THE THEORY OF ELECTRODE REACTIONS

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A striking peculiarity of electrode reactions is the fact that their rate may be described by means of the empirical law developed by Tafel, which relates the rate constant to the electrode potential thus:

$$K \sim \exp[-\alpha e(\varphi - \varphi_{\text{eq}})/kT] = \exp(-\alpha e\eta/kT)$$

where φ_{eq} is the equilibrium potential, η is the overpotential, and α a transfer coefficient. The Tafel Law describes the elementary act involving the transfer of a charge during the electrode reaction. It cannot be applied to reactions complicated by additional factors, such as those occurring in several stages, or affected by transport-limitations, or involving chemical reactions occurring in the bulk solution in association with electrode processes (kinetic and catalytic electrode processes). In general, the transfer coefficient varies only slowly with change in the overpotential η. For a number of reactions, particularly those involving discharge of hydrogen ions at the surface of many metals, $\alpha = 1/2$ for a wide range of variation in η. The general nature of these regularities indicates that the mechanism of charge transfer in many processes is one of general application.

The present paper is devoted to a consideration of a number of works on the theory of electrode reactions, which have been carried out with the object of elucidating the mechanism of these reactions, and deriving theoretically the rate constants of electrode processes.

In its most general form the rate of an electrode reaction characterized by current density i may be expressed in the form:

$$i = e\int C(x)\,W(x, \varepsilon)\,n(\varepsilon)\,\rho\,d\varepsilon\,dx, \tag{1}$$

where e is the charge transferred; C(x) is the concentration of reacting particles at a distance x from the electrode; and $n(\varepsilon)\rho$ is the concentration of electrons with energy ε in the metal. The probability W of charge transfer from particles to electrode (or the reverse) per unit time depends on the energy ε, the properties of the particles and of the solvent, and also on the distance x. Since the probability W as a function of x diminishes to zero at distances of atomic dimensions (the Bohr radius), while C(x) varies within quasi-macroscopic dimensions (the thickness of the double layer), it follows that $W(\varepsilon, x)C(x)$ will always possess a sharp maximum which determines the optimum distance for discharge x^*. This distance practically coincides with the geometrical plane representing the closest approach of the hydrated ion to the electrode. Accurate determination of x^* requires a knowledge of the function C(x), and therefore of the distribution of the field within the inner region of the double layer.

In the general case the rate constant may be written in the form:

$$K = \frac{i}{C(x^*)} \simeq e\int W(\varepsilon;\ x^*)\,\rho(\varepsilon)\,n(\varepsilon)\,d\varepsilon, \tag{2}$$

where the functional form of $W(\varepsilon, x^*)$ is determined exclusively by the properties of solvent and of the particles, which x^* represents a parameter which affects the numerical, but not the functional, expression $W(\varepsilon, x^*)$.

Hence, the mechanism of change transfer, represented by the form of $W(\varepsilon, x^*)$, is independent of the statistical distribution of the ions in the double layer.

Calculations indicate that the value of K is determined as a function of $\rho n(\varepsilon)$, which describes the properties of the electrode, and of $W(\varepsilon, x^*)$ which is determined by the properties of the particles before and after discharge, and by the properties of the solvent.

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Calculations indicate that the value of K is determined as a function of $\rho n(\varepsilon)$, which describes the properties of the electrode, and of $W(\varepsilon, x^*)$ which is determined by the properties of the particles before and after discharge, and by the properties of the solvent.

Earlier works on this subject took into account: 1) only the properties of the electron distribution in the metal $n(\varepsilon)$ [1]; 2) only the properties of the particles before and after discharge, the effect of the properties of the solvent and the part played by $n(\varepsilon)$ being completely ignored [2-4]; 3) the effect of the solvent on W in redox-systems in which the state of the particles before and after discharge was regarded as unchanged. No account was taken of the effect of $\rho n(\varepsilon)$, or of possible changes in the state of the particles before and after discharge [5].

The present work involves fundamentally the evaluation of K by means of the accurate form (1).

The transfer probability which forms a part of this may, in its general form, be described by an accurate quantum-mechanical expression which must, of course, include the case where transition occurs according to the laws of classical mechanisms:

$$W = \frac{2\pi}{\hbar} Av\, \Sigma \left| \langle \psi^f_{ee} \varphi^f_p \chi^f_s \,|\, V \,|\, \psi^i_{ee} \varphi^i_p \chi^i_s \rangle \right|^2, \tag{3}$$

where ψ_{es}, φ_p, and χ_s, represent the wave function of an electron, of heavy particles, and of solvent particles respectively in the initial (i) and final (f) states; while the symbols < > designate a quantum-mechanical, and Av a statistical, averaging.

