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EFFECT OF SURFACE POTENTIAL ON THE RATE OF ELECTRON TRANSFER STEP OF HYDROGEN ELECTRODE REACTION ON METALS^{*})

By

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Abstract

The galvanostatic transient method has been applied to the hydrogen evolution reaction on gallium, gold, silver, nickel and platinum metals in aqueous sodium hydroxide and gold in sulfuric acid, in order to determine the overvoltage component η_1 which is caused by charging up of the electric double layer at the metal-solution interface.

It has been found that (i) the hydrogen overvoltage η is composed of two independent components η_1 and the other component η_a which is caused by the change of the surface potential of the electrode due to specifically adsorbed Na atoms in alkaline solutions or H atoms in acid which is produced by the electron transfer step, and (ii) the polarization curve of the overall reaction $\log i$ vs. η is divided into two independent parts $\log i$ vs. η_1 and $\log i$ vs. η_a which correspond respectively to the polarization curve of the electron transfer step $\text{Na}^+ + \text{e}^- \rightarrow \text{Na(a)}$ or $\text{H}^+ + \text{e}^- \rightarrow \text{H(a)}$ and to that of the recombination of adsorbed H atoms. In alkaline solutions η_a controls the activity of H(a) through the decomposition of water molecule by Na(a).

On the basis of the FRUMKIN's electrode potential theory η_a has been given as the difference of the chemical potential of Na(a) or H(a) $-\Delta\mu_{\text{Na}}$ or $-\Delta\mu_{\text{H}}$ between the reversible and polarization states which means a compensation effect between the changes of the surface potential and the free energy of adsorption of Na(a) or H(a). As the result of the application of the compensation effect to the activation free energy of the electron transfer step which is given by the HORIUTI-POLANYI's rule, it has been shown by the rate theory developed by HORIUTI in the frame of the transition state method that the rate of the electron transfer step can be expressed by the Tafel equation in terms of η_1 independent of the surface potential of the electrode in accordance with the experimental results.

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Introduction

The hydrogen electrode reaction (h.e.r.) on metals may occur as a sequence of several elementary steps and the hydrogen overvoltage η may be composed of a series of components:

$$\eta = \sum_j \eta_j, \quad (1)$$

where η_j means the overvoltage of the j -th elementary step which may be given by the chemical affinity ΔG_j and the stoichiometric number ν_j of the step¹⁾:

$$2F\eta_j = \nu_j \Delta G_j, \quad (2)$$

in which F is the Faraday and the coefficient 2 comes from the number of electrons in the h.e.r., and the rate of each individual step should not be given in general as a function of the overvoltage of the overall reaction which is measurable in the steady state method, but should be expressed in terms of its own component of overvoltage which may be different in the physical conception among different steps.

As pointed out by FRUMKIN²⁾, the establishment of the electrode potential is caused by a number of factors, *i. e.* the adsorption of ions, neutral atoms and molecules, the orientation of surface active substances or solvent dipoles and the Galvani potential of the electrode. All these factors may also result in the build up of the hydrogen overvoltage by charging up of the electric double layer at the metal-solution interface or by the change of the surface potential of the electrode.

The overvoltage caused by charging up of the double layer has been introduced by FRUMKIN in the rate expression of the h.e.r.³⁾, and the polarization characteristics in many electrochemical reaction systems have been successfully explained on the basis of this theory.

On the other hand, the surface states of a metal hydrogen electrode usually show complicated change under polarization which are still at present far from the comprehensive understanding because of the experimental difficulties, and we have little informations on the effect of the surface potential on the rate of the electron transfer step of the h.e.r. However in such complicated systems the overvoltage component caused by charging up of the double layer, which will be denoted hereafter as η_1 , may be determined separately by a galvanostatic transient method at steady states of polarization. In the present work the polarization characteristics of the electron transfer step determined in this way on high and low overvoltage

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metals will be discussed in connection with the change of the surface states of the electrodes.

The principle of the determination of the values of η_1 from the galvanostatic transient curves has been described previously^{4,5,22}, but will be briefly described here. The polarization resistance r_1 of the electron transfer through the electric double layer which is defined as the derivative of η_1 with respect to the net rate of the electron transfer can be determined at a steady state of polarization with the current density i and the overvoltage η from the perturbation of η by a current impulse, the transient curves observed being analyzed by the following equations^{4,5}:

$$\ln(-\Delta i/\dot{\eta}) = \frac{t}{\tau_1} + \ln C_D, \quad (3)$$

$$\tau_1 = C_D r_1, \quad (4)$$

in which Δi is the height of the current pulse, $\dot{\eta}$ is the time derivative of the transient curve observed, C_D is the differential capacity of the double layer and τ_1 is the time constant of the electron transfer step. These equations have been derived assuming a simple equivalent circuit for the metal-solution interface as shown in Fig. 1. The assumption of this simple model for the electrode-solution interface will not affect the validity of deducing the kinetic parameters of the electron transfer step from the transient curves insofar as these curves are observed through a very early time window.

The value of η_1 can be obtained on the basis of the definition of r_1 from the following integral equation as a function of the current density i , taking into consideration that the net rate of the electron transfer step in a steady state equals $i^{(5)}$:

$$\eta_1 = -\int_0^i r_1 di. \quad (5)$$

In this way we obtain the po-

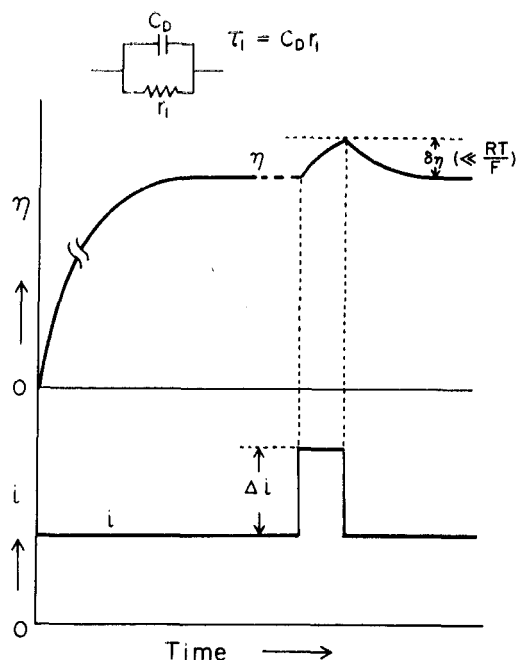


Fig. 1. A galvanostatic transient curve and an equivalent circuit.

larization curve of the electron transfer step separately. From the comparison of the polarization curve of the electron transfer step $\log i$ vs. η_1 and that of the overall reaction $\log i$ vs. η , we can obtain one more polarization curve $\log i$ vs. η_a where $\eta_a \equiv \eta - \eta_1$, which may offer informations on the overvoltage components due to the change of the surface potential.

The polarization characteristics of the electron transfer step will be discussed in the following sections comparing three kinds of polarization curves on gallium, gold, nickel, silver and platinum hydrogen electrodes in alkaline solutions and on gold in sulfuric acid.

Experimental results

(1) The gallium hydrogen electrode in sodium hydroxide solutions

The liquid gallium electrode of 99.99999% purity (geometrical area 1 cm²) shows a rest potential around -550 mV of η in aqueous sodium hydroxide solutions under atmospheric hydrogen bubbling at 32°C, but in the hydrogen overvoltage region the polarization curves have a slope of 120 mV as shown in Fig. 2, and show a good coincidence with those obtained by BAGOZKAYA and POTAPOVA⁶⁾.

The pH-dependence of η at $i=10^{-3}$ amp/cm² shows a gradient 125 mV as seen from Fig. 3, in accordance with the water molecule discharge me-

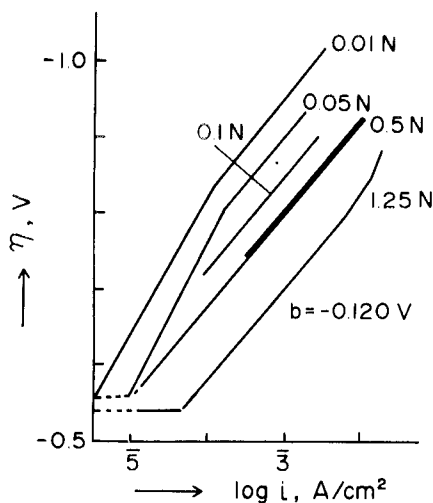


Fig. 2. Polarization curves of the overall reaction on Ga in NaOH solutions at 32°C; thick line—BAGOZKAYA and POTAPOVA⁶⁾.

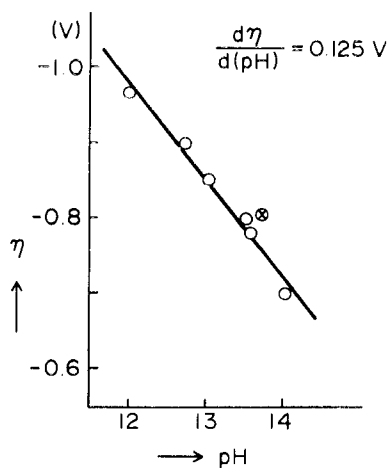


Fig. 3. pH-dependence of overvoltage at 10^{-3} A/cm²; (⊗)—BAGOZKAYA and POTAPOVA⁶⁾.

