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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

Michio ENYO\*) and Takamitsu YOKOYAMA\*)

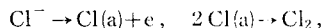
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### Abstract

A new method for determining the stoichiometric number,  $\nu_r$ , 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,  $2\text{Cl}^- = \text{Cl}_2 + 2\text{e}$ , on Pt in 2N  $\text{H}_2\text{SO}_4$  containing HCl at various concentrations. The value of  $\nu_r$  was found to be practically independent of chlorine pressure (1~0.089 atm) and of  $\text{Cl}^-$  concentration (0.2~0.006 N), but dependent upon the electrode potential;  $\nu_r$  was found to be two in the potential region more positive than the reversible potential at 1 atm  $\text{Cl}_2$  and 0.2N 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  $1.1 \pm 0.1$  for  $\text{Cl}^-$  and  $-0.03 \pm 0.05$  for  $\text{Cl}_2$ . In the potential region more negative than  $-100$  mV, that of the chlorine ionization reaction was approximately unity for  $\text{Cl}_2$  and  $0 \pm 0.05$  for  $\text{Cl}^-$ . On the basis of these values and the above  $\nu_r$ -values, it was concluded that the chlorine electrode reaction proceeds by the scheme,



where  $\text{Cl(a)}$  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,  $\nu_r$ , of the rate-determining step, first introduced by HORIUTI,<sup>1,2)</sup> 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.<sup>3-7)</sup>

According to the general theory of reaction rates<sup>2)</sup>, the ratio of the unidirectional forward rate of the overall reaction  $V_+$  to the reverse rate  $V_-$  is given as

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

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  $\nu_r$ . 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  $V$

$$V = V_+ - V_-. \quad (2)$$

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 unduly large value for the unidirectional rate and hence to an erroneously large value of  $\nu_r$ . The first problem has been solved in the case of the hydrogen electrode reaction<sup>6,7)</sup> 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,  $\mu_e$ , while keeping the chemical potentials,  $\mu_j$ , of all the chemical substances,  $j$  (reactants and products), constant, Eq. (1) yields

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

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

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

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

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

The expression for the net current density  $i$

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$$i = i_+ - i_- = i_+(1 - i_-/i_+), \quad (6)$$

follows as

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

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

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

If the Tafel constants  $\alpha_+$  and  $\alpha_-$ , defined respectively as

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

and

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

are independent of  $\varphi$ , we obtain the linear relations;

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

and

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

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

Thus, a new method which requires neither isotope exchange nor the assumption of constant  $\alpha_+$  and  $\alpha_-$  is desirable. The present work is concerned with development 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



(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

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\*) For the same reason, it is not generally valid to determine  $\nu_r$  by the equation,  $\alpha_+ - \alpha_- = n/\nu_r$ , which follows readily from Eq. (5) and (9),<sup>4)</sup> if the  $\alpha$ -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<sup>8)</sup> the reaction orders with respect to A and B which appear in Eq. (11):

$$\zeta_+(A) \equiv (\partial \ln i_+ / \partial \ln a_A)_{a_B, \varphi} = RT(\partial \ln i_+ / \partial \mu_A)_{\mu_B, \varphi}, \quad (12. +)$$

$$\zeta_-(A) \equiv (\partial \ln i_- / \partial \ln a_A)_{a_B, \varphi} = RT(\partial \ln i_- / \partial \mu_A)_{\mu_B, \varphi}, \quad (12. -)$$

$$\zeta_+(B) \equiv (\partial \ln i_+ / \partial \ln a_B)_{a_A, \varphi} = RT(\partial \ln i_+ / \partial \mu_B)_{\mu_A, \varphi}, \quad (13. +)$$

and

$$\zeta_-(B) \equiv (\partial \ln i_- / \partial \ln a_B)_{a_A, \varphi} = RT(\partial \ln i_- / \partial \mu_B)_{\mu_A, \varphi}, \quad (13. -)$$

