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APPLICATION OF FRUMKIN'S ELECTRODE POTENTIAL THEORY TO HYDROGEN OVERVOLTAGE ON PLATINUM IN ALKALINE SOLUTIONS

By

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Abstract

The setting up of the hydrogen overvoltage on platinum in alkaline solutions was discussed on the basis of FRUMKIN's electrode potential theory. It was found that the hydrogen overvoltage was composed of the two independent parts, *i.e.* the one due to free charges on the electrode surface which was given by a function of the chemical potential of the alkali metal ion in solution and the other due to adsorbed intermediate alkali atom which depended on the chemical potential of the adsorbed alkali metal atom, and that the former turned out to be the overvoltage of the electron transfer step of the hydrogen evolution reaction and the latter the overvoltage of the step of the recombination of adsorbed hydrogen atoms.

Taking into consideration the functional relations between these two components of the hydrogen overvoltage and the chemical potentials of the alkali ion in solution and the adsorbed alkali metal atom, it was concluded that the exchange rate of the electron transfer step of the hydrogen evolution reaction was proportional to the square root of the alkali metal ion concentration in agreement with the experimental results.

FRUMKIN[1] has developed a theory on the setting up of the electrode potential on the basis of Gibbs thermodynamics in the reversible hydrogen electrode system. It is possible to apply FRUMKIN's theory extensively to the setting up of the hydrogen overvoltage in the irreversible system, provided that the electron transfer step of the hyrogen evolution reaction is followed by the rate-determining step of the reaction.

In the case of the platinum hydrogen electrode in alkaline solutions it has been found by the galvanostatic transient method[2,3] that the overvoltage caused by free charges on the electrode surface can be separated from that due to the intermediate species on the electrode surface, and the former is responsible for the rate of the electron transfer step and the latter for the rate of the recombination of adsorbed hydrogen atoms. From the comparison of these two kinds of overvoltages it has been concluded that the electron transfer

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step can be regarded as practically in equilibrium at low current densities.

The aim of the present paper is to clarify the mechanism of the setting up of the platinum hydrogen electrode potential in alkaline solutions on the basis of FRUMKIN's theory in the overvoltage region where the electron transfer step is practically in equilibrium.

The theoretical basis of the galvanostatic transient method and the experimental facts will be surveyed briefly which are useful to understand the applicability of FKUMKIN's theory to the setting up of the hydrogen overvoltage.

§ 1. Theoretical basis for the analysis of the overvoltage-time curves

Let us consider a hydrogen electrode on which the hydrogen evolution reaction is occuring steadily with a current density i_s at an overvoltage η_s, where suffix s means a steady state. When the polarizing current is changed impulsively by a constant value from i_s to $i_s+\Delta i$, the overvoltage begins to change until it attains a new steady value. The overvoltage-time curves thus obtained, η, t-curves, are available for the determination of the differential capacity of the electric double layer at the electrode-solution interface and the kinetic relation between the rate of the electron transfer step of the hydrogen evolution reaction and the overvoltage caused by the free charge on the electrode surface. The theoretical basis will first be developed for the analysis of the overvoltage-time curves.

In the course of the build up of overvoltage a part of electrons imparted impulsively to the electrode is used for the charging up of the double layer and the remaining part for the electron transfer step producing intermediate species, *i. e.*, Δi is divided into a non-faradaic part and a faradaic one. At the initial moment of the current impulse, however, Δi is entirely non-faradaic. Therefore it is possible to deduce the differential capacity of the double layer C_D at η_s from the initial tangent of the η, t-curve by the equation:

$$\Delta i = -C_D\dot{\eta}(0), \qquad (1)$$

where $\dot{\eta}(0)$ is the time derivative of η at $t=0$. The sign of the current is taken positive and that of η negative in the cathodic direction. It is usually difficult, however, to determine the reliable valus of $\dot{\eta}(0)$ because of slight distortions of the instantaneous change of overvoltage at the initial moment due to the arrangements of the electric circuit and instrumentations. Therefore it is desirable from the experimental point of view to use the later stage of the η, t-curve.

In the course of the build up of η the faradaic part of Δi increases with

time, while the non-faradaic one decreases. We find a region of the η, t-curve in which the non-faradaic part is comparable in its value with the faradaic one. In this region the non-faradaic part of Δi is given by $-C_D\dot{\eta}$ inspite of the accumulation of the intermediate species on the electrode surface, provided that C_D is much smaller than the pseudo-capacity due to the intermediate species, as usually observed in the case of the platinum hydrogen electrode[2]. Consequently the faradaic component of Δi is given in this region by the equation:

$$\delta i_1 = \Delta i + C_D\dot{\eta}\,, \tag{2}$$

where δi_1 shows the excess of the rate of the electron transfer step i_1 over that at η_s expressed in terms of the electric unit.

On the other hand, i_1 is given by a function of η in the course of the build up of overvoltage. Expanding $i_1(\eta)$ in a series in the neighbourhood of η_s, we obtain

$$i_1(\eta) = i_1(\eta_s) + \left(\frac{di_1}{d\eta}\right)_{\eta_s}\delta\eta + \frac{1}{2}\left(\frac{d^2i_1}{d\eta^2}\right)_{\eta_s}(\delta\eta)^2 + \cdots\,, \tag{3}$$

where $\delta\eta = \eta - \eta_s$. Neglecting the terms higher than the second order, we obtain

$$\delta i_1 = i_1(\eta) - i_1(\eta_s) = \left(\frac{di_1}{d\eta}\right)_{\eta_s}\delta\eta\,,$$

or

$$\delta\eta = -r_1\delta i_1\,, \tag{4}$$

where

$$r_1 = -\left(\frac{d\eta}{di_1}\right)_{\eta_s}. \tag{5}$$

Assuming the constancy of C_D at potentials close to η_s, we obtain from Eqs. (2) and (4):

$$\ln\left(-\frac{\Delta i}{\dot{\eta}}\right) = \frac{t}{\tau_1} + \ln C_D\,, \tag{6}$$

where

$$\tau_1 = C_D r_1\,. \tag{7}$$

It is possible to deduce τ_1, C_D and r_1 on the basis of Eqs. (6) and (7) from the η, t-curve in the neighbourhood of η_s.

