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A STUDY OF THE ELECTRIC DOUBLE LAYER AND THE KINETICS OF THE ELECTRON TRANSFER STEP OF HYDROGEN EVOLUTION REACTION ON SILVER IN SULFURIC ACID SOLUTIONS BY A GALVANOSTATIC TRANSIENT METHOD

By

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Abstract

The double layer capacity measurement and the kinetic study of h. e. r. on silver were carried out by a galvanostatic transient method. The p. z. c. was found at -0.6 ± 0.02 V (NHE) from the position of the minimum in the capacity~potential curves in dilute sodium sulfate solutions. The kinetics of the electron transfer step of h. e. r. on silver in sulfuric acid solutions (1.73 N~1.57×10^{-3} N) was studied over an extended range of the overvoltage of the step. There was an unique linear relationship between the polarization resistance of the step and the polarizing current density in a log-log scale at higher current densities, which was common to all the solutions studied. It was shown from this result that the relation between the unidirectional rate and the overvoltage of the step was expressed by an ordinary Tafel-type equation with a Tafel constant $\alpha=0.5$.

The exchange current density of the step, i_{10}, and that of the overall h. e. r., i_0, were determined in each solution. The ratio i_{10}/i_0 varied from 184 at 1.73 N to a value close to unity in very dilute solutions around 10^{-5} N, which suggests existence of a rate determining step following the electron transfer around the equilibrium potential in concentrated solutions.

Introduction

Many attempts have been made to elucidate the mechanism of h. e. r. on silver in acid solutions[1~14] mainly based on the data obtained by steady state measurements such as the b-balue of Tafel lines, pH-effect and the stoichiometric number of the rate determining step. Enyo and Matsusima[15] studied the mechanism in 1 N H_2SO_4 in terms of the ratio of the rates of the constituent elementary steps and found that the exchange rate of the electron transfer step was three to five times greater than that of the follow-

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ing recombination step of adsorbed hydrogen atoms.

On the other hand, the galvanostatic transient method[16] has been found to be useful in this approach and particulary successful in determining the kinetic law of the electron transfer step of h. e. r. separately from the kinetics of the overall reaction. The mechanism of h. e. r. on some metals was thus elucidated by comparing the rate and the overvoltage of the elementary steps.

Among the metals studied, only gallium[17] behaved like a mercury electirode, on which all the overvoltage was imposed on the electron transfer step. On other metals such as Pt,[16,18~20] Ni,[21,22] Au[23] and Ti,[24] the overvoltage of the electron transfer step was restricted in a small range because the rate of the step was much higher than that of the overall reaction. The kinetics was shown, however, to be well expressed by the following equation,

$$i_1 = i_{10}\left(e^{-\frac{F\eta_1}{2RT}} - e^{\frac{F\eta_1}{2RT}}\right) \tag{1}$$

where i_{10} and i_1 are respectively the exchange current density and the rate of the electron transfer step at a steady state and η_1 is the overvoltage associated with the step at the steady state.

Silver is known to behave as a mercury-like electrode as classified by Frumkin[25] through the studies on the double layer structure. In fact the differential capacity～potential curves on silver single crystal electrodes[26~29] as well as on a polycrystaline electrode[30~33] in neutral solutions are similar to that of an ideally polarized electrode.

It is expected therefore that we could study the kinetics of the electron transfer step of h. e. r. over an extended range of overvoltage in the case of the silver electrode.

The present work is concerned with a kinetic study of the electron transfer step of h. e. r. on silver in sulfuric acid solutions by the galvanostatic transient method.

The principle of the galvanostatic transient method has been described elsewhere[16,18] and the basic equations only will be outlined here.

The electrode is first polarized galvanostatically to a steady state with overvoltage η and current density i and then a constant current pulse Δi is superimposed on i giving rise to a transient curve of η. The double layer capacity C_D and the time constant of the electron transfer step τ_1 at the steady state can be obtained by the analysis of the $\eta \sim t$ curve by the equation,

$$\ln(-\Delta i/\dot{\eta}) = t/\tau_1 + \ln C_D \tag{2}$$

$$\tau_1 = C_D r_1 \tag{3}$$

where $\dot{\eta}$ is the time derivative of η at time t and r_1 is the polarization resistance of the electron transfer step of h. e. r. defined by,

$$r_1 = -(\partial\eta_1/\partial i_1)_{i_1=i}\,. \qquad (4)$$

i_1 and η_1 are the rate and the overvoltage of the step at the steady state. Equation (2) should be applied to the initial stage of the transient curve where the change of η is much smaller than RT/F.

The overvoltage of the electron transfer step of h. e. r. at a given steady state can be obtained by the integration of eq. (4) using the values of r_1 at various values of the polarizing current density,

$$\eta_1 = -\int_0^i r_1 \mathrm{d}i\,. \qquad (5)$$

The polarization curve of the electron transfer step is given by the relation between η_1 and $\log i$ thus determined. In eqs. (4) and (5) it is assumed that electron transfer occurs through only one elementary step so that we can put $i_1 = i$ at a steady state. The validity of this assumption can be discussed on the basis of the results obtained based on it.

The exchange current density i_{10} of the electron transfer step is obtained from the relation,

$$i_{10} = \mathrm{RT/F}\, r_{10} \qquad (6)$$

where r_{10} is the value of r_1 at the equilibrium potential.

Experimental

Special care has been taken to ensure the cleanliness of the whole system which was all pyrex glass made and completely air-tight. The construction of such a system is described elsewhere.[16] The silver electrode used throughout the study was made by melting silver powder (99.99%) in a small vessel of fused quartz under a helium stream. The silver powder was degassed beforehand by heating close to the melting point. A thin platinum foil was sealed through the bottom of the quartz vessel to have an electrical contact. The sealing was done in vacuo by placing a platinum foil at a constricted portion of a quartz tube which was then heated from outside by propane-oxygen fiame. The electrode made in this way is shown in Fig. 1. The geometrical surface area of

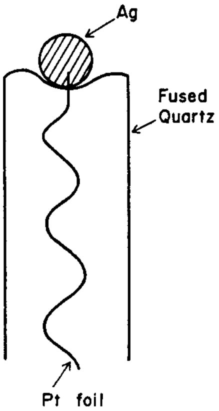

Fig. 1. The silver bead electrode.

the electrode was calculated as 0.28 cm^2 assuming a spherical form. All the data in the present study is referred to the unit geometrical area.