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

Since  $\alpha$ 's and  $\zeta$ 's are, generally, functions of  $\varphi$  and  $a$ 's, the plot of  $\ln i_+$  or  $\ln i_-$  against  $\varphi$  is not always linear. However, there exists a range of  $\varphi$  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:

$$i_+ = k_+ (a_A)^{\zeta_+(A)} (a_B)^{\zeta_+(B)} \exp(\alpha_+ F \varphi / RT), \quad (14. +)$$

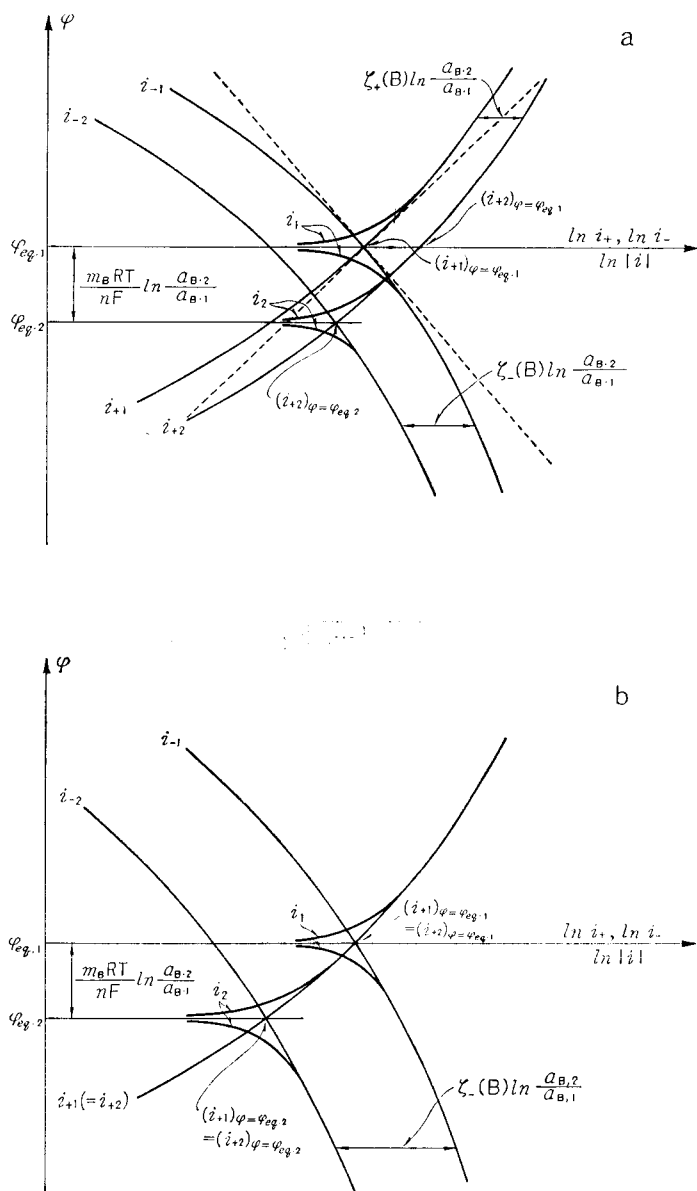
and

$$i_- = k_- (a_A)^{\zeta_-(A)} (a_B)^{\zeta_-(B)} \exp(\alpha_- F \varphi / RT), \quad (14. -)$$

where  $k$ 's are constant. In Fig. 1a are shown schematically the general relation between  $i_+$  or  $i_-$  and  $\varphi$  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  $a_{B,1}$  to  $a_{B,2}$ . In Fig. 1a, 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  $a_{B,1}$ :  $a_B = a_{B,1}$  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  $\varphi$  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  $\nu_r$  enters into Eq. (7). In accordance with the shift of  $a_B$  from  $a_{B,1}$  to  $a_{B,2}$  while keeping  $a_A$  constant, the equilibrium potential is shifted from  $\varphi_{eq,1}$  to  $\varphi_{eq,2}$ . By varying  $\varphi$  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  $\nu_r$ . 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  $\varphi$  is related to the reaction order with respect to B (at that value of  $\varphi$  and the fixed value of  $a_A$ ), *i. e.*,

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**Fig. 1.** Schematic representation of relations between  $\varphi$  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  $\zeta_-(B) \neq 0$ .

