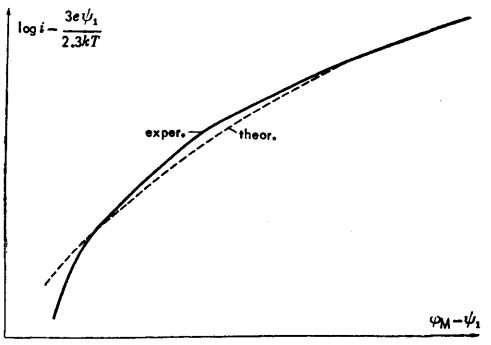


Fig. 8.

3. Kinetics at Semiconductor Electrodes

The basic physical mechanism of current flow at a semiconductor electrode is the same as for a metallic electrode. The most characteristic features of semiconductor electrodes are that the Fermi level in a semiconductor is situated in the forbidden gap, and that the filling of energy levels by electrons is a sensitive function of temperature and of the distribution of potential in the system. A consequence of the first characteristic is that the integration in (3.3) and (3.4) must be carried out over both the conduction and the valence band of the semiconductor. The resulting expressions will be called the electron current (i^e) and the hole current (i^p) respectively. From the second characteristic, it follows that in a semiconductor the variation of current with potential and with temperature will be determined not exclusively (or even mainly) by the effect of these parameters on the transition probability, but rather by their effect on the concentration of free carriers.

We can point out immediately that the procedure used to derive formulae (3.12) and (3.13) makes it obvious that the formulae are applicable to each of the components (electrons and holes) of the total current[44,49]. We shall therefore quote only the expressions for cathodic currents. The expressions for anodic currents are easily obtained by using the formulae given above.

Semiconductor with non-degenerate surface. We shall assume that the Fermi level does not extend into either band, i.e. that the following condition is satisfied (see Fig. 6):

$$\Delta_{e,p} - e|\varphi_{sc} - \varphi_c| > 4\,kT. \tag{3.18}$$

In this case the integration in (3.4) gives[47,49]

$$i_c^p = i_0^p \exp\left\{-\beta_p \frac{e(\eta_c - \eta_d)}{kT}\right\} \exp\left\{-\frac{ze\eta_d}{kT}\right\}; \tag{3.19}$$

$$i_c^e = i_0^e \exp\left\{-\beta_e \frac{e(\eta_c - \eta_d)}{kT}\right\} \exp\left\{-\frac{ze\eta_d}{kT}\right\} \exp\left\{-\frac{e(\eta - \eta_c)}{kT}\right\}. \tag{3.20}$$

where i_0^e and i_0^p are the electron and hole exchange currents,

$$\beta_p = \frac{1}{2} - \frac{\varepsilon_p^c - \varepsilon_F}{2E_s};\ \varepsilon_p^c - \varepsilon_F = -(\Delta_p - e(\varphi_{sc}^0 - \varphi_c^0)); \tag{3.21}$$

$$\beta_e = \frac{1}{2} - \frac{\varepsilon_e^c - \varepsilon_F}{2E_s};\ \varepsilon_e^c - \varepsilon_F = \Delta_e + e(\varphi_{sc}^0 - \varphi_c^0). \tag{3.22}$$

The remaining symbols are illustrated in Figs. 6 and 9.

The second terms in (3.19) and (3.20) give the potential dependence of the probability of electronic transition. Of course, this quantity depends only on the difference in potential between the electrode surface and the point where the ion undergoing discharge is situated. The third terms describe the potential dependence of the concentration of ions in the reaction region (ψ_1-effect). Lastly, the third term in (3.20) describes the potential variation of the concentration of electrons close to the semiconductor surface.

Brønsted's rule. It can be shown[44,47,49] that with semiconductor electrodes Brønsted's rule can only be

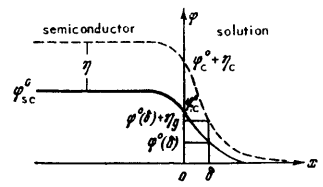


Fig. 9.

applied, generally speaking, to the electron and the hole current separately. The β coefficients are given by formulae (3.21) and (3.22), and are not usually the same. In a semiconductor with a non-degenerate surface, the inequalities $\beta_e \leqslant \frac{1}{2} \leqslant \beta_p$ are always satisfied. Only when E_S is large enough do we find $\beta_e = \beta_p = \frac{1}{2}$ (i.e. just as in the case of a metal electrode).