The electrode made in this way showed a high activity which was stable over a few days in the same solution.

Sulfuric acid solutions were made from Merck Suprapur H_2SO_4 and four times distilled water obtained from a still with alkaline permanganate solution at the first stage.

The reference and counter electrodes were both platinized platinum nets. The former was contained in a separated compartment connected to the main compartment by a Luggin capirally and the latter was placed symmetrically around the silver electrode. All the measurements were done at room temperature.

For the analysis of a great number of $\eta\sim t$ curves observed by the galvanostatic transient method an off-line system has been developed by employing a transient recorder (biomation Type 801), a tape punch buffer and a tape puncher (made by Takeda Riken) and a mini-computer (OKITAC 4300). The final result of the analysis was plotted out on a teletype as a $\log(-\Delta i/\dot{\eta})\sim t$ curve.

Results and Discussion

1. *Double layer capacity in neutral solutions*

Before the kinetic study in sulfuric acid solutions the double layer capacity measurement was carried out in dilute solutions of sodium sulfate to observe the diffuse double layer minimum at the p. z. c. in the capacity$\sim$potential curve.

First, the equilibrium potential of h. e. r. on silver in these neutral solutions was confirmed by observing an $i\sim\eta$ relationship around the equilibrium potential as shown in Fig. 2. These measurements were carried out usually after polarizing the silver electrode to $-\eta=0.3\sim0.4$ V for one hour.

The double layer capacity of the silver hydrogen electrode was then determined from the overvoltage transient curves at various steady overvoltages. In these dilute neutral solutions it is fairly easy to observe the ideally polarized region of the transient curves on silver by applying a suitable large current pulse to the electrode. This is clearly seen in Fig. 3 in which all the transient curves at various overvoltages are linear. So, the capacity value can be calculated from the slope of each straight line. The double layer capacity$\sim$potential curves for dilute solutions of sodium sulfate determined in this way are given in Fig. 4, which shows clear minima at -0.6 ± 0.02 V (NHE) which deepen with dilution of the solution. These data confirm the

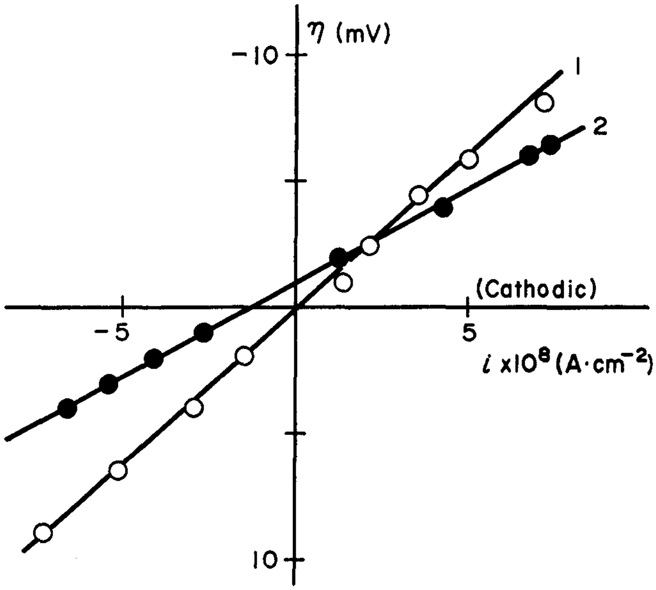

Fig. 2. $i \sim \eta$ relationship around the equilibrium potential on silver in sodium sulfate solutions.
1) 4.7×10^{-3} 2) 1.92×10^{-3} N

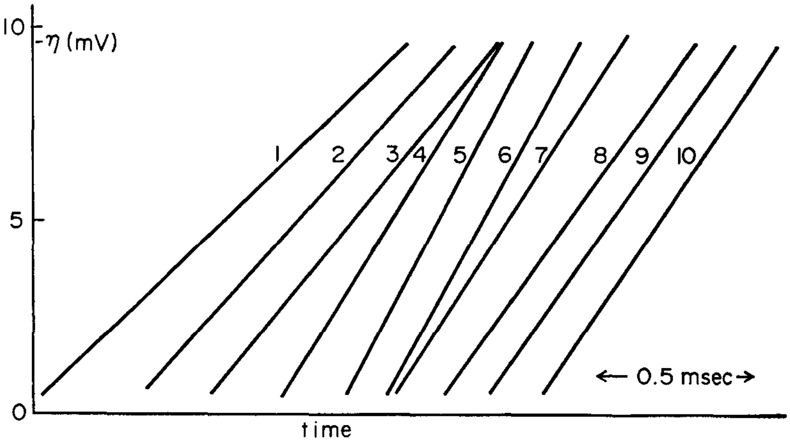

Fig. 3. Determination of the double layer capacity from the linear $\eta \sim t$ curves observed at various starting overvoltages by applying a constant pulse current $\Delta i = 5.01 \times 10^{-4}$ A·cm^{-2} in 3.78×10^{-3} N Na_2SO_4.
The overvoltage is

1) +150 mV 2) +100 mV 3) 0 4) −100 mV
5) −150 mV 6) −200 mV 7) −250 mV 8) −300 mV
9) −400 mV 10) −500 mV