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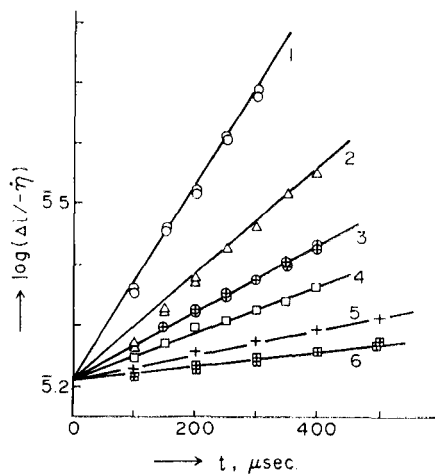


Fig. 4. $\log(-\Delta i/\bar{\eta})$ vs. t relations obtained from potential-time curves on Ga in 0.01 N NaOH; the starting overvoltage in mV, (1) -1050; (2) -1008; (3) -965; (4) -932; (5) -895; (6) -720.

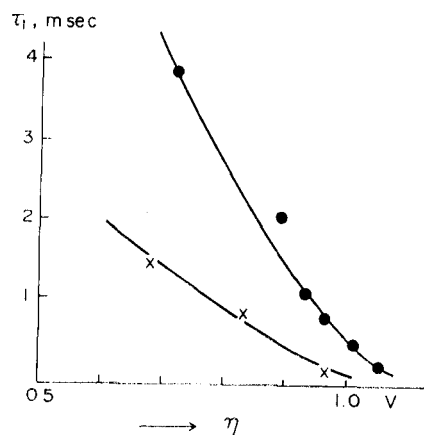


Fig. 5. η -dependence of the time constant of the electron transfer step τ_1 on Ga in NaOH solutions; (●) 0.01 N, (×) 0.075 N.

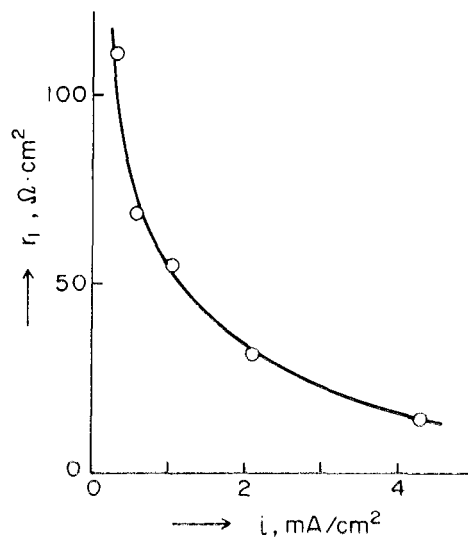


Fig. 6. The relation between the polarization resistance of the electron transfer step and the current density on Ga in 0.01 N NaOH solution.

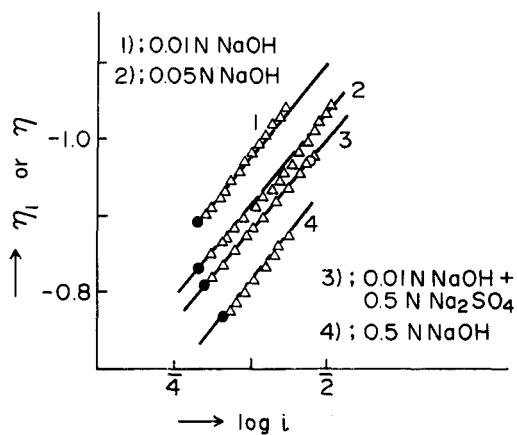


Fig. 7. Polarization curves of the electron transfer step (Δ), and of the overall reaction (line) in NaOH solutions.

chanism proposed by FRUMKIN, KORSHUNOV and BAGOZKAYA^{7,8)} on gallium.

The experimental results of the galvanostatic transient study are shown in Figs. 4~8. It can be seen from Fig. 4 that the values of $\log(-\Delta i/\dot{\eta})$ calculated from the transient curves change linearly with time in accordance with Eq. (3), and the double layer capacity has a constant value $16 \mu\text{F}/\text{cm}^2$ independent of η , but the values of τ_1 strongly depend on η as shown in Fig. 5. A typical τ_1 vs. i curve in 0.01 N NaOH is shown in Fig. 6.

The polarization curves of the electron transfer step $\log i$ vs. η_1 in NaOH solutions obtained from the integration of the τ_1 vs. i curves according to Eq. (5) are illustrated in Fig. 7 with a symbol of triangle, and the polarization curves of the overall reaction $\log i$ vs. η in the same solutions are also shown in this Figure by straight lines. It can be seen that the two kinds of the polarization curves coincide with each other in every solution used. It follows from this fact that η equals η_1 , *i. e.* the hydrogen overvoltage is entirely caused by charging up of the double layer on gallium in NaOH solution.

This conclusion is also supported by the result of the comparison of the $\log i$ vs. η curve of the overall reaction with the polarization curve of the electron transfer step $\log i_1$ vs. η obtained from the decay of overvoltage after switching off the polarizing current, as will be seen in the following. In the course of the potential decay the rate of the electron transfer i_1 may be given by the following equation if the overvoltage is caused by the change of the free charge density on the electrode surface:

$$i_1 = C_D \dot{\eta}. \quad (6)$$

The values of $\log i_1$ determined in this way are plotted against the values of overvoltage at which $\dot{\eta}$ is calculated in the course of decay in Fig. 8. As seen from this Figure, $\log i_1$ vs. η curve in the course of decay coincides with $\log i$ vs. η curve in steady states.

In order to find the chemical species which accepts a metal electron in the double layer, the values

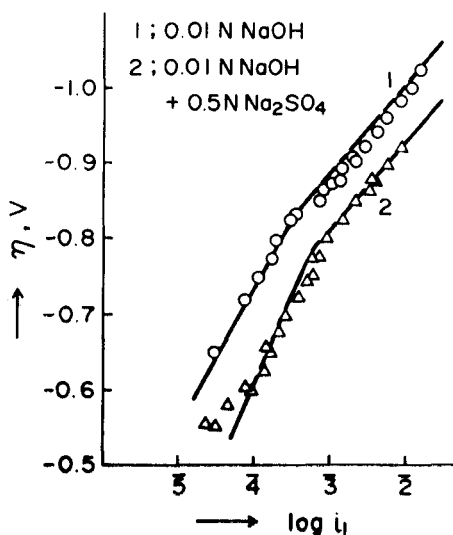


Fig. 8. Polarization curves of the electron transfer step obtained from the potential decay after switching off the current (\circ) and (\triangle), and of the overall reaction (line).

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of τ_1 at a constant potential drop between the metal surface and the Helmholtz plane are plotted against the pH or pNa of the solution in Fig. 9, the FRUMKIN correction being used for the calculation of the potential of the Helmholtz plane⁹⁾ ϕ_1 . Taking into consideration the constancy of the value of C_D , the values of τ_1 are used for convenience as a measure of the rate of the electron transfer step, since its value is measurable independent of the surface area of the electrode. As seen from this Figure, the values of τ_1 at a constant potential drop across the compact double layer show no pH nor pNa dependence. It can be concluded from this fact that the metal electron transfers to a water molecule in the double layer. All the evidences obtained from the galvanostatic transient study confirm the mechanism of the water molecule discharge proposed by FRUMKIN, KORSHUNOV and BAGOZKAYA,⁷⁾ and the hydrogen overvoltage is entirely caused by charging up of the double layer.

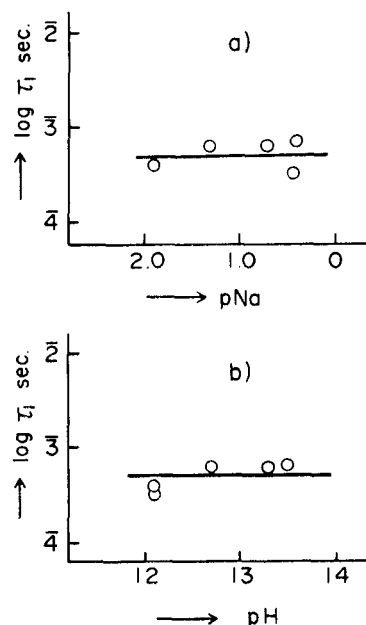


Fig. 9. pNa- (a) or pH-dependence (b) of the time constant of the electron transfer step at constant $\varphi - \phi_1$ in NaOH and NaOH + Na₂SO₄ solutions.

(2) **The gold hydrogen electrode in sulfuric acid and sodium hydroxide solutions**

The mechanism of the hydrogen electrode reaction on gold has been discussed by several authors based mainly on the b -value of the Tafel slope^{9,10,11)}, but the mechanism has not yet been generally accepted because of its wide variety among different authors. The mechanism of the establishment of the hydrogen overvoltage and the reaction mechanism will be discussed here from the comparison of the polarization characteristics between the individual step of the electron transfer and the overall reaction in sulfuric acid and sodium hydroxide solutions. Special attention was paid for the preparation and purification of the electrode metal and the solutions. A gold foil degassed or gold film prepared in vacuum was used as the working electrode and the electrolytic cell was made of silica glass.

(2 a) *Polarization curves in sulfuric acid.*

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Sulfuric acid was prepared by dissolution of SO_3 gas into water in a vacuum system. The gold hydrogen electrode showed very high activity and good reproducibility after an anodic treatment at about 1.8 V (*vs.* R.H.E.) for a few seconds. The double layer capacity was found to be constant independent of the value of η and the concentration of the solution from the galvanostatic transient study, whereas the time constant τ_1 changed remarkably depending on η and the solution concentration.

Fig. 10 shows the polarization curves of the electron transfer step $\log i$ *vs.* η_1 determined by the galvanostatic transient method and $\log i$ *vs.* η curves of the overall reaction.¹²⁾ The polarization curve of the overall reaction in 1 N H_2SO_4 shows a straight line with the b -value of 29 mV, but in dilute solutions it shows a deviation from this line and the b -value tends to approach to 120 mV with the increase of the current density.