It is interesting to note that, in principle, the values $\beta_p \geqslant 1$ and $\beta_e \leqslant 0$ are possible. The cases of strict inequality correspond to the distribution of energy levels shown in Fig. 10). The cases of equality denote that the corresponding level is non-activated. These situations can evidently be realised in the discharge of large ions, for which the transpolarisation energy E_S is relatively small, and when the equilibrium bending of the bands is large. Let us examine in greater detail the expressions for the currents i^e and i^p. To simplify matters, we shall ignore the ψ_1-effect and assume that $\eta_g = 0$. The quantity η_k is determined by the properties of the semiconductor surface. However, if the concentration of surface states is large, we find[44,50] that $\eta_k \simeq \eta$. This is precisely the case of interest when the situation $\beta_p > 1$ and $\beta_e < 0$ occurs, because an unusual current–voltage relation is observed. Thus, for $\eta_k = \eta$, say, the expression for i^p takes the form

$$i^p = i_0^p \left\{ e^{\frac{e(1-\beta_p)\eta}{kT}} - e^{-\frac{e\beta_p\eta}{kT}} \right\}, \qquad (3.23)$$

and if $\beta_p > 1$ the current i^p initially increases with increase of η, but reaches a maximum and then begins to fall off. It should be noted, however, that a curve of this type, showing a maximum, can only be obtained if for any reason the electron current vanishes or is very small. In the opposite case the electron current can mask the effect, since it will usually show a normal potential variation (it is very unlikely that the inequalities $\beta_p > 1$ and $\beta_e < 0$ can both be satisfied at the same time). A similar effect can take place for $\beta_e < 0$. The possibility of a maximum in the electron or the hole current was envisaged in a qualitative argument by Gerischer[51]. However, Gerischer considers that this can occur only if the semiconductor surface is degenerate. He gives[51] only a qualitative discussion, and does not derive the β coefficients.

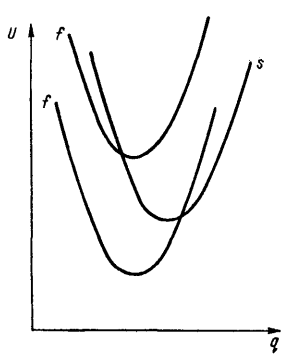


Fig. 10.

Transfer coefficients. The coefficient α, introduced by formula (3.17), is indistinguishable from β for a metallic electrode (in the absence of the ψ_1-effect). Such is not the case with a semiconductor. When the system comprises a semiconductor electrode, the following relations apply:

$$\alpha^e = 1 - (1 - \beta_e)\, d\eta_k/d\eta, \qquad (3.24)$$

$$\alpha^p = \beta_p\, d\eta_k/d\eta. \qquad (3.25)$$

In the absence of surface states, $d\eta_k/d\eta \ll 1$ and α^e and α^p are equal to 1 and 0 respectively[43,44]. Surface states can, on the one hand, affect the potential distribution in the system and thus influence the electron exchange between the solution and the bands of the semiconductor, and, on the other hand, they can themselves exchange electrons with the solution and thus contribute to the current. The former effect can make the transfer coefficients differ appreciably from 1 and 0, and be a function of the overvoltage, which should lead to departures from the Tafel relation[47,49]. The latter effect leads to a change in the nature of the current–potential relationship[47,49] (from electronic to hole current) as the surface states become gradually filled, if the concentration of surface states is high.

Exchange currents. The general expressions for the exchange currents are extremely cumbersome[44,47,49], and there is no simple relation, in general, between i_0^p and i_0^e. However, if the condition $|\Delta_p, e \pm e(\varphi_{sc} - \varphi_c)| \ll E_S$ is satisfied, the two exchange currents are related by the simple expression[47]

$$i_0^e = i_0^p \exp\left\{ -(1 + \Delta_0/E_s)\, \frac{e\,(\varphi_{sc}^0 - \varphi_c^0) - (\Delta_p - \Delta e)/2}{kT} \right\}, \qquad (3.26)$$

where Δ_0 is the half-width of the forbidden gap. This expression coincides with the formula given by Dewald[52]. It is evident from (3.26) that, in the absence of surface states, the ratio of exchange currents is independent of the impurity concentration in the semiconductor over a wide range. If a large density of surface states is present, the quantity $\varphi_{sc}^0 - \varphi_c^0$ is practically constant, and the ratio of currents becomes a function of impurity concentration.

Degenerate surface. If the Fermi level intersects either of the bands, the surface of the semiconductor assumes metallic properties. In this case the expression for the current is similar to the analogous expression for a metallic electrode, and the major part of the current is carried by electrons located close to the Fermi level[44,49].

