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A NEW METHOD FOR DETERMINING THE STOICHIOMETRIC NUMBER OF THE RATE-DETERMINING STEP.—APPLICATION TO THE CHLORINE ELECTRODE REACTION ON PLATINUM

By

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Abstract

A new method for determining the stoichiometric number, ν_r, of the rate-determining step was developed with special reference to electrode reactions. The method is based on a comparison of the electrode potential-current relations obtained under different conditions, and involves neither an isotope exchange reaction nor an extrapolation of a Tafel line to the reversible potential.

The method was applied to the chlorine electrode reaction, $2Cl^- = Cl_2 + 2e$, on Pt in 2 N H_2SO_4 containing HCl at various concentrations. The value of ν_r was found to be practically independent of chlorine pressure (1~0.089 atm) and of Cl^- concentration (0.2~0.006 N), but dependent upon the electrode potential; ν_r was found to be two in the potential region more positive than the reversible potential at 1 atm Cl_2 and 0.2 N HCl, and to decrease toward unity upon change of the electrode potential toward more negative values.

In the positive potential region, the order of the chlorine evolution reaction was 1.1 ± 0.1 for Cl^- and -0.03 ± 0.05 for Cl_2. In the potential region more negative than -100 mV, that of the chlorine ionization reaction was approximately unity for Cl_2 and 0 ± 0.05 for Cl^-. On the basis of these values and the above ν_r-values, it was concluded that the chlorine electrode reaction proceeds by the scheme,

$$Cl^- \rightarrow Cl(a) + e, \quad 2Cl(a) \rightarrow Cl_2,$$

where Cl(a) is the chlorine adatom, and the first determines the rate (the "slow-discharge" mechanism) in the positive region and the second (the "catalytic" mechanism) in the negative region.

Introduction

The stoichiometric number, ν_r, of the rate-determining step, first introduced by HORIUTI,[1,2] is of primary importance in analyzing reaction kinetics and

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hence a great deal of work has been devoted to its experimental determination.[3~7]

According to the general theory of reaction rates[2], the ratio of the unidirectional forward rate of the overall reaction V_+ to the reverse rate V_- is given as

$$V_+/V_- = \exp(-\Delta G/\nu_r RT), \tag{1}$$

where $-\Delta G$ is the affinity of the overall reaction. This equation is rewritten as

$$\nu_r = -\Delta G/RT \ln(V_+/V_-),$$

which is the form widely used in the experimental determination of ν_r. Here, the ratio V_+/V_- is usually determined by means of an isotopic tracer, *i.e.* by observing under a given value of $-\Delta G$ either of the unidirectional rates simultaneously with the net rate V

$$V = V_+ - V_-. \tag{2}$$

The utilization of an isotopic tracer, however, introduces new difficulties: (a) the isotope effect frequently has a significant magnitude especially in reactions involving hydrogen; (b) the isotope may by-pass the rate-determining step of the reaction under study, thus fallaciously giving rise to an undully large value for the unidirectional rate and hence to an erronously large value of ν_r. The first problem has been solved in the case of the hydrogen electrode reaction[6,7] but not, so far, for other reactions.

Another method of determination of V_+ or V_- has been used in the case of electrode reactions. If we vary the electrode potential or the chemical potential of the electron, μ_e, while keeping the chemical potentials, μ_j, of all the chemical substances, j (reactants and products), constant, Eq. (1) yields

$$V_+/V_- = \exp\left\{-n(\mu_e - \mu_{e,eq})/\nu_r RT\right\}, \tag{3}$$

where $\mu_{e,eq}$ is the value of μ_e at equilibrium under the given conditions and n is the stoichiometric coefficient of the electron in the overall reaction. The difference in μ_e is in turn given by the difference in the electrode potential φ as

$$\mu_e - \mu_{e,eq} = -F(\varphi - \varphi_{eq}), \tag{4}$$

where φ_{eq} is the value of φ at equilibrium and F the Faraday. Consequently, we obtain, expressing V_+ and V_- in terms of the current densities, i_+ and i_-, respectively,

$$i_+/i_- = \exp\left\{nF(\varphi - \varphi_{eq})/\nu_r RT\right\}. \tag{5}$$

The expression for the net current density i

$$i = i_+ - i_- = i_+(1 - i_-/i_+), \tag{6}$$

follows as

$$i = i_+ \left[1 - \exp\left\{-nF(\varphi - \varphi_{eq})/\nu_r RT\right\}\right]. \tag{7}$$

