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Title	TAFEL'S CONSTANT AND HYDROGEN ION CONCENTRATION DEPENDENCE OF OVERVOLTAGE IN HYDROGEN EVOLUTION REACTION : Part Ⅰ: Slow Discharge and Electrochemical Mechanisms
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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 6(3), 231-249
Issue Date	1958-12
Doc URL	https://hdl.handle.net/2115/24684
Type	departmental bulletin paper
File Information	6(3)_P231-249.pdf

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TAFEL'S CONSTANT AND HYDROGEN ION CONCENTRATION DEPENDENCE OF OVERVOLTAGE IN HYDROGEN EVOLUTION REACTION

Part I: Slow Discharge and Electrochemical Mechanisms

By

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(Received December 27, 1958)

Both the TAFEL's constant and the dependence of overvoltage on hydrogen ion concentration at constant current density are important characteristics of hydrogen evolution reaction, which may be taken as criteria for the underlying mechanim.

Experimentally the TAFEL's constant has been observed with much stress. Although the classical kinetics leads to a linear relation between the logarithm of the current density $\ln i$ and overvoltage η with inclinations in terms of the TAFEL's constant $\tau=(RT/F)(\partial \ln i/\partial\eta)$ of values 1/2, 2 and 3/2 respectively for the slow discharge, catalytic and electrochemical mechanisms, such simple values of τ are not always observed but there occurs a break on the $\log i, \eta$ -curve, *i.e.*, a jump of τ from a value to another or even an utter deviation from the linear relation.[1-7] HORIUTI and collaborators have deduced in some special cases allowing for the interaction between adsorptives by statistical mechanical method[8] that the TAFEL's constant of the catalytic mechanism is kept constant near 0.5[9] over an appreciable range of η as observed,[6),11),12] while that of the electrochemical mechanism switches from a constant value 1.5 at lower cathodic polarization to another constant value 0.5 at higher cathodic polarization[10] in accordance with experiments.[1] It seems usual however to conclude from the value of the TAFEL's constant near 0.5 exclusively the slow discharge mechanism just in accordance with the classical kinetics taking no notice of the possible forthcoming of the same value from other mechanisms.

FRUMKIN *et al.*[13] have extensively studied the dependence of overvoltage on hydrogen ion concentration experimentally, which is an

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important complementarity to the TAFEL's constant as the criterion. Theoretically the effect has been formulated by FRUMKIN[14], PARSONS[15] and BOCKRIS[16] without however taking the specific adsorption of hydrogen on the electrode surface explicitly into account in the formula.

One of the present authors[17] has recently developed a systematic theory of specific adsorption of charged and uncharged hydrogen intermediates, *i.e.*, hydrogen ion $H^+(a)$, a hydrogen atom H(a) and hydrogen molecule ion $H_2^+(a)$ which are hitherto severally assumed to exist in accounting for the experimental results of hydrogen evolution reaction. It is the purpose of the present paper theoretically to establish these characteristics of hydrogen evolution reaction as the criteria of the underlying mechanisms in extension of the above work.[17]

§ 1. Model of Hydrogen Electrode

Hydrogen electrode going to be treated in the present paper is modelled as follows.[17] There exists, parallel to the electrode surface C, an adsorption plane P, which holds on it the centers of adsorbed hydrogen intermediates as well as the critical complex of the rate-determining step of hydrogen evolution reaction each situated in one of physically identical sites of adsorption but inside which no ion is admitted. The electrostatical potential E and the charge density vary one-dimensionally along x-axis taken normal to P towards the interior of the solution with its origin at the electrode surface C, as shown in Fig. 1; the electrostatic potential E_P at P is thus determined by the potential of the electrode E_C, the charge density s on P-plane given by the coverage of charged hydrogen intermediates, and the charge density ρ, satisfying the condition that $\rho \lesseqgtr 0$ according as $E \gtreqless 0$, of the electrolyte at outside P-plane according to one-dimensional POISSON equation. Besides the electrostatical potential, there exists the potential of interaction exerted additionally among hydrogen intermediates each with one electron, *i.e.*, H(a) and $H_2^+(a,)$ which is proportional to the sum of coverages of H(a) and $H_2^+(a)$ with the common proportionality constant uRT.