When r_1 is given as a function of η_s or i_s, it is possible to obtain the overvoltage η_{1s} which is caused by charging up of the double layer in a

steady state from the integration of Eq. (5):

$$\eta_{1s}=\int_0^{\eta_{1s}} d\eta=-\int_0^{i_1} r_1 di_1=-\int_0^{i_s} r_1 di_s\,, \tag{8}$$

since i_1 equals i_s in a steady state. Eq. 8 enables us to determine the relation between the rate of the electron transfer step and the overvoltage caused by free charges on the electrode surface in the steady states of the hydrogen evolution reaction.

In the particular case of the reversible hydrogen electrode potential, *i. e.* at $\eta_s=0$, r_1 can be related to the exchange rate of the electron transfer step i_{10} by the equation:

$$r_1=RT/Fi_{10}\,, \tag{9}$$

where R, F and T denote respectively the gas constant, the Faraday and the absolute temperature.

The i_1 in the course of the build up of overvoltage started from the reversible hydrogen electrode potential is expressed by the following equation in place of Eq. (2) insofar as the overvoltage is caused by charging up of the double layer:

$$i_1=i+C_D\dot{\eta}\,. \tag{10}$$

Eq. (10) enables us to determine the relation between the rate of the electron transfer step and the overvoltage caused by free charges on the electrode surface in the transient states of the build up of overvoltage.

The experimental results will be described in the following sections which have been obtained with evaporated platinum film electrodes in aqueous sodium and cesium hydroxides or sulfates.[2,3]

§ 2. Experimental results

(i) The exchange rate of the electron transfer step

The τ_1 at $\eta_s=0$ strongly depends on the concentration of solution, while C_D remains constant independent of the overvoltage and the concentration of solution. Fig. 1 shows the $\log\tau_1$ plotted against pH or $\log C_{M^+}$ in sodium and cesium hydroxides or sulfates, where C_{M^+} is the concentration of alkali metal ion.[2,3] As seen from this Figure, in pure hydroxides $\log\tau_1$ varies linearly with pH with a gradient $-1/2$, but no regularity can be seen in the pH-dependence of $\log\tau_1$ in sulfate solutions. However, when $\log\tau_1$ is plotted against $\log C_{M^+}$, a definite linear relation is obtained with gradient $-1/2$ in any case of pure hydroxides and sulfate solutions. These results mean that the exchange rate i_{10} calculated by Eqs. (7) and (9) is proportional

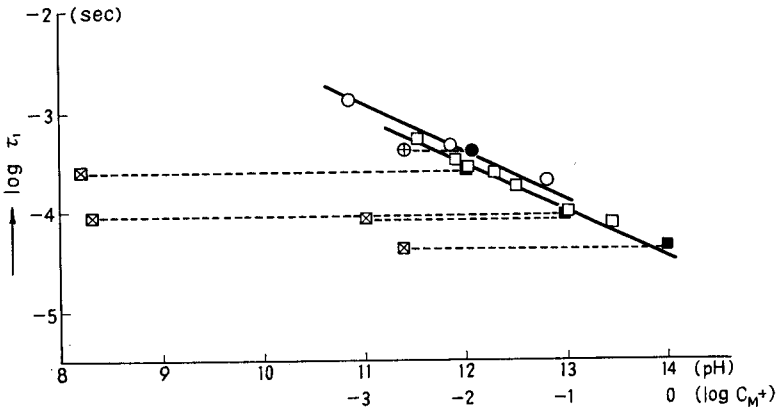

Fig. 1. log τ_1 at the reversible hydrogen electrode potential plotted against pH or log C_{M^+} :
(□)—$NaOH_{aq}$; (⊠)—$Na_2SO_{4,aq}$ plotted against pH;
(■)—$Na_2SO_{4,aq}$ plotted against log C_{M^+} ;
(○)—$CsOH_{aq}$; (⊕)—$Cs_2SO_{4,aq}$ plotted against pH;
(●)—$Cs_2SO_{4,aq}$ plotted against log C_{M^+}.

to the square root of the alkali metal ion concentration, since C_D remains constant, *i.e.*,

$$i_{10} = k(C_{M^+})^{1/2}. \tag{11}$$

It can be concluded from this fact that the electron transfer step of the hydrogen evolution reaction in alkaline solutions consists in the discharge of an alkali metal ion, but not of a water molecule.

(ii) The rate and overvoltage of the electron transfer step

The overvoltage η_{1s} which is caused by charging up of the double layer in a steady state can be obtained from the r_1, i_s-curve on the basis of Eq. (8). The log i_s, η_{1s}-curve thus obtained shows the relation between the rate and overvoltage of the electron transfer step in the steady states. Fig. 2 shows the log i_s, η_{1s}-curve in $CsOH_{aq}$ of pH 12.8.[3] It can be seen from this Figure that the log i_s, η_{1s}-curve can be expressed by the simplified FRUMKIN equation in which the Ψ_1-potential term is omitted[4] :

$$i_s = i_{10}\left\{\exp(-F\eta_{1s}/2RT) - \exp(F\eta_{1s}/2RT)\right\}, \tag{12}$$

where i_{10} is the exchange rate of the electron transfer step calculated from the value of τ_1 at $\eta_s = 0$.