Expansion of the exponential term near equilibrium where $\varphi \simeq \varphi_{eq}$, yields

$$\nu_r = (i_+)_{\varphi=\varphi_{eq}} (nF/RT)(\partial\varphi/\partial i)_{\varphi=\varphi_{eq}}. \tag{8}$$

If the Tafel constants α_+ and α_-, defined respectively as

$$\alpha_+ \equiv (RT/F)(\partial \ln i_+/\partial\varphi)_{\mu_j} = -RT(\partial \ln i_+/\partial\mu_e)_{\mu_j}, \tag{9.+}$$

and

$$\alpha_- \equiv (RT/F)(\partial \ln i_-/\partial\varphi)_{\mu_j} = -RT(\partial \ln i_-/\partial\mu_e)_{\mu_j}, \tag{9.-}$$

are independent of φ, we obtain the linear relations;

$$\ln i_+ = (\ln i_+)_{\varphi=\varphi_{eq}} + \alpha_+ F(\varphi - \varphi_{eq})/RT, \tag{10.+}$$

and

$$\ln i_- = (\ln i_-)_{\varphi=\varphi_{eq}} + \alpha_- F(\varphi - \varphi_{eq})/RT. \tag{10.-}$$

Consequently, extrapolation to φ_{eq} of a linear Tafel line, established in the potential region far apart from φ_{eq}, yields the value of $(i_+)_{\varphi=\varphi_{eq}} = (i_-)_{\varphi=\varphi_{eq}}$, *i.e.*, we obtain ν_r according to Eq. (8). However, the application of this method is often questionable in the absence of sufficient justification to assume α to remain constant over a wide range of φ.*)

Thus, a new method which requires neither isotope exchange nor the assumption of constant α_+ and α_- is desirable. The present work is concerned with developement of such a method and its application to the chlorine electrode reaction on platinum.

Theoretical

We develop the method with respect to a general electrode reaction expressed as

$$m_A A = m_B B + n e. \tag{11}$$

(Essentially the same argument as below can be made for non-electrochemical reactions by replacing e by a chemical reagent.) The Tafel constant, according to its definition, Eq. (9), may be considered as the reaction order with respect

*) For the same reason, it is not generally valid to determine ν_r by the equation, $\alpha_+ - \alpha_- = n/\nu_r$, which follows readily from Eq. (5) and (9),[4] if the α-values are evaluated in the anodic and cathodic region, respectively, and not at the same electrode potential.

to the electron. In an analogous way we define[8] the reaction orders with respect to A and B which appear in Eq. (11):

$$\zeta_+(\mathrm{A}) \equiv (\partial \ln i_+ / \partial \ln a_\mathrm{A})_{a_\mathrm{B},\varphi} = RT(\partial \ln i_+ / \partial \mu_\mathrm{A})_{\mu_\mathrm{B},\varphi}\,, \qquad (12.+)$$

$$\zeta_-(\mathrm{A}) \equiv (\partial \ln i_- / \partial \ln a_\mathrm{A})_{a_\mathrm{B},\varphi} = RT(\partial \ln i_- / \partial \mu_\mathrm{A})_{\mu_\mathrm{B},\varphi}\,, \qquad (12.-)$$

$$\zeta_+(\mathrm{B}) \equiv (\partial \ln i_+ / \partial \ln a_\mathrm{B})_{a_\mathrm{A},\varphi} = RT(\partial \ln i_+ / \partial \mu_\mathrm{B})_{\mu_\mathrm{A},\varphi}\,, \qquad (13.+)$$

and

$$\zeta_-(\mathrm{B}) \equiv (\partial \ln i_- / \partial \ln a_\mathrm{B})_{a_\mathrm{A},\varphi} = RT(\partial \ln i_- / \partial \mu_\mathrm{B})_{\mu_\mathrm{A},\varphi}\,, \qquad (13.-)$$

where a_A and a_B are the activities of A and B.

