THE KINETICS OF CERTAIN ELECTROCHEMICAL OXIDATION-REDUCTION REACTIONS OF METALS

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There have recently been carried out numerous experimental and theoretical investigations, devoted to a study of the kinetics of heterogeneous oxidation-reduction reactions. Since the general understanding of the expression "oxidation-reduction reactions" is very comprehensive, including systems different in those qualities which may involve differences in kinetic properties, it will be convenient to adopt the following classification.

1. Reactions proceeding with the formation or the decomposition of chemical bonds. Reactions belonging to this class include, in particular, those which proceed through an adsorption stage. An example is the ionization of hydrogen: $H_{ads} \rightarrow H^+$ (hydr.) + e, is the elementary act of this reaction, which consists not only of the transfer of an electron from the atoms of the metal and the corresponding migration of water from the solvent, but also of the disruption of a chemisorption bond between the metal and the hydrogen.

2. Reactions accompanied by deformation of bonds in the first coordination sphere of the ion. An example of this is the system Fe^{2+}/Fe^{3+}, in which, when the reaction $Fe^{3+} + e \rightarrow Fe^{2+}$ occurs, the bonds in the first hydration sphere are distorted.

3. Reactions in the course of which the internal coordination sphere may be regarded as undeformed. The example usually quoted is the system $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$.

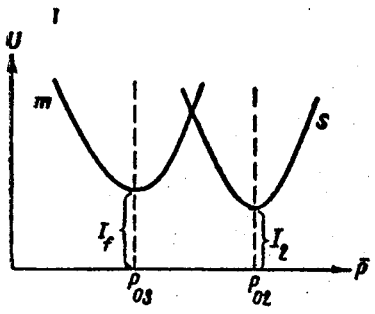

Fig. 1.

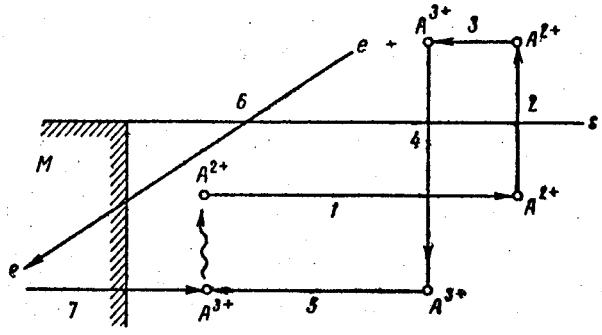

Fig. 2.

Reactions of types 1 and 2, are the most widespread and of the greatest interest. At the same time, they are the most difficult from the point of view of theoretical study. It is for this reason that, in the studies of Gerisher [1], where reactions of this type were studied, no concrete results were obtained which could be submitted to comparison with experiment. Reactions of type 3 are met quite rarely. Nevertheless such a case is of great interest, since it permits of quantitative investigation, the result of which may be to obtain a numerical expression for the kinetic parameter a. This case has been investigated by Marcus [2]. He employed the theory of absolute reaction rates, which is not strictly applicable to reactions involving electron transfer. If we postulate, as Marcus in this article does, an activation relationship of the reaction rate, the problem is reduced to a calculation of the free energy of activation, ΔF^*. To calculate ΔF^*, Marcus uses results obtained previously by himself [3] for homogeneous reactions, by the well known methods of thermodynamic nonequilibrium states. It is unfortunate that the der-

ivation of the formula for the case of electronic reactions has not been published in an accessible form. The thermodynamic method used by Marcus has, together with some advantages, this defect, that it does not permit of calculation of the exchange current; it is not possible within the framework of this method to calculate the difference between reactions on metals and semi-conductors.

We consider a reaction of the third type, proceeding according to the scheme: $A^{2+} \rightarrow A^{3+} + e$ (in a metal). In the resolution of the quantum-mechanical problem on the transfer of an electron from a solution to a metal, we are limited to a "one particle" approximation. That is, we shall consider the system: solvent, ion A^{3+}, metal, and an electron which may be present either in the ion A^{3+}, forming the ion A^{2+}, or in the metal. The remaining ions will be taken account of by means of the self-consistent field $\varphi(x)$.

In the fundamental theory, the following suppositions will be made:

1. The solvent, outside the first coordination sphere, may be considered as a continuous medium, characterized by a non-equilibrium polarization $\mathbf{P}(r, t)$.

2. The electron present in the ion has a powerful effect on the polarization of the medium, that is, its energy, when the ion is found in the solvent, is appreciably different from that when the ion exists in the gas phase. This eliminates the possibility of considering the electron transfer as an ordinary tunnel transition.

3. We accept the Frank-Condon principle, that is, the adiabatic approximation, according to which the energy of an electron is a unique function of the coordinates characterizing the solvents.

4. The double layer is weakened by the ions undergoing discharge. This limitation, as the calculation shows, is the least rigid.