As seen from Fig. 10, the rate of the electron transfer step i_1 can be expressed by the following equation in terms of η_1 :

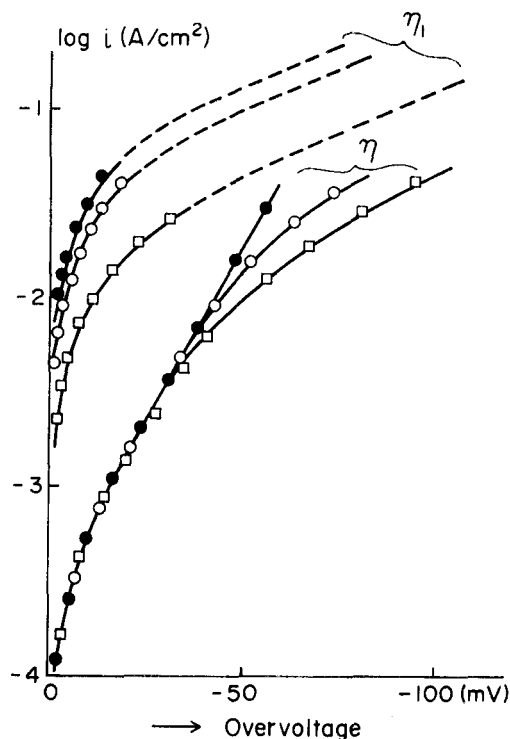


Fig. 10. Polarization curves of the electron transfer step $\log i$ *vs.* η_1 , and of the overall reaction $\log i$ *vs.* η on Au in sulfuric acid, (●) 1.3 N, (○) 0.67 N and (□) 0.30 N, and (---) theoretical curves calculated by Eq. (7).

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$$i_1 = i_{10} \left\{ \exp(-\alpha F \eta_1 / RT) - \exp(\beta F \eta_1 / RT) \right\}, \quad (7)$$

with the transfer coefficient $\alpha = \beta = 0.5$. The exchange current density of the electron transfer step i_{10} is obtained from the polarization resistance at the reversible potential by the equation:

$$i_{10} = RT / r_{10} F. \quad (8)$$

The polarization resistance r_{10} is obtained from the time constant τ_{10} at the reversible potential according to Eq. (4). $\log \tau_{10}$ is found to change linearly with the pH of the solution with a gradient 0.5 as shown in Fig. 11, and consequently i_{10} is proportional to the square root of the concentration of the hydronium ion. It may be concluded from these facts that the electron transfer step is the discharge of the hydronium ion, and its rate can be expressed by Eq. (7) in terms of the overvoltage component caused by charging up of the double layer.

As seen from the comparison of η_1 and η at a constant current density in Fig. 10, η_1 is negligibly small at low current densities, but with the increase of the current density it grows to such an extent that η_1 accounts for the considerable part of η particularly in dilute solutions.

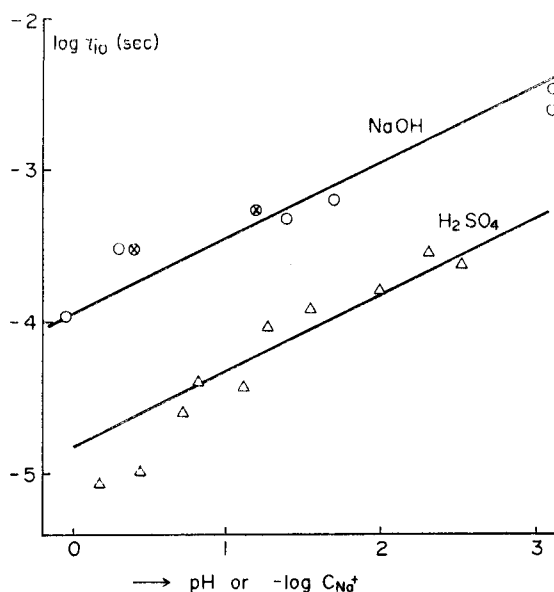


Fig. 11. Time constant τ_{10} of the electron transfer step at the reversible potential on Au plotted against pH in acid, or pNa in alkaline solutions, (⊗) in NaOH+Na₂SO₄ solutions of pH 10.8 and 12.1.

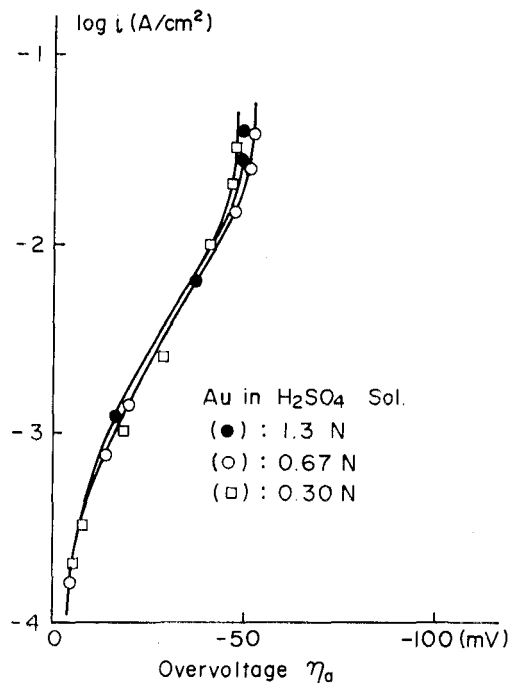
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Fig. 12. Current density plotted against overvoltage difference $\eta - \eta_1 \equiv \eta_a$ on Au in sulfuric acid obtained from Fig. 10.

From the two kinds of polarization curves in Fig. 10, it is possible to deduce $\log i$ vs. η_a curves which may reveal the mechanism of the setting up of the surface potential. As seen from Fig. 12, the $\log i$ vs. η_a curves practically coincide with each other with the b -value of 29 mV and the value of η_a has a tendency to approach a saturation value of *ca.* -50 mV independent of the concentration of the solution. These facts may be explained by assuming that η_a is caused by the adsorption of hydrogen atoms on the electrode surface which result in the change of the surface potential due to dipoles with the positive end toward the solution side, and that its surface coverage is very low but it attains saturation at η_a about -50 mV.

From the comparison of the $\log i$ vs. η_1 and $\log i$ vs. η_a curves, it may be concluded that η_1 grows according to Eq. (7) but η_a attains a saturation value with the increase of the current density, or in other words, the rate-determining step switches over from the recombination of adsorbed hydrogen atoms to the discharge of hydronium ion. This conclusion contradicts to the mechanism of KUHN and BYRNE^{1D} in which the transition of the rate-determining step occurs from the recombination of adsorbed hydrogen atoms

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to the electrochemical desorption.

(2 b) *Polarization curves in sodium hydroxide solutions.*

The gold hydrogen electrode in aqueous NaOH shows a wide variety of the polarization curves of the overall reaction as shown by the shaded area in Fig. 13. However it gives good reproducible results on the $\log i$ vs. η_1 curves, which enable us to deduce some definite conclusions on the kinetic behavior of the electron transfer step.

Fig. 13 shows examples of the polarization curves $\log i$ vs. η_1 . These curves can also be expressed by Eq. (7), and i_{10} is now proportional to the square root of Na^+ ion independent of the pH of the solution, as seen from Fig. 11. It may be concluded that the electron transfer step is the discharge of Na^+ ion, in contrast to the case of the gallium hydrogen electrode.

The change of τ_1 with η is shown in Fig. 14. As seen from the Figure, τ_1 remains at a constant value which equals τ_{10} in the wide range of overvoltage from 0 to -300 or -400 mV, *i.e.* the electron transfer step can be regarded as very close to its reversible state in spite of the remarkable

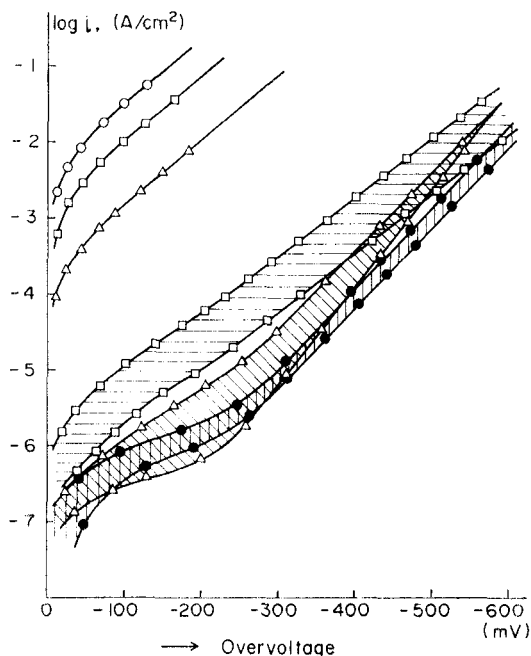


Fig. 13. Polarization curves of the electron transfer step and the overall reaction (shaded area) on Au in alkaline solutions, (○) 1 N NaOH, (●) 0.56 N NaOH, (△) 0.007 N NaOH, (□) 0.43 N $\text{Na}_2\text{SO}_4 + 0.01$ N NaOH.