The i_1 in the course of the build up of overvoltage can be calculated

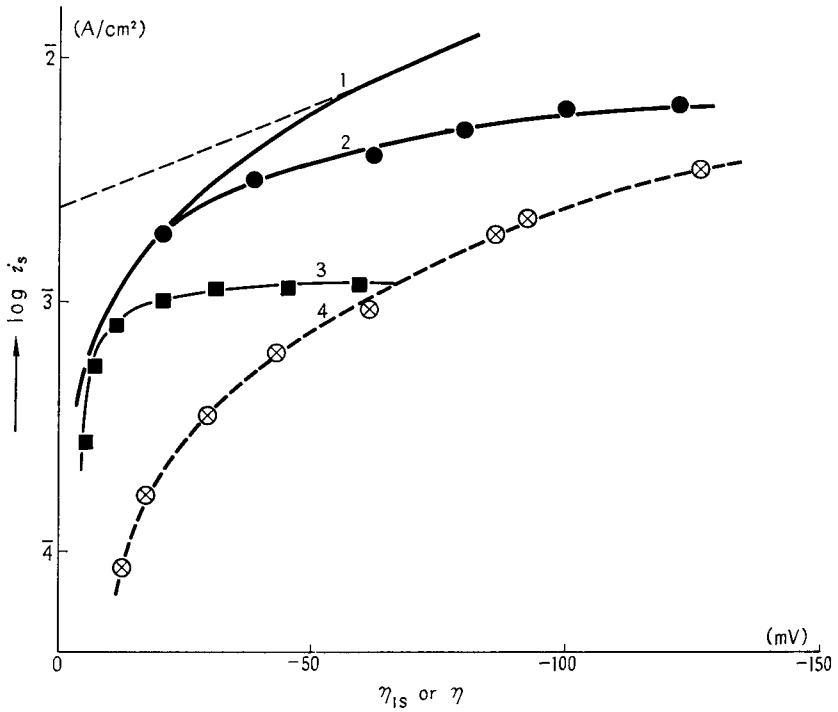

Fig. 2. The relation between the rate and overvoltage of the electron transfer step in $CsOH_{aq}$ of pH.
1—log i_s, η_{1s}-curve in the steady states,
2, 3—log i_1, η-curve in the course of the build up of η,
4—log i_s, η_s-curve of the overall reaction in the steady states.

by Eq. (10) from the η, t-curve started from $\eta_s=0$. The log i_1, η-curves thus obtained in the transient states in $NaOH_{aq}$ are shown in Fig. 3.[2] It can be seen from this Figure that log i_1 shows sharp increase with η in the first stage along the theoretical line calculated by FRUMKIN equation and then moves to the second stage where η increases sharply, i_1 being practically kept constant close to the polarizing current i. This fact suggests that the overvoltage is first caused by charging up of the double layer and second by the accumulation of the intermediate species on the electrode surface in the course of the build up of overvoltage.

The log i_1, η-curves in the transient states in $CsOH_{aq}$ are also shown in Fig. 2. It can be seen from this Figure that log i_1 in the transient states increases with η first along the log i_s, η_{1s}-curve in the steady states and then moves to the second stage. It can be concluded from these facts that the

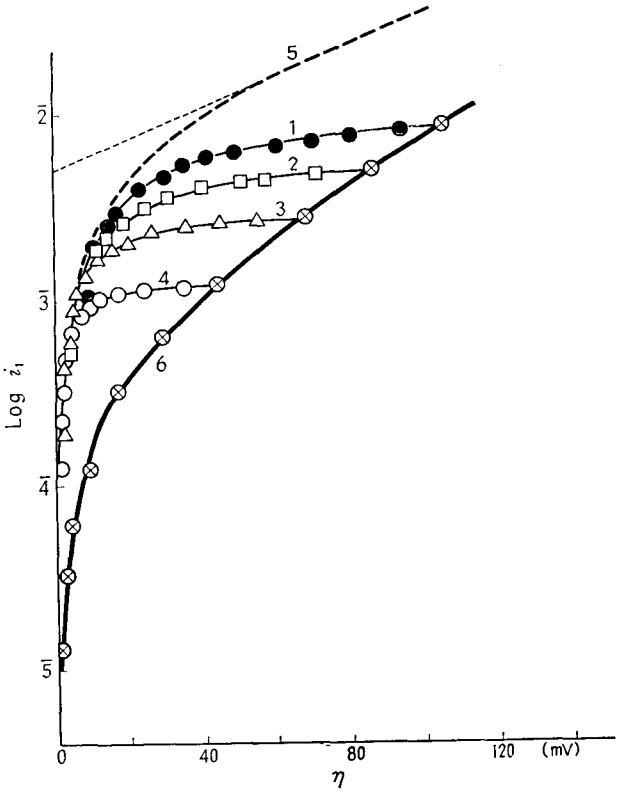

Fig. 3. The relation between $\log i_1$ and η in the course of the build up of η in $NaOH_{aq}$ of pH 13.0.
1, 2, 3, 4—$\log i_1$, η-curves in the course of the build up,
5—the theoretical curve calculated by FRUMKIN equation,
6—$\log i_s$, η_s-curve of the overall reaction.

overvoltage caused by free charges on the electrode surface in the course of the build up of overvoltage remains unchanged in the steady state, and that the electrode potential caused by free charges on the electrode surface is responsible for the acceleration of the electron transfer step whether the electrode is in a steady state or in a transient state. It should be noted that the degree of the accumulation of the intermediate species on the electrode surface is different between the transient state and the steady state.