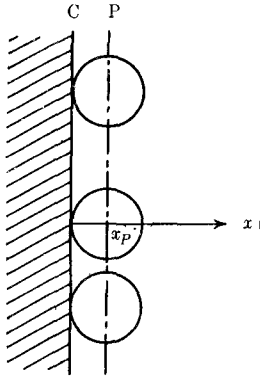

Fig. 1.
Model of electrode-solution boundary.

The slow discharge (SDM) and the electrochemical mechanisms

(ECM) are dealt with on the base of the model described above in the present paper. The rate-determining step of the respective mechanisms and the appropriate equilibrium relations are expressed as:

$$H^+(a)+e \longrightarrow H(a),\ 2H(a) \rightleftharpoons H_2,\ H^+(a) \rightleftharpoons H^+ \qquad (1.S.a),\ (1.S.b),\ (1.S.c)$$

or

$$H_2^+(a)+e \longrightarrow H_2,\ H_2^+(a) \rightleftharpoons 2H^+(a)+e,\ H^+(a) \rightleftharpoons H^+ \qquad (1.E.a),\ (1.E.b),\ (1.E.c)$$

for SDM or ECM*) respectively, where e is an electron in the electrode metal and (a) shwos the adsorbed state and $\longrightarrow$ or $\rightleftharpoons$ the rate-determining step or the equilibrium relation respectively. Similar general treatment of catalytic mechanism is left to later papers, which has been treated by HORIUTI[9] taking the repulsive potential among H(a)'s into account in a special case when $H^+(a)$ is absent.

§ 2. General Formulation of TAFEL's Constant and Dependence of Overvoltage on Hydrogen Ion Concentration

The steady current density i of the respective mechanisms is generally formulated below, from which the TAFEL's constant $\tau \equiv -(RT/F)(\partial \ln i/\partial\eta)$ and the dependence $\gamma \equiv -(\partial F\eta/\partial\mu^{H^+})_i$ of η on the hydrogen ion concentration or on the appropriate chemical potential μ^{H^+} are deduced.

The steady current density at cathodic polarization is generally expressed by the rate $\vec{v}_r$ of the rate-determining step and its stoichiometric number ν_r as[8]:

$$i = \frac{2F}{N_A}\frac{\vec{v}_r}{\nu_r} = \frac{2F}{N_A}\frac{\varkappa}{\nu_r}\frac{kT}{h}\frac{p^*}{p^1}, \qquad (2.1)$$

where $\varkappa$ is the transmission coefficient, h or k the PLANCK or BOLTZMANN

*) The initial complex of the rate-determining step of ECM was originally suggested (Ref. 18) as consisting of a neutral hydrogen atom and a proton respectively linked to surface metal atom and to a water molecule. It has been later shown (Ref. 10) that both its electronic and the nuclear configuration worked out quantum-mechanically was adequately covered by the word "hydrogen-molecule-ion adsorbed on the electrode". The following inference on ECM holds invariably to its original form in so far as the initial complex I in the latter consists of $H^+(a)$ and H(a) situated in a single σ^*, in which case the fundamental relation (2.6) reasonablly follows.

constant, T the absolute temperature and F or N_A the FARADAY's constant or the AVOGADRO's number respectively. The p^* or p^{I} is the BOLTZMANN factor of the chemical potential of the critical complex $*$ or the initial complex I, *i.e.*,

$$\mu^* = -RT\ln p^*, \quad \mu^{\mathrm{I}} = -RT\ln p^{\mathrm{I}} . \qquad (2.2^*), (2.2.\mathrm{I})$$

