DETERMINATION OF THE CHARGE OF A REACTING PARTICLE FROM THE DEPENDENCE OF THE KINETICS OF ELECTROLYTIC REDUCTION ON THE POTENTIAL AND THE CONCENTRATION OF THE SUPPORTING ELECTROLYTE

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Translated from Doklady Akademii Nauk SSSR, Vol. 147, No. 2,
pp. 418-421, November, 1962
Original article submitted June 21, 1962

In the assumption of equilibrium between the transition state of a reaction and the reacting particles in solution (the theory of retarded discharge), allowance for the influence of the double layer (d.l.) leads to the following expression for the rate constant k of a reduction reaction involving one electron [1]:

$$k = k_0 \exp \frac{F}{RT} [-\alpha(\varphi - \psi_1) - n_1\psi_1], \quad (1)$$

where n_1 is the charge of the reacting particle in the bulk of the solution, ψ_1 is the potential at a point corresponding to the position of the charge center of the transition state of the reaction, produced by the other charged particles, φ is the metal–electrolyte potential difference, and $0 < \alpha < 1$. To check Eq. (1) it is necessary to know the dependence of ψ_1 on φ and the concentration of the supporting electrolyte, and this involves certain assumptions regarding the structure of the d.l. The simplest assumption, according to which ψ_1 can be taken as equal to the mean value of the potential in the outer Helmholtz layer (Grahame's ψ_0), is not justified in all cases. The actual calculation of ψ_0 involves a number of approximations (for example, no allowance is made for the discrete character of the d.l. structure, the degree of covering of the surface, etc.). From the observed deviations from Eq. (1), it has been concluded that the charge in the surface differs from the charge in the bulk of the solution (formation of ion pairs), and also that other types of interaction are involved between the reacting anion and the cations of the d.l. [2]. We shall show that, in the case of a surface carrying a sufficiently high negative charge at least, it is possible to select experimental conditions which make it possible to check unambiguously the theory regarding the influence of the d.l. structure of the kinetics of electrode processes. We shall compare the course of the reaction involved in the attachment of an electron to a particle M^{n_1} in two systems I and II, which have identical values of $[M^{n_1}]$ and which satisfy the following conditions:

1. The adsorption of the anions of the supporting electrolyte Γ_A and the adsorption of the reacting particle are small compared with the adsorption of the cation Γ_C, i.e., $|\Gamma_A| \ll |\Gamma_C|$. From this condition, in the case where the solutions are dilute and the values of the density of the charge ε are not too small, it follows that at sufficiently short distances from the interface it is possible to neglect the concentration of anions compared with the concentration of cations.

2. On going from system I to system II, the relationship $\varphi - (RT/n_2F)\ln c = \text{const}$ (where n_2 is the charge, and c the concentration of the cations of the supporting electrolyte) applies. It is assumed that all the cations in the solution have charges of equal magnitude. From the fundamental electrocapillarity equation in the case of dilute solutions, it follows that*

$$d\sigma = -\varepsilon d\varphi - RT\Gamma_A d\ln c - RT\Gamma_K d\ln c \quad (2)$$

(σ is the metal–solution boundary tension). Taking account of condition 1 and the electrical-neutrality condition, which in our case reduces to $\varepsilon = -n_2\Gamma_C F$, we obtain

*For nonideal solutions, the concentrations should be replaced by the activities $a_\pm$.

$$\left(\frac{\partial \varepsilon}{\partial \ln c}\right)_{\varphi} = -\frac{RT}{n_2 F}\left(\frac{\partial \varepsilon}{\partial \varphi}\right)_{\ln c}, \qquad \varepsilon = f\left(\varphi - \frac{RT}{n_2 F}\ln c\right). \tag{3}$$

which, combined with condition 2, leads to ε = const. The invariant nature of ε corresponds also to invariant nature in the potential at sufficiently short distances from the surface, at which condition 1 is satisfied.