Now $\log i_s$ is expressed in Fig. 4 as a function of η_{1s} or the remaining part of overvoltage in a steady state $\eta_{2s}=\eta_s-\eta_{1s}$, which are obtained in $CsOH_{aq}$ of different concentrations.[3] Fig. 4 shows that the $\log i_s$, η_{1s}-curve

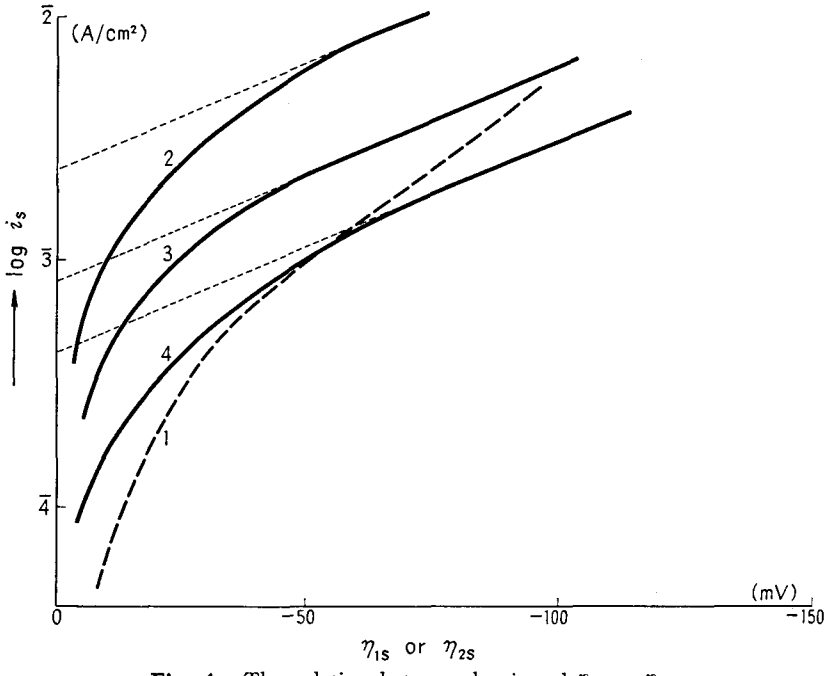

Fig. 4. The relation between $\log i_s$ and η_{1s} or η_{2s}.
1—$\log i_s$, η_{2s}-curve in $CsOH_{aq}$ of pH 10.86, 11.86 and 12.80,
2, 3, 4—$\log i_s$, η_{1s}-curves in $CsOH_{aq}$ of pH 12.80, 11.86 and10.86 respectively.

strongly depends on the concentration of solution as expected from the fact that the electron transfer step is the discharge of Cs^+ ion, while the $\log i_s$, η_{2s}-curve does not depend on the concentration of cesium hydroxide. It can be concluded from this fact that η_{2s} is imposed upon the step of the recombination of adsorbed hydrogen atoms.

Taking into consideration that the electron transfer step consists in the discharge of alkali metal ion and that the last step is the recombination of adsorbed hydrogen atoms, the elementary steps of the hydrogen evolution reaction can be expressed as:

$$M^+ + e \longrightarrow M, \qquad (I)$$

$$M + H_2O \longrightarrow H + OH^- + M^+, \qquad (II)$$

$$H + H \longrightarrow H_2, \qquad (III)$$

where M and H denote respectively the intermediate alkali atom and the hydrogen atom adsorbed on the electrode surface. The overvoltage of the

overall reaction η_s is given by the summation of those of stops (I) and (III), as mentioned above, *i. e.*,

$$\eta_s = \eta_{1s} + \eta_{2s}, \tag{13}$$

so that the step (II) can be regarded as practically in equilibrium.

On the other hand, η_{1s} is also negligibly small as compared with η_{2s} at low current densities, as seen from Fig. 4 or 3. This fact means that the electrode potential due to free charges on the electrode surface is kept nearly constant in this region inspite of the increase of η_{2s}, and consequently the charge density on the electrode surface is nearly kept constant because of the constancy of C_D.

(III) The intermediate species

As seen from the reaction scheme of the hydrogen evolution reaction, the intermediate species M and/or H are responsible for the setting up of the hydrogen overvoltage η_{2s}. It is possible to determine the intermediate species which changes its surface concentration with overvoltage by the differential capacity measurements.[2)]

The differential capacity C of the hydrogen electrode can be calculated by the following equation from the decay curve of overvoltage after switching off of the polarizing current:

$$C = -i/\dot{\eta}, \tag{14}$$

where i means the rate of removal of the intermediate species from the electrode surface at an overvoltage at which $\dot{\eta}$ is taken, and it can be identified approximately with i_s at the same value of overvoltage in the steady state.

Fig. 5 shows the capacities of the platinum hydrogen electrode in 1N sodium sulfate solutions of varying pH plotted against the electrode potential φ referred to the normal hydrogen electrode[2)]; the C, φ-curves show a maximum at about $\varphi = -0.8$ v independent of the pH of solution. It has been found that the maximum value of C decreases with the decrease of the concentration of sodium ion. It can be concluded from these facts that the intermediate species which changes its surface concentration with overvoltage is not the hydrogen atom but the alkali metal atom. According to the graphic integration of the C, φ-curve, the excess of the surface concentration of the intermediate sodium atom over that at the reversible hydrogen electrode potential attains about 7×10^{15} atoms per ture unit area at $\varphi = -0.9$ v in 1N sodium sulfate solution. The true area of the electrode surface has been determined from the C_D-value, assuming that the platinum electrode has the