Since α's and ζ's are, generally, functions of φ and a's, the plot of $\ln i_+$ or $\ln i_-$ against φ is not always linear. However, there exists a range of φ and a's in which the reaction order values are practically constant, although its extent varies from one system to another. The following expressions for i_+ and i_- hold in such a range:

$$i_+ = k_+ (a_\mathrm{A})^{\zeta_+(\mathrm{A})} (a_\mathrm{B})^{\zeta_+(\mathrm{B})} \exp(\alpha_+ F\varphi / RT)\,, \qquad (14.+)$$

and

$$i_- = k_- (a_\mathrm{A})^{\zeta_-(\mathrm{A})} (a_\mathrm{B})^{\zeta_-(\mathrm{B})} \exp(\alpha_- F\varphi / RT)\,, \qquad (14.-)$$

where k's are constant. In Fig. 1 a are shown schematically the general relation between i_+ or i_- and φ at constant a_A and a_B by solid lines. The relations given by Eq. (14) are given by dotted straight lines.

We consider now the effect upon the curves of shifting the activity of A or B; for example a_B from $a_{\mathrm{B},1}$ to $a_{\mathrm{B},2}$. In Fig. 1 a, the curves i_{+1} and i_{-1} respectively represent the value of i_+ and i_- under the condition that (a) the activity of the reactant B has the value $a_{\mathrm{B},1}$: $a_\mathrm{B} = a_{\mathrm{B},1}$ while (b) the activity of the reactant A remains constant. The equilibrium potential $\varphi_{eq,1}$ then has the value of $\varphi_{eq,1}$: $\varphi_{eq} = \varphi_{eq,1}$. The curve i_1 represents the relation between φ and the *net* current density in the anodic or cathodic region under this condition. Since only i_1 at given $(\varphi - \varphi_{eq,1})$ is experimentally observable, while i_{+1} as well as i_{-1} need to be calculated using Eq. (7), a second equation is required because also ν_r enters into Eq. (7). In accordance with the shift of a_B from $a_{\mathrm{B},1}$ to $a_{\mathrm{B},2}$ while keeping a_A constant, the equilibrium potential is shifted from $\varphi_{eq,1}$ to $\varphi_{eq,2}$. By varying φ again, we would observe the curve i_2 and hence we obtain the curves i_{+2} and i_{-2} as a function of $\varphi - \varphi_{eq,2}$ and unknown value of ν_r. The horizontal distance, on a logarithmic scale, from the curve i_{-1} or i_{+1} to i_{+2} or i_{-2}, respectively, at a given value of φ is related to the reaction order with respect to B (at that value of φ and the fixed value of a_A), *i.e.*,