In conclusion, we should stress the fact that the use of semiconductors as electrodes in the study of electron transfer processes between an electrode and a solution offers some definite advantages over metallic electrodes. The current at a semiconductor electrode is a function of semiconductor parameters such as the position of the Fermi level in the forbidden gap, the equilibrium bending of the bands, and the width of the forbidden gap. These parameters can be varied over wide limits, either by working with different semiconductors or by controlling the bending

of the bands for the same semiconductors. Therefore, a semiconductor offers very wide possibilities for research in this field. However, one serious disadvantage of semiconductors in this respect is that it is not always possible to determine unambiguously some of the semiconductor characteristics, and this can make the interpretation of experimental results very difficult.

4. Kinetics of Electrochemical Reactions in the Metal–Semiconducting Film–Electrolyte Solution System

In the study of various processes at metal surfaces one often has to deal with metals whose surface is covered with a natural oxide film. A considerable number of experimental and theoretical papers[53-59] have been devoted to oxide films on metal surfaces. The interest in studies of this type springs from the profound effect of oxide films on the course of many catalytic, corrosion, and electrochemical processes. Most contemporary workers consider that the semiconductor nature of oxide films must be taken into account when discussing the effect of these films on the above processes. Since we share this view, we have examined[46,49] a number of electrochemical processes in the metal–semiconducting film–electrolyte solution system.

In our discussion of the kinetics at a clean metallic electrode (III, 2) and at a clean semiconductor electrode (III, 3), we showed that there is an essential difference between these systems as regards their electrochemical behaviour. In a mixed metal–semiconductor–solution system we can expect to find properties both of the metallic and of the semiconductor electrode. Real oxide films are very complex structures, and are difficult to discuss theoretically. We have therefore considered[46,49] a highly idealised model, which, however, allows a qualitative study of some of the properties of these systems.

The film is treated as a uniform semiconductor to which the normal band theory can be applied. This limitation excludes very thin films from our discussion. An oxidation–reduction reaction of the type (*), satisfying all the conditions laid down at the beginning of this chapter, is proceeding at the surface of the film. It is assumed that the composition of the film does not change during the reaction, i.e. that the material of the film does not take part in the reaction.

A direct study of the kinetics of reaction (*) has shown[46] that the expressions obtained for a semiconductor electrode are quite general and can be modified for the present system by allowing for the difference between the energy diagram of this system (Fig. 11) and that of the semiconductor–solution system. The potential distribution in the two systems is also different, so that different quantitative results can be expected.

The expressions for the hole and the electron current are given, as before, by formulae (3.19) and (3.20), with the proviso that the values of $\epsilon_F - \epsilon_p^s$ and $\epsilon_e^c - \epsilon_F$ now take the form

$$\varepsilon_F - \varepsilon_p^c = \Delta_p - e(\varphi_M^0 - \varphi_c^0) + \chi_{sc}^0 - \chi_M^0, \qquad (3.27)$$

$$\varepsilon_e^c - \varepsilon_F = \Delta_e + e(\varphi_M^0 - \varphi_c^0) - \chi^0 + \chi_M^0, \qquad (3.28)$$

where χ_{sc}^0 and χ_M^0 are the work functions of the isolated semiconductor and metal respectively, and φ_c^0 is the equilibrium potential at the film–solution interface.

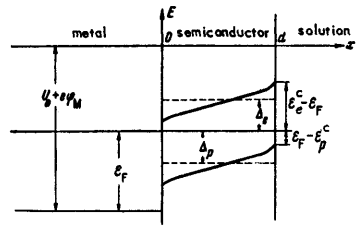


Fig. 11.

It follows from (3.27) and (3.28) that the properties of the system depend on the potential distribution (values of $\varphi_M^0 - \varphi_c^0$, η_c, η_g) and on the work function of the metal and the semiconductor (χ_M^0 and χ_{sc}^0). The whole of the above treatment is applicable to a uniform semiconductor under conditions of small departures from equilibrium in the semiconductor. The formulae can be generalised to include significant departures from equilibrium[48,49]. With weakly non-uniform semiconductors the general expressions remain valid, but the position of the bands at the interface with the solution with respect to the Fermi level ($\epsilon_{p,e}^s - \epsilon_F$) ceases to be defined by formulae (3.27) and (3.28), and becomes a function of the physical structure of the film.