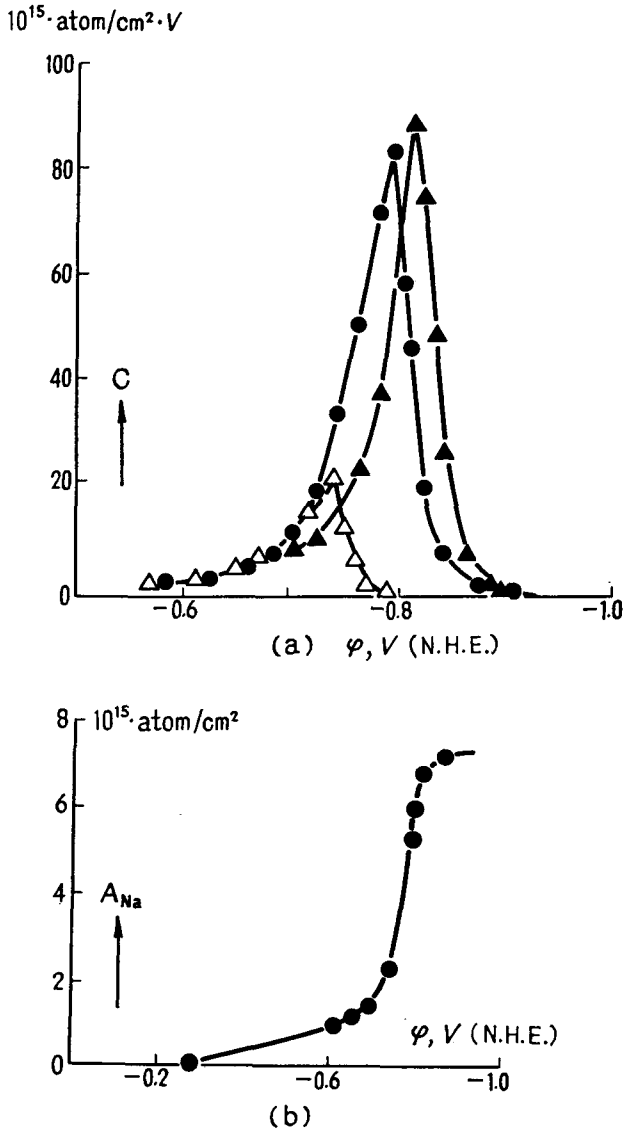

Fig. 5. (a) Differential capacity plotted against φ,
-●-: 1N $Na_2SO_{4,aq}$, pH 4.7;
-▲-: 1N $Na_2SO_{4,aq}$, pH 11.4;
-△-: 0.01N $Na_2SO_{4,aq}$, pH 8.2.
(b) Surface concentration of the intermediate Na atom in 1N $Na_2SO_{4,aq}$ of pH 4.7.

same C_D-value as the mercury electrode $18\,\eta F/\mathrm{cm}^2$ determined by FRUMKIN and VORSINA.[5] The large value of the surface concentration of the intermediate species as compared with that at the full coverage of the electrode surface suggests that the intermediate sodium atom is not only adsorbed on the electrode surface, but also it penetrates into the bulk of the platinum electrode.

With respect to the adsorbed hydrogen atom it has already been shown by BURSHTEIN and her coworkers in acid solutions[18] and by FRUMKIN and SLYGIN in alkaline solutions[8] that its surface concentration attains nearly a saturation value at the reversible hydrogen electrode potential in the case of the platinum hydrogen electrode.

It can be concluded from these facts that the adsorbed hydrogen atom does not take part in the setting up of the hydrogen overvoltage in the cathodic polarization region in alkaline solutions.

§ 3. The mechanism of the setting up of the hydrogen overvoltage

The hydrogen evolution reaction occurs in alkaline solutions as the sequence of the following elementary steps, as described in the previous section:

$$M^+ + e \longrightarrow M, \qquad (I)$$

$$M + H_2O \longrightarrow H + OH^- + M^+, \qquad (II)$$

$$H + H \longrightarrow H_2, \qquad (III)$$

in which the step (III) is rate-determining at low current densities. In this particular case both of the steps (I) and (II) can be regarded as practically in equilibrium:

$$M^+ + e \rightleftharpoons M, \qquad (Ia)$$

$$M + H_2O \rightleftharpoons H + OH^- + M^+, \qquad (IIa)$$

Insofar as these two elementary stops are concerned, the system can be regarded as quasi-reversible although the hydrogen evolution reaction is going on steadily. It is possible in this quasi-reversible system to discuss the setting up of the electrode potential on the basis of the electrode potential theory established by FRUMKIN and his school.[1,6-15]

The thermodynamic relations in this system are given by the chemical potentials of the species which take part in the reactions (Ia) and (IIa):

$$d\mu_{M^+} + d\mu_e = d\mu_M, \qquad (15)$$

$$d\mu_{M} = d\mu_{H} + d\mu_{OH^-} + d\mu_{M^+}\,, \tag{16}$$

where μ_{M^+} etc. denote the chemical potentials of M^+ etc. expressed in terms of the electric unit. The μ_e and μ_H can be expressed by the electrode potentials φ and φ_r referred respectively to the normal hydrogen electrode and to the reversible hydrogen electrode in the same solution under the atmospheric pressure of hydrogen:

$$d\mu_e = -d\varphi\,, \tag{17}$$

$$d\mu_H = -d\varphi_r\,. \tag{18}$$

From Eqs. (15) and (17) we obtain:

$$d\varphi = d\mu_{M^+} - d\mu_M\,. \tag{19}$$

The free energy density of the electrode-solution interface σ in this system is expressed by Gibbs equation:

$$d\sigma = -\sum_j \Gamma_j d\mu_j\,, \tag{20}$$

where j means the chemical species e, M, H, OH^- and anion A^- which are found at the electrode-solution interface, and Γ_j the adsorbed quantity of the j-th species per unit area in the sense of Gibbs thermodynamics.[1,8]