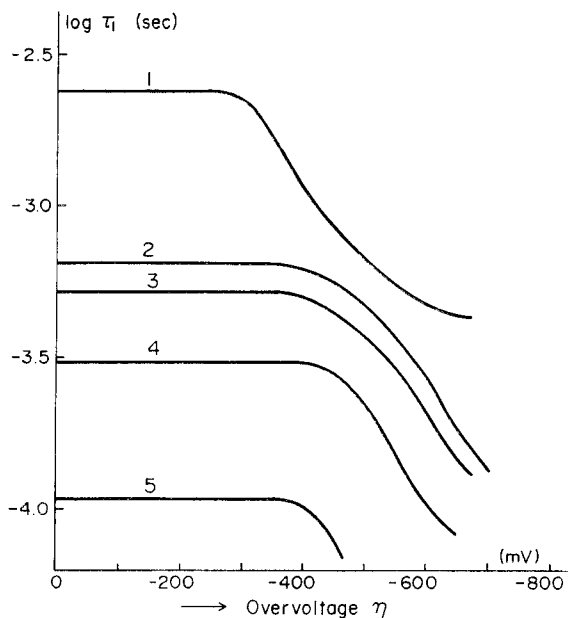


Fig. 14. Time constant of the electron transfer step plotted against η on Au in alkaline solutions, 1—0.007 N NaOH, 2—0.02 N NaOH, 3—0.001 N NaOH+0.1 N Na₂SO₄, 4—0.5 N NaOH, 5—1 N NaOH.

growth of η . This fact suggests that the electron transfer step occurs independent of the surface states of the electrode. This may be the reason why a definite polarization curve of good reproducibility can be obtained with respect to the electron transfer step in spite of the wide variety of the polarization curves of the overall reaction. The rate equation and the effect of the surface potential on the rate of the electron transfer step will be discussed in detail in a later section.

(3) The silver hydrogen electrode in sodium hydroxide solution

A silver electrode of a bead shape of geometrical area 0.2 cm² was used after heat treatment in a stream of helium gas. The silver electrode prepared in this way showed good reproducibility in NaOH solutions.

Fig. 15 shows the $\log(-\Delta i/\dot{\eta})$ vs. time curves obtained at different overvoltages in $5.6 \cdot 10^{-8}$ N NaOH. The values of C_D given by $-\Delta i/\dot{\eta}$ at $t=0$ are plotted against η in Fig. 16. It can be seen from this Figure that the η -dependence of C_D on silver is different from that on gallium or gold. There exists a minimum in the C_D -curve in Fig. 16 at about -0.9 V (*vs.* N.H.E.) in agreement with the result of LEIKIS *et al.*¹⁰, which may corresponds to

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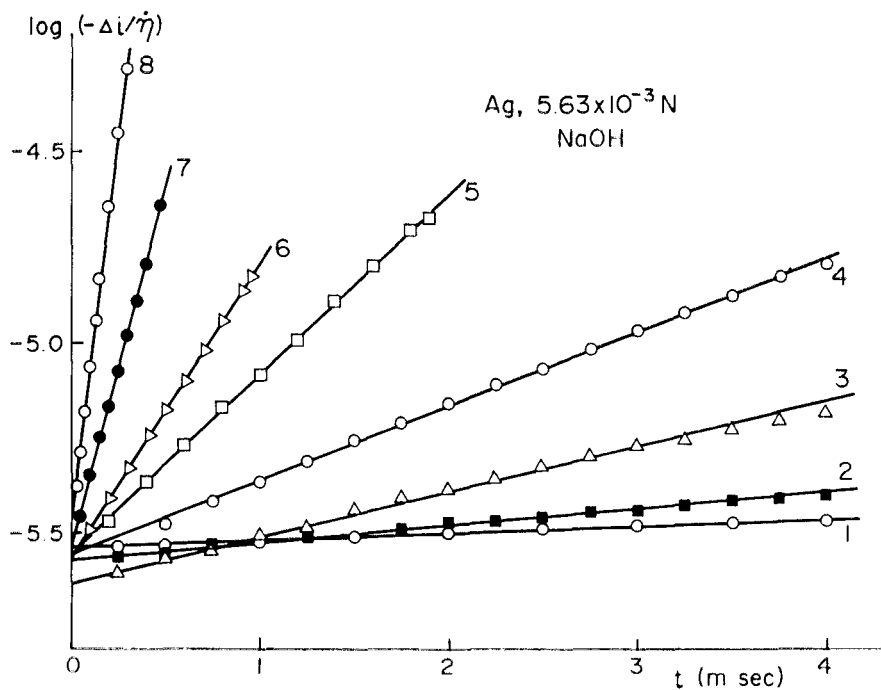


Fig. 15. $\log(-\Delta i/\dot{\eta})$ vs. t curves on Ag in $5.63 \cdot 10^{-3}$ N NaOH, the starting overvoltage of the transient in mV, (1) 0; (2) -100; (3) -200; (4) -240; (5) -300; (6) -330; (7) -400; (8) -490.

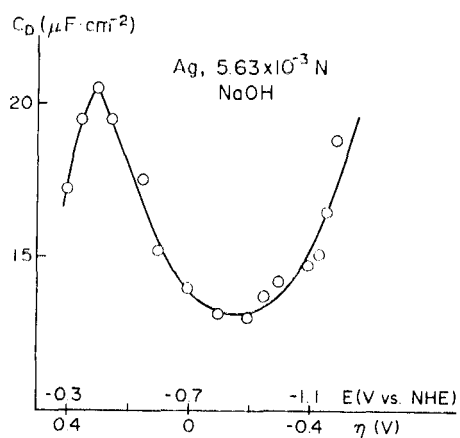


Fig. 16. Potential dependence of the double layer capacitance of Ag in $5.63 \cdot 10^{-3}$ N NaOH obtained from Fig. 15.

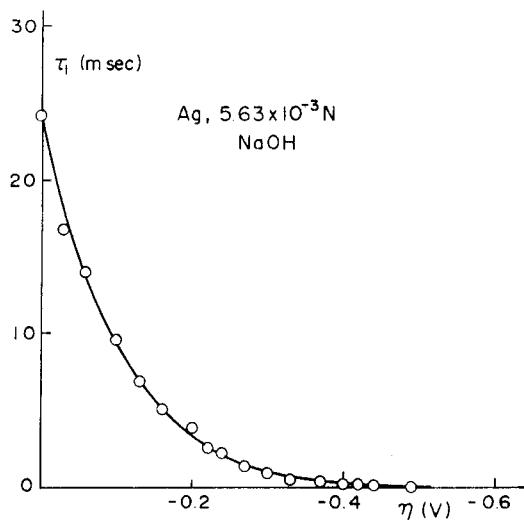
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Fig. 17. Time constant of the electron transfer step on Ag obtained from Fig. 15.

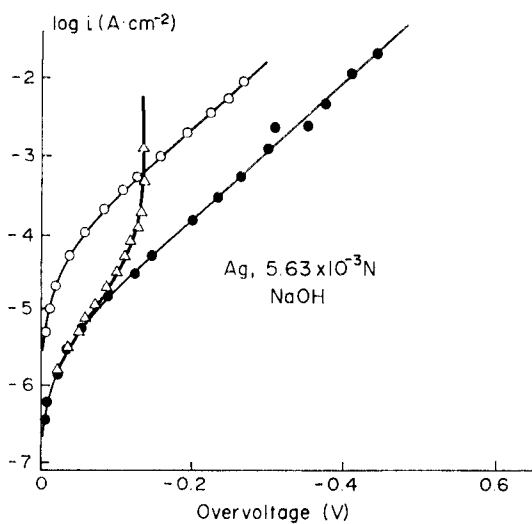


Fig. 18. $\log i$ plotted against τ_1 (\circ), η (\bullet), and η_a (Δ) on Ag in $5.63 \cdot 10^{-3} \text{ N}$ NaOH.

the zero-charge potential.

The τ_1 vs. η curve shows a gradual decrease as in the case of gallium with no plateau, as seen from Fig. 17. Fig. 18 shows the $\log i$ vs. η_1 curve obtained from Fig. 17 together with the $\log i$ vs. η of the overall reaction

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in a NaOH solution. As seen from this Figure, the $\log i$ vs. η_1 curve can also be expressed by Eq. (7) and η_1 cannot be neglected as compared with η except in the reversible region, and η_1 accounts for a greater part of η at higher current densities. The $\log i$ vs. η_a curve obtained from the two kinds of polarization curves is also shown in Fig. 18 with the symbol of triangle, which has the b -value of 60 mV and the saturation value of η around -0.14 V as in the case of gold in sulfuric acid.

It is interesting to compare the $\log i$ vs. η_a curve in Fig. 18 with the polarization curve on silver observed by KRISHTALIK and BYSTROV¹⁵⁾ at low current densities in hydrochloric acid. It is found that the two polarization curves have the same b -value of 60 mV and are almost in the same region of the current density and overvoltage. It may be concluded from this fact that η_a is attributed to the recombination of adsorbed hydrogen atoms, the existence of which has already been demonstrated by SHUMILOVA *et al.*¹⁶⁾

(4) The nickel hydrogen electrode in alkaline solutions

The nickel hydrogen electrode in alkaline solutions has been extensively studied and its polarization characteristics has been explained on the basis of the catalytic mechanism¹⁷⁾ in which the recombination of adsorbed hydrogen atoms is rate-determining. However the kinetic study of the individual steps of the reaction by the galvanostatic transient method has required some modification as to the mechanism of the establishment of the hydrogen overvoltage and the reaction mechanism.

(4 a) The polarization curves in sodium hydroxide solutions.

The polarization curves of the electron transfer step $\log i$ vs. η_1 and those of the overall reaction $\log i$ vs. η in aqueous NaOH are shown in Fig. 19.¹⁸⁾ As seen in this Figure, the Tafel line of the overall reaction has a break in any concentration which suggests the change of the reaction mechanism. In the region lower than the break point the Tafel line has the b -value of *ca.* 80 mV and is independent of the solution concentration, but after the break point the b -value changes to 120 mV and the Tafel line is lowered with the increase of the solution concentration.