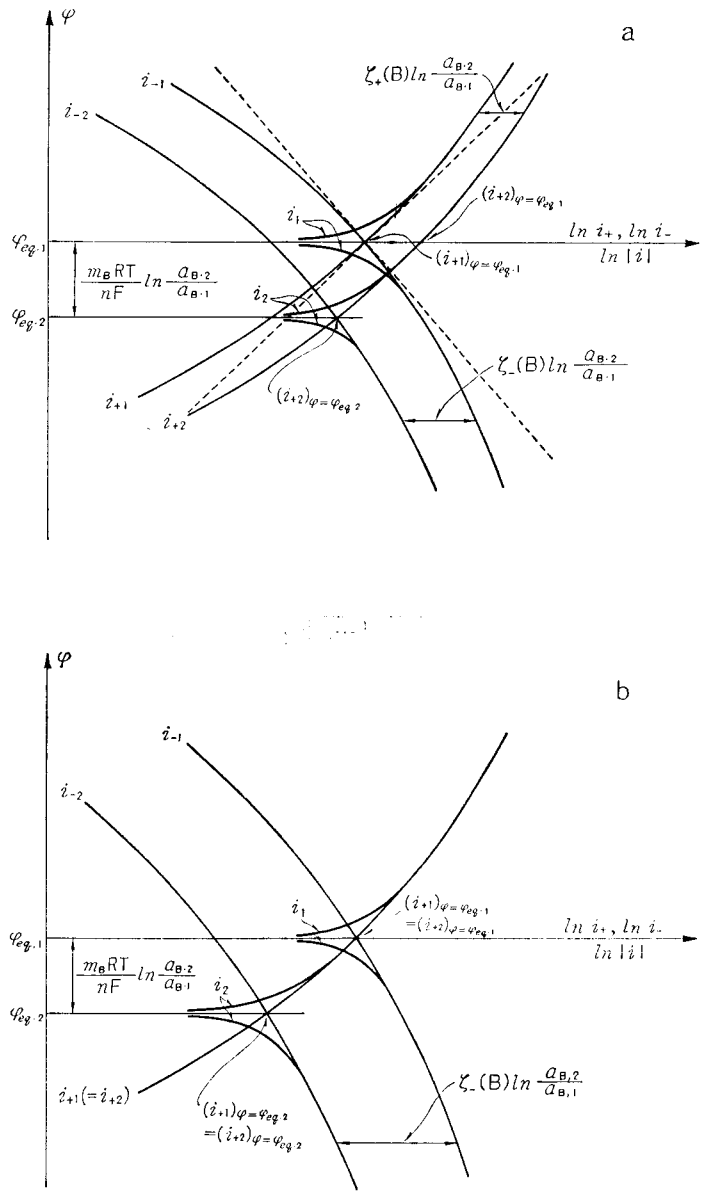

Fig. 1. Schematic representation of relations between φ and $\ln i_+$, $\ln i_-$ or $\ln |i|$. Quantities with subscript 1 indicate those under the condition $a_A = a_A$ and $a_B = a_{B,1}$ and subscript 2 those under $a_A = a_A$ and $a_B = a_{B,2}$.

a, $\zeta_+(B) \neq 0$ and $\zeta_-(B) \neq 0$; b, $\zeta_+(B) = 0$ and $\zeta_-(B) \neq 0$.

$\zeta_+(\mathrm{B})$ or $\zeta_-(\mathrm{B})$ multiplied by $\ln(a_{\mathrm{B},2}/a_{\mathrm{B},1})$.

In the case where $\zeta_+(\mathrm{B})$ is zero in the potential region concerned, as is frequently the case but cannot be expected *a priori*, the curve i_{-1} alone would be shifted to the position of the curve i_{-2} in accordance with the shift of φ_{eq} from $\varphi_{eq,1}$ to $\varphi_{eq,2}$ (Fig. 1 b). In this case, the value of i_{+1} is equal to i_{+2} at any value of φ. Hence, writing down two equations for i_{+1} and i_{+2}, respectively, using Eq. (7), and then equating to each other, we obtain

$$\frac{i_1}{1-\exp\{-nF(\varphi-\varphi_{eq,1})/\nu_r RT\}} = \frac{i_2}{1-\exp\{-nF(\varphi-\varphi_{eq,2})/\nu_r RT\}}. \quad (15)$$

Consequently, by selecting a position of φ where i_1 appreciably deviates from i_2, we can determine the value of ν_r. Likewise, if we select φ at $\varphi_{eq,1}$, we have a common value of $(i_{+1})_{\varphi=\varphi_{eq,1}}=(i_{+2})_{\varphi=\varphi_{eq,1}}$. This magnitude is given on the one hand from the reaction resistance $(\partial\varphi/\partial i_1)_{\varphi=\varphi_{eq,1}}$ by Eq. (8) and on the other hand from $(i_2)_{\varphi=\varphi_{eq,1}}$ and $\varphi_{eq,1}-\varphi_{eq,2}$ by Fq. (7). Hence, equating those, we obtain

$$\frac{\nu_r}{(nF/RT)(\partial\varphi/\partial i_1)_{\varphi=\varphi_{eq,1}}} = \frac{(i_2)_{\varphi=\varphi_{eq,1}}}{1-\exp\{-nF(\varphi_{eq,1}-\varphi_{eq,2})/\nu_r RT\}}. \quad (16)$$

In the case where $\varphi_{eq,1}-\varphi_{eq,2}$ is sufficiently greater than RT/F, this equation reduces to a simpler from, that is,

$$\nu_r = (i_2)_{\varphi=\varphi_{eq,1}}(nF/RT)(\partial\varphi/\partial i_1)_{\varphi=\varphi_{eq,1}}. \quad (17)$$

The value of ν_r is, thus, determined by Eq. (15), (16) or (17) at any value of φ, at least in principle. (In practice, the range of φ where we can apply this method is roughly 200 mV.) An entirely analogous procedure is also possible by varying a_{A} while keeping a_{B} constant. The basic requirement in this method that is $\zeta_+(\mathrm{B})=0$, can readily be tested by observing the coincidence of the Tafel lines, $\ln i_1$ and $\ln i_2$ in the potential region where the contributions of the reverse rates i_{-1} and i_{-2} are negligible.