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

In the case where  $\zeta_+(B)$  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  $\varphi_{eq}$  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  $\varphi$ . 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  $\varphi$  where  $i_1$  appreciably deviates from  $i_2$ , we can determine the value of  $\nu_r$ . Likewise, if we select  $\varphi$  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 Eq. (7). Hence, equating those, we obtain

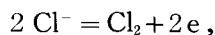
$$\frac{\nu_r}{(nF/RT)(\partial\varphi/\partial i_1)_{\varphi=\varphi_{eq,1}}} = \frac{(i_2)_{\varphi=\varphi_{eq,1}}}{1 - \exp \{-nF(\varphi_{eq,1} - \varphi_{eq,2})/\nu_r RT\}}. \quad (16)$$

In the case where  $\varphi_{eq,1} - \varphi_{eq,2}$  is sufficiently greater than  $RT/F$ , this equation reduces to a simpler form, 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  $\nu_r$  is, thus, determined by Eq. (15), (16) or (17) at any value of  $\varphi$ , at least in principle. (In practice, the range of  $\varphi$  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  $\zeta_+(B)=0$ , 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,



on platinum. It is known<sup>9)</sup> that a homogeneous isotope exchange proceeds through the complex-formation reaction,  $\text{Cl}^- + \text{Cl}_2 = \text{Cl}_3^-$ , and hence we are unable to determine  $\nu_r$  of the chlorine electrode reaction by utilizing the exchange of a chlorine isotope.

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## **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  $\text{Cl}^-$  and  $\text{Cl}_2$  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  $\text{Cl}_2$ .

Solutions of 2 N  $\text{H}_2\text{SO}_4$  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 ( $300^\circ\text{C}$ ) Pt-net and through a trap containing 2 N  $\text{H}_2\text{SO}_4$  solution. Helium used to vary the partial pressure of  $\text{Cl}_2$  was purified by means of a rare-gas purifier (Japan Pure Hydrogen, type RT-025) which uses a heated ( $1000^\circ\text{C}$ ) 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  $\pm 1$  mV and were stable within  $\pm 20$   $\mu\text{V}$ . The experimental temperature was  $25 \pm 0.5^\circ\text{C}$ . The polarization measurements were then made by means of a galvanostatic pulse technique. After the measurements, the  $\text{Cl}_2$ -flow was replaced by He-flow, and when the activity of  $\text{Cl}_2$  was decreased to a desired value, as judged from the potential difference between the test electrode and the  $\text{Cl}_2$ -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  $\text{Cl}^-$  at 1 atm of  $\text{Cl}_2$ .