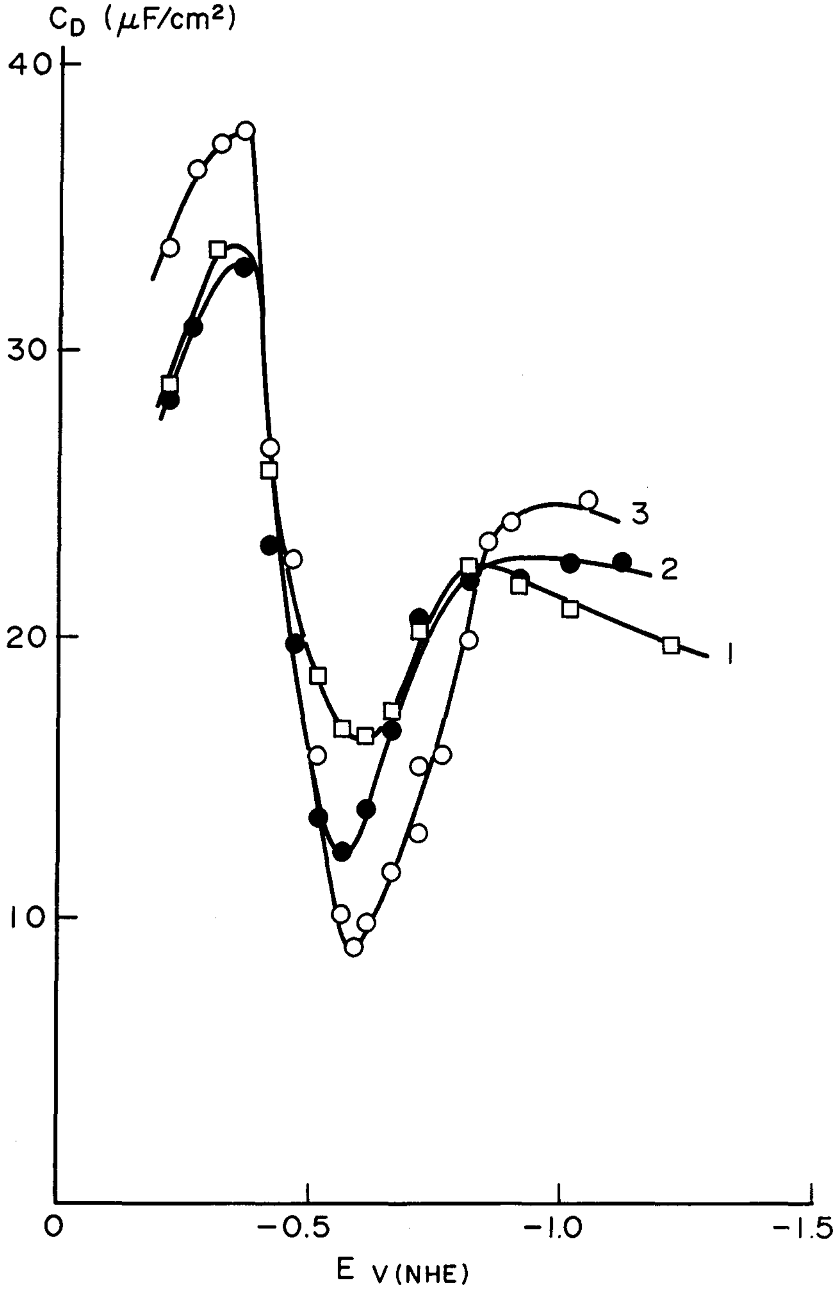

Fig. 4. Differential capactiy~potential curves on silver in dilute sodium sulfate solutions determined by the galvanostatic transient method.
1) 3.78×10^{-3} N 2) 7.25×10^{-4} N 3) 2.83×10^{-4} N

clealiness of the solution and the electrode surface.

The capacity~potential curves for the concentration below 10^{-3} N Na_2SO_4 have not yet been measured before by the AC method either on a polycrystaline or on single crystal silver electrodes. This demonstrates an advantage of the DC method over the AC method in studying the double layer structure in very dilute solutions.

The potential for the minimum capacity observed here is nearly 0.1 V more positive than the well established p. z. c. of polycrystaline silver, *i. e.*, -0.7 V (NHE)[30~33] determined by AC measurements. This difference may have been caused by the formation, to some extent, of an Ag single crystal when the electrode was made, which is known to have the p. z. c. more positive than a polycrystaline electrode.[26~29]

2. *Kinetic study in sulfuric acid*

2. 1 **Steady state measurements**

The polarization curves in steady states measured in sulfuric acid are shown in Fig. 5_a and 5_b. The Tafel slope of these polarization curves is 125~130 mV in the region of high current densities but in very dilute solutions there appears an effect due to a limited diffusion of H^+ to the electrode surface as seen from the bending of curve-5 in Fig. 5_b above 1 mA/cm^2 for 1.57×10^{-3} N H_2SO_4.

We can see a systematic concentration dependence of $i \sim \eta$ relations around the equilibrium potential in Fig. 5_a and of $\log i \sim \eta$ curves in Fig. 5_b. These are in conformity with that observed in hydrochloric[2,12] and sulfuric[30] acid but in contrast to that reported by Gossner and Mansfeld.[13] The presence or absence of the pH-effect on the Tafel lines has been very often a crucial matter in discussing the mechanism of h. e. r. but the conflicting data on the pH-effect on sliver may probably result from difficulties to keep the activity of the electrode unchanged in a series of experiments at various concentrations. But it should be pointed out that the activity of the silver reported by Gossner and Mansfeld is 2~4 order of magnitude lower than that obtained in the present work.

The presence of two Tafel sections with the slopes of 60 mV at lower current densities and 120 mV at higher current densities was also reported by a number of authors[2,4,6,8~10,12] and was interpreted by Krishtalik[34] as an evidence for switching over from the barrierless slow discharge to the ordinary slow discharge. However, there is no sign of the presence of the two Tafel sections in the present work as seen from Fig. 5_b. The reason of this difference is not clear but again it should be pointed out that the activity of the silver reported by these authors is almost one order of mag-

