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Kinetics of Some Electrochemical Oxidation-Reduction Reactions on Metals

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In recent years, numerous experimental and theoretical works have been carried out devoted to the study of the kinetics of heterogeneous oxidation-reduction reactions. Since the generally accepted concept of "oxidation-reduction reactions" is very broad and includes systems that differ in such features as may give rise to differences in kinetic properties, it is convenient to use the following classification.

1. **Reactions proceeding with the formation or rupture of chemical bonds.** This class should include, in particular, reactions that pass through an adsorption stage. An example is the ionization reaction of hydrogen
$H_{ads} \rightarrow H^{+}$ (hydr) $+e$, since the elementary act of the reaction consists not only in the transfer of an electron from the atom into the metal and the corresponding rehydration of the solvent, but also in the rupture of the chemisorption bond metal—hydrogen.
2. **Reactions accompanied by deformation of bonds in the first coordination sphere of the ion.** An example is the system Fe^{2+}/Fe^{3+}, in which, in the reaction
$Fe^{3+} + e \rightarrow Fe^{2+}$, the bonds in the first hydration shell are deformed.
3. **Reactions in the course of which the inner coordination sphere may be regarded as undeformed.** The system $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ is usually cited as an example.

Reactions of types 1 and 2, the most widespread and of the greatest interest, are at the same time the most difficult from the point of view of theoretical investigation. Precisely for this reason, in Gerischer' s works ([1]), where reactions of this type are considered, no concrete results permitting comparison with experiment were obtained. Reactions of type 3 occur extremely rarely. Nevertheless, this case is of considerable interest, since it permits a quantitative investigation, as a result of which a numerical expression may be obtained for the kinetic parameter α. Case 3 was considered by Marcus ([2]); he used the theory of absolute reaction rates, which, by his own admission, is not applicable to electron-transfer reactions. If, as is done in ([2]), one postulates an activation dependence of the reaction rate, the problem reduces to calculating the free energy of activation ΔF^*. To calculate ΔF^*, Marcus uses results obtained earlier by him ([3]) for homogeneous reactions by known methods of the thermodynamics of nonequilibrium states. Unfortunately, the derivation of the formulas for the case of electrode reactions has not been published in accessible print. The thermodynamic method used by Marcus, along with a number of merits, has the defect that it does not allow the exchange current to be calculated; within the framework of this method it is impossible to take into account differences between reactions on metals and on semiconductors.

We shall consider reactions of type 3 proceeding according to the scheme:
$A^{2+} \to A^{3+} + e$ (in the metal). In solving the quantum-mechanical problem of the transition of an electron from the solution into the metal, we shall restrict ourselves to the "one-particle" approximation, i.e., we shall consider the system: solvent, ion A^{3+}, metal

and the electron, which is located either on the ion A^{3+}, forming the ion A^{2+}, or in the metal. The remaining ions will be taken into account by means of a self-consistent field $\varphi(x)$.

The theory will be based on the following assumptions:

1. The solvent outside the first coordination sphere may be regarded as a continuous medium characterized by nonequilibrium polarization $\mathbf{P}(\mathbf{r}, t)$.
2. The electron located on the ion interacts strongly with the polar medium; i.e., its energy in the case where the ion is in the solvent differs substantially from its energy when the ion is placed in the gas phase. This makes it impossible to treat the electron transition as an ordinary tunneling transition.
3. The Franck–Condon principle is valid, i.e., the adiabatic approximation, according to which the energy of the electron is a single-valued function of the coordinates characterizing the solvent.
4. The double layer is depleted of discharging ions. This restriction, as follows from the calculation, is the least stringent.

Fig. 1

In the adiabatic approximation it is convenient to describe the system by means of potential-energy curves (electronic terms). In Fig. 1 the left term m corresponds to the state of the system in which the electron is in the metal and the solvent is characterized by the equilibrium polarization $\mathbf{P}_{03}(\mathbf{r})$. The right term s corresponds to the electron on the ion and to the equilibrium polarization $\mathbf{P}_{02}(\mathbf{r})$. Fig. 1 is schematic, since only one "coordinate" of the solvent, P, is plotted along the abscissa, whereas in reality the medium is characterized by many coordinates, and the electronic terms are multidimensional. Along the ordinate is plotted the total energy of the system, excluding the kinetic energy of the solvent particles. According to the Franck-Condon principle, the transition of the electron from state s to state m can occur only at the point of intersection of the terms. (Within assumption 4 we may restrict ourselves to the case in which the separation of the terms is small.) The probability of such a transition, calculated by us earlier ([4]), in the harmonic approximation has the form:

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

where I_f and I_2 are the equilibrium energies in the initial and final states, respectively; E_s is the repolarization energy, equal to

$$\frac{c}{8\pi}\int (\mathbf{D}_{03} - \mathbf{D}_{02})^2\, dv;$$

$\mathbf{D}_{02}$ and $\mathbf{D}_{03}$ are the values of the field induction 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. Let us note that abandoning restriction 4 leads to adiabatic transitions and affects 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 can be explained with the aid of Fig. 1. Indeed, if one uses the formula of the theory of absolute reaction rates $k \sim e^{-\Delta E^*/kT}$, then ΔE^* can be calculated by finding the point of intersection of the curves s and m, which in the harmonic approximation are parabolas. It is easy to see that simple algebraic operations lead to formula (2) for ΔE^*.