The p^* is expressed in the case of a heterogeneous step expediently as[8]

$$p^* = G\theta^*_{\sigma(0)} q^* , \qquad (2.3)$$

where G is the number of adsorption sites σ^*'s of the critical complex per unit area of the electrode surface, $\theta_{\sigma^*(0)}$ the probability that σ^* is free to admit the critical complex, q^* the BOLTZMANN factor of the reversible work ε^* required to bring up a critical complex to a definite preliminarily evacuated σ^* from standard states of its constituents, *i.e.*,

$$\varepsilon^* = -RT\ln q^* \qquad (2.4)$$

We have the current equation from (2.1), (2.2), (2.3) and (2.4)

$$i = \frac{2F}{N_A}\frac{\kappa}{\nu_r}\frac{kT}{h} G\theta_{\sigma^*(0)} \exp\left\{-(\varepsilon^* - \mu^{\mathrm{I}})/RT\right\}$$

or

$$RT\ln i = -\varepsilon^* + \mu^{\mathrm{I}} + RT\ln\theta_{\sigma^*(0)} + C , \qquad (2.5)$$

where $C = 2F/N_A \cdot \kappa/\nu_r \cdot kT/h \cdot G$ is a constant at a constant temperature.

The increment $\delta\varepsilon^*$ of ε^* is expressed, on the other hand, by that $\delta\varepsilon^{\mathrm{I}}$ of ε^{I} according to HORIUTI and POLANYI[19] and HORIUTI and OKAMOTO[18] as

$$\delta\varepsilon^* = \alpha\delta\varepsilon^{\mathrm{I}} , \qquad (2.6)$$

so that the current equation (2.5) is given in the differential form

$$RT\delta\ln i = -\alpha\delta\varepsilon^{\mathrm{I}} + \delta\mu^{\mathrm{I}} + RT\delta\ln\theta_{\sigma^*(0)} , \qquad (2.7)$$

where α is a proper fraction and $\delta\varepsilon^{\mathrm{I}}$ is the increment of the reversible work ε^{I} required to bring up I from the standard state of its constituents onto a definite, unoccupied σ^* to form there a specified state, which consists of an electron in electrode metal and H^+ or H_2^+ situated in σ^* respectively in the case of SDM and ECM; denoting the reversible work for H^+ or H_2^+ in σ^* in particular by $\varepsilon^{\mathrm{H}^+}$ or $\varepsilon^{\mathrm{H}_2^+}$, we have

$$\varepsilon^{\mathrm{I}} = \varepsilon^{\mathrm{H}^+} + \mu^{\mathrm{e}} \ (\mathrm{SDM}), \quad \varepsilon^{\mathrm{I}} = \varepsilon^{\mathrm{H}_2^+} + \mu^{\mathrm{e}} \ (\mathrm{ECM}) , \qquad (2.8.\mathrm{S}.\varepsilon), (2.8.\mathrm{E}.\varepsilon)$$

and for μ^{I} in accordance with (1.S) and (1.E)

$$\mu^{\mathrm{I}}=\mu^{\mathrm{H}^+}+\mu^{\mathrm{e}}\ (\mathrm{SDM}),\quad \mu^{\mathrm{I}}=\mu^{\mathrm{H}_2^+}+\mu^{\mathrm{e}}\ (\mathrm{ECM}). \qquad (2.8.\mathrm{S}.\mu),\ (2.8.\mathrm{E}.\mu)$$

Substituting ε^{I} and μ^{I} from (2.8) into (2.7) and identifying σ^* with the physically identical sites of adsorption in accordance with §1 and hence $\theta_{\sigma^*(0)}$ with θ_0, we have

$$RT\delta\ln i=-\alpha(\delta\varepsilon^{\mathrm{H}^+}+\delta\mu^{\mathrm{e}})+\delta l+RT\delta\ln\theta_0\ (\mathrm{SDM}), \qquad (2.9.\mathrm{S})$$

$$RT\delta\ln i=-\alpha(\delta\varepsilon^{\mathrm{H}_2^+}+\delta\mu^{\mathrm{e}})+2\delta l+RT\delta\ln\theta_0\ (\mathrm{ECM}), \qquad (2.9.\mathrm{E})$$

where

$$l\equiv\mu^{\mathrm{H}^+}+\mu^{\mathrm{e}}. \qquad (2.9.l)$$

The $\varepsilon^{\mathrm{H}^+}$ or $\varepsilon^{\mathrm{H}_2^+}$ in the above equation, represented by ε^j, is expressed in terms of θ_0 and the occupied fraction θ_j of the sites according to the relation[17]