The method developed above was applied to the chlorine electrode reaction,

$$2\,\mathrm{Cl}^- = \mathrm{Cl}_2 + 2\,\mathrm{e},$$

on platinum. It is known[9] that a homogeneous isotope exchange proceeds through the complex-formation reaction, $\mathrm{Cl}^- + \mathrm{Cl}_2 = \mathrm{Cl}_3^-$, and hence we are unable to determine ν_r of the chlorine electrode reaction by utilizing the exchange of a chlorine isotope.

Experimental

Experiments were carried out in a two-compartment all-glass cell. In the main compartment were placed the test (Pt-wire), reference (Ir-wire) and counter (Pt-net) electrodes. An Ag/AgCl-reference electrode, which was used to evaluate the change in activity of Cl^- and Cl_2 in the main compartment, was placed in the side compartment which was separated from the former compartment with a ground-glass stopper so as to be free of Cl_2.

Solutions of 2 N H_2SO_4 containing HCl at various concentrations were prepared from carefully purified water and special grade chemicals. Chlorine gas was prepared by electrolysis of 6 N HCl. The gas was purified by passing it over a heated (300°C) Pt-net and through a trap containing 2 N H_2SO_4 solution. Helium used to vary the partial pressure of Cl_2 was purified by means of a rare-gas purifier (Japan Pure Hydrogen, type RT-025) which uses a heated (1000°C) titanium compounds.

Soon after the cell was set up, the potentials of all the electrode in the main compartment came to the reversible chlorine potential within ± 1 mV and were stable within $\pm 20\ \mu$V. The experimental temperature was 25 ± 0.5°C. The polarization measurements were then made by means of a galvanostatic pulse technique. After the measurements, the Cl_2-flow was replaced by He-flow, and when the activity of Cl_2 was decreased to a desired value, as judged from the potential difference between the test electrode and the Cl_2-free Ag/AgCl-reference electrode, the He-flow was stopped and then the polarization measurements were repeated. Similar experiments were made at various values of activity of Cl^- at 1 atm of Cl_2.

Results and Discussion

The polarization data obtained are plotted for different values of a_{Cl_2} (Fig. 2 a) and for those of a_{Cl^-} (Fig. 2 b). The electrode potential was referred to the potential of the reversible chlorine electrode at 1 atm Cl_2 and 0.2 N HCl (*ca.* $+1.42$ *V* on the NHE scale). In both cases, the curves were reproducible when the same condition was restored after having shifted the activity to a different value (92% of the initial value of $(\partial\varphi/\partial i)^{-1}_{\varphi=\varphi_{eq,1}}$ for the case of variation of a_{Cl_2}, and 82% for the case of variation of a_{Cl^-}, respectively).

In Fig. 2 a, the agreement of the Tafel lines at the potential region in which we can equate i to i_+ is excellent, which shows $\zeta_+(Cl_2)$ to be zero. Similarly, from Fig. 2 b, $\zeta_-(Cl^-)$ is also found to vanish. These facts enable us to use Eq. (15), (16) or (17) derived above for both cases of variation of activity of Cl^- or Cl_2.