There exist, however, no electron and no alkali metal atom in the bulk of the solution and gas phase of the system. Therefore the change of free charges on the electrode surface occurs through the reaction (Ia) only, and the change of the surface density of alkali metal atom through the reactions (Ia) and (IIa), so that

$$\Gamma_e = 0\,, \tag{21 a}$$

$$\Gamma_M = 0\,. \tag{21 b}$$

All chemical species but A^- take part in the chemical reactions (Ia) and/or (IIa), so that Γ_H, Γ_{M^+} and Γ_{OH^-} can be expressed by the following equations:

$$\Gamma_H = A_H + A_M - \varepsilon\,, \tag{22}$$

$$\Gamma_{M^+} = A_M + \Gamma^{\varepsilon}_{M^+}\,, \tag{23}$$

$$\Gamma_{OH^-} = A_M - \varepsilon + \Gamma^{\varepsilon}_{OH^-}\,, \tag{24}$$

where A_H, A_M and ε denote respectively the density of H, M and free charges on the electrode surface, and $\Gamma^{\varepsilon}_{M^+}$ and $\Gamma^{\varepsilon}_{OH^-}$ mean the surface density of M^+ and OH^- which take part in the formation of the electric double layer. From the electric neutrality of the electric double layer, we obtain:

$$\varepsilon = \Gamma_{A^-} + \Gamma^i_{OH^-} - \Gamma^i_{M^+} . \tag{25}$$

BARASHOVA and KAZARINOV[16,17] have shown by the radiochemical measurements of the adsorption of ions in the potential region more positive than the reversible hydrogen electrode potential that the adsorption of anions on the platinum hydrogen electrode can be neglected insofar as the electrode surface is negatively charged, so that we can expect in the potential region more negative than the reversible hydrogen electrode potential region that:

$$\Gamma_{A^-} = 0 . \tag{26}$$

It follows from Eqs. (21a)–(26) that Gibbs equation can be simplified as:

$$d\sigma = -(A_M + A_H - \varepsilon)d\mu_M - (\varepsilon + \Gamma^i_{M^+} - A_H)(d\mu_{M^+} + d\mu_{OH^-}) . \tag{27}$$

It can be seen from Eq. (27) that the states of the system can be determined by the independent variables μ_M, μ_{M^+} and μ_{OH^-}. The setting up of the electrode potential in the reversible system will be discussed on the basis of Eq. (27) in the two cases of constant μ_{OH^-} and of constant μ_{M^+}.

(i) μ_{OH^-} = **constant**

In this case the states of the system can be determined by two independent variables μ_M and μ_{M^+}, and the following relation can be obtained from Gibbs equation (27):

$$\left\{\delta(A_M + A_H - \varepsilon)/\delta\mu_{M^+}\right\}_{\mu_M} = \left\{\delta(\varepsilon + \Gamma^i_{M^+} - A_H)/\delta\mu_M\right\}_{\mu_{M^+}} . \tag{28}$$

We discuss here each term in the right and left hand sides of Eq. (28).

(a). $(\delta A_H/\delta\mu_{M^+})_{\mu_M}$ and $(\delta A_H/\delta\mu_M)_{\mu_{M^+}}$. According to Eqs. (16) and (18), $\delta\mu_{M^+}$ equals $\delta\varphi_r$ at constant μ_{OH^-} and μ_M, and $\delta\mu_M$ equals $-d\varphi_r$ at constant μ_{OH^-} and μ_{M^+}. It follows that:

$$(\delta A_H/\delta\mu_{M^+})_{\mu_M} = (\delta A_H/\delta\varphi_r)_{\mu_M} , \tag{29 a}$$

$$(\delta A_H/\delta\mu_M)_{\mu_{M^+}} = -(\delta A_H/\delta\varphi_r)_{\mu_{M^+}} . \tag{29 b}$$

On the other hand, the major intermediate which changes its concentration with φ_r is not H but M,[2] as shown in the experimental part, so that the right hand sides of Eqs. (29a) and (29b) can be regarded as equal to zero, *i.e.*,

$$(\delta A_H/\delta\mu_{M^+})_{\mu_M} = 0 , \tag{30 a}$$

$$(\delta A_H/\delta\mu_M)_{\mu_{M^+}} = 0 . \tag{30 b}$$

(b). $(\delta\varepsilon/\delta\mu_M)_{\mu_{M^+}}$ and $(\delta\Gamma^i_{M^+}/\delta\mu_M)_{\mu_{M^+}}$. The ε remains constant independent of φ_r inasmuch as the elementary step (I) is in equilibrium, as conclued in

§2. (ii), so that we obtain:

$$(\delta\varepsilon/\delta\mu_{\mathrm{M}})_{\mu_{\mathrm{M}^+}} = 0\,. \tag{31}$$

SLYGIN, FRUMKIN and MEDWEDOWSKY[7] and recentry PETRY, FRUMKIN and KOTLOV[12] have shown that the charge density on the electrode surface in alkaline solutions is kept nearly constant at potentials more positive than the reversible hydrogen electrode potential. Eq. (31) shows that the constancy of ε found by FRUMKIN school in the anodic polarization region can also be extended to the cathodic polarization region in which the elementary steps (I) and (II) are in equilibrium.