$$\theta_j=\theta_0\exp(-\omega^j/RT), \qquad (2.10.\mathrm{a})$$

where

$$\sum_j\theta_j+\theta_0=1 \qquad (2.10.\mathrm{b})$$

and

$$\omega^j=\varepsilon^j-\mu^j, \qquad (2.10.\mathrm{c})$$

so that we have eliminating ε^j and ω^j from (2.9) and (2.10)

$$RT\delta\ln i=(1-\alpha)\delta l+\alpha RT\delta\ln\frac{\theta}{\theta_0}+RT\delta\ln\theta_0\ (\mathrm{SDM}), \qquad (2.11.\mathrm{S})$$

$$RT\delta\ln i=2(1-\alpha)\delta l+\alpha RT\delta\ln\frac{\theta}{\theta_0}+RT\delta\ln\theta_0\ (\mathrm{ECM}), \qquad (2.11.\mathrm{E})$$

where θ in (2.11.S) or (2.11.E) denotes the covered fraction of H^+(a) or H_2^+(a) respectively.

The θ and θ_0 in (2.11) are, as shown in the next section, functions of l and h, *i.e.*,

$$h\equiv\mu^{\mathrm{H}^+} \qquad (2.12.\mathrm{a})$$

at constant temperature, while

$$l=\frac{1}{2}\mu^{\mathrm{H}_2}-F\eta \qquad (2.12.\mathrm{b})$$

according to (2.9.l) and to the definition of overpotential $F\eta=\frac{1}{2}\mu^{\mathrm{H}_2}-$

$\mu^{H^+}-\mu^e$. It follows from (2.11) that i is a function of l and h and hence

$$\tau \equiv -\frac{RT}{F}\left(\frac{\partial \ln i}{\partial \eta}\right)_h = RT\left(\frac{\partial \ln i}{\partial l}\right)_h$$
$$= RT\left(\frac{\partial \ln i}{\partial l}\right)_{\theta,\theta_0} + RT\left(\frac{\partial \ln i}{\partial \theta}\right)_{l,\theta_0}\left(\frac{\partial \theta}{\partial l}\right)_h + RT\left(\frac{\partial \ln i}{\partial \theta_0}\right)_{l,\theta}\left(\frac{\partial \theta_0}{\partial l}\right)_h , \qquad (2.13.\tau)$$

and

$$\gamma \equiv -\left(\frac{\partial F\eta}{\partial \mu^{H^+}}\right) = \left(\frac{\partial l}{\partial h}\right)_i = -\left(\frac{\partial \ln i}{\partial h}\right)_l \Big/ \left(\frac{\partial \ln i}{\partial l}\right)_h$$

as deduced from the equation

$$RT\,\delta \ln i = RT\left(\frac{\partial \ln i}{\partial l}\right)_h \delta l + RT\left(\frac{\partial \ln i}{\partial h}\right)_l \delta h = 0 ,$$

or according to (2.13.τ)

$$\gamma = -\frac{RT}{\tau}\left\{\left(\frac{\partial \ln i}{\partial \theta}\right)_{l,\theta_0}\left(\frac{\partial \theta}{\partial h}\right)_l + \left(\frac{\partial \ln i}{\partial \theta_0}\right)_{l,\theta}\left(\frac{\partial \theta_0}{\partial h}\right)_l\right\} . \qquad (2.13.\gamma)$$

The $\left(\frac{\partial \theta}{\partial l}\right)_h$, $\left(\frac{\partial \theta_0}{\partial l}\right)_h$, $\left(\frac{\partial \theta}{\partial h}\right)_l$ and $\left(\frac{\partial \theta_0}{\partial h}\right)_l$ are yet to be determined for evaluating τ and γ in the respective cases of mechanism.