The most significant feature of this system is that the parameters which determine the current–voltage characteristic (exchange currents and transfer coefficients) depend on the thickness of the film. In fact, the transfer coefficients [see Eqns. (3.21) and (3.22)] and the exchange currents depend on $\epsilon_{p,e}^s - \epsilon_F$. The latter quantity is a function of the potential distribution in the system and therefore of the thickness of the film. For a uniform semiconductor, it is possible to investigate in a general way the variation of the exchange currents with film thickness[46,49]. The expressions obtained[46,49] for the exchange currents show that the hole exchange current decreases and the electron exchange current increases with increase of φ_c^0 potential. Therefore, the problem becomes one of determining the variation of φ_c^0 with film thickness at a fixed value of φ_M^0. This relationship was investigated in Ref. 53, where the potential distribution in the film is examined under different conditions.

1. Consider the case of a uniform potential gradient in the film, with $\varphi_c^0 < \varphi_M^0$. As the thickness of the film decreases, φ_c^0 increases and approaches the value of φ_M^0, so that the hole exchange current decreases while the electron current increases. If $\varphi_c^0 > \varphi_M^0$, the reverse is true.

2. If the fall of potential in the film is not monotonic, the variation of φ_c^0 (and therefore also of i_0^p and of i_0^e) with film thickness may or may not be monotonic[49]. Not surprisingly, the behaviour of the total exchange current $i_0 = i_0^p + i_0^e$ will be very complex, depending on the relative values of the individual exchange currents. We must stress that all the above effects will be appreciable only with film thicknesses smaller than the Debye length in the semiconductor.

The variation of the exchange currents and of the transfer coefficients with film thickness becomes particularly simple if the fall of potential in the film is linear. To make the problem concrete, let $\varphi_M > \varphi_c$, and also

$|\epsilon_{p,e}^{c} - \epsilon_F| \ll 2\sqrt{E_S kT}$. The exchange currents and the transfer coefficients are then given by[46]

$$\ln i_0^{p,e} = (\text{const})^{p,e} \mp (\chi_{sc}^0 - \chi_M^0) \pm e\varphi_M^0 \frac{1}{1 + \frac{\delta}{d}\frac{\epsilon_{sc}}{\epsilon_H}}, \quad (3.29)$$

$$\alpha_p = \frac{1}{2}\frac{1}{1 + \frac{d}{\delta}\frac{\epsilon_H}{\epsilon_{sc}}}; \alpha_e = 1 - \alpha_p, \quad (3.30)$$

where d is the film thickness, δ is the thickness of the Helmholtz layer, ϵ_{sc} and ϵ_H are the dielectric constants of the semiconductor and of the Helmholtz layer. It is obvious that for large film thicknesses ($d \gg \delta\epsilon_{sc}/\epsilon_H$) α_p and α_e will approach 0 and 1 respectively, i.e. the film behaves as an ordinary semiconductor. As the thickness decreases, α_p increases and α_e decreases. In the limit of $d = 0$ we obtain $\alpha_{p,e} = 1/2$, i.e. the same result as for a metallic electrode. The condition of linear potential gradient in the film for small values of φ_M ($e\varphi_M \ll kT$) leads to $\varkappa d \ll 1$, where $\varkappa$ is the Debye screening length in the semiconductor. If φ_M is large, this condition becomes insufficient, and one must proceed with some care.

It follows from what has been said that the current–voltage characteristics of these systems are determined by the energy diagram of the system and by the potential distribution. Therefore, to obtain the variation of current with voltage for any system we must know the energy diagram and the potential distribution for the system. On the other hand, it is possible to form an opinion of the electronic structure of the film by comparing the theoretical relations derived from a definite model of the system with experimental results.

5. Stationary Photoeffect in the Semiconductor–Electrolyte Solution System

Methods relying on illumination of the electrode are widely used in studies of electrochemical processes at the semiconductor–solution interface. There are also theoretical papers devoted to the photoeffect at the semiconductor–solution interface. The influence of illumination on the potential of a semiconductor electrode has been examined[60,61] by a combination of a thermodynamic argument and of the Tafel formula. This method leads to a number of relationships containing experimentally determinable parameters. The stationary photoeffect, considered in the light of the above adiabatic theory of electron transfer reactions, is of interest in this context.