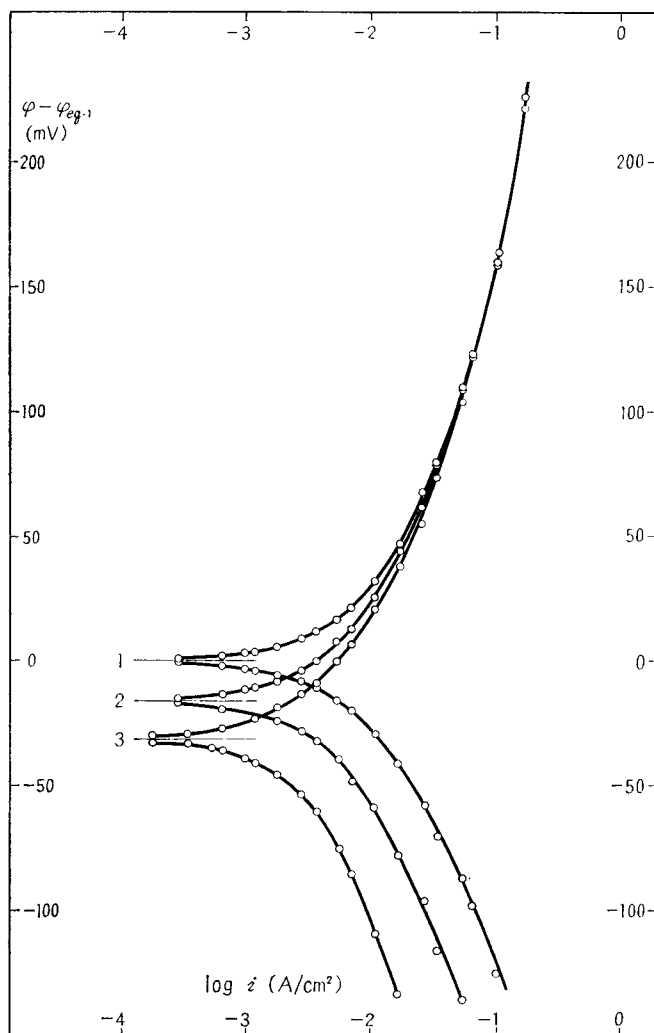
## **Results and Discussion**

The polarization data obtained are plotted for different values of  $a_{\text{Cl}_2}$  (Fig. 2a) and for those of  $a_{\text{Cl}^-}$  (Fig. 2b). The electrode potential was referred to the potential of the reversible chlorine electrode at 1 atm  $\text{Cl}_2$  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  $(\partial\varphi/\partial i)_{\varphi=\varphi_{\text{eq},1}}^{-1}$  for the case of variation of  $a_{\text{Cl}_2}$ , and 82% for the case of variation of  $a_{\text{Cl}^-}$ , respectively).

In Fig. 2a, the agreement of the Tafel lines at the potential region in which we can equate  $i$  to  $i_+$  is excellent, which shows  $\zeta_+(\text{Cl}_2)$  to be zero. Similarly, from Fig. 2b,  $\zeta_-(\text{Cl}^-)$  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  $\text{Cl}^-$  or  $\text{Cl}_2$ .