§ 3. Functions θ_j's and θ_0 of l and h

The ε^j in (2.10) is given as[17]

$$\varepsilon^j = \varepsilon_0^j + z_j F E_P , \qquad (3.1)$$

where ε_0^j is a constant at constant temperature, z_j the number of charge of j-th intermediate; $F'E_P$ has beed worked out as a function of l and h,[17)*] *i.e.* as

$$\delta(FE_P) = \alpha_h \delta h - \alpha_l \delta l , \qquad (3.2)$$

where

$$\alpha_h = -\frac{\dfrac{D_P}{4\pi x_P} + F\left(\dfrac{\partial s}{\partial h}\right)_{l,E_P}}{\dfrac{D_P}{4\pi x_P} - \dfrac{D_P}{4\pi}\dfrac{\partial}{\partial E_P}\left(\dfrac{\partial E}{\partial x}\right)_a - \left(\dfrac{\partial s}{\partial E_P}\right)_{h,l}} , \qquad (3.3.h)$$

*) See Appendix.

$$\alpha_l = \frac{\dfrac{D_P}{4\pi x_P} - F\left(\dfrac{\partial s}{\partial l}\right)_{h,E_P}}{\dfrac{D_P}{4\pi x_P} - \dfrac{D_P}{4\pi}\dfrac{\partial}{\partial E'_P}\left(\dfrac{\partial E}{\partial x}\right)_a - \left(\dfrac{\partial s}{\partial E_P}\right)_{h,l}} . \qquad (3.3.l)$$

The μ^j is on the other hand given as a function of l and h by (2.9.l) and (2.12.a) according to the appropriate equilibrium relations, so that θ_j and θ_0 are functions of l and h according to (2.10) at constant temperature. Differential coefficients $(\partial\theta/\partial l)_h$, $(\partial\theta_0/\partial l)_h$, $(\partial\theta/\partial h)_l$ and $(\partial\theta_0/\partial h)_l$ required for evaluating τ and γ depend of course on the sort of I and the coexisting intermediates. These will be developed in subsequent sections for the slow discharge and the electrochemical mechanism severally.

§ 4. The Slow Discharge Mechanism

It is assumed in this case that H(a) and H^+(a) are only intermediates existent in the sites on the P-plane*), although H_2^+(a) is not altogether excluded from being a predominant intermediate inspite of the rate-determining step of (1.S.a).*) We have by (2.10) for the intermediate H(a)

$$\delta\omega^H = \delta\varepsilon^H, \quad \delta\omega^H = -RT\delta \ln \frac{\theta_H}{\theta_0} , \qquad (4.1.a), (4.1.b)$$

since $\delta\mu^{H(a)}=0$ according to the equilibrium relation (1.S.b). The increment $\delta\varepsilon^H$ of adsorption energy due to the interaction potential exerted by surrounding adsorptives is given according to §1 as

$$\delta\varepsilon^H = uRT\delta\theta_H \qquad (4.2)$$

and hence we have from (4.1) and (4.2)

$$RT\delta \ln \frac{\theta_H}{\theta_0} + uRT\delta\theta_H = 0 . \qquad (4.3)$$

For the intermediate H^+(a) we have according to (2.10), (3.1), (2.12.a) and (1.S.c)

$$\delta\omega^{H^+} = \delta\varepsilon^{H^+} - \delta\mu^{H^+(a)} = \delta\varepsilon_0^{H^+} + \partial(FE_P) - \delta h , \qquad (4.4.a)$$

$$\delta\omega^{H^+} = -RT\delta \ln \frac{\theta}{\theta_0} . \qquad (4.4.b)$$

*) According to the conclusion of the previous work[17] H^+(a) and H_2^+(a) appear rather alternatively coexisting only in a narrow range of η or l, whereas H(a) exists in the case of SDM constantly in equilibrium with gaseous hydrogen.