Consider a reaction of the type of (*), proceeding at a semiconductor electrode. In the absence of illumination, both the net current in the external circuit and the individual hole and electron currents must be equal to zero at equilibrium. When the semiconductor is illuminated, the latter requirement ceases to apply. The increase in electron and hole concentration in the semiconductor resulting from illumination produces an increase in the currents of both electron and hole transfer into the solution at a given potential. Therefore the potentials φ_p^0 and φ_e^0 at which the hole and the electron current respectively vanish are not equal to each other or to the equilibrium potential of the system φ_{sc}^0. When the semiconductor is illuminated, a steady state which we shall call a quasi-equilibrium state is established: in other words, we assume that the quasi-Fermi levels for electrons (Φ_e) and for holes (Φ_p) are constant over the entire space-charge region. Proceeding as in the derivation of formula (3.12), it is possible to obtain[45,47,49] the following expressions for the currents in a semiconductor with a non-degenerate surface not at equilibrium:

$$i^{e,p} = i_c^{e,p}\left[\exp\left\{\frac{e(\varphi - \varphi_{sc}^0) + \varepsilon_F - \Phi_{e,p}}{kT}\right\} - 1\right]. \quad (3.31)$$

It follows that the potentials φ_p^0 and φ_e^0 are related to the quasi-Fermi levels by the expressions

$$e\varphi_{p,e}^0 = e\varphi_{sc}^0 + \Phi_{p,e} - \varepsilon_F. \quad (3.32)$$

This result agrees with that obtained thermodynamically by Brattain and Garrett[60]. When there is no net current in the system (open circuit), a potential φ_{st} is set up for which (see Fig. 12).

$$i^p = -i^e. \quad (3.33)$$

Since the quasi-Fermi level for electrons lies above the Fermi level when the semiconductor is illuminated, we have $\varphi_e^0 > \varphi_{sc}^0$. For holes, $\varphi_p^0 < \varphi_{sc}^0$. The quasi-Fermi levels for electrons and holes are related by the expression[62]

$$\left[\exp\left(\frac{\varepsilon_F - \Phi_p}{kT}\right) - 1\right]\left[\exp\left(-\frac{\varepsilon_F - \Phi_e}{kT}\right) - 1\right]^{-1} = n_0/p_0, \quad (3.34)$$

where n_0 and p_0 are the electron and hole concentrations in the bulk of the semiconductor.

The solution of the electrostatic problem taking account of Eqns. (3.33) and (3.34) determines the deviation of the potential from its equilibrium value in terms of the positions of the quasi-Fermi levels for electrons and holes. To find the variation of the steady-state potential φ_{st} with the intensity of illumination S, we have to introduce an expression relating the position of the quasi-Fermi level to S. We shall assume that the semiconductor is illuminated with light in the fundamental absorption region and that the light is absorbed over a distance which is small compared with the diffusion length of minority carriers but not necessarily smaller than the Debye length: we assume, in other words, that the diffusion length of minority carriers is much greater than the Debye length. Taking an n-type semiconductor as a concrete example, we can write[62]

$$I - i_c^p = I_s^p\left[\exp\left(\frac{\varepsilon_F - \Phi_p}{kT}\right) - 1\right], \quad (3.35)$$

where I is the number of hole–electron pairs generated by the light in unit time and per cm² of semiconductor surface (a quantity proportional to S), $I_S^p = ep_0[D_p/L_p + v_S^p]$, D_p and L_p are the diffusion coefficient and diffusion length of holes, and v_S^p is the surface recombination velocity.

At small departures from equilibrium, solution of Eqn. (3.33) gives

$$\frac{e(\varphi_{st} - \varphi_{sc}^0)}{kT} \simeq \frac{I}{I_s^p}\left[\frac{p_0}{n_0} - \exp\left\{\left(1 + \frac{\Delta_0}{E_s}\right)\frac{e(\varphi_{sc}^0 - \varphi_c^0) - (\Delta_p - \Delta_e)/2}{kT}\right\}\right] \text{ for } i_0^p \ll I_s^p. \quad (3.36)$$

It is evident from Eqn. (3.36) that the photoeffect can have either sign, according to the relative values of $\varphi_{sc}^0 - \varphi_c^0$ and $\Delta_p - \Delta_e$. In particular, the photoeffect vanishes at $e(\varphi_{sc}^0 - \varphi_c^0) \simeq (\Delta_e - \Delta_p)/2$ (since $\Delta_0 \ll E_S$). If $e(\varphi_{sc}^0 - \varphi_c^0) < (\Delta_e - \Delta_p)/2$, the photoeffect is positive. If the opposite is true, the photoeffect is negative. Analogous expressions can be written for a p-type semiconductor.

If the potential drop in the solution is ignored, expressions for φ_{st} can be obtained also for the case of high illumination intensities[48,49] ($I \simeq I_S^p$). To simplify the problem, we shall assume that the condition $i^p \ll I_S^p$ holds true. Several different cases are possible.

1. $(i_0^p/i_0^e)^{1/2} \gg 1$.

$$e(\varphi_{st} - \varphi_{sc}^0)/kT \simeq -\ln(1 + I/I_s^p) = (\Phi_p - \varepsilon_F)/kT, \qquad (3.37)$$

i.e. the potential is shifted by the same amount as the quasi-Fermi level Φ_p.