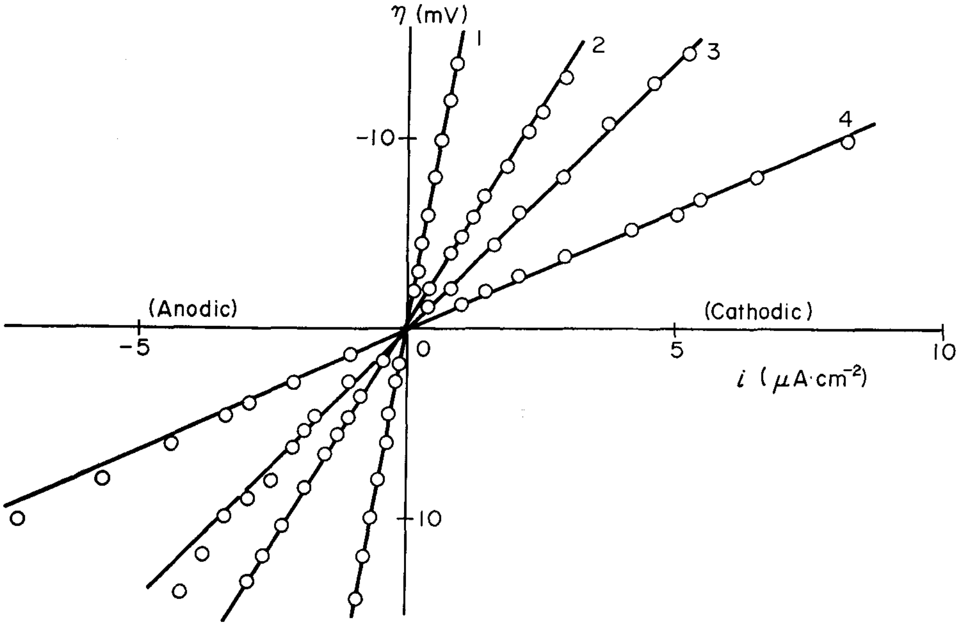

Fig. 5. (a) $i \sim \eta$ relationship around the equilibrium potential of silver hydrogen electrode in sulfuric acid solutions.
1) 1.57×10^{-3} N 2) 1.04×10^{-3} N 3) 7.15×10^{-2} N 4) 1.73 N

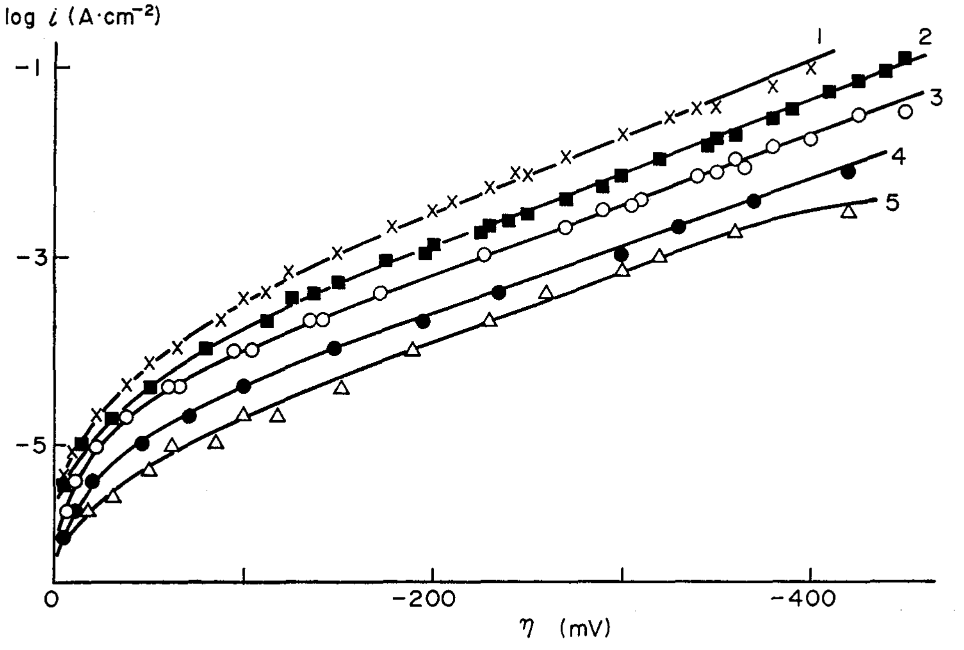

Fig. 5. (b) Tafel lines of over-all h. e. r. on silver in sulfuric acid solutions.
1) 1.73 N 2) 0.276 N 3) 7.15×10^{-2} N 4) 1.04×10^{-2} N
5) 1.57×10^{-3} N

nitude lower than that in Fig. 5_b.

A jump of the overvoltage is also reported at a high overvoltage around $-0.6 \sim -0.7$ V,[13,14] keeping the Tafel slope 120 mV before and after the jump. This high overvoltage region, however, was not accessible in the present study because of the high electrode activity.

The $i \sim \eta$ relations around the equilibrium potential are all straight lines crossing the origin, as seen from Fig. 5_a. The polarization resistance of the overall reaction $r_0 = -\left(\frac{d\eta}{di}\right)_{\eta=0}$ can be determined from these straight lines and the exchange rate of the overall reaction i_0 can be estimated from r_0 by the following relation

$$i_0 = \nu(r)\,\mathrm{RT}/2\mathrm{F}\,r_0 \qquad (7)$$

where $\nu(r)$ is the stoichiometric number of the rate-determining step. The dependence on pH of i_0 estimated by eq. (7) assuming $\nu(r)=1$ are given in Table 1 and Fig. 13. The assumption can be justified at least in concentrated solutions for which $i_{10} \gg i_0$.

TABLE 1.

$\log a_{\mathrm{H}^+}$	$i_{10}\,(\mathrm{A\cdot cm^{-2}})$	$i_0\,(\mathrm{A\cdot cm^{-2}})$	i_{10}/i_0
-0.62	1.84×10^{-3}	1.00×10^{-5}	184
-1.20	4.65×10^{-4}	5.01×10^{-6}	92.8
-1.60	9.39×10^{-5}	4.41×10^{-6}	21.3
-2.20	4.90×10^{-5}	2.75×10^{-6}	17.8
-2.88	1.30×10^{-5}	8.17×10^{-7}	15.9
-3.46	3.64×10^{-6}	6.69×10^{-7}	5.4

2.2 Kinetic law of the electron transfer step

An example of a series of overvoltage tansient curves observed at various pulse current densities are shown in Fig. 6. The curves are linear at larger current densities showing the ideally polarized region but become curved at lower current densities due to the leakage current across the double layer by the electron transfer step.

