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![Fig. 1](image)

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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KINETICS OF THE IONIZATION OF MOLECULAR CHLORINE

We have investigated the kinetics of the process of electroreduction of chlorine on a rotating platinum disk electrode. The electrode consisted of a platinum wire fastened into a brass rod and sealed into glass; after the end of the cylinder thus obtained was ground off, a disk-shaped surface of the wire was exposed. The surface of the electrode was 0.78 mm^2. Chlorine was obtained by electrolysis of 15% HCl and was washed by passing it through the solution under investigation; a platinum–rhodium wire served as the anode in the electrolyzer. Before use, the electrode under investigation was activated by repeated changes of potentials from $+1.8$ to -0.1 V vs. the normal hydrogen electrode in 0.05 N HCl. Before each point of the polarization curve was taken, the electrode was subjected to cathodic polarization to the potential of hydrogen evolution for 3 sec. Then the electrode was set to a potential value that was kept constant for 15 sec., after which the current was recorded. This procedure was necessitated by the fact that the current at a given potential did not remain constant with time, but gradually decreased because of passivation of the electrode. The overvoltage of the chlorine-reduction reaction η_k was determined relative to a platinum electrode in the same solution, used as an equilibrium chlorine electrode at atmospheric pressure of chlorine.

Fig. 1. Polarization curves for the ionization and evolution of chlorine from a solution of 0.023 N HCl+0.6 N HClO_4. $m = 1500$ rpm. $P_{\text{Cl2}} = 1$ atm. η_k is the overvoltage of the cathodic process of chlorine ionization; η_a is the overvoltage of the anodic process of discharge of Cl ions.

It was found that at not very high overvoltages the current of chlorine ionization depends on whether the voltage is changed from more anodic potentials to more cathodic ones or in the reverse direction. In this case, if one proceeds from more anodic potentials to more cathodic ones, the curve lies lower than the curve recorded in the reverse run, but at a sufficiently high overvoltage these two curves merge (Fig. 1). Evidently, at a sufficiently high cathodic overvoltage the reaction, even in the case of a less active electrode, is accelerated to such an extent that diffusion of chlorine to the electrode surface becomes the limiting factor. In addition, when a sufficiently high cathodic overvoltage is reached, adsorbed oxygen is removed from the electrode surface; this oxygen is the cause of the lowered activity of platinum, which facilitates the attainment of the limiting value of the diffusion current.

The magnitude of the limiting current of the chlorine-ionization reaction, attainable at large η_k, in accordance with the equation of V. G. Levich (1), is proportional to

$\sqrt{m}$, where m is the number of revolutions per second. However, at not very high overvoltages, for example at $\eta_k = 40$ mV, the points expressing the value of the current density i no longer lie on a straight line passing through the origin (Fig. 2). Under these conditions, as was shown in (2), by extrapolating the dependence of $1/i$ on $1/\sqrt{m}$ to an infinite value of m, one can find the value of the kinetic current i_∞, expressing the reaction rate when the concentration of the reacting substance is unchanged by the passage of current (segment AC in Fig. 2). As was shown in the same work, from the value of the ratio AB/BC it is possible to draw a conclusion about the order of the electrode reaction; here $BC = i_{m_0}$ is the current value at $m = m_0$, i.e., at the value of m at which the limiting diffusion current i_d is made equal to i_∞. The value of i_d at any m can be found by drawing a tangent to the curve $i, \sqrt{m}$ at the origin of coordinates.

Fig. 2. Dependence of the chlorine ionization current density on $\sqrt{m}$ at $\eta_k = 40$ mV. Composition of the solution: $0.1\,N$ HCl + $1.9\,N$ H_2SO_4.

From the relation $\frac{AB}{BC} = \frac{i_\infty - i_{m_0}}{i_{m_0}}$, denoting AB/BC by x, it follows:

$$x = \frac{C^p - C_s^p}{C_s^p}, \tag{1}$$

where p is the order of the reaction, C is the concentration in the bulk of the solution, and C_s is the concentration at the electrode surface during passage of current at $m = m_0$.