Insofar as ε remains constant, we can expect the constancy of $\Gamma^{i}_{\mathrm{M}^+}$ at potentials more negative than the reversible hydrogen electrode potential, which has already been verified in the anodic polarization region by the radiochemical measurements of BARASHOVA and KAZARINOV[16]. It follows that:

$$(\delta\Gamma^{i}_{\mathrm{M}^+}/\delta\mu_{\mathrm{M}})_{\mu_{\mathrm{M}^+}} = 0\,. \tag{32}$$

Substituting Eqs. (30a)-(32) into Eq. (28), we obtain:

$$(\delta A_{\mathrm{M}}/\delta\mu_{\mathrm{M}^+})_{\mu_{\mathrm{M}}} = (\delta\varepsilon/\delta\mu_{\mathrm{M}^+})_{\mu_{\mathrm{M}}}\,. \tag{33}$$

It can be seen from Eqs. (31) and (33) that $(\delta\Gamma_{\mathrm{M}}/\delta\mu_{\mathrm{M}^+})_{\mu_{\mathrm{M}}} = (\delta\varepsilon/\delta\mu_{\mathrm{M}})_{\mu_{\mathrm{M}^+}} = 0$, where $\Gamma_{\mathrm{M}} = A_{\mathrm{M}} - \varepsilon$. Hence the system under consideration can be identified with the reversible alkali metal electrode under the isoelectric conditions $(\delta\varphi/\delta\mu_{\mathrm{M}^+})_{\Gamma_{\mathrm{M}}} = 1$. The setting up of the electrode potential in this system can be treated just in the same way as the reversible hydrogen electrode in acid solutions under the isoelectric conditions $(\delta\varphi/\delta\mu_{\mathrm{H}^+})_{\Gamma_{\mathrm{H}}} = 1$, where $\Gamma_{\mathrm{H}} = A_{\mathrm{H}} - \varepsilon$, which has already been discussed in the previous work.[19]

On the other hand, the electrode potential in this system can be determined by the intermediate species M and free charges on the electrode surface, so that we obtain:

$$d\varphi = (\delta\varphi/\delta A_{\mathrm{M}})_{\varepsilon} dA_{\mathrm{M}} + (\delta\varphi/\delta\varepsilon)_{A_{\mathrm{M}}} d\varepsilon\,. \tag{34}$$

Putting

$$X \equiv (\delta\varphi/\delta A_{\mathrm{M}})_{\varepsilon}\,, \qquad Y \equiv (\delta\varphi/\delta\varepsilon)_{A_{\mathrm{M}}}\,, \tag{35 a), (35 b)}$$

we obtain

$$d\varphi = X dA_{\mathrm{M}} + Y d\varepsilon\,, \tag{36}$$

where the reciprocals of X and Y mean the differental capacities respectively due to M and the free charge and can be determined by the galvanostatic

transient method.

The A_M and ε are also functions of μ_M and μ_{M^+}, so that

$$XdA_M = X(\delta A_M/\delta\mu_M)_{\mu_{M^+}}d\mu_M + X(\delta A_M/\delta\mu_{M^+})_{\mu_M}d\mu_{M^+}\,, \tag{37}$$

$$Yd\varepsilon = Y(\delta\varepsilon/\delta\mu_M)_{\mu_{M^+}}d\mu_M + Y(\delta\varepsilon/\delta\mu_{M^+})_{\mu_M}d\mu_{M^+}\,. \tag{38}$$

On the other hand, we obtain from Eqs. (19) and (36):

$$X(\delta A_M/\delta\mu_M)_{\mu_{M^+}} + Y(\delta\varepsilon/\delta\mu_M)_{\mu_{M^+}} = -1\,, \tag{39}$$

$$X(\delta A_M/\delta\mu_{M^+})_{\mu_M} + Y(\delta\varepsilon/\delta\mu_{M^+})_{\mu_M} = 1\,. \tag{40}$$

Substituting Eqs. (31) and (33) into Eqs. (39) and (40), we obtain:

$$X(\delta A_M/\delta\mu_M)_{\mu_{M^+}} = -1\,, \tag{41}$$

$$(X+Y)(\delta\varepsilon/\delta\mu_{M^+})_{\mu_M} = 1\,. \tag{42}$$

Substituting Eqs. (31), (33), (41) and (42) into Eqs. (37) and (38), we obtain:

$$XdA_M = -d\mu_M + \left(\frac{X}{X+Y}\right)d\mu_{M^+}\,, \tag{43}$$

$$Yd\varepsilon = \left(\frac{Y}{X+Y}\right)d\mu_{M^+}\,. \tag{44}$$

In the particular case when $|X| \ll |Y|$, as realized in the case of the platinum hydrogen electrode,[2] we obtain:

$$XdA_M = -d\mu_M\,, \tag{45}$$

$$Yd\varepsilon = d\mu_{M^+}\,. \tag{46}$$

Eqs. (45) and (46) show that the potential of the platinum hydrogen electrode under consideration can be separated into two independent parts: the one due to the intermediate alkali atom which depends only on μ_M and the other due to the charge density on the electrode surface which depends only on μ_{M^+}. It can readily be seen that Eqs. (45) and (46) or (43) and (44) satisfy the thermodynamic relation (15).

Let us denote these two components of the potential φ_{20} and φ_{10} respectively, then we have

$$XdA_M = d\varphi_{20}\,, \quad \text{and} \quad Yd\varepsilon = d\varphi_{10}\,, \tag{47a), (47b}$$

or

$$\varphi_{10} = (RT/F)\ln a_{M^+} + \text{const.}\,, \tag{48}$$

$$\varphi_{20} = -(RT/F)\ln a_M + \text{const.}\,, \tag{49}$$

where a_{M^+} and a_M are the activities of M^+ and M.