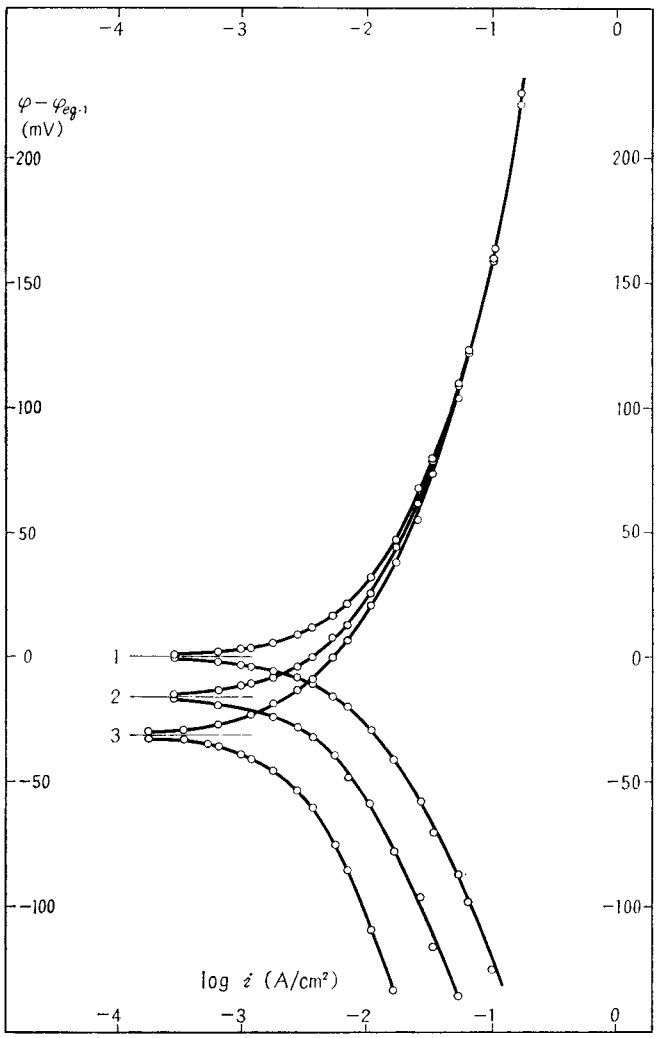

Fig. 2. a Tafel plot of the chlorine electrode reaction on Pt in 0.2N HCl +2N H_2SO_4 solution at 25°C. Chlorine pressure, (1), 1 atm; (2), 0.288 atm and (3), 0.0891 atm.

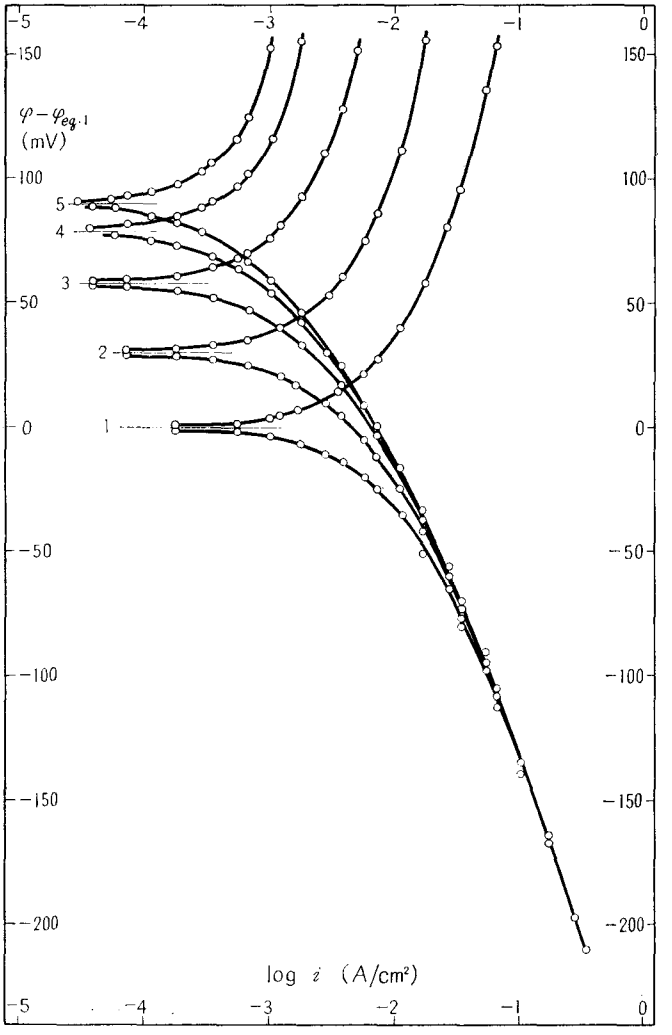

Fig. 2.b Tafel plot of the chlorine electrode reaction on Pt in solutions of 2 N H_2SO_4 containing HCl of various concentration under 1 atm Cl_2 at 25°C. (1), 0.20; (2), 0.062; (3), 0.021; (4), 0.0092 and (5) 0.0060 N.