From (1) it follows:

$$p = \frac{\lg(x+1)}{\lg \dfrac{C}{C_s}}. \tag{2}$$

According to the equations of diffusion kinetics,

$$\frac{C}{C_s} = \frac{i_d}{i_d - i_{m_0}} = \frac{i_\infty}{i_\infty - i_{m_0}} = \frac{AC}{AB} = 1 + \frac{1}{x}. \tag{3}$$

From (2) and (3) it follows:

$$p = \frac{\lg(x+1)}{\lg(x+1) - \lg x}. \tag{4}$$

Fig. 3. Dependence of the logarithm of the chlorine ionization current on the overvoltage η_k at different values of φ_r.
1—$\varphi_r = 1.073$; 2—$\varphi_r = 1.087$ V; 3—$\varphi_r = 1.102$ V; 4—$\varphi_r = 1.115$ V; 5—$\varphi_r = 1.141$ V (potentials relative to the normal calomel electrode, without introducing a correction for the diffusion potential). Background: $2.2\,N$ $\mathrm{HClO_4}$.

The derivation presented is valid only under the assumption that at $m \gg m_0$ the rate of the reverse reaction can be neglected in comparison with the rate of the forward one, and that at small m, when the polarization has a purely concentration character, the concentration established at a definite polarization at the electrode surface is small in comparison with the initial one. These assumptions can be realized only if η_k is not too small. As is seen from Fig. 2, for the case of the chlorine ionization reaction the ratio

$x = AB/BC$ is close to unity; consequently, according to equation (4), the ionization reaction of chlorine is a first-order reaction with respect to chlorine.

The first order of the reaction with respect to chlorine was also confirmed by determining the dependence of the cathodic current i_∞ on the chlorine concentration at constant potential.

The electrode process of chlorine ionization can be decomposed into successive stages, for example, as follows:

$$\mathrm{Cl_2} \rightleftharpoons 2\mathrm{Cl_{ads}} \tag{a}$$

$$2\mathrm{Cl_{ads}} + 2e \rightleftharpoons 2\mathrm{Cl^-} \tag{b}$$

If the first stage is slow and the second reversible, then for the process of chlorine ionization, under the assumption of uniformity and low coverage of the electrode surface by chlorine, an equation should be applicable analogous to the equation derived under similar assumptions for the process of hydrogen ionization:

$$\eta_k = -\frac{RT}{2F} \ln\left(1 - \frac{i}{i_0}\right). \tag{5}$$

It follows from (5) that the value of i cannot exceed the value of the exchange current at stage (a), i_0; consequently, there must exist a limiting ionization current, the magnitude of which is determined by the rate of dissociation of chlorine molecules. In addition, a linear dependence between the overvoltage and the logarithm of the cathodic current is not obtained.

However, if the overvoltage values are plotted on the ordinate axis, and on the abscissa axis the logarithms of the cathodic current obtained by extrapolating the experimental data to $m = \infty$, i.e., corresponding to an unchanged chlorine concentration in the solution, then between $\lg i$ and η_k, for $\eta_k > 50$ mV, a linear dependence is observed with a slope coefficient of 85 mV, which can be checked up to $\eta_k = 150$ mV.

It follows from (5) that the density of the cathodic current at a given overvoltage should not depend on the concentration of chloride ions $[\mathrm{Cl}^-]$, since the exchange current i_0 is completely determined by the concentration of chlorine. If the equilibrium potential of the electrode is changed by changing $[\mathrm{Cl}^-]$ at constant chlorine concentration, then all points expressing current densities at a definite overvoltage and different values of $[\mathrm{Cl}^-]$ should coincide. As is seen from Fig. 3, experiment does not confirm this conclusion, which follows from the assumption that the first stage is slow and, what is especially important, does not depend on additional assumptions about the state of the electrode surface.