Ignoring $\delta\varepsilon_0^{H^+}$ in accordance with §1, we have for $H^+(a)$

$$\delta h-\delta(FE_P)=RT\delta\ln\frac{\theta}{\theta_0} \tag{4.5}$$

or according to (3.2) as

$$(1-\alpha_h)\delta h+\alpha_l\delta l=RT\delta\ln\theta-RT\delta\ln\theta_0. \tag{4.6}$$

It follows from (4.3), (4.6) and the relation

$$\theta+\theta_H+\theta_0=1 \tag{4.7}$$

that

$$\frac{RT}{\alpha_l}\left(\frac{\partial\theta}{\partial l}\right)_h=\frac{RT}{1-\alpha_h}\left(\frac{\partial\theta}{\partial h}\right)_l=\frac{\theta(1-\theta+u\theta_H\theta_0)}{1+u\theta_H(1-\theta_H)}, \tag{4.8.a}$$

$$\frac{RT}{\alpha_l}\left(\frac{\partial\theta_0}{\partial l}\right)_h=\frac{RT}{1-\alpha_h}\left(\frac{\partial\theta_0}{\partial h}\right)_l=-\frac{\theta\theta_0(1+u\theta_H)}{1+u\theta_H(1-\theta_H)}. \tag{4.8.b}$$

The τ and γ for the slow discharge are now given substituting $(\partial\theta/\partial l)_h$ *etc.* from (4.8) into (2.13) refering to (2.11) as

$$\tau=(1-\alpha)+\frac{\alpha-\theta+u\theta_H\{(1-\theta_H)\alpha-\theta\}}{1+u\theta_H(1-\theta_H)}\alpha_l \tag{4.9.τ}$$

$$\gamma=-\frac{1}{\tau}\frac{\alpha-\theta+u\theta_H\{(1-\theta_H)\alpha-\theta\}}{1+u\theta_H(1-\theta_H)}(1-\alpha_h) \tag{4.9.γ}$$

or in the absence of H(a) in particular, simply as

$$\tau=(1-\alpha)+(\alpha-\theta)\alpha_l, \tag{4.10.τ}$$

$$\gamma=-\frac{1}{\tau}(\alpha-\theta)(1-\alpha_h). \tag{4.9.γ}$$

The α_h and α_l in the above equations are developed for SDM as follows. Differential coefficients $(\partial s/\partial h)_{l,E_P}$, $(\partial s/\partial l)_{h,E_P}$ and $(\partial s/\partial E_P)_{h,l}$ in (3.3) are given by (4.3), (4.5) and (4.7), expressing the charge density s on P-plane by the surface coverage of $H^+(a)$ as

$$\delta s=\frac{GF'}{N_A}\delta\theta \tag{4.11}$$

in the form

$$F\left(\frac{\partial s}{\partial h}\right)_{l,E_P}=-\left(\frac{\partial s}{\partial E_P}\right)_{h,l}=\frac{GF^2}{N_ART}\frac{\theta(1-\theta+u\theta_H\theta_0)}{1+u\theta_H(1-\theta_H)} \tag{4.12.$h.E_P$}$$

$$F\left(\frac{\partial s}{\partial l}\right)_{h,E_P}=0\,. \qquad (4.12.l)$$

We have thus substituting $(\partial s/\partial h)_{l,E_P}$ *etc.* from (4.12) into (3.3)

$$\alpha_h=\frac{\dfrac{D_P}{4\pi x_P}+\dfrac{GF^2}{N_ART}\dfrac{\theta(1-\theta+u\theta_H\theta_0)}{1+u\theta_H(1-\theta_H)}}{\dfrac{D_P}{4\pi x_P}-\dfrac{D_P}{4\pi}\dfrac{\partial}{\partial E_P}\left(\dfrac{\partial E}{\partial x}\right)_a+\dfrac{GF^2}{N_ART}\dfrac{\theta(1-\theta+u\theta_H\theta_0)}{1+u\theta_H(1-\theta_H)}}\,, \qquad (4.13.h)$$

$$\alpha_l=\frac{\dfrac{D_P}{4\pi x_P}}{\dfrac{D_P}{4\pi x_P}-\dfrac{D_P}{4\pi}\dfrac{\partial}{\partial E_P}\left(\dfrac{\partial E}{\partial x}\right)_a+\dfrac{GF^2}{N_ART}\dfrac{\theta(1-\theta+u\theta_H\theta_0)}{1+u\theta_H(1-\theta_H)}}\,, \qquad (4.13.l)$$