The transient curves with curvature were analyzed on the basis of eq. (2) to determine the time constant τ_1 and the double layer capacity C_D at various overvoltages in each solution. An example of the analysis is given in Fig. 7 for 1.73 N H_2SO_4, which shows a good linearity between $\log(-\Delta i/\eta)$ and time. The η-dependence of τ_1 and C_D determined in this way are shown in Figs. 8 and 9 respectively.

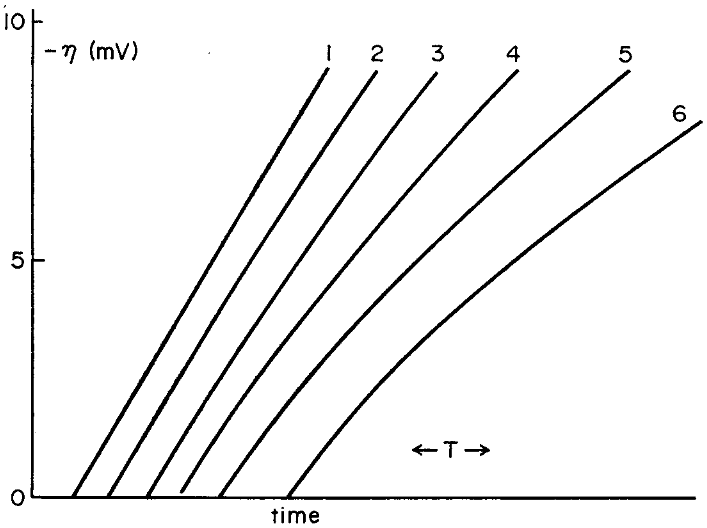

Fig. 6. $\eta \sim t$ curves observed from the equilibrium potential on silver in 1.04×10^{-2} N H_2SO_4 at various time windows. The pulse current Δi and the time scale T for each curve are chosen so that the tangential lines at $t=0$ remain parallel each other for the same value of the double layer capacity.

	1	2	3	4	5	6
Δi(A•cm^{-2})	1.06×10^{-3}	5.03×10^{-4}	2.65×10^{-4}	1.06×10^{-4}	5.03×10^{-5}	2.65×10^{-5}
T(msec)	0.1	0.2	0.4	1	2	4

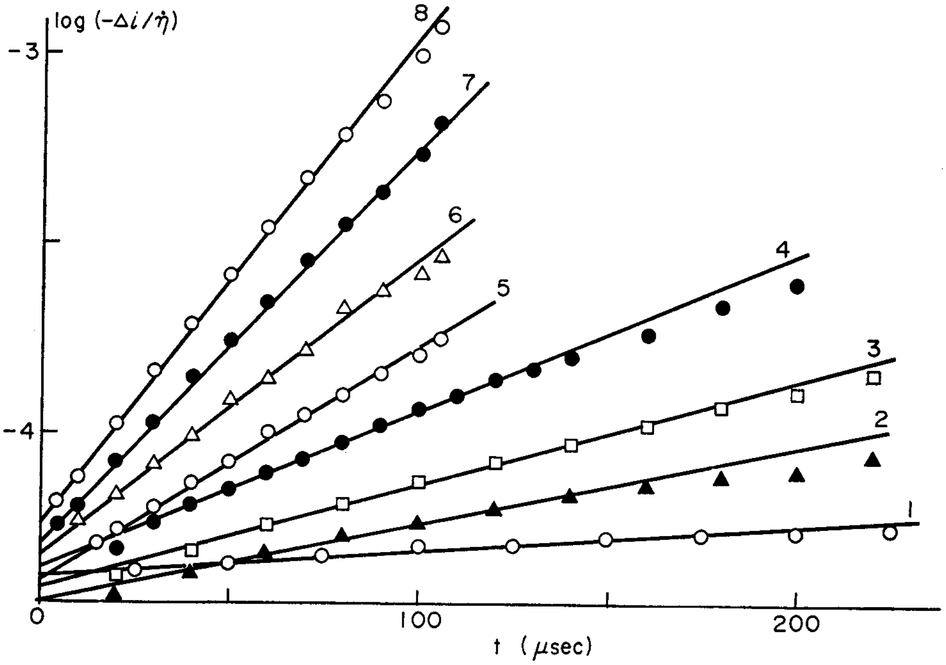

Fig. 7. Analysis of $\eta \sim t$ curves at various overvoltages in 1.73 N H_2SO_4 on the basis of eq. (2). The overvoltage is; 1) 0, 2) −250 mV, 3) −290 mV, 4) −325 mV, 5) −350 mV, 6) −380 mV, 7) −400 mV, 8) −430 mV.