The polarization curve of the electron transfer step $\log i$ vs. η_1 in Fig. 19 can also be expressed by Eq. (7) with $\alpha=\beta=0.5$, and the value of η_1 is negligibly small at current densities lower than that at the break point of the Tafel line of the overall reaction, at which it becomes detectable, and at higher current densities the Tafel line of the electron transfer step becomes parallel to that of the overall reaction, as seen from Fig. 19. On the other hand, $\log \tau_{10}$ changes linearly with $\log C_{\text{Na}^+}$ with a coefficient 0.5 in NaOH

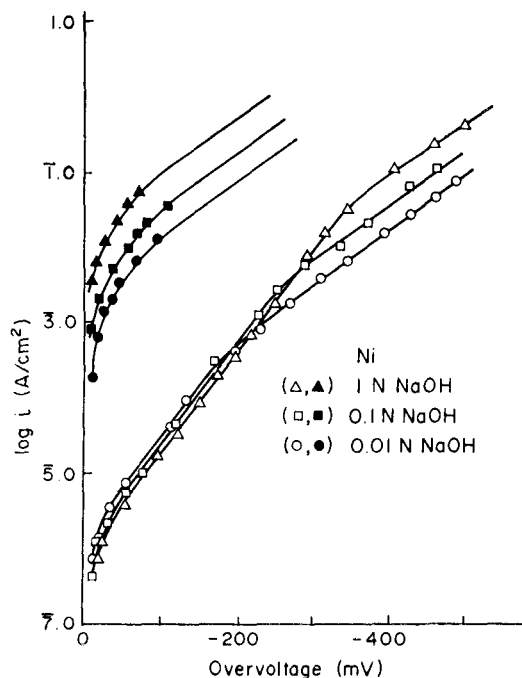
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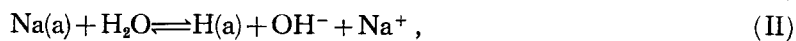
Fig. 19. Polarization curves of the electron transfer step $\log i$ vs. η (filled symbols), and of the overall reaction (open symbols) on Ni in NaOH solutions.

or Na_2SO_4 solutions as in the case of gold in alkaline solutions, as seen in Fig. 21.¹⁰ It may be concluded from these facts that the electron transfer step is composed of the discharge of Na^+ ion.

The $\log i$ vs. η_a curves calculated from $\log i$ vs. η_1 and $\log i$ vs. η curves in Fig. 19 are shown in Fig. 20. As seen from this Figure, these polarization curves nearly coincide with each other and also with the polarization curve of the overall reaction in the region lower than the break point, but the value of η_a has a tendency to approach a saturation value with the increase of the current density as in the case of gold and silver. On the other hand, it has been found from the concentration dependence of the pseudo-capacitance of the nickel hydrogen electrode in alkaline solutions that the key intermediate which causes η_a has been determined to be Na atom adsorbed on the electrode surface, but not adsorbed hydrogen atoms.

On the basis of the arguments mentioned above it may be concluded that the hydrogen electrode reaction occurs as the sequence of the following elementary steps :

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in which the step (II) can be regarded as practically in equilibrium, but the

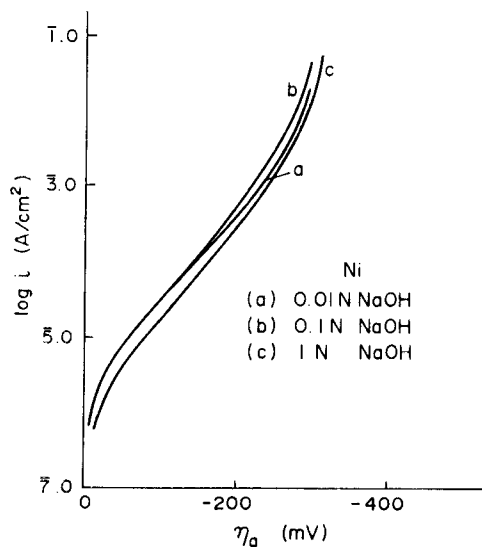


Fig. 20. $\log i$ vs. η_a curves obtained from Fig. 19.

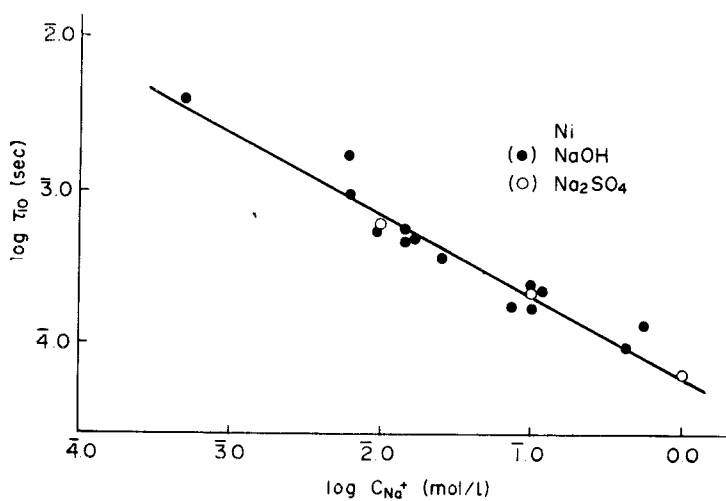


Fig. 21. Concentration dependence of the time constant τ_{10} on Ni in alkaline solutions.

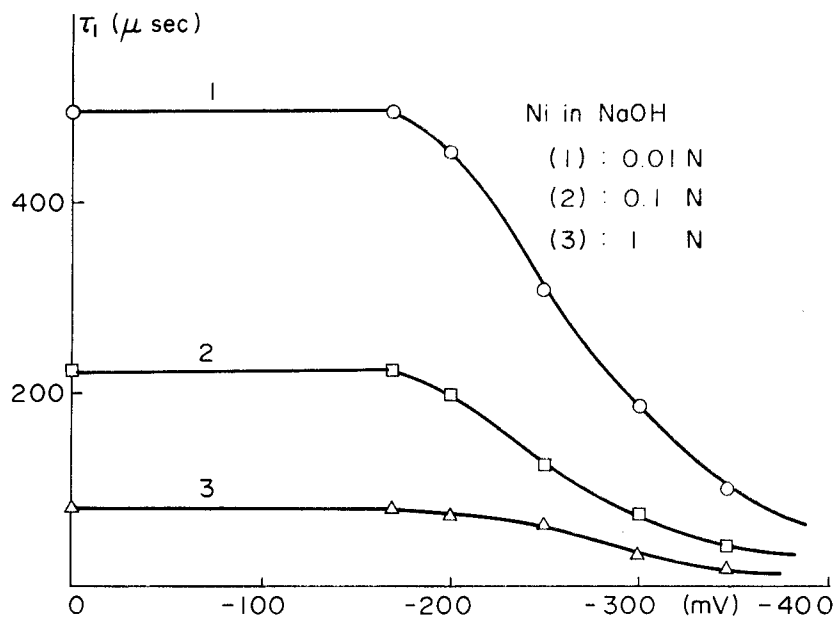
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Fig. 22. η -dependence of the time constant τ_1 on Ni in NaOH solutions.

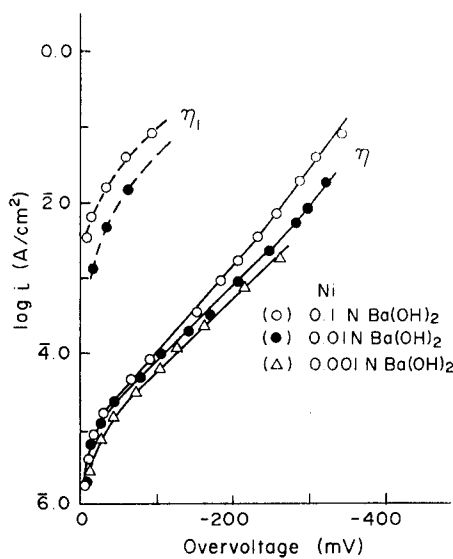


Fig. 23. Polarization curves of the electron transfer step $\log i$ vs. η_1 and of the overall reaction on Ni in Ba(OH)₂ solutions.

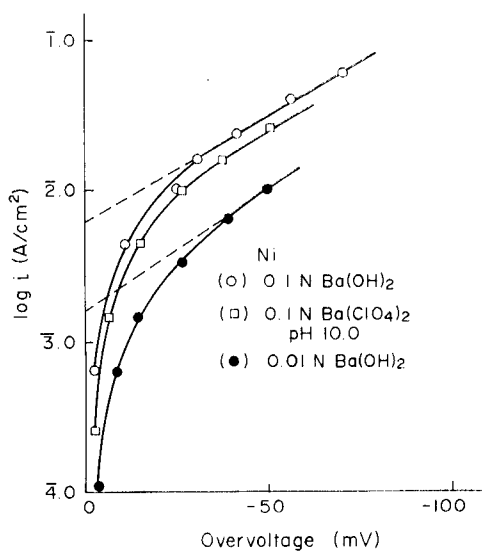


Fig. 24. $\log i$ vs. η_1 curves on Ni in alkaline solutions containing Ba²⁺ ion.

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transition of the rate-determining step occurs from step (III) to (I) with the increase of the current density, on which basis the break of the Tafel line of the overall reaction may be explained.