or when (Ha) is absent in particular

$$\alpha_h=\frac{\dfrac{D_P}{4\pi x_P}+\dfrac{GF^2}{N_ART}\theta(1-\theta)}{\dfrac{D_P}{4\pi x_P}-\dfrac{D_P}{4\pi}\dfrac{\partial}{\partial E_P}\left(\dfrac{\partial E}{\partial x}\right)_a+\dfrac{GF^2}{N_ART}\theta(1-\theta)}\,, \qquad (4.14.h)$$

$$\alpha_l=\frac{\dfrac{D_P}{4\pi x_P}}{\dfrac{D_P}{4\pi x_P}-\dfrac{D_P}{4\pi}\dfrac{\partial}{\partial E_P}\left(\dfrac{\partial E}{\partial x}\right)_a+\dfrac{GF^2}{N_ART}\theta(1-\theta)}\,. \qquad (4.14.l)$$

It can be seen from (4.13) that α_h and α_l are positive proper fractions since $\dfrac{D_P}{4\pi}\dfrac{\partial}{\partial E_P}\left(\dfrac{\partial E}{\partial x}\right)_a$ is negative,*) *i.e.*,

$$0<\alpha_h<1,\quad 0<\alpha_l<1. \qquad (4.15.h),\ (4.15.l)$$

The τ is expressed identically by transforming (4.9.τ) as

$$\tau=1-\left\{\alpha(1-\alpha_l)+\frac{\theta(1+u\theta_H)}{1+u\theta_H(1-\theta_H)}\alpha_l\right\}=(1-\alpha)(1-\alpha_l)+\frac{1-\theta+u\theta_H(1-\theta-\theta_H)}{1+u\theta_H(1-\theta_H)}\alpha_l\,.$$

The second member of the above equation shows that τ never exceed 1 since the second term of the member is positive according to (4.15.*l*), while the third member that τ is positive inasmuch as $1-\theta-\theta_H$ as well as $1-\theta$ is positive according to (4.7), *i.e.*,

$$0<\tau<1\,. \qquad (4.16)$$

Particularly when there is no specific adsorption on the electrode sur-

*) See Appendix.

face and E_P-potential is kept constant, *i. e.* $\alpha_h=\alpha_l=0$, τ and γ are simply given by (4.10) as

$$\tau = 1-\alpha\,, \quad \gamma = -\frac{\alpha}{1-\alpha}\,, \qquad (4.17.\tau),\ (4.17.\gamma)$$

as has been previously derived by FRUMKIN[14] for the particular case.

§ 5. The Electrochemical Mechanism

As shown in (1.E) intermediates $H^+(a)$ and $H_2^+(a)$ are involved in the hydrogen electrode reaction of the electrochemical mechanism, although H(a) is not altogether excluded similarly as $H_2^+(a)$ in the case of SDM. The isotherm of $H_2^+(a)$ is written according to (2.10) and (3.1) as

$$\delta\omega^{H_2^+} = \delta\varepsilon^{H_2^+} - \delta\mu^{H_2^{+(a)}} = \delta\varepsilon_0^{H_2^+} + \delta(FE_P) - \delta\mu^{H_2^{+(a)}}\,, \qquad (5.1.a)$$

$$\delta\omega^{H_2^+} = -RT'\delta\ln\frac{\theta}{\theta_0}\,, \qquad (5.1.b)$$

where

$$\delta\mu^{H_2^{+(a)}} = 2\delta\mu^{H^+} + \delta\mu^e \qquad (5.2)$$

by (1.E.b) and (1.E.c) and

$$\delta\varepsilon_0^{H_2^+} = uRT\delta\theta \qquad (5.3)$$

according to § 1.
We have thus from (5.1), (5.2), (5.3), (2.9.l) and (2.12.a)

$$\delta h + \delta l - \delta(FE_P) = RT\delta\ln\frac{\theta}{\theta_0} + uRT\delta\theta \qquad (5.4)$$