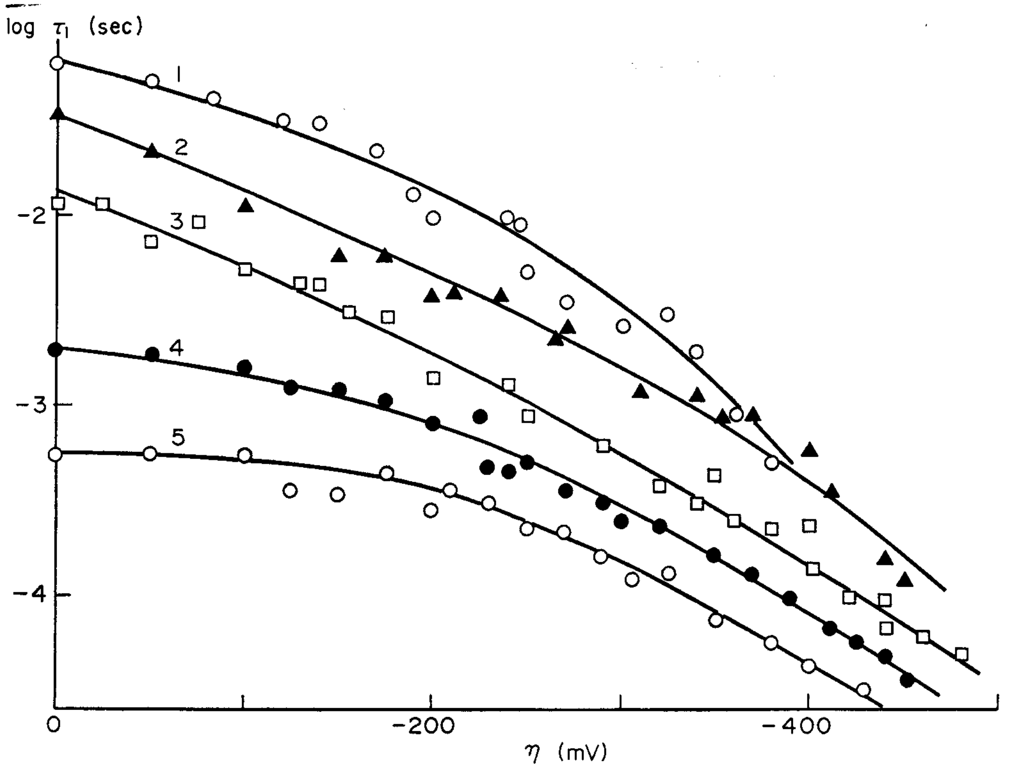

Fig. 8. Dependence of the time constant of the electron-transfer step on overvoltage in sulfuric acid solutions; 1) 1.75×10^{-3} N, 2) 1.04×10^{-2} N, 3) 7.15×10^{-2} N, 4) 0.276 N, 5) 1.73 N.

We see in Fig. 9 that C_D in dilute sulfuric acid solutions decreases sharply at higher overvoltages probably reaching the capacity minimum of the diffuse double layer at p. z. c. in acid solutions. From the comparison of Figs. 4 and 9 it can be seen also that the polarization curves are taken on the highly positively charged electrode surface.

As seen from Fig. 8, τ_l decreases gradually at first with overvoltage but it decreases sharply at higher overvoltages in all the solutions studied. Kinetically, however, the reaction resistance r_l has more significance than τ_l since τ_l reflects the change of both C_D and r_l according to eq. (3). The values of r_l calculated by eq. (3) from τ_l using the value of C_D are shown in Fig. 10 for 0.276 N H_2SO_4 as a function of the polarizing current density. The overvoltage component η_l can be determined by integration of the $r_l \sim i$ curve on the basis of eq. (5).

It is interesting to convert the $r_l \sim i$ curves into a log-log scale as shown

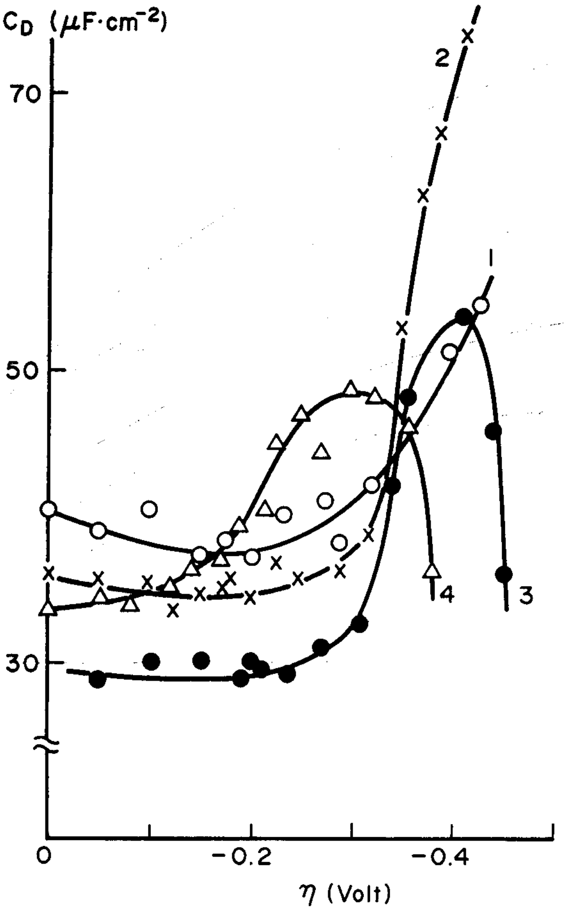

Fig. 9. Dependence on overvoltage of the differential capacity of electric double layer on silver in sulfuric acid solutions ; 1) 1.73 N, 2) 0.276 N, 3) 1.04×10^{-2} N, 4) 1.57×10^{-3}.

in Fig. 11. All the $\log r_1 \sim \log i$ curves tend to coincide each other at higher current densities giving a straight line which can be experessed by the following relation,

$$\log r_1 = -1.26 - \log i\,. \qquad (8)$$

From eq. (8) we can derive an expression for the unidirectional rate of the electron transfer step as a function of η_1. The polarizing current density i is given by the difference between the unidirectional rates of the electron transfer step in the right and reverse directions as $i = \vec{i}_1 - \overleftarrow{i}_1$. At high current

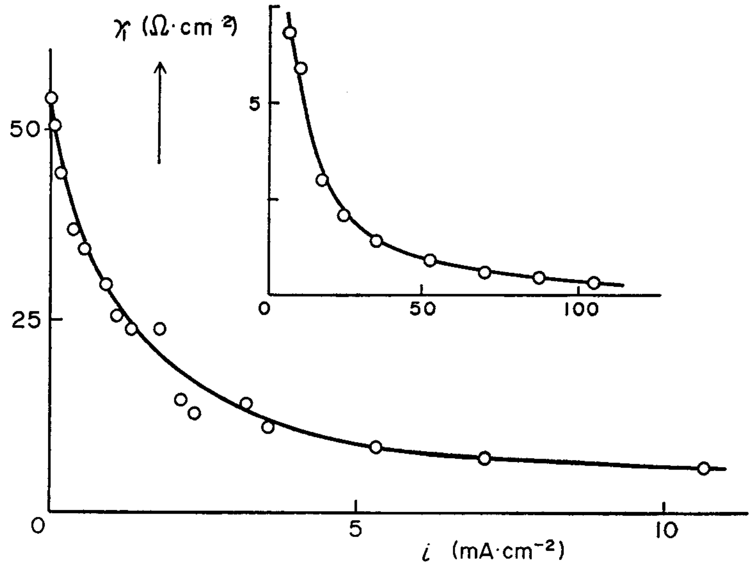

Fig. 10. Dependence of the polarization resistance of the electron-transfer step of the h. e. r. on silver on the polarizing current density in 0.276 N H_2SO_4.