It has already been shown in §2 that the hydrogen overvoltage due to free charges on the electrode surface can be separated from that due to the intermediate species in the irreversible system, and the former turns out to be the overvoltage of the electron transfer step and the latter that of the recombination step of adsorbed hydrogen atoms. Now it can be seen that the overvoltage due to the intermediate species is given by Eq. (45) on the basis of FRUMKIN's theory. Eq. (45) shows also a functional relation for the change of the electronic work function of platinum metal due to the adsorption of alkali metal atoms on the surface which may be measured in a vacuum system.

(ii) μ_{M^+} = **constant**

In this case the independent variables of the system are μ_M and μ_{OH^-}, and the following equation can be obtained from Eq. (27):

$$\left\{\delta(A_M+A_H-\varepsilon)/\delta\mu_{OH^-}\right\}_{\mu_M}=\left\{\delta(\varepsilon+\Gamma^i_{M^+}-A_H)/\delta\mu_M\right\}_{\mu_{OH^-}}. \tag{50}$$

We obtain the following relations based on the arguments described in §3. (i),

$$(\delta A_H/\delta\mu_{OH^-})_{\mu_M}=0\,,\quad (\delta A_H/\delta\mu_M)_{\mu_{OH^-}}=0\,,\quad (\delta\varepsilon/\delta\mu_M)_{\mu_{OH^-}}=0\,,$$
$$(\delta\Gamma^i_{M^+}/\delta\mu_M)_{\mu_{OH^-}}=0\,. \tag{51 a), (51 b), (51 c), (51 d)}$$

It follows from Eqs. (50) and (51) that:

$$(\delta A_M/\delta\mu_{OH^-})_{\mu_M}=(\delta\varepsilon/\delta\mu_{OH^-})_{\mu_M}\,. \tag{52}$$

The left hand side of Eq. (52) becomes equal to zero, since A_M depends on φ and μ_{M^+} independent of μ_{OH^-}, as shown in § 2. (iii), so that we have:

$$(\delta\varepsilon/\delta\mu_{OH^-})_{\mu_M}=0\,. \tag{53}$$

On the other hand, ε is a function of μ_M and μ_{OH^-}, so that we have from Eqs. (51 c) and (53):

$$d\varepsilon=(\delta\varepsilon/\delta\mu_M)_{\mu_{OH^-}}d\mu_M+(\delta\varepsilon/\delta\mu_{OH^-})_{\mu_M}d\mu_{OH^-}=0\,. \tag{54}$$

It follows from Eqs. (36) and (54) that:

$$Yd\varepsilon=d\varphi_{10}=0\,, \tag{55}$$

$$XdA_M=d\varphi_{20}=d\varphi=-d\mu_M\,. \tag{56}$$

It can be seen from Eq. (55) that the electrode potential due to free charges on the electrode surface is kept constant independent of the pH of solution insofar as μ_{M^+} remains constant.

(iii) The rate equation of the electron transfer step

The rate equation of the electron transfer step of the hydrogen evolution reaction in alkaline solutions can be expressed by the simplified FRUMKIN equation on the basis of the experimental results as a function of the electrode potential φ_1 which is caused by free charges on the electrode surface:

$$i_1 = k_{1+}(a_{M^+}) \exp(-F\varphi_1/2RT) - k_{1-} \exp(F\varphi_1/2RT). \tag{57}$$

Eq. (57) can be transformed as:

$$i_1 = i_{10}\left\{\exp(-F\eta_1/2RT) - \exp(F\eta_1/2RT)\right\}, \tag{58}$$

in which

$$i_{10} = k_{1+}(a_{M^+}) \exp(-F\varphi_{10}/2RT) = k_{1-} \exp(F\varphi_{10}/2RT), \tag{59}$$

and

$$\eta_1 = \varphi_1 - \varphi_{10}. \tag{60}$$

Putting Eq. (48) into Eq. (59), the exchange rate i_{10} can be written as:

$$i_{10} = \text{const.}\,(a_{M^+})^{1/2}. \tag{61}$$

Eq. (61) can explain the experimental results of the concentration dependence of the exchange rate of the electron transfer step. From the constancy of φ_{10} at constant μ_{M^+}, as seen from Eq. (55), it can be concluded that the exchange rate of the electron transfer step does not depend on the pH of solution as experimentally verified.[2)]

The rate equation (57) can also be expressed by the electrode potential φ and the component of the potential φ_2 which is caused by the intermediate alkali metal atom on the electrode surface as:

$$i_1 = k'_{1+}(a_{M^+}) \exp\left\{-F(\varphi-\varphi_2)/2RT\right\} - k'_{1-} \exp\left\{F(\varphi-\varphi_2)/2RT\right\}. \tag{62}$$

Taking into consideration that φ_2 is given by Eq. (49) as a function of a_M, we obtain from Eq. (62):

$$i_1 = k_{1+}(a_{M^+})(a_M)^{-1/2} \exp(-F\varphi/2RT) - k_{1-}(a_M)^{1/2} \exp(F\varphi/2RT). \tag{63}$$

Eq. (63) is the same in formula as the rate equation derived by FRUMKIN and ALADJALOVA[20)] in the case of the discharge of proton on the palladium hydrogen electrode.

Concluding remarks

It has been established on the basis of the FRUMKIN's electrode potential theory that the hydrogen overvoltage on platinum in alkaline solutions is composed of two independent parts: the one due to free charges on the electrode surface which depends on the activity of the alkali metal ion in solution and the other due to the intermediate alkali metal atom on the electrode surface which depends on the activity of the alkali metal atom, and that the former is responsible for the acceleration of the electron transfer step of the hydrogen evolution reaction and the latter for the rate of the recombination step of the adsorbed hydrogen atoms on the electrode surface.

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