2. $(i_0^p/i_0^e)^{1/2} \ll 1$.

$$e(\varphi_{st} - \varphi_{sc}^0)/kT \simeq \ln(1 + p_0 I/n_0 I_s^p) \simeq (\Phi_e - \varepsilon_F)/kT, \qquad (3.38)$$

i.e. the potential shifts by the same amount at Φ_e.

3. $i_0^p \simeq i_0^e$.

$$e(\varphi_{st} - \varphi_{sc}^0) \simeq [\Phi_e - \varepsilon_F + \Phi_p - \varepsilon_F]/2. \qquad (3.39)$$

These results are readily understood by reference to Fig. 12. The exchange currents determine the slope of the lines with respect to the φ axis. In case 1 the left-hand line is very steep and the right-hand line is shallow. Thus their intersection is close to φ_p^0. In the second case the opposite situation occurs and the straight lines intersect close to φ_e^0. In the third case the picture is symmetrical and the lines intersect in the middle.

Let us now consider, in a sense, the opposite problem. We shall examine the variation of the current in the system under illumination at a given potential. It is easy to show that, for small light intensities [$e(\varphi_{st} - \varphi_{sc}^0) \ll kT$] and small values of $\varphi - \varphi_{st}$, the current varies linearly with $\varphi - \varphi_{st}$, and the exchange current is equal to its dark value. For appreciable intensities of illumination ($I \simeq I_S^p$), the expression for the total current is of the form[48,49]

$$i = i_0^{eff}[\exp\{e(\varphi - \varphi_{st})/kT\} - \exp\{-e(\varphi - \varphi_{st})/kT\}]. \qquad (3.40)$$

This expression is correct only for small deviations of the potential from φ_{st}. The effective exchange current is

$$i_0^{eff} = \sqrt{i_0^p i_0^e}\,\exp[e(\Phi_e - \Phi_p)/2kT]. \qquad (3.41)$$

It is evident from (3.41) that at high light intensities the exchange current is greater than the dark exchange current. This is not surprising, since the effective exchange current is the current flowing in one direction in the absence of net current in the external circuit. Under illumination this current can be very significantly higher than the dark exchange current.

The stationary photoeffect shows a distinct similarity to other steady-state processes: two oxidation–reduction reactions occur simultaneously at the semiconductor electrode under conditions such that the concentrations of the oxidised and the reduced form of both the first and the second species remain constant in the bulk of the solution. When the semiconductor is illuminated, the potentials φ_p^0 and φ_e^0 (at which the electron and the hole currents vanish) take on different values because the quasi-Fermi levels for electrons and holes no longer coincide. As a result, a steady state in which the total current is zero but the individual hole and electron currents are finite is established in the system. In a similar way, in a two-reaction system the potentials φ_1^0 and φ_2^0 ($\varphi_1^0 > \varphi_2^0$, say) at which the currents of the first and the second reaction go through zero do not coincide. (Of course, this difference does not arise from the difference in quasi-Fermi levels in the semiconductor, but is due to differences in the concentration and in the nature of the ions.) Therefore, we can again observe a state of zero net current but finite currents of the first and the second reaction:

$$i_1 = -i_2.$$

The solution of this equation defines the stationary potential φ_{st} of the system. We shall not reproduce all the equations (see Refs. 48 and 49); they are similar to the corresponding equations for the stationary photoeffect. For small values of $\varphi_1^0 - \varphi_2^0$ and $\varphi - \varphi_{st}$, the variation of the current with $\varphi - \varphi_{st}$ is linear, and the exchange current equals the sum of the exchange currents of the first and the second reaction. If $\varphi_1^0 - \varphi_2^0$ is large, the expressions obtained are similar to (3.40) and (3.41) except for the replacement of Φ_e by φ_1^0, Φ_p by φ_2^0, and $\sqrt{i_0^p i_0^e}$ by $\sqrt{i_{20}^p i_{10}^e}$.

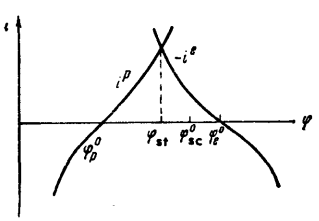


Fig. 12.