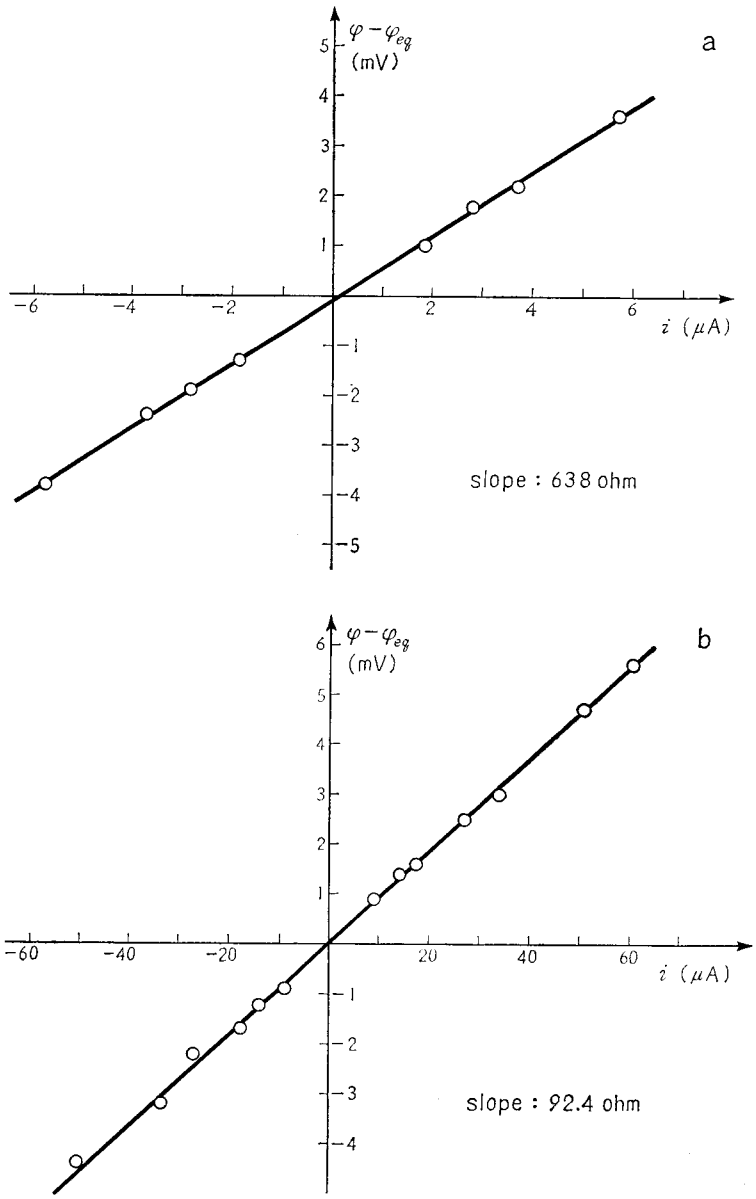

Fig. 3. Typical current-overpotential relations of the chlorine electrode reaction on Pt at 25°C near the reversible potential, φ_{eq}, where i is the *net* current (surface area: 0.05 cm²).

a, 1 atm Cl_2 and 0.021 N HCl in 2 N H_2SO_4;
b, 0.288 atm Cl_2 and 0.20 N HCl in 2 N H_2SO_4.