Eq. (3) shows that the probability of transfer is determined by the overlap in the initial and final states of the wave functions both of the electrons on the one hand, and of heavy particles and solvent particles on the other, so involving all particles involved in the act of transfer.

To provide a basis for a specific calculation on the basis of equation (3), we have used the fact that electrons, being light particles, move much more quickly than the other particles. This fact allows us to use an adiabatic approximation in evaluating equation (3). Calculation shows that, using the adiabatic approximation, the overlap of the electronic wave functions enters into W in the form of a separate numerical factor L_{el}. Thus, the subsequent task resolves itself into an evaluation of the overlap integrals of the heavy particles and the solvent. In redox reactions, occurring without the breaking of chemical bonds, the wave functions for the heavy particles are unchanged, and the evaluation of W is reduced to a calculation of the values which determine the overlap of the wave functions of the solvent (taking thermal movement into account):

$$W = L_{el} Av \Sigma \left| \langle \chi_s{}^f | \chi_s{}^i \rangle \right|^2 = L_{el} \exp(-E_a / kT). \tag{4}$$

This expression was first evaluated by Markus within the framework of classical mechanics for reactions occurring in bulk, while in its general quantum form it has been evaluated in our own works [6]. Qualitatively, the two sets of results agreed with other. It has been found that the properties of the thermal movement of the solvent determined the transition probability. In such a case better agreement with experiment is attained using a continuous model for the medium. The physical mechanism of transfer, corresponding to equation (4), consists in this, that the position of the energy levels of the ion in the solvent depend on the polarization of the latter. Fluctuation in the latter polarization leads to the development of a reaction situation, when the energy levels of the electrons in the initial and final states coincide. In this situation a quantum (tunnel) transition of the electron into the final state takes place. The activation energy in this case which plays a part in the value of W is equal to the energy of reorganization of the solvent on charge transfer.

The difference between the general quantum and the classical calculation, apart from the obvious peculiarities of the former, consists basically of this, that in the quantum calculation: 1) it is possible to employ the difference between adiabatic and nonadiabatic reactions in evaluating the pre-exponential factor; 2) it is possible to show that the activation energy, which in the classical calculation depends only on the radius of the hydrated ions, actually also depends on the dielectric structure of the solvent, that is, on the correlation of the dipole moments of the medium.

Since the theory of redox-reactions gives good agreement with experiment, it may be suggested that a continuous model for the solvent is a good approximation capable of being employed in the consideration of more complex reactions.

For reactions in which transfer of heavy particles occurs it is necessary to choose a satisfactory model by which they can be depicted. When the heavy particles in question are protons, this selection reduces itself to the following: the proton in the initial state (the hydroxonium ion) and in the final state (H_{ads}) is in a strongly-bonded condition and undergoes low-temperature oscillations. On this assumption, the probability of transfer has been calculated approximately on the basis of an adiabatic theory of excitation, and also more accurately using the harmonic oscillation approximation. The two calculations lead to results which agree with each other. It appears that the quantum transfer of the proton is the most probable. Thus, the probability of proton transfer takes a form similar to (4):

$$W = \frac{2\pi}{\hbar} L_{\mathrm{el}} L_{\mathrm{pr}} Av \, \Sigma \, | \langle \chi_s^f | \chi_s^i \rangle |^2 = \mathrm{const} \cdot L_{\mathrm{el}} L_{\mathrm{pr}} \exp \left[- E_{\mathrm{a}} (\varepsilon) / kT \right]. \tag{5}$$

Here $E_a(\varepsilon)$ is the activation energy for the transition corresponding to a given initial energy of the electron in the metal, which in the final state binds the proton in the adsorbed condition to the electrode:

$$E_{\mathrm{a}} (\varepsilon) = \left[E_s + \Delta Q (\varepsilon, \eta) \right]^2 / 4E_s, \tag{6}$$

where $\Delta Q(\varepsilon, \eta)$ is the "heat" of the reaction corresponding to electron energy ε and a given value of the overpotential $\eta = -(\varphi - \varphi_{\mathrm{eq}})$:

$$\Delta Q = \Delta Q_{\mathrm{eq}} + e(\varphi - \varphi_{\mathrm{eq}}) - (\varepsilon - \varepsilon_F) = \Delta Q_{\mathrm{eq}} - e\eta - (\varepsilon - \varepsilon_F), \tag{7}$$

where ε_F is the Fermi energy, and ΔQ_{eq} is the equilibrium heat of reaction. The quantity $\Delta Q(\varepsilon)$ represents the difference between the minima of the terms in the initial and final states. It is clear that both $E_a(\varepsilon)$ and $\Delta Q(\varepsilon)$ are devoid of any macroscopic significance. Of course the energy difference of the proton in the initial and final states makes no contribution to $E_a(\varepsilon)$. This difference, and also the difference in the energy of an electron in the initial and final states, enters into the value of the equilibrium potential. Thus, the mechanism of the electron transfer and that of the proton transfer are similar. The reaction situation is arrived at as a result of fluctuations in the solvent. In arriving at the reaction situation transitions both of electrons and of protons are of a quantum nature.