1. N.F. Mott and H.S.W. Massey, "Theory of Atomic Collisions" (Translated into Russian), Inostr. Lit., 1951.
2. A.S. Davydov, Zhur. Eksper. Teor. Fiz., 18, 913 (1948).
3. M.F. Deigen, Trudy Inst. Fiz. Akad. Nauk Ukrain. SSR, No. 5, 119 (1954).
4. S.I. Pekar, "Issledovaniya po Elektronnoi Teorii Kristallov" (Studies on the Electronic Theory of Crystals), Fizmatgiz, 1951.
5. V.G. Levich in "Advances in Electrochemistry and Electrochemical Engineering" (Edited by Delahay and Tobias), Vol. 5 (1965).
6. V.G. Levich and R.R. Dogonadze, Coll. Czech. Chem. Comm., 26, 193 (1961).
7. R.A. Marcus, "Modern Aspects of Electrochemistry", No. 3, Butterworth, London, 1964, p. 155.
8. E. Sacher and K.J. Laidler, "Modern Aspects of Electrochemistry", No. 3, Butterworth, London, 1964, p. 1.
9. T. Holstein, Ann. Physik, 8, 325 (1959).
10. H. Fröhlich, Adv. Phys., 3, 325 (1964).
11. R.A. Marcus, J. Chem. Phys., 24, 979 (1956).
12. V.G. Levich and R.R. Dogonadze, Dokl. Akad. Nauk SSSR, 124, 123 (1959).
13. V.G. Levich and R.R. Dogonadze, Dokl. Akad. Nauk SSSR, 133, 158 (1960).
14. R.R. Dogonadze, Candidate's Thesis, Moscow Physical Engineering Institute, Moscow, 1961.
15. R.R. Dogonadze, Dokl. Akad. Nauk SSSR, 142, 1108 (1962).
16. R.R. Dogonadze, Dokl. Akad. Nauk SSSR, 133, 1368 (1960).
17. R.A. Marcus, J. Chem. Phys., 24, 966 (1956); 26, 867 (1957).
18. L.D. Landau and E.M. Lifshits, "Statisticheskaya Fizika" (Statistical Physics), Fizmatgiz, Moscow, 1951.
19. G. Stein and A. Treinin, Trans. Faraday Soc., 55, 1091 (1959).
20. A.F. Ioffe, Fiz. Tverd. Tela, 1, 1 (1959).
21. R.R. Dogonadze and Yu.A. Chizmadzhev, Fiz. Tverd. Tela, 3, 3712 (1961).
22. R.R. Dogonadze, Yu.A. Chizmadzhev, and A.A. Chernenko, Fiz. Tverd. Tela, 3, 3720 (1961).