In the adiabatic approximation, it is satisfactory to describe the system by means of potential energy curves (electronic terms). In Fig. 1, the left-hand term, m, corresponds to such a state of the system as would arise when the electron is present in the metal, while the solvent is characterized by the equilibirum polarization $\mathbf{P}_{03}(r)$. The right-hand term, s, corresponds to the electron in the ion and the equilibrium polarization $\mathbf{P}_{02}(r)$. Figure 1 is schematic in nature, since the axis of abscissae uses only one "coordinate" for the solvent, P, while in actual fact the medium is characterized by many coordinates, and the electronic term is also many dimensional. The axis of ordinates depicts the complete energy of the system, except for the kinetic energy of the solvent particles. According to the Frank-Condon principle, the transfer of an electron from the s state to the m state may only occur at the point where the terms intersect. (Within the scope of assumption 4, we are limited to the case in which the divergence of the terms is small). The probability of such a transfer, calculated by ourselves at an earlier stage [4], has, in a harmonic approximation, the form:

$$w_{sm} = \left(\frac{\pi}{\hbar^2 kT E_s}\right)^{1/2} |L|^2 \exp\left\{-\frac{[I_f - I_2 + E_s]^2}{4E_s kT}\right\}, \tag{1}$$

where I_f and I_2 represent the equilibrium energies in the initial and final states respectively; E_s is the energy of transpolarization, given by $\frac{c}{8\pi}\int (\mathbf{D}_{03} - \mathbf{D}_{02})^2\, dv$; D_{02} and D_{03} are the values of the induction field of the ions A^{2+} and A^{3+}; L is the exchange integral [4]; $c = \frac{1}{\varepsilon_0} - \frac{1}{\varepsilon_s}$, where ε_s is the static, and ε_0 the optical dielectric constant. We should note that rejection of condition 4 leads to an adiabatic transition, and would influence only the form of the pre-exponential factor. According to (1), the activation energy ΔE^* has the form:

$$\Delta E^* = \frac{[I_f - I_2 + E_s]^2}{4E_s}. \tag{2}$$

This formula may be explained by means of Fig. 1. Actually, if the formula of the theory of absolute reaction is used, $k \sim e^{-\Delta E^*/kT}$, where ΔE^* may be calculated, finding the point of intersection of the curves of s and m, which are parabolas in the harmonic approximation. It is easy to see that simple algebraic operations result in formula (2) for ΔE^*.

The quantity $I_f - I_2 = \Delta I$, which we have calculated earlier [4], has the form:

$$\Delta I = \varepsilon_f - e\varphi_m - U'_0 - \varepsilon_2 + \frac{\varepsilon_s - 1}{8\pi\varepsilon_s}\int (D_{02}^2 - D_{03}^2)\,dv + e\varphi(x), \tag{3}$$

where ε_f is some energy level in the metal; φ_m is the Volta-potential; U'_0 is the potential energy of an electron in the metal; ε_2 is the energy of the electron in the ion, if this is in the gas phase; $\varphi(x)$ is the potential of the self-consistent field of the double layer at the distance x from the electrode; ε_s is the static dielectric constant; $\frac{\varepsilon_s - 1}{8\pi\varepsilon_s}\int (D_{02}^2 - D_{03}^2)\,dv = \Delta\alpha$, where $\Delta\alpha$ is the difference in the hydration energy of the ions. This quantity may be omitted from ΔE^* by means of the following thermodynamic cycle, which makes possible a transition to a consideration of the equilibrium and the kinetics for small deviations from the latter.

Figure 2 shows all stages of the cycle, in equilibrium conditions the work in the stages 1, 5, and 7 is zero. The work in stage 2 and 4 is:

$$\bar{\mu}_2 = \psi_2 + kT \ln c_2 + 2e\varphi_s, \quad \bar{\mu}_3 = \psi_3 + kT \ln c_3 + 3e\varphi_s, \tag{4}$$

where $\Psi_2 = kT \ln N + \alpha_2$, $\Psi_3 = kT \ln N + \alpha_3$; N is the number of particles of the solvent; φ_s is the potential in the bulk of the solution; the potential at infinity in the gas phase is equal to zero. The signficance of α_2 and α_3 is easy to see from the equation for the complete thermodynamic potential of the solution: $\Phi = \Phi_0 + n\alpha + kT \ln n! + ze\varphi_s$, in which the number of ions n = 1: $\Phi = \Phi_0 + \alpha + ze\varphi_s$, where Φ_0 is the thermodynamic potential of the pure solvent. Thus $(\alpha + ze\varphi_s)$ is equal to the change in the thermodynamic potential of the system when one ion is introduced into the pure solvent. This quantity is called the real hydration energy. According to Born [5]

$$\alpha = -\frac{\varepsilon_s - 1}{8\pi\varepsilon_s}\int D^2 dv.$$

If we denote by α_m^e the work of emission of an electron from the metal, and equate to zero the work of the closed cycle, we obtain

$$-\bar{\mu}_2 - \varepsilon_2 + \bar{\mu}_3 - e\varphi_m^0 - \alpha_m^e = 0, \tag{5}$$

where φ_m^0 is the equilibrium Volta-potential of the metal. If we insert (4) in (5), we obtain an equation for the equilibrium Volta-potential of the metal:

$$e(\varphi_m^0 - \varphi_s) = \Delta\alpha - kT \ln (c_2/c_3) - \varepsilon_2 - U_0 + \varepsilon_F - e_m\varphi_0, \tag{6}$$

where ε_F is the Fermi level of the metal; and $_m\varphi_0$ is the potential jump at the metal-gas boundary. The difference between the Galvani-potentials at the metal-solution boundary is equal to:

$$_m\varphi_s = \varphi_m^0 - \varphi_s + {}_m\varphi_0 = \frac{1}{e}(\Delta\alpha - kT \ln (c_2/c_3) - \varepsilon_2 - U_0 + \varepsilon_F). \tag{7}$$