In actual fact, if we assume arbitrarily that the potential in the metal in both systems is equal to zero and if we write the expressions for the electrochemical potentials of the cations $\mu_C = \mu_C^0 - \varphi n_2 F + RT \ln c$ at an infinitely great distance from the interface, we reach the conclusion that the values of μ_C are equal if condition 2 is observed. Since in accordance with condition 1 only cations take part in the equilibrium close to the interface, the fact that the values of μ_C are equal means that the composition and structure of the surface layer remain unchanged on going from system I to system II.* This means that the value of $\varphi - \psi_x$ is invariant on going from system I to system II and thus leads to the relationship

$$\psi_x = \text{const} + \frac{RT}{n_2 F}\ln c, \tag{4}$$

where ψ_x is the potential at a distance x from the interface (here and subsequently, the potential is measured from a point in the bulk of the solution). Thus, the study of the kinetics of processes in systems for which condition 2 applies makes it possible to determine the influence, on the rate of the process, of the potential difference between the point at which the reacting particle is situated in the surface layer, and the bulk of the solution, so long as the other conditions under which the reaction takes place remain strictly constant. When the bulk concentration of the reacting particle remains constant, its concentration close to the surface of the electrode (at distances at which condition 1 applies) is proportional to $\exp[-n_1 \psi_x F/RT]$. Thus the rate of the process is proportional to c^{-n_1/n_2} or

$$(\partial \ln i / \partial \ln c)_{\varphi - \frac{RT}{n_2 F}\ln c} = -n_1/n_2. \tag{5}$$

This conclusion is independent of the assumptions on which the theory of the diffusion d. l. is based, and remains applicable at any degree of covering of the surface, and also in the presence of specific adsorption of cations and reacting particles, so long as condition 1 is satisfied.** The result is also independent of the nature of the interaction between the reacting particle and the cations of the d.l., and, in particular, of the formation of ion pairs in the d.l. The study of the dependence of the kinetics of the process on c cannot therefore serve as a diagnostic criterion for determining the nature of the charge on a reacting particle in the d.l. Examination of the equilibrium between ion pairs in the bulk and in the surface leads to the same result [4].

Comparison of the kinetics in systems for which the condition $\varphi - (RT/n_2F) \ln c$ = const applies was first used to deduce rigorously that hydrogen overvoltage is independent of concentration in acid solutions containing no indifferent electrolyte [5]. Equations of type (5) were also used by Gierst [2] to examine the mechanism of reduction of various cations and anions; his treatment had a different basis from ours, however, and this partly explains the difference between his interpretation of the data and ours. In the case of the reduction of $S_2O_8^{2-}$ on a supporting electrolyte of NaF, there is also a difference between the experimental data obtained by Gierst and those which we have obtained. The above comparison makes it possible to estimate the upper limit of x. For this, however, it is necessary to resort to a

*The conclusion that the structure and composition of the surface layer remain unchanged must be made more precise. Beyond the limits of the layer in which the concentrations of the anions can be neglected, the solution contains anions. Since the coulombic forces are long-range forces, the presence of these anions may have an influence on the structure of the d.l., even at intermediate distances, at which their concentration is still small.

**Instead of considering the equilibrium between a reacting particle in the bulk of the solution and in the surface layer, we can examine the equilibrium with a particle in the transition state of the reaction; this leads to the same result, as has been shown for the case of the discharge of the H_3O^+ ion [3]. In fact, if we regard the transition state as a state in which a fraction α of the positive charge is neutralized by an electron, the probability of the transition state is proportional to $\exp\left[-\frac{n_1\psi_x F}{RT} - \frac{\alpha(\varphi - \psi_x)F}{RT}\right]$, and this leads to the same result, since $\varphi - \psi_x$ = const.