The η -dependence of τ_1 is shown in Fig. 22.¹⁸⁾ As seen from this Figure, a plateau appears in the τ_1 vs. η curve as in the case of gold, which also

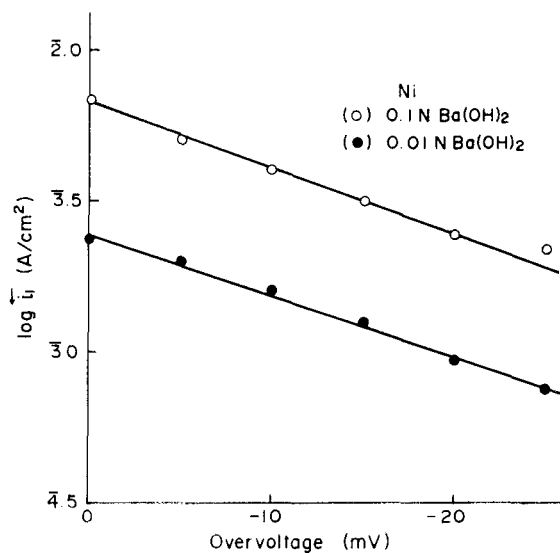


Fig. 25. Polarization curves of the electron transfer step in the reverse direction $\log i$ vs. η_1 on Ni in $\text{Ba}(\text{OH})_2$ solutions.

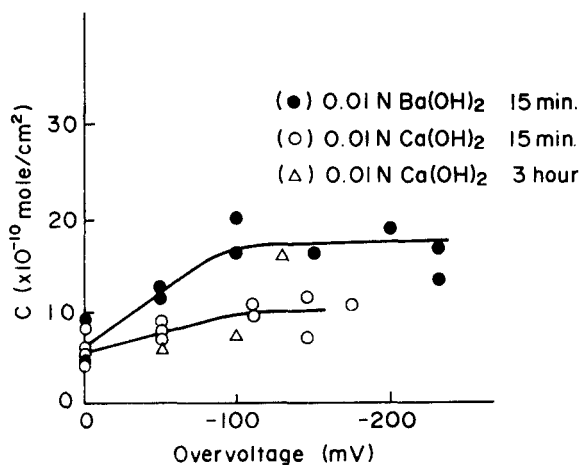


Fig. 26. Surface concentration of Ba or Ca atom under polarization on Ni determined by atomic absorption spectroscopy.

means that the electron transfer step is close to the reversible state in spite of the remarkable growth of η .

(4 b) *The polarization curves in barium hydroxide solutions*

In aqueous $\text{Ba}(\text{OH})_2$ the polarization curves of the overall reaction are quite similar to those in aqueous NaOH as shown in Fig. 23¹⁹⁾, and the rate of the electron transfer step can also be expressed by Eq. (7) with $\alpha=0.68$, as seen from Fig. 24.¹⁹⁾

The rate of the electron transfer step in the reverse direction \bar{i} can be determined as a function of η_1 from the following equations:

$$i = \bar{i} - \bar{i}, \quad (9)$$

$$\bar{i} = i_{10} \exp(-\alpha F \eta_1 / RT), \quad \alpha = 0.68. \quad (10)$$

The polarization curves $\log \bar{i}$ vs. η_1 determined in this way are shown in Fig. 25. The transfer coefficient β in the reverse direction is found to be 1.37 from Fig. 25 and the sum $\alpha + \beta$ is quite close to 2 which may be obtained as the result of the discharge of Ba^{II} ion. In fact, the intermediate species of the electrolytic hydrogen evolution in aqueous $\text{Ba}(\text{OH})_2$ has been found to be Ba atom by atomic absorption spectroscopy²⁰⁾, and its surface concentration varies with η as shown in Fig. 26. It may be concluded that the hydrogen electrode reaction on nickel in $\text{Ba}(\text{OH})_2$ solutions occurs in the same frame of the reaction mechanism as in the aqueous NaOH with the intermediate species of Ba atom which causes the change of the surface potential of the electrode.

(5) **The platinum hydrogen electrode in alkaline solutions**

The polarization characteristics of the electron transfer step has been found quite similar to those on nickel in alkaline solutions^{4,5)}. The value of τ_{10} in NaOH , LiOH ²¹⁾ and CsOH ²²⁾ is also proportional to the square root of the cation concentration as shown in Fig. 27, and it does not show a remarkable distinction among alkali ions, but slightly increases in the order $\text{Li}^+ < \text{Na}^+ < \text{Cs}^+$, for instance, 75, 90 and 120 μsec in 0.1 N concentration respectively.

The polarization curves of the electron transfer step $\log i$ vs. η_1 can also be expressed by Eq. (7) and its exchange rate is proportional to the square root of the cation concentration, but the $\log i$ vs. η_a curves do not depend on the solution concentration and have the b -value of 60 mV, as exemplified in Fig. 28 in the case of CsOH solutions.

The adsorption capacitance determined from the potential decay after switching off the current has shown a strong dependence on the cation concentration with a sharp maximum at the potential *ca.* -800 mV (*vs.* N.H.E.)^{21,22,23)}.

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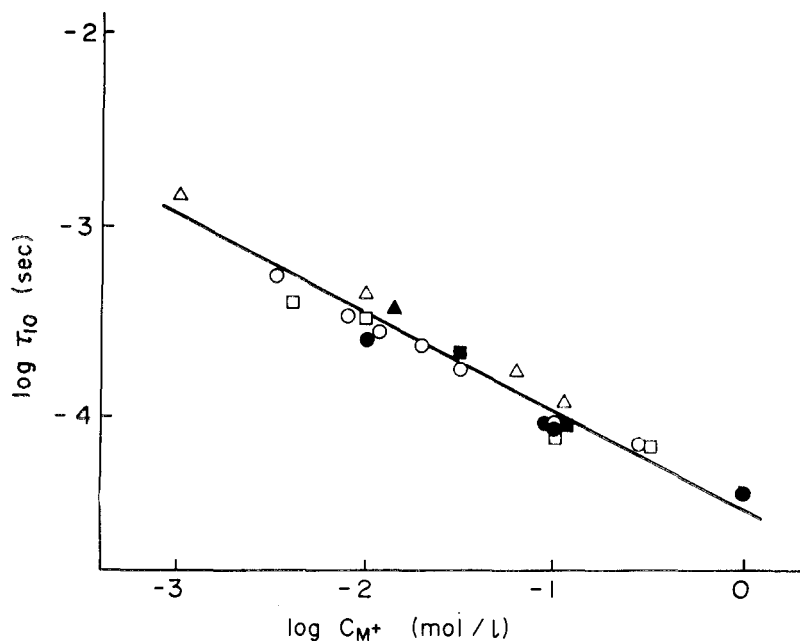


Fig. 27. Concentration dependence of τ_{10} on Pt in LiOH (\square), NaOH (\circ), CsOH (\triangle), and LiOH+Li₂SO₄ (\blacksquare), NaOH+Na₂SO₄ (\bullet), CsOH+Cs₂SO₄ (\blacktriangle).

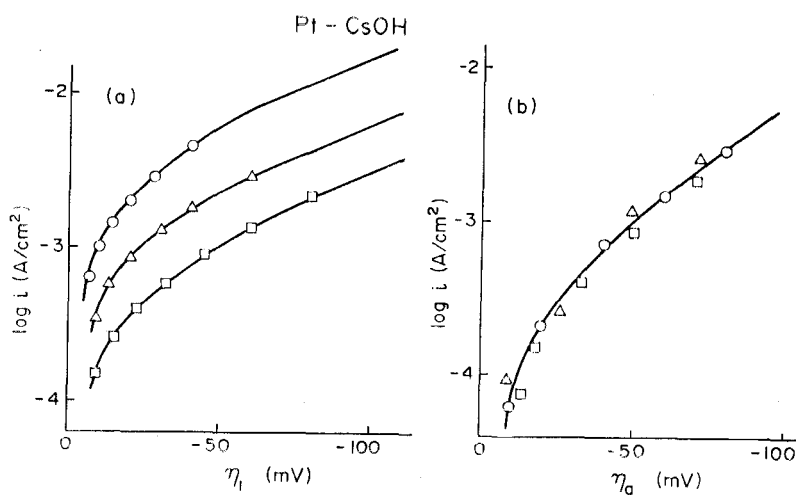


Fig. 28. (a)—Polarization curves of the electron transfer step $\log i$ vs. η_1 , (b)—Polarization curves $\log i$ vs. η_a on Pt in CsOH, (\circ) pH 12.8, (\triangle) pH 11.86 and (\square) 10.86.

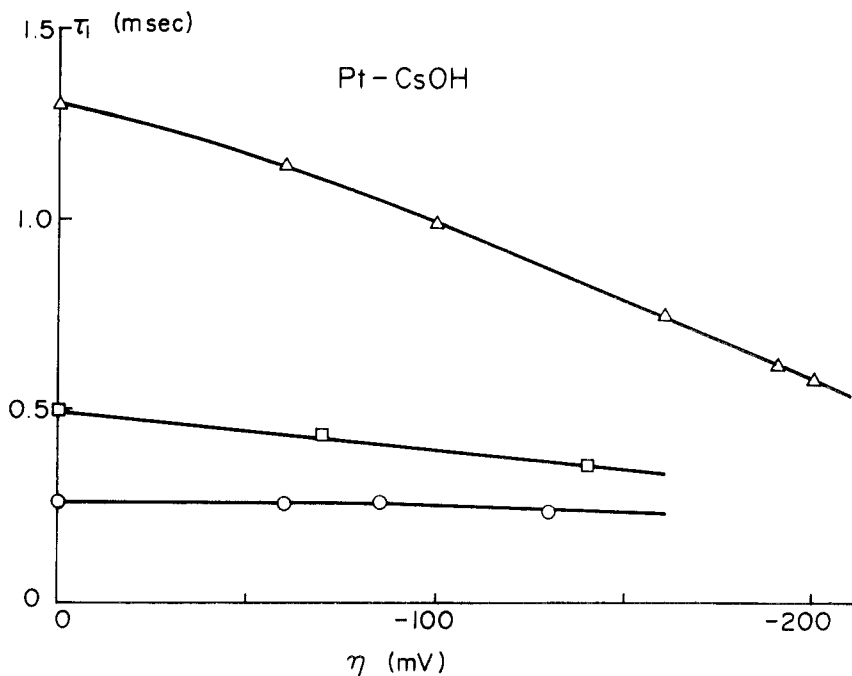
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Fig. 29. η -dependence of the time constant τ_1 on Pt in CsOH of the same concentration as in Fig. 28.