23. E.A.Nagaev, Fiz.Tverd.Tela, 4, 2201 (1962).
24. M.I.Klinger, Fiz.Tverd.Tela, 4, 3075, 3086 (1962).
25. I.G.Lang and Yu.A.Firsov, Zhur.Eksper.Teor.Fiz., 43, 1843 (1962).
26. L.Friedman, Phys.Rev., 135, A233 (1964).
27. M.Matheson, Radiation Res.Supplement, 4, 269 (1964).
28. E.M.Kosower, "Molecular Biochemistry" (Translated into Russian), Izd.Mir, Moscow, 1964.
29. I.Z.Fisher, "Statisticheskaya Teoriya Zhidkosti" (Statistical Theory of Liquids), Fizmatgiz, Moscow, 1961.
30. I.M.Lifshits, Uspekhi Fiz.Nauk, 83, 617 (1964).
31. A.N.Frumkin, V.S.Bagotskii, Z.A.Iofa, and B.N.Kabanov, "Kinetika Elektrodnykh Protsessov" (Kinetics of Electrode Processes), Izd.Moskov.Univ., Moscow, 1952.
32. Yu.A.Vdovin, V.G.Levich, and V.A.Myamlin, "Nekotorye Voprosy Teoreticheskoi Fiziki" (Some Problems in Theoretical Physics), Atomizdat, 1958.
33. V.A.Myamlin, Dokl.Akad.Nauk SSSR, 126, 1296 (1959).
34. S.Glasstone, K.J.Laidler, and H.Eyring, "The Theory of Rate Processes" (Translated into Russian), Inostr.Lit., Moscow, 1948.
35. J.E.B.Randles, Trans.Faraday Soc., 48, 828 (1952).
36. N.S.Hush, J.Chem.Phys., 28, 962 (1958).
37. H.Gerischer, Z.phys.Chem.(Frankfurt), 26, 223, 325 (1960); 27, 48 (1961).
38. R.A.Marcus, J.Chem.Phys., 24, 966, 979 (1956).
39. R.A.Marcus, in "Transactions of the Symposium on Electrode Processes" (Edited by E.Yaeger), McGraw-Hill, New York, 1960.
40. R.A.Marcus, Trans.Faraday Soc., 56, 21 (1960).
41. R.R.Dogonadze and Yu.A.Chizmadzhev, Dokl.Akad.Nauk SSSR, 144, 1077 (1962).
42. R.R.Dogonadze and Yu.A.Chizmadzhev, Dokl.Akad.Nauk SSSR, 145, 849 (1962).
43. R.R.Dogonadze and Yu.A.Chizmadzhev, Dokl.Akad.Nauk SSSR, 150, 333 (1963).
44. R.R.Dogonadze, A.M.Kuznetsov, and Yu.A.Chizmadzhev, Zhur.Fiz.Khim., 38, 1195 (1964) [Russ.J.Phys.Chem., 652 (1964)].
45. R.R.Dogonadze and A.M.Kuznetsov, Izv.Akad.Nauk SSSR, Ser.Khim., 1885 (1964).
46. R.R.Dogonadze and A.M.Kuznetsov, Izv.Akad.Nauk SSSR, Ser.Khim., 2140 (1964).
47. R.R.Dogonadze and A.M.Kuznetsov, Elektrokhimiya, 1, 742 (1965).
48. R.R.Dogonadze and A.M.Kuznetsov, Elektrokhimiya, 1, 1008 (1965).
49. A.M.Kuznetsov, Candidate's Thesis, Moscow Physical Engineering Institute, Moscow, 1965.
50. J.O'M.Bockris (Editor), "Modern Aspects of Electrochemistry" (Translated into Russian), Inostr.Lit., 1958.
51. H.Gerischer in "Advances in Electrochemistry and Electrochemical Engineering, Vol.1" (Edited by P.Delahay), Interscience, 1961.
52. J.Dewald in "Surface Chemistry of Metals and Semiconductors" (Edited by H.C.Gatos), New York, 1960.
53. F.F.Vol'kenshtein, V.S.Kuznetsov, and V.B.Sandomirskii, Kinetika i Kataliz, 3, 712 (1962).
54. J.N.Butler, J.Chem.Phys., 35, 636 (1961).
55. L.Young, "Anodic Oxide Films", Academic Press, London–New York, 1961.
56. V.I.Veselovskii, "Trudy Soveshchaniya po Elektrokhimii" (Proceedings of the Conference on Electrochemistry), Izd.Akad.Nauk SSSR, Moscow, 1953.
57. A.A.Yakovleva, T.I.Borisova, and V.I.Veselovskii, Zhur.Fiz.Khim., 36, 1426 (1962) [Russ.J.Phys.Chem., 763 (1962)].
58. J.Dewald, Bell.System.Techn.J., 39, 3 (1960).
59. I.L.Rozenfel'd and E.K.Oshe, Dokl.Akad.Nauk SSSR, 125, 139 (1959); "Trudy Vtorogo Vsesoyuznogo Soveshchaniya po Radiatsionnoi Khimii" (Proceedings of the Second All-Union Conference on Radiation Chemistry), 1962.
60. W.H.Brattain and C.G.B.Garrett, Bell System Techn.J., 34, 192 (1955).
61. R.M.Lazorenko-Manevich, Zhur.Fiz.Khim., 36, 2066 (1962) [Russ.J.Phys.Chem., 1110 (1962)].
62. C.G.B.Garrett and W.H.Brattain, Phys.Rev., 99, 376 (1955).
63. A.N.Frumkin, O.A.Petry, and N.V.Nikolaeva-Fedorovich, Electrochim.Acta, 8, 177 (1963).
64. O.A.Petrii, Candidate's Thesis, Institute of Electrochemistry of the Academy of Sciences of the USSR, Moscow, 1962.

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ELECTROCHEMICAL IMPLANTATION OF ALKALI METALS

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I. INTRODUCTION

The alkali metals are deposited on cathodes at potentials so negative that hydrogen evolution makes them inaccessible in aqueous solutions, even when the electrodes consist of metals with a high hydrogen overvoltage such as lead or mercury. The highest potentials attainable under ordinary experimental conditions are more positive than the equilibrium potentials of the alkali metals by about 1 V. However, if liquid mercury is used as cathode, the alkali metals can be discharged at not too negative potentials because the discharge potential is shifted towards more positive values. This phenomenon is well known, and has been used in industry for a long time and has been investigated by physical chemists for over a hundred years. The cause of this shift is the strong chemical interaction between the alkali metals and mercury, with formation of amalgams. Electrolysis of aqueous solutions has produced amalgams not only of the alkali and alkaline earth metals, but also of ammonium and of some organic cations such as tetramethylammonium [1,2].