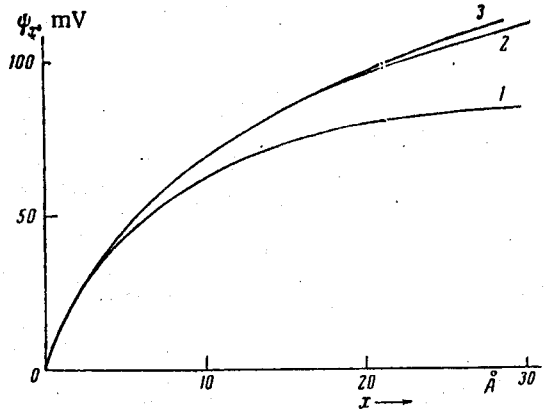

Fig. 1. Distribution of potential in the diffusion layer, measured relative to the potential at the boundary of the dense and diffuse regions of the double layer, for solutions of a 1–1-valent electrolyte at concentrations of: 1) 10^{-1}; 2) 10^{-2}; 3) 10^{-3} N and $\varepsilon = -10\ \mu C/cm^2$.

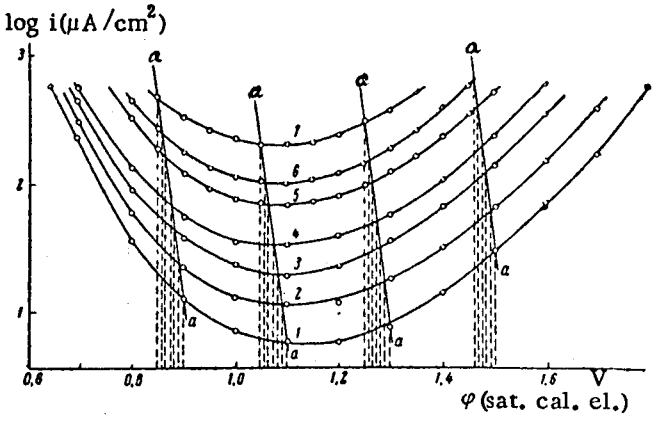

Fig. 2. Relationship between the rate of reduction of 10^{-3} N $Na_2S_2O_8$ and potential in the presence of NaF at concentrations of: 1) 3×10^{-3}; 2) 5×10^{-3}; 3) 7×10^{-3}; 4) 10^{-2}; 5) 1.5×10^{-2}; 6) 2×10^{-2}; 7) 3×10^{-2} N.

definite picture of diffuse d.l. structure. Comparison of the change in potential in the diffuse layer in Fig. 1, calculated from Gouy's theory, shows that the quantity $\psi_x - (RT/n_2F) \cdot \ln \underline{c}$ ceases to be invariant, on going from 10^{-3} to 10^{-2} N solutions, at distances more than 15 A from the outer Helmholtz plane, and, on going from 10^{-2} to 10^{-1} N solutions, at distances > 5 A. It should be noted that when equilibrium is not observed between the transition state of the reaction and the reacting particles in the solution, analysis of the relationship between $\ln \underline{i}$ and $\ln \underline{c}$ also leads to the charge of particle in the bulk of the solution.*

Thus the possibility of carrying out a rigorous determination of the value of n_1 depends only on the extent to which condition 1 is observed. The latter can be checked independently of kinetic measurements, from the ε, φ-curves or from the displacement of the descending branch of the electrocapillary curve with change in $\underline{c}$. As follows from A. N. Frumkin's measurements [7], and also from the ε,φ-curves calculated from the values of the differential capacity in solutions of LiCl, NaF, KCl, and CsCl of different concentrations, according to [8] and [9], condition 1 is observed for the solutions studied, within the limits of accuracy of the measurements.