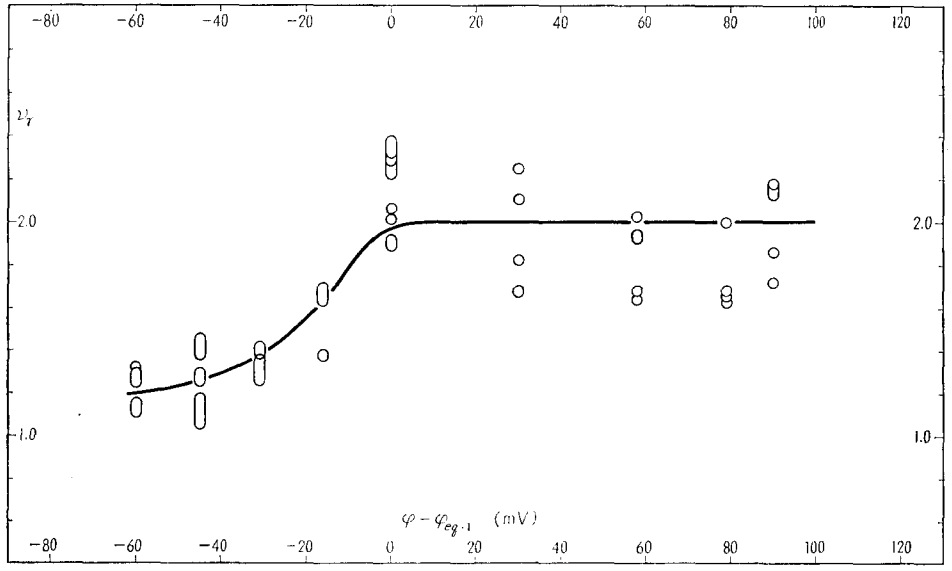

Fig. 4. Variation with the electrode potential φ of the observed stoichiometric number of the rate-determining step of the chlorine electrode reaction on Pt in 2 N H_2SO_4 at 25°C.

Cl_2, 1~0.0891 atm and HCl, 0.20~0.0060 N.

We evaluated the ν_r-value by (1) combining two i-values obtained at a fixed φ-value but under a different activity of either Cl^- or of Cl_2 and (2) by combining the reaction resistance values at the equilibrium potential under a given set of concentrations with an i-value at this potential but obtained under a different condition, *cf.* Eq. (16). The results are plotted against φ in Fig. 4. The ν_r-value was found to be two at potentials positive with respect to $\varphi_{eq,1}$ but showed a tendency to decrease toward unity as the electrode potential was shifted in more negative direction.*)

From the above data we deduce the reaction mechanism. Comparing with the various mechanisms considered for the hydrogen electrode reaction,[6] we find that the possible mechanisms which yield $\nu_r=2$ are (the "slow-discharge" mechanism)

$$Cl^- \overset{\rightarrow}{\rightarrow} Cl(a)+e\,, \qquad 2\,Cl(a) \rightleftharpoons Cl_2\,, \tag{19. a, b}$$

and

$$Cl_2 \rightleftharpoons 2\,Cl(a)\,, \qquad Cl(a)+Cl^- \overset{\rightarrow}{\rightarrow} Cl_2+e\,, \tag{20. a, b}$$

where $\overset{\rightarrow}{\rightarrow}$ denotes the rate-determining step and Cl(a) is a chlorine adatom.

If a simple mass-action law holds for the rate-determining step in (19) or (20), the orders of the reaction are expected to be

$$\zeta_+(Cl^-)=1 \quad \text{and} \quad \zeta_+(Cl_2)=0\,,$$

for (19) and

$$\zeta_+(Cl^-)=1 \quad \text{and} \quad \zeta_+(Cl_2)=0.5\,.$$

for (20). The values observed in the anodic polarization region were

$$\zeta_+(Cl^-)=1.1\pm0.1 \quad \text{and} \quad \zeta_+(Cl_2)=-0.03\pm0.05\,.$$

Hence, we exclude the possibility of the mechanism (20). The chlorine electrode reaction at the positive potentials is thus concluded to follow the slow-discharge mechanism (19).

As the potential moves to more negative values, the mechanism appears to change to the "catalytic" one, *viz.* rapid discharge of Cl^- followed by slow recombination of Cl(a) as indicated by the decrease of ν_r toward unity. The reaction orders observed in the potential region $\varphi-\varphi_{eq,1}<-100$ mV, $\zeta_-(Cl^-)\simeq0$ and $\zeta_-(Cl_2)\simeq1$, are in good agreement with this conclusion. The

*) FRUMKIN and TEDORADSE[5] determined the ν_r-value to be two in the negative potential region by the extrapolation method mentioned in the Introduction; no variation of ν_r with φ was considered in that work.

chlorine electrode reaction on Pt thus changes over from the slow-discharge to the catalytic mechanism as the potential becomes more and more negative.

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