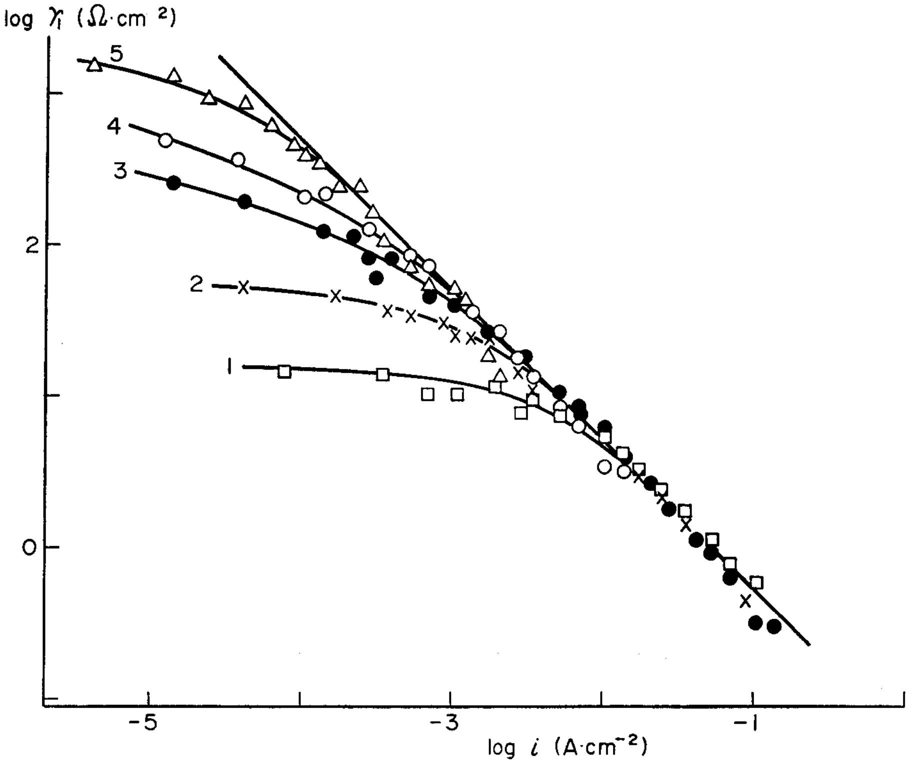

Fig. 11. Dependence of the polarization resistance of the electron-transfer step of h. e. r. on silver in sulfuric acid solutions on the polarizing current density plotted in a log-log scale; 1) 1.73 N, 2) 0.276 N, 3) 7.15×10^{-2} N, 4) 1.04×10^{-2} N, 5) 1.57×10^{-3} N.

densities i can be identified with $\vec{i}_1$ and r_1 with $\vec{r}_1 = -\frac{d\eta_1}{d\vec{i}_1}$. Equation (8) can therefore be identified with the following one,

$$\log \vec{r}_1 = -1.26 - \log \vec{i}_1 . \tag{9}$$

It follows from eq. (9) that

$$\vec{r}_1 \vec{i}_1 = 0.055\,(\mathrm{V}),$$

or combined with eq. (4)

$$-\frac{d\eta_1}{d \ln \vec{i}_1} = 0.055\,(\mathrm{V}) . \tag{10}$$

Integrating eq. (10), we obtain

$$-\eta_1 = 0.055 \ln \frac{\vec{i}_1}{i_{10}} ,$$

which can be expressed at the room temperature by the following equation

$$\vec{i}_1 = i_{10} \exp(-\alpha F \eta_1 / RT), \tag{11}$$

with the coefficient $\alpha = 0.5$. Equation (11) is the typical rate equation for the unidirectional rate of an one-electron transfer reaction.

On the other hand, we can obtain $\eta_1 \sim \log i$ relations in the range of the current density from 0 to i from integration of the $r_1 \sim i$ plot in Fig. 10 on the basis of eq. (5). The log $i \sim \eta_1$ curves obtained in this way are shown in Fig. 12 together with the polarization curves of the overall reaction. It is found that log i can be expressed by eq. (11) at high current densities and in the whole range of the current density eq. (1) can be obtained as the rate equation of the electron transfer step.

It was found on other metals too[16~24] that the rate of the electron trasfer step of h. e. r. in alkaline and sulfuric acid solutions was expressed by eq. (1) but existence of a common line given by eq. (8) was not found since the measurements on these metals could not be extended enough to the region of the higher values of η_1. Equation (1) was also found to be applicable to the proton discharge step on palladium in sulfuric acid in both cathodic and anodic polarization regions by Enyo and Maoka.[35]

The kinetic law of the electron transfer step of h. e. r. on silver so far obtained strongly suggests that electron transfer occurs through the proton discharge step, *i. e.*,

$$H^+ + e \longrightarrow H(a) \tag{I}$$

As seen from Fig. 12, the $\log \eta_1 \sim i$ relations show pronounced concentration dependence. The dependence on the proton activity of i_{10} determined from r_{10} by eq. (5) is shown in Table 1 and Fig. 13. The i_{10} was determined also by exptrapolating the Tafel lines of the electron transfer step given in Fig. 12 to the equilibrium potential and the result is also shown in Fig. 13. It is seen that values of i_{10} determined by two methods agree well in each solution.