If one assumes that the limiting stage is the process of transition of adsorbed chlorine atoms into chloride ions, while stage (a) is reversible, then, according to the theory of slow discharge, for the cathodic process at sufficiently high values of η_k and constant chlorine concentration the equation should be valid:

$$\varphi = \text{const} - \frac{RT}{\alpha F} \ln i, \tag{6}$$

where φ is the electrode potential. Taking into account that $\eta_k = \varphi_r - \varphi$, where φ_r is the equilibrium potential of the electrode, we obtain:

$$\eta_k = \text{const} + \varphi_r + \frac{RT}{\alpha F} \ln i. \tag{7}$$

It follows from (6) and (7) that, if the second assumption is correct, there must be a linear dependence between the logarithm of the current density and the potential or overvoltage. As indicated above, experiment confirms this conclusion. It also follows from (6) and (7) that, upon changing φ_r and keeping the chlorine concentration constant, the polarization curves should merge if the electrode potential is plotted on the ordinate axis, and diverge if

if, instead of the potential, the overvoltage is plotted. As can be seen from Figs. 3 and 4, experiment also confirms this conclusion, which remains valid independently of any assumptions about the state of the electrode surface.

Fig. 4. Dependence of the logarithm of the chlorine ionization current on the potential at different values of φ_r. The designations are the same as in Fig. 3.

The independence of the current density at a given φ from $[\mathrm{Cl}^-]$ proves the irreversibility of the stage of ionization proper; however, from the assumption of reversibility of stage (a) there follows, at least in the case of a homogeneous

Fig. 4. Dependence of the logarithm of the chlorine ionization current on the potential at different values of φ_r. The designations are the same as in Fig. 3.

Figure 2: Fig. 4. Dependence of the logarithm of the chlorine ionization current on the potential at different values of φ_r. The designations are the same as in Fig. 3.

weakly filled surface, a half-order of the reaction with respect to Cl_2, whereas experimentally, as has already been indicated, first order is observed. One may try, while retaining the conclusions about the irreversibility of stage (b), to consider stage (a) also irreversible, or else to abandon the assumption of homogeneity and weak filling of the surface. However, as a more detailed analysis shows, within the framework of these assumptions a simultaneous explanation of the first order of the reaction with respect to chlorine, the absence of a limiting cathodic current, and the absence of a dependence of i on $[Cl^-]$ appears difficult. The experimental data fit well within the theory if it is assumed that the process of ionization of Cl_2, apart from the diffusion stage of Cl_2, proceeds through the following two stages:

$$Cl_2 + e \rightleftarrows Cl_{ads} + Cl^- \qquad ( )$$

$$Cl_{ads} + e \rightleftarrows Cl^- \qquad ( )$$

of which the first, at sufficiently high η_k, is irreversible. From the theory of slow discharge, under these assumptions, taking the concentration Cl_{ads} $[Cl_a]$ to be small, it follows that

$$i_\infty = 2k_1[Cl_2]e^{-\frac{\alpha_1 F}{RT}\varphi}, \tag{8}$$

where k_1 is the rate constant of reaction ( ).

Equation (8) correctly expresses the dependence of i on φ, the first order of the reaction with respect to Cl_2, and the absence of a dependence of i_∞ on $[Cl^-]$. On the basis of the data obtained at considerable η_k, no conclusions can be drawn about the character of stage ( ). From observations on the kinetics of oxidation of Cl^- ions at a Pt electrode (^{3}) and from the magnitude of the so-called stoichiometric number (^{4})

$$\nu = \frac{2F}{RT} i_0 \left(\frac{\partial \eta_k}{\partial i_\infty}\right)_{\eta=0},$$

which in the case under consideration is close to 2 (i_0 is the exchange current, which is found by extrapolating the right-hand side of equation (8) to the value

$\varphi = \varphi_r$), it follows that stage ( ) at sufficiently high overvoltages must also be irreversible, and that the exchange currents of stages ( ) and ( ) are quantities of the same order.

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