Inserting (7) in (3) we obtain

$$\Delta I = \Delta I^0 - e\eta; \quad \Delta I^0 = \varepsilon_f - \varepsilon_F + kT \ln [c_2(x)/c_3(x)], \tag{8}$$

where the overpotential $\eta = \varphi_m - \varphi_m^0$.

To calculate the exchange current, it is necessary to take into account the transitions of the electron at all unfilled places in the metal. Denoting by δ the distance at which the transitions basically take place, we obtain

$$i_0 = \left(\frac{\pi e^2}{\hbar^2 kT E_s}\right)^{1/2} \frac{df}{d\varepsilon_f}\, c_2(\delta)\,\delta\, |L|^2 \int_{\varepsilon_F}^{U_0} \exp\left\{\frac{-(\varepsilon_f - \varepsilon_F + kT \ln [c_2(\delta)/c_3(\delta)] + E_s)^2}{4E_s kT}\right\} d\varepsilon_f$$

or, finally

$$i_0 = \sqrt{\frac{\pi e^2}{\hbar^2}} \sqrt{\frac{kT}{E_s}}\, \delta \frac{df}{d\varepsilon_f} |L|^2 \sqrt{c_2(\infty)\, c_3(\infty)} \exp\left\{-\frac{10e\varphi'(\delta) + E_s}{4kT}\right\}, \tag{9}$$

where $\varphi'(\delta) = \varphi(\delta) - \varphi_s$; $df/d\varepsilon_f = \rho_f$ is the density of such positions in the metal. The exchange current depends on the nature of the metal through the quantities ρ_f, $|L|^2$ and $\varphi'(\delta)$. The dependence on $\varphi'(\delta)$ is equivalent to the known Ψ_1 effect. Similar calculations for the presence of overpotential lead to the formula

$$i = \sqrt{\frac{\pi e^2}{\hbar^2}} \sqrt{\frac{kT}{E_s}}\, \rho_f c_2(\delta)\, \delta |L|^2 \exp\left\{\frac{-(e\varphi'(\delta) + kT \ln(c_2/c_3) + E_s - e\eta)^2}{4E_s kT}\right\}. \tag{10}$$

Since $e\eta$ is always small in comparison with E_s(~10 ev), the activation energy may be set out in a series

$$\frac{(e\varphi'(\delta) + kT \ln(c_2/c_3) + E_s - e\eta)^2}{4E_s} \simeq \frac{E_s}{4} + \frac{e\varphi'(\delta)}{2} - \frac{e\eta}{2} + \frac{1}{2} kT \ln \frac{c_2}{c_3}$$

and the current may be written in the form

$$i = (\pi e^2/\hbar^2)^{1/2} \sqrt{kT/E_s}\, \rho_f \sqrt{c_2(\infty)\, c_3(\infty)}\, \delta |L|^2 e^{-E_s/4kT} e^{[e\eta - 5e\varphi'(\delta)]/2kT}. \tag{11}$$

If the potential jump outside the reaction region $\varphi'(\delta)$ is equal to the equilibrium value, equation (11) takes the simple form: $i = i_0 e^{e\eta/2kT}$.

From the results obtain, the following conclusions may be drawn:

1. The well known Tafel [6] formula for reactions of type 3 is approximate, and is obtained from the points in (10) by replacing it for small overpotentials by steps in $e\eta/E_s$.

2. The transition coefficient α in the region of application of equation (11) is strictly equal to 0.5.

3. Deviations from the Tafel formula may be increased through the terms omitted in (10): $\exp\left\{-\frac{e^2\eta^2}{4E_s kT}\right\}$ and $\exp\left\{-\frac{e\eta \ln[c_2(\delta)/c_3(\delta)]}{2E_s}\right\}$. For overpotentials of the order of 1 volt, the first member is estimated to be about 2. For lower overpotentials, if $\ln(c_2/c_3)$ is large, the second term may cause a deviation of α from the value of 0.5.

It is interesting to note that formula (11) is, with respect to its exponential part, in agreement with the results of Marcus, which were obtained by another means. Comparison of the theory set out above with experimental results is at present a matter of some difficulty. This is due to the fact that reliable experimental data on the coefficient α, are available only for such complicated reactions as the ionization of hydrogen, which are not considered in the present theory. However, systems of type 3 have not yet been investigated to such an extent that a basis is available for comparison with the present data, so as to confirm or refute the conclusions of the theory here set out.

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