All these evidences for the platinum hydrogen electrode in alkaline solutions are in favor of the mechanism on nickel described in the previous section. The τ_1 vs. η curve also has a plateau as shown in Fig. 29.

The role of the surface potential in the rate equation of the electron transfer step

It has already been established by FRUMKIN²⁴⁾ and KRISHTALIK²⁵⁾ from the theoretical point of view and experimentally by FEDOROVICH *et al.*²⁶⁾ that for the comparison of the rate of the electron transfer between metals of different work function on which no change of the surface potential is observed under polarization, the rate of the reaction should be compared at a constant potential referred to a definite reference electrode, but not at a potential referred to the zero charge potential of the electrode, or in other words, the work function of the metal electrode into vacuum does not appear explicitly in the rate equation of the electron transfer reaction, but the work function into solution plays an important role in the promotion of the rate of the electron transfer reaction.

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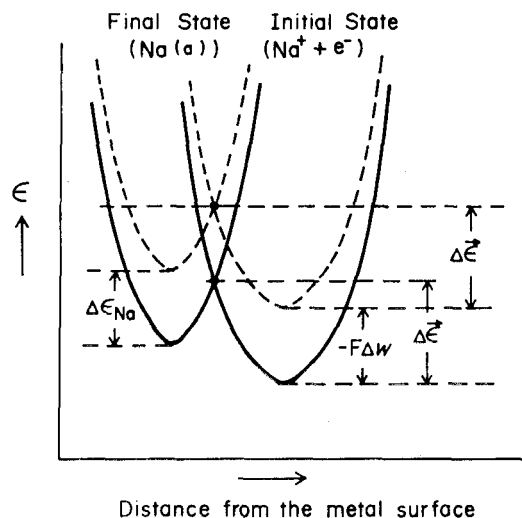


Fig. 30. The compensation of the free energy between the initial and final states.

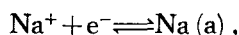
However, the situation seems to be quite different in the case of the hydrogen evolution reaction on low overvoltage metals. As already described in the previous sections, the overvoltage component appears on low overvoltage metals which is caused by the change of the surface potential due to the specific adsorption of the intermediate species on the electrode surface, for instance, $H(a)$ on gold in sulfuric acid, or $Na(a)$ on gold, nickel and platinum in sodium hydroxide solutions. The rate of the electron transfer step in these systems, however, can simply be expressed experimentally by the Tafel equation in terms of the overvoltage component due to charging up of the double layer, but not in terms of the overvoltage of the overall reaction referred to the reversible hydrogen electrode. These experimental results seem to be contradictory to the conclusion attained by FRUMKIN *et al.*

In the present section the two kinds of the overvoltage components which are caused respectively by charging up of the double layer and the change of the surface potential will be given quantitatively on the basis of the electrode potential theory developed by FRUMKIN and his school²⁷⁾ in the reversible systems, and the effect of the change of the surface potential due to the specific adsorption of the intermediate species on the rate of the electron transfer will be discussed on the basis of the rate theory developed by HORIUTI²⁸⁾ in the frame of the transition state method for the heterogeneous systems. As a result it will be shown that the change of the free energy of adsorption of the intermediate species with the increase of the surface

coverage will be compensated in the expression of the activation free energy by the change of the surface potential caused by adsorbed dipoles as seen from Fig. 30, and consequently the surface potential does not appear in the rate equation of the electron transfer step.

(1) **The two kinds of overvoltage components η_1 and η_a**

As described in the previous sections, there appears a plateau in the τ_1 vs. η curves, for instance, on gold, nickel and platinum in sodium hydroxide solutions, as shown respectively in Figs. 14, 22 and 29, and the values of η_1 is negligibly small and the growth of overvoltage in this region can be attributed substantially to η_a , as seen from the comparison of the polarization curves of the electron transfer step and the overall reaction in Figs. 13 and 14. Therefore the electron transfer step can be regarded as practically in equilibrium in this polarization region:



and the charge density on the electrode surface may be kept nearly constant although the electrode potential caused by Na(a) shows a marked growth in this region.

In such a quasi-reversible system the FRUMKIN's theory may be applicable for the estimation of the amount of the growth of the electrode potential caused by charging up of the double layer which will be denoted as $\delta\varphi_0$, and that caused by the change of the surface potential due to the adsorbed Na(a) which will be denoted as $\delta\omega$.

These two quantities have been found on the basis of the FRUMKIN's theory to be mutually independent and given by the following equations respectively in terms of the chemical potentials of Na^+ ion in the solution and the adsorbed Na atom⁵⁾:

$$F\delta\varphi_0 = \delta\bar{\mu}_{\text{Na}^+}, \quad (11)$$

$$F\delta\omega = -\delta\mu_{\text{Na}}. \quad (12)$$

These equations mean that the Nernst equation which represents the equilibrium relation of the electron transfer step in the differential form

$$\delta\bar{\mu}_{\text{Na}^+} + \delta\bar{\mu}_{e,0} = \delta\mu_{\text{Na}} \quad (13)$$

can be divided into two independent parts. As seen from Eq. (11), φ_0 is constant in a given solution of definite concentration of Na^+ ion.

η_1 is given by the difference of the electrostatic potential caused by charging up of the double layer between the polarized and reversible states,

$$\eta_1 = \varphi - \varphi_0, \quad (14)$$

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and η_a is given by the difference of w between the reversible and the polarized states according to Eq. (12) as,

$$\eta_a = w - w_0, \quad (15)$$

where suffix 0 means the reversible state.

In the frame of the reaction mechanism in sodium hydroxide solutions described in the previous section, η_1 turns to the affinity of the electron transfer step (I) ΔG_1 ,

$$\begin{aligned} \Delta G_1 &= \mu_{Na} - \bar{\mu}_{Na^+} - \bar{\mu}_e = (\mu_{Na} - \mu_{Na,0}) - (\bar{\mu}_e - \bar{\mu}_{e,0}) \\ &= -F(\eta_a - \eta) = F\eta_1, \end{aligned} \quad (16)$$

and η_a turns to the affinity of the recombination of the adsorbed hydrogen atoms ΔG_3 through the equilibration of the step (II),

$$\eta_a = \mu_{Na,0} - \mu_{Na} = \mu_{H,0} - \mu_H = \frac{1}{2} \Delta G_3. \quad (17)$$

In the case of the discharge of hydronium ion which produces adsorbed hydrogen atom as an intermediate, the components of the electrode potential have been found to be expressed as²⁰⁾,

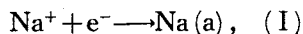
$$F\delta\varphi_0 = \delta\bar{\mu}_{H^+}, \quad (11')$$

$$F\delta w = -\delta\mu_H. \quad (12')$$

(2) The rate equation of the electron transfer step

The effect of the change of the surface potential on the rate of the electron transfer step will be discussed here on the basis of Eq. (12) in the frame of the transition state method developed by HORIUTI^{17,20)} for the heterogeneous reaction systems.

The electron transfer step in the sodium hydroxide solutions will be taken as an example for the rate expression:



in which Na^+ is the sodium ion on the Helmholtz-plane in the electric double layer at the metal-solution interface. The absolute rate of the step (I) in the right or reverse direction will be given by the following equation in the frame of the transition state method:

$$\bar{i} = e_0 \kappa \frac{kT}{h} \cdot \exp\left(-\frac{\bar{\mu}^* - \bar{\mu}_i}{RT}\right) \quad (18)$$

or

$$\bar{i} = e_0 \kappa \frac{kT}{h} \cdot \exp\left(-\frac{\bar{\mu}^* - \bar{\mu}_f}{RT}\right) \quad (19)$$

where e_0 is the elementary charge of an electron, κ is the transmission coefficient, k , T and h are respectively the Boltzmann constant, absolute temperature and the Planck constant, $\bar{\mu}^*$, $\bar{\mu}_i$ and $\bar{\mu}_f$ are respectively the electrochemical potential of the activated complex and the initial and final states,

$$\bar{\mu}_i = \bar{\mu}_{\text{Na}^+} + \bar{\mu}_e \quad (20)$$

$$\bar{\mu}_f = \mu_{\text{Na}} \quad (21)$$

$\bar{\mu}^*$, $\bar{\mu}_{\text{Na}^+}$ and μ_{Na} are given by the statistical mechanical theory of HORIUTI^{28,34} as:

$$\bar{\mu}^* = \varepsilon^* - RT \ln G \theta_0^*, \quad (22)$$

$$\mu_{\text{Na}} = \varepsilon_{\text{Na}} + RT \ln \frac{\theta}{1-\theta}, \quad (23)$$

$$\bar{\mu}_{\text{Na}^+} = \varepsilon_{\text{Na}^+} + RT \ln C_{\text{Na}^+,D} \quad (24)$$

where ε^* , $\varepsilon_{\text{Na}^+}$ and ε_{Na} denote respectively the reversible work per mole required to bring an activated complex, Na(a) and Na⁺ ion to the definite adsorption site from their standard states, θ_0^* is the surface coverage of the vacant site for the activated complex which equals unity practically, G is the number of adsorption site for the activated complex per unit area, θ is the surface coverage of Na(a), and $C_{\text{Na}^+,D}$ is the concentration of Na⁺ ion on the Helmholtz-plane which is given by the concentration of Na⁺ ion in the solutions as:

$$C_{\text{Na}^+,D} = C_{\text{Na}^+} e^{-\frac{F\psi_1}{RT}}, \quad (25)$$

where ψ_1 is the electrostatic potential at the Helmholtz-plane referred to that in the bulk of the solution.