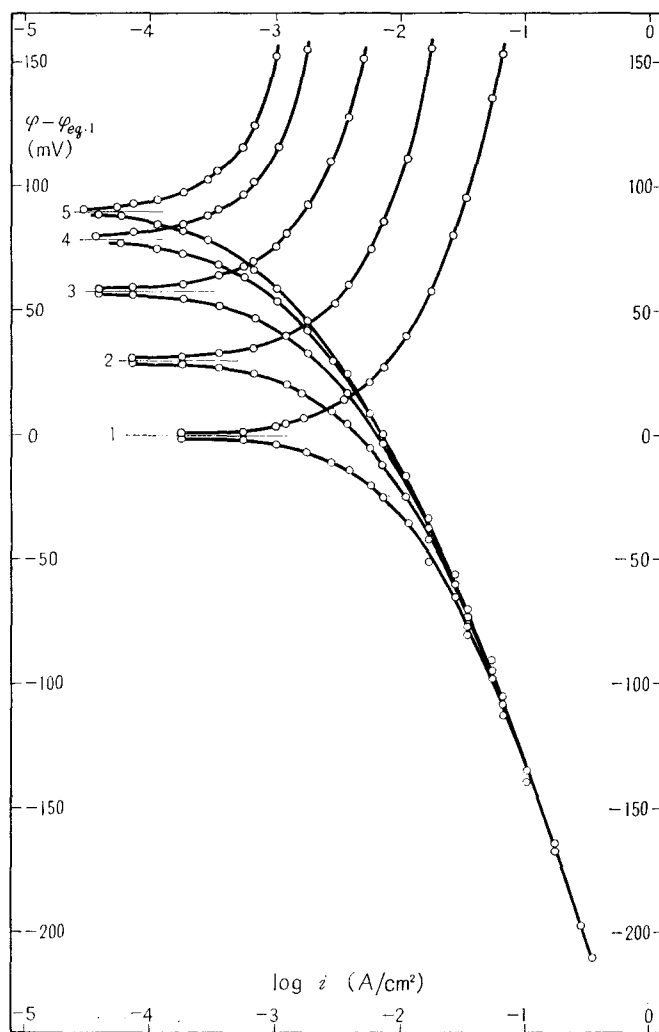


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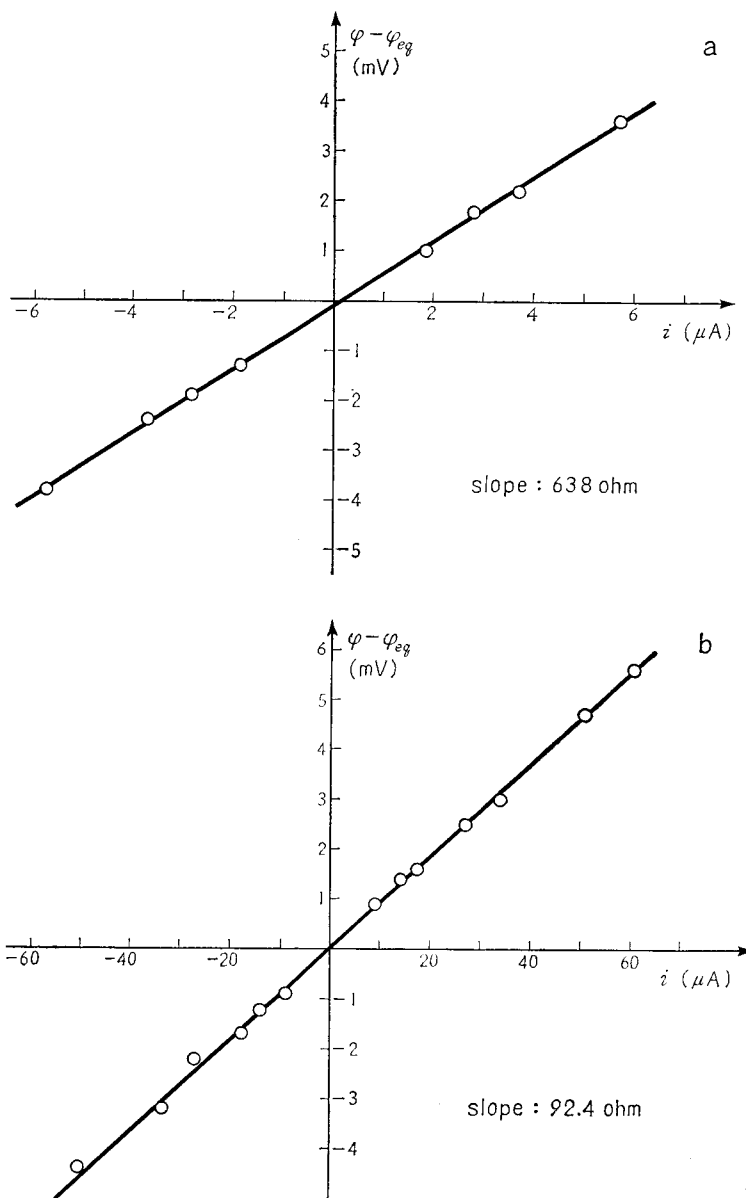
**Fig. 2. a** Tafel plot of the chlorine electrode reaction on Pt in 0.2N HCl + 2N H<sub>2</sub>SO<sub>4</sub> solution at 25°C. Chlorine pressure, (1), 1 atm; (2), 0.288 atm and (3), 0.0891 atm.