This method of calculating n_1 can also be used in the case where the anion R^{n_1} being reduced is obtained as a result of a reaction $A^n \rightleftharpoons R^{n_1} \pm pX^m$ ($n = n_1 \pm mp$) preceding the discharge. If the rate of the process is determined by the retarded discharge of R^{n_1}, with equilibrium observed between the bulk of the solution and the surface layer, and if the supporting electrolyte has no influence on the ratio $[A^n]:[R^{n_1}]$, analysis of the relationship between $\ln \underline{i}$ and $\ln \underline{c}$ leads to the charge of R^{n_1}. If the added electrolyte contains ions capable of influencing the chemical equilibrium, it is necessary to make allowance for the fact that the bulk concentration of R^{n_1} does not remain constant. When R^{n_1} and A^n undergo reduction immediately, the shape of the curve with coordinates $\ln i - \ln c$ should depend on the ratio $[A^n]:[R^{n_1}]$, φ, and $\underline{c}$, and also on the change in the ratio $[A^n]:[R^{n_1}]$, if the added electrolyte contains X^m. The part played by the more highly charged anions in the discharge process should decrease with decrease in $\underline{c}$ and increase in $-\varphi$, in accordance with the related increase in $-\psi_1$. If the rate of the process is determined by the retarded attainment of equilibrium according to the above reaction and the thickness of the reaction layer is small compared with the thickness of the d.l., we reach the conclusion, taking account of the Boltzmann distribution for A^n and X^m present in equi-

*In actual fact, according to Levich's theory [6], the rate constant for the reduction of an anion on a supporting electrolyte consisting of a 1-1-valent electrolyte is proportional to $\lambda^{-1} \exp(|n_1| - \frac{1}{2}) F\psi_1/RT$, where λ is the Debye length. Using (4) and making allowance for the fact that λ is inversely proportional to the value of $\sqrt{c}$, we obtain the relationship [6]

$$\left(\frac{\partial \ln i}{\partial \ln c}\right)_{\psi - \frac{RT}{n_2 F} \ln c} = -\frac{n_1}{n_2}.$$

librium in the volume of the solution, that the proposed method again gives the charge of R^{n_1}. Thus while making it possible to reach conclusions regarding the value of n_1, consideration of the relationship between ln $\underline{i}$ and ln $\underline{c}$ does not answer the question of whether the rate of the process is determined by the chemical reaction preceding the discharge in the d.l. or by retarded discharge.

Examination of relationship (5) for the reduction of H_3O^+ on mercury from the data in [10, 11] leads to values of n_1 close to 1. Calculation of n_1 for the reduction of $Fe(CN)_6^{3-}$ from the data in [4] gives −2.7 for a supporting electrolyte of LiCl and −3.0 for a supporting electrolyte of KCl or CsCl. We have measured the polarization curves for the reduction of 10^{-3} N $Na_2S_2O_8$, $K_2S_2O_8$, and $Cs_2S_2O_8$ at a dropping mercury electrode on supporting electrolytes of different concentrations, containing respectively NaF and NaCl (3×10^{-3}-3×10^{-2} N), KCl (2×10^{-3}-10^{-2} N), and CsCl (5×10^{-4}-5×10^{-3} N), and also in a solution of 10^{-3} N $Na_2S_2O_8$ containing different concentrations of LiCl + NaCl (10^{-2}-7×10^{-2} N), the ratio $[Li^+]:[Na^+]$ being kept equal to 10:1. The curves in the solutions with added NaF and NaCl practically coincided at potentials more negative than that of the zero charge point. After introducing a correction for concentration polarization according to the Meiman–Bagotskii theory [4], we calculated n_1 as shown in Fig. 2 (the lines aa connect points corresponding to the condition $\varphi - (RT/n_2F) \ln a_{\pm} = \text{const}$). The calculated mean values of n_1 for different values of $-\varepsilon$ are equal to −1.78 on a supporting electrolyte of LiCl + NaCl, −1.85 on a supporting electrolyte of NaF, −1.90 on a supporting electrolyte of KCl, and −1.93 on a supporting electrolyte of CsCl, and are closer to $n_1 = -2$, the higher the value of $-\varepsilon$. Gierst's conclusion [2] regarding the different charge of a reacting particle for the reduction of $S_2O_8^{2-}$ at potentials on the ascending and descending branches of the curve is not confirmed. The lower values of n_1 obtained on a supporting electrolyte of LiCl can apparently be attributed to the fact that in this case, because of the lower rate of the process in this supporting electrolyte, higher concentrations of additives were used, so that condition 1 is satisfied to a smaller extent.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