The quantity $I_f - I_2 = \Delta I$, which was calculated by us earlier ([4]), has the form:

$$\Delta I = \varepsilon_f - e\varphi_m - U_0' - \varepsilon_2 + \frac{\varepsilon_s - 1}{8\pi\varepsilon_s}\int \left(\mathbf{D}_{02}^2 - \mathbf{D}_{03}^2\right)\, dv + e\varphi(x), \tag{3}$$

where ε_f is a certain energy level in the metal; φ_m is the Volta potential of the metal; U_0' is the potential energy of an electron in the metal; ε_2 is the energy of an electron in an ion located in the gas phase; $\varphi(x)$ is the potential of the self-consistent field of the double layer at a distance x from the electrode; ε_s is the static dielectric constant;

$$\frac{\varepsilon_s - 1}{8\pi\varepsilon_s}\int \left(\mathbf{D}_{02}^2 - \mathbf{D}_{03}^2\right)\, dv = \Delta\alpha,$$

Fig. 2

Figure 1: Fig. 2

where $\Delta\alpha$ is the difference in the hydration energies of the ions. This quantity can be excluded from ΔE^* by means of the following thermodynamic cycle, which will make it possible to pass to the consideration of equilibrium and kinetics at small deviations from it.

All stages of the cycle are shown in Fig. 2. Under equilibrium conditions the work in stages 1, 5, and 7 is equal to zero. The work in stages 2 and 4 is equal to:

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

where $\psi_2 = kT \ln N + \alpha_2$, $\psi_3 = kT \ln N + \alpha_3$; N is the number of solvent particles; φ_s is the potential in the bulk of the solution; the potential at infinity in the gas phase is equal to zero. The meaning of α_2 and α_3 is easily clarified from the expression for the total thermodynamic potential of the solution,

$$\Phi = \Phi_0 + n\alpha + kT \ln n! + ze\varphi_s,$$

putting 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)],

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

Fig. 2

Denoting by α_m^e the work function of an electron from the metal and setting the work of the closed cycle equal to zero, we obtain

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

where φ_m^0 denotes the equilibrium Volta potential of the metal. Substituting (4) into (5), we obtain an expression for the equilibrium Volta potential of the metal

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

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

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

Substituting (7) into (3), we obtain

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

where the overvoltage is $\eta = \varphi_m - \varphi_m^0$.

To calculate the exchange current it is necessary to take into account electron transitions into all unfilled states of the metal. Denoting by δ the distance from which the transitions mainly occur, we obtain

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

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 states in the metal. The exchange current depends on the nature of the metal through ρ_f, $|L|^2$, and $\varphi'(\delta)$. The dependence on $\varphi'(\delta)$ is equivalent to the known ψ_1-effect. Analogous calculations in the presence of an overvoltage lead to the formula

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

Since $e\eta$ is always small in comparison with E_s (~ 10 eV), the activation energy can be expanded in a series

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

and the current written in the form

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

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

From the results obtained the following conclusions may be drawn:

1. The known Tafel formula (*) for reactions of type 3 is an approximate one and is obtained from the exact formula (10) as a result of expansion in powers of $e\eta/E_s$ at small overvoltages.

2. The transfer coefficient α in the range of applicability of (11) is strictly equal to 0.5.

3. Deviations from the Tafel formula may arise because of the terms omitted in (10):

$$\exp\left\{-\frac{e^2\eta^2}{4E_s kT}\right\} \quad \text{and} \quad \exp\left\{-\frac{e\eta\ln[c_2(\delta)/c_3(\delta)]}{2E_s}\right\}.$$

At overvoltages ~ 1, according to estimates, the first term is approximately 2. At smaller overvoltages, if $\ln(c_2/c_3)$ is large, the second term may cause deviations of α from 0.5.

It is interesting to note that formula (11), in its exponential part, agrees with Marcus' s results, which were obtained by another method. A comparison of the theory set forth above with experiment is as yet difficult. This is connected with the fact that reliable experimental data on the coefficients α are available for such complex reactions as hydrogen ionization, which are not considered in the present theory. Systems of type 3, however, have not yet been studied to such an extent that, on the basis of comparison with the available data, it would be possible to confirm or refute the conclusions of the proposed theory.

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Note: Figure translations are in progress. See original paper for figures.