On the other hand, the second term of the right hand side of Eq. (23) can be neglected as compared with the first term when θ is not close to zero nor unity, *i. e.*,

$$|\varepsilon_{\text{Na}}| \gg \left| RT \ln \frac{\theta}{1-\theta} \right|. \quad (26)$$

In the frame of this approximation the rate equation is written by Eqs. (18)~(24) as:

$$\bar{i}_1 = e_0 \kappa \frac{kT}{h} G \cdot C_{\text{Na}^+} \cdot e^{-\frac{F\psi_1}{RT}} \cdot \exp\left[-(\varepsilon^* - \varepsilon_{\text{Na}^+} - \bar{\mu}_e)/RT\right], \quad (27)$$

in which $\varepsilon^* - \varepsilon_{\text{Na}^+} - \bar{\mu}_e \equiv \Delta\bar{\varepsilon}$ is the activation free energy of the reaction. According to the theory of HORIUTI and POLANYI³⁰⁾ for the change of the activation free energy $\delta(\Delta\bar{\varepsilon})$, we have

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$$\delta(\Delta\bar{\epsilon}) = \alpha\delta(\varepsilon_{\text{Na}} - \varepsilon_{\text{Na}^+} - \bar{\mu}_e)$$

and in the integral form

$$\Delta\bar{\epsilon} = \Delta\varepsilon_0 + \alpha(\varepsilon_{\text{Na}} - \varepsilon_{\text{Na}^+} - \bar{\mu}_e), \quad (28)$$

where $\Delta\varepsilon_0$ is a constant which means the activation free energy at the electrode potential $\bar{\mu}_e = \varepsilon_{\text{Na}} - \varepsilon_{\text{Na}^+}$, and it does not depend on the surface potential of the electrode and equals in the right and reverse directions.

On the other hand, we can obtain the following relation between ε_{Na} and w from Eqs. (12) and (23) within the accuracy of Eq. (26):

$$F\Delta w + \Delta\varepsilon_{\text{Na}} = 0. \quad (29)$$

This equation means a compensation effect between the change of the surface potential and that of the free energy of the adsorbed atom at a definite adsorption site, being equally reflected respectively in the free energy curves of the initial and final states, as illustrated in Fig. 30.

Furthermore $\bar{\mu}_e$, ε_{Na} and $\varepsilon_{\text{Na}^+}$ can be expressed as,

$$\bar{\mu}_e = -F(\varphi + w_0 + \Delta w) \quad (30)$$

$$\varepsilon_{\text{Na}} = \varepsilon_{\text{Na},0} + \Delta\varepsilon_{\text{Na}} \quad (31)$$

$$\varepsilon_{\text{Na}^+} = \varepsilon_{\text{Na}^+,0} + F\phi_1, \quad (32)$$

where $\varepsilon_{\text{Na},0}$ is ε_{Na} on the bare surface, w_0 is the work function of the base metal into vacuum and $\varepsilon_{\text{Na}^+,0}$ is $\varepsilon_{\text{Na}^+}$ at $\phi_1 = 0$. Putting Eqs. (29)~(32) into Eq. (28), we obtain the activation free energy as:

$$\Delta\bar{\epsilon} = \Delta\varepsilon_0 + \alpha(\varepsilon_{\text{Na},0} - \varepsilon_{\text{Na}^+,0}) + \alpha F w_0 + \alpha F \varphi, \quad (33)$$

and the rate equation from Eqs. (27) and (33) as:

$$\vec{i}_1 = \vec{k} C_{\text{Na}^+} \cdot e^{-\frac{(1-\alpha)F\psi_1}{RT}} \cdot e^{-\frac{\alpha F \varphi}{RT}} \quad (34)$$

where

$$\vec{k} = e_0 \kappa \frac{kT}{h} G \cdot \exp\left[-\alpha(\varepsilon_{\text{Na},0} - \varepsilon_{\text{Na}^+,0})/RT\right] \cdot e^{-\frac{\Delta\varepsilon_0}{RT}} \cdot e^{-\frac{\alpha F w_0}{RT}}, \quad (35)$$

is a constant which does not depend on the surface potential of the electrode. It can be seen from Eq. (34) that the rate of the electron transfer step does not depend on the surface potential of the electrode caused by the specific adsorption of the intermediate species, but depend only on the electrostatic potential caused by charging up of the double layer as the result of the compensation between the adsorption free energy and the surface potential. This is the reason why the polarization curve of the electron transfer step can be

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determined separately independent of the surface potential of the electrode.

In the special case where there is no change of the surface potential under polarization, Eq. (34) can be reduced simply to the equation derived by FRUMKIN²⁴⁾,

$$\bar{i}_1 = \bar{k}' e^{-\frac{F(1-\alpha)\psi_1}{RT}} \cdot e^{-\frac{\alpha\bar{\mu}_e}{RT}}, \quad (36)$$

since in this case $\bar{\mu}_e$ equals simply $-F(\omega_0 + \varphi)$, and the rate of the electron transfer step on gallium can be expressed by this equation, as shown in the previous section.

The rate of the electron transfer step in the reverse direction can be expressed in the same procedure:

$$\bar{i}_1 = \bar{k} e^{-\frac{\beta F \psi_1}{RT}} \cdot e^{\frac{\beta F \varphi}{RT}} \quad (37)$$

and

$$\bar{k} = e_0 \kappa \frac{kT}{h} G \frac{\theta}{1-\theta} \cdot e^{-\frac{J_{i_0}}{RT}} \cdot \exp[-\beta(\varepsilon_{\text{Na}^+,0} - \varepsilon_{\text{Na},0})/RT] \cdot e^{\frac{\beta F \omega_0}{RT}}. \quad (38)$$

It can readily be seen from Eqs. (34) and (37) that

$$RT \ln \frac{\bar{i}_1}{\bar{i}_1} = -F\eta_1, \quad (39)$$

and also from Eqs. (18) and (19):

$$RT \ln \frac{\bar{i}_1}{\bar{i}_1} = \bar{\mu}_{\text{Na}^+} + \bar{\mu}_e - \mu_{\text{Na}} \equiv -\Delta G_1, \quad (40)$$

and consequently we obtain

$$F\eta_1 = \Delta G_1, \quad (41)$$

which has already been derived in Eq. (16) from the thermodynamic consideration of the overvoltage components.

The exchange rate of the electron transfer step i_{10} can be expressed by Eq. (34) as:

$$i_{10} = k C_{\text{Na}^+} \cdot e^{-\frac{\alpha F \varphi_0}{RT}}, \quad (42)$$

assuming that ψ_1 -potential may reasonably be regarded as constant in the case of low overvoltage metals, since the greater part of the overvoltage is caused by the surface potential. Taking into consideration Eq. (11), we obtain the concentration dependence from Eq. (42),

$$i_{10} = \text{const} \cdot (C_{\text{Na}^+})^\beta, \quad (43)$$

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which shows that in the case of the monovalent cation i_{10} is proportional to the square root of the Na^+ ion concentration in accordance with the experimental results, since $\beta=0.5$.

FLINN and SCHULDINER³⁶⁾ has recently reported that the exchange rate of the electron transfer step of the h.e.r. on platinum in sulfuric acid remains constant with the increase of the reversible potential which is attained by diminishing the partial pressure of hydrogen and that the exchange rate of the electron transfer step is proportional to the square root of the concentration of the hydronium ion. These phenomena are quite similar to those on gold in sulfuric acid and can be explained on the basis of Eqs. (11') and (12') and the rate theory described above.

Thus the polarization characteristics of the electron transfer step which have been found experimentally in the case of low overvoltage metals can well be explained on the basis of the compensation effect between the free energy of adsorption and the surface potential in the frame of the transition state method.

Recently, many theoretical and experimental reports have been accumulated in the vacuum systems, which concern with the relation between the binding energy of the adsorption bond and the work function of the metal substrate or the adsorption states.³¹⁾ If the adsorption bond is completely ionic, the increase of the surface potential with the increase of the surface coverage may result in the decrease in the binding energy of the adsorption bond as shown in the classical theory of LANGMUIR and TAYLOR³²⁾, and consequently the compensation effect can be seen between these two quantities.

However, recent studies on monocrystal surfaces in the ultra high vacuum systems show that the nature of the adsorption bond cannot be explained by the classical theory and the covalent nature cannot be neglected even in the case of alkali adsorption on metals^{33,35)}.

Although at present we cannot find a conclusive physical conception which can explain the relation between the binding energy of the adsorption bond and the work function of the substrate or the surface potential of the adsorption states in the vacuum systems, the change of the surface potential in the hydrogen electrode system which takes part in the setting up of the hydrogen overvoltage can be expressed by Eq. (12) in terms of the chemical potential of the intermediate adsorbate. The existence of the two independent components of the electrode potential as expressed in Eqs. (11) and (12) or in Eqs. (11') and (12') can explain the reason why the polarization curve of the hydrogen electrode reaction can be divided into two independent

parts.

DOGONADZE, KUZNETSOV and LEVICH³⁷⁾ have recently developed a quantum mechanical rate theory of the electron transfer step in the case of high overvoltage metal on which no specific adsorption is observed under polarization. In order to extend their theory to the case of low overvoltage metals, the compensation effect between the surface potential and the free energy of adsorption of an intermediate should probably be taken into consideration in the quantum mechanical treatment of the rate of the electron transfer step, since the potential energy curves of the initial and final states of the electron transfer step may equally be affected in the same extent by the change of the surface coverage of the intermediate.

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