We obtain from Fig. 13

$$\mathrm{d} \ln i_{10}/\mathrm{d} \ln a_{\mathrm{H}^+} = 0.99 \tag{12}$$

where a_{H^+} is the proton activity in the solution. The dependence of i_{10} on the activity of proton for step (I) can be expressed as,[36]

$$\mathrm{d} \ln i_{10}/\mathrm{d} \ln a_{\mathrm{H}^+} = (1-\alpha)\left(1 - \frac{\mathrm{F}}{\mathrm{RT}}\, \mathrm{d}\Psi_1/\mathrm{d} \ln a_{\mathrm{H}^+}\right) \tag{13}$$

taking into account the a_{H^+}-dependence of the electrostatic potential Ψ_1 of

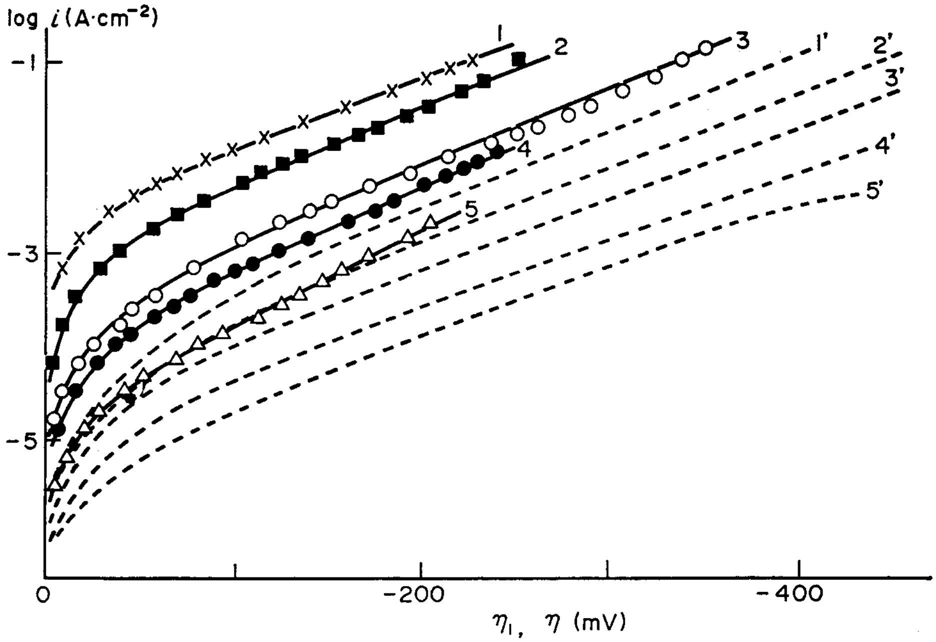

Fig. 12. Tafel lines of the electron-transfer step compared to that of the over-all h. e. r. on silver in sulfuric acid solutions; (1–5) the electron-transfer step and (1′–5′) the over-all reaction. (1, 1′) 1.73 N, (2, 2′) 0.276 N, (3, 3′) 7.15×10^{-2} N, (4, 4′) 1.04×10^{-2} N, (5, 5′) 1.57×10^{-3} N.

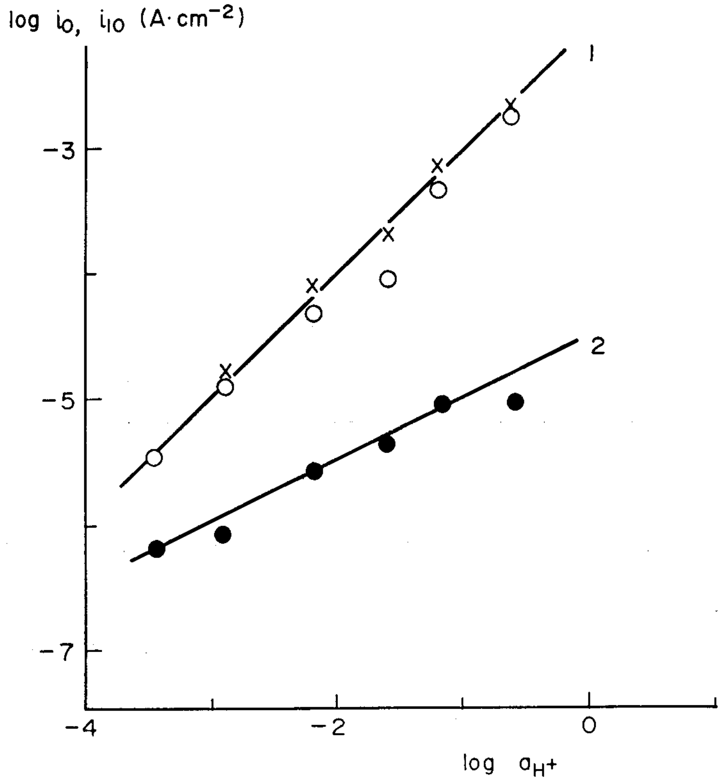

Fig. 13. Dependence of the exchange current densities of h. e. r. on silver on the activity of proton in sulfuric acid solutions; 1) Exchange current density of the electron-transfer step determined from the polarization resistance of the step at the equilibrium potential (○) and by the extrapolation of $\eta_1 \sim \log i$ curves in Fig. 12 (×), 2) Over-all exchange current density determined from the over-all polarization resistance at the equilibrium potential assuming $\nu(r)=1$.

the outer Helmholtz plane referred to the bulk of the solution. The pH-effect on i_{10} expressed by eq. (13) would be zero in dilute solutions of acids if the step (I) takes place on a highly negatively charged electrode surface[36] for which $-\Psi_1 \gg RT/F$ and $\Psi_1=(RT/F)\ln a_{H^+}+\text{const.}$. In the case of silver, however, this is not the case as the equilibrium potential of h. e. r. in an acid solution is several hundreds millivolts more positive than the p. z. c. as seen from Figs. 4 and 9. It follows from eqs. (12) and (13)

$$\frac{d\Psi_1}{d\ln a_{H^+}} = -RT/F \tag{14}$$

The a_{H^+}-dependence of Ψ_1 given by eq. (14) may be accepted reasonable as an approximate expression for the highly positively charged equilibrium silver hydrogen electrode.

From the comparison of i_{10} and i_0 given in Table 1 and Fig. 13 we can expect existence of the rate-determining step which follows the proton discharge in the neighbourhood of the equilibrium potential in concentrated solutions. The nature and the kinetics of the following step will be discussed later in a following paper.

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