Knowing the transition probability, it is possible to determine the rate constant, that is the quantity:

$$K = \mathrm{const} \cdot \int W(\varepsilon) n(\varepsilon) \, d\varepsilon = \mathrm{const} \cdot L_{\mathrm{el}} L_{\mathrm{pr}} \int n(\varepsilon) \exp \left\{ - \frac{[E_s + \Delta Q(\varepsilon, \eta)]^2}{4E_s kT} \right\} d\varepsilon. \tag{8}$$

Calculation has shown that replacement of a continuous Fermi distribution of electrons in the metal, $n(\varepsilon)$, by a model in which only electrons with Fermi energies ε_F participate (as was done, for example, by Markus) is unacceptable. Since, according to equation (7), $\Delta Q(\varepsilon, \eta)$ diminishes with increase in ε, and $n(\varepsilon)$ diminishes with increase in ε, the expression within the integral has a sharp maximum. Physically this indicates that the transition occurs in such a way that some energy level ε^* represents the major contribution to the current. This value of ε^* is determined by the condition:

$$d(Wn) / d\varepsilon = 0,$$

which leads to the equation:

$$n(\varepsilon) = 1 - \partial E_{\mathrm{a}} / \partial \Delta Q(\varepsilon) = 1 - \alpha(\varepsilon) \tag{9}$$

for the determination of ε^*. It is clear that ε^* is a function of the overpotential. The value of $\alpha(\varepsilon)$ represents an analog of the transfer coefficient envisaged by Brønsted. However, $\alpha(\varepsilon)$, like $E_a(\varepsilon)$ and $\Delta Q(\varepsilon)$, refer to a given electron energy, and have no direct macroscopic significance. The measurable quantity is the value of $\alpha(\varepsilon^*)$.

We may write approximately:

$$K = \mathrm{const} \cdot W(\varepsilon^*) n(\varepsilon^*) = \mathrm{const} \cdot \exp[-\alpha^*(\eta) e\eta / kT] \tag{10}$$

The presence of a spectrum of electrons in the metal leads to the appearance of three regions in the curve of K against η:

I. A region of low overpotential. Solution of equation (9) leads to a value $\varepsilon^* > \varepsilon_F$, that is, in the reaction involving the discharge of a hydrogen ion electrons from largely incompletely filled levels take part preferentially. In this case $n(\varepsilon^*) \ll 1$, and $\alpha(\varepsilon^*) \sim 1$. These transitions correspond to terms located in such a way that the transition should be of a barrierless nature.

II. Region of normal overpotential, in which the transition is mainly effected from levels close to the Fermi level $\varepsilon^* \sim \varepsilon_F$, $n(\varepsilon^*) \sim 1/2$, and $\alpha(\varepsilon^*) \sim 1/2$.

III. Region of high overpotentials in which the transition occurs mainly from filled levels $\varepsilon^* < \varepsilon_F$, $n(\varepsilon^*) \sim 1$, and $\alpha \sim 0$. This is a region of transitions without activation energy. It is clear that neglect of the Fermi spectra would lead to an omission of regions I and II.

The results obtained in relation to redox-systems and proton transfers, are not difficult to generalize to cases involving heavy ions within the framework of the harmonic approximation.

However, without a model calculation, it is clear that a number of relations are of a quite general significance, and relate in the same degree to a wide range of electrochemical reactions.

Actually, equations (2) and (7) are to a known extent independent of the model of the process, and are of a very general character. Experiments show that for reactions in which the slow stage is charge transfer, the rate constant takes the form of the Tafel formula:

$$K \sim \exp(-\alpha e\eta / kT).$$

Starting from general kinetic considerations, we may suppose that the probability of transition is described by the Arrhenius equation:

$$W \sim \exp[-E_a(\varepsilon) / kT].$$

In these cases too competition between the factor W and n in equation (2) still exists. The condition for the determination of the position of the maximum retains the form of equation (9). It follows from this that in the very general case regions I, II, and III should exist. If the charge transfer in an electrode reaction is associated with the removal of an electron from the Fermi level, then $\alpha(\varepsilon^*) \sim 1/2$ for any reactions of this type. This conclusion should be confirmed by model calculations.

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