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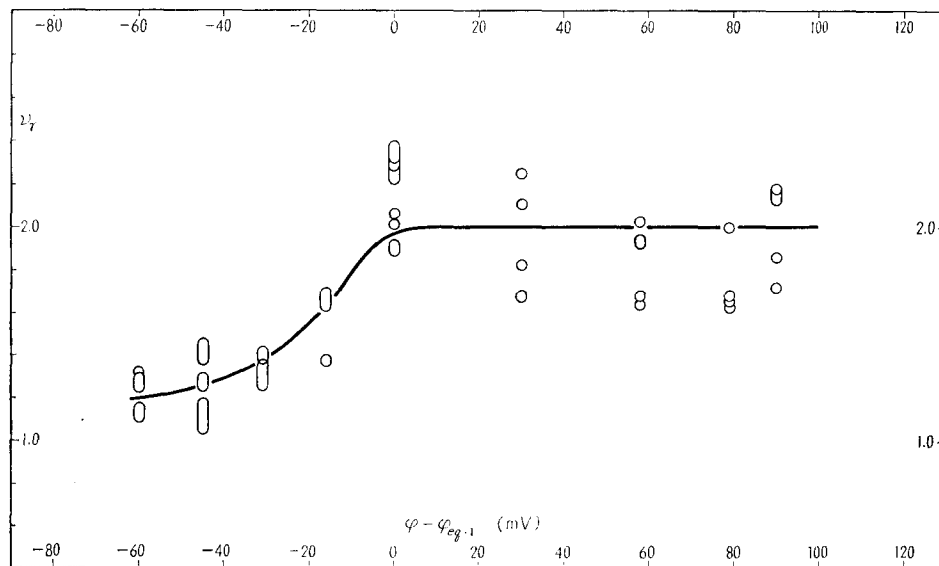
**Fig. 2. b** Tafel plot of the chlorine electrode reaction on Pt in solutions of 2N H<sub>2</sub>SO<sub>4</sub> containing HCl of various concentration under 1 atm Cl<sub>2</sub> at 25°C. (1), 0.20; (2), 0.062; (3), 0.021; (4), 0.0092 and (5) 0.0060 N.

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**Fig. 3.** Typical current-overpotential relations of the chlorine electrode reaction on Pt at 25°C near the reversible potential,  $\varphi_{eq}$ , where  $i$  is the net current (surface area: 0.05 cm<sup>2</sup>).

- a, 1 atm Cl<sub>2</sub> and 0.021 N HCl in 2 N H<sub>2</sub>SO<sub>4</sub>;  
 b, 0.288 atm Cl<sub>2</sub> and 0.20 N HCl in 2 N H<sub>2</sub>SO<sub>4</sub>.

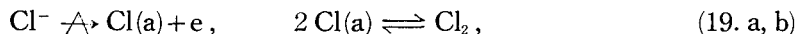


**Fig. 4.** Variation with the electrode potential  $\phi$  of the observed stoichiometric number of the rate-determining step of the chlorine electrode reaction on Pt in 2 N  $\text{H}_2\text{SO}_4$  at 25°C.

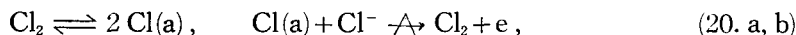
$\text{Cl}_2$ , 1~0.0891 atm and  $\text{HCl}$ , 0.20~0.0060 N.

We evaluated the  $\nu_r$ -value by (1) combining two  $i$ -values obtained at a fixed  $\varphi$ -value but under a different activity of either  $\text{Cl}^-$  or of  $\text{Cl}_2$  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  $\varphi$  in Fig. 4. The  $\nu_r$ -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,<sup>6)</sup> we find that the possible mechanisms which yield  $\nu_r=2$  are (the "slow-discharge" mechanism)



and



where  $\xrightarrow{\text{A}}$  denotes the rate-determining step and  $\text{Cl(a)}$  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

$$\zeta_+(\text{Cl}^-) = 1 \quad \text{and} \quad \zeta_+(\text{Cl}_2) = 0,$$

for (19) and

$$\zeta_+(\text{Cl}^-) = 1 \quad \text{and} \quad \zeta_+(\text{Cl}_2) = 0.5.$$

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

$$\zeta_+(\text{Cl}^-) = 1.1 \pm 0.1 \quad \text{and} \quad \zeta_+(\text{Cl}_2) = -0.03 \pm 0.05.$$

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  $\text{Cl}^-$  followed by slow recombination of  $\text{Cl(a)}$  as indicated by the decrease of  $\nu_r$  toward unity. The reaction orders observed in the potential region  $\varphi - \varphi_{eq,1} < -100$  mV,  $\zeta_-(\text{Cl}^-) \simeq 0$  and  $\zeta_-(\text{Cl}_2) \simeq 1$ , are in good agreement with this conclusion. The

\*) FRUMKIN and TEDORADSE<sup>5)</sup> determined the  $\nu_r$ -value to be two in the negative potential region by the extrapolation method mentioned in the Introduction; no variation of  $\nu_r$  with  $\varphi$  was considered in that work.

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

**Acknowledgement**

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