We have on the other hand from (4.5) for $H^+(a)$

$$\delta h - \delta(FE_P) = RT\delta\ln\frac{\theta_{H^+}}{\theta_0}\,, \qquad (5.5)$$

rewriting θ there into θ_{H^+}. Eq. (5.4) and (5.5) are written in accoordance with (3.2) as

$$(1-\alpha_h)\delta h + (1+\alpha_l)\delta l = RT\delta\ln\frac{\theta}{\theta_0} + uRT\delta\theta\,, \qquad (5.6.\ H_2^+)$$

$$(1-\alpha_h)\delta h + \alpha_l\delta l = RT\delta\ln\frac{\theta_{H^+}}{\theta_0}\,, \qquad (5.6.\ H^+)$$

from which we have $(\partial\theta/\partial l)_h$ *etc.* remembering $\delta\vartheta+\delta\theta_{H^+}+\delta\theta_0=0$ as

$$RT\left(\frac{\partial\theta}{\partial l}\right)_{h,E_P}=\frac{\theta(1-\theta+\theta_0\alpha_l)}{1+u\theta(1-\theta)}\,, \tag{5.7.a}$$

$$RT\left(\frac{\partial\theta_0}{\partial l}\right)_{h,E_P}=-\frac{\theta_0\{\theta+(1-\theta_0+u\vartheta\theta_{H^+})\alpha_l\}}{1+u\vartheta(1-\theta)}\,, \tag{5.7.b}$$

$$RT\left(\frac{\partial\theta}{\partial h}\right)_{l,E_P}=\frac{\theta\theta_0(1-\alpha_h)}{1+u\theta(1-\theta)}\,, \tag{5.7.c}$$

$$RT\left(\frac{\partial\theta_0}{\partial h}\right)_{l,E_P}=-\frac{\theta_0\{1-\theta_0+u\theta\theta_{H^+}\}(1-\alpha_h)}{1+u\vartheta(1-\theta)}\,. \tag{5.7.d}$$

The τ and γ are now expressed by (2.13) and (5.7) in the form

$$\tau=2(1-\alpha)+\frac{\alpha-\theta}{1+u\vartheta(1-\theta)}+\frac{\alpha+\theta_0-1+(\alpha-1)u\theta\theta_{H^+}}{1+u\vartheta(1-\theta)}\alpha_l\,, \tag{5.8.τ}$$

$$\gamma=-\frac{1}{\tau}\frac{\alpha+\theta_0-1+(\alpha-1)u\vartheta\theta_{H^+}}{1+u\vartheta(1-\theta)}(1-\alpha_h)\,, \tag{5.8.γ}$$

or particularly in the absence of H^+(a) simply

$$\tau=2(1-\alpha)+\frac{\alpha-\theta}{1+u\vartheta(1-\theta)}(1+\alpha_l)\,, \tag{5.9.τ}$$

$$\gamma=-\frac{1}{\tau}\frac{\alpha-\theta}{1+u\vartheta(1-\theta)}(1-\alpha_h)\,. \tag{5.9.γ}$$

Differential coefficients $(\partial s/\partial h)_{l,E_P}$ *etc.* in the expressions of α_h and α_l are given according to (5.4) and (5.5) by expressing the charge density s on P-plane as

$$\delta s=\frac{GF}{N_A}(\delta\theta+\delta\vartheta_{H^+})\,, \tag{5.10}$$

and noting the relation $\delta\vartheta+\delta\theta_{H^+}+\delta\theta_0=0$ as

$$F\left(\frac{\partial s}{\partial h}\right)_{l,E_P}=-\left(\frac{\partial s}{\partial E_P}\right)_{h,l}=\frac{GF^2}{N_ART}\frac{\theta_0(1-\theta_0+u\theta\theta_{H^+})}{1+u\theta(1-\theta)}\,, \tag{5.11.$h.E_P$}$$

$$F\left(\frac{\partial s}{\partial l}\right)_{h,E_P}=\frac{GF^2}{N_ART}\frac{\theta\theta_0}{1+u\vartheta(1-\theta)}\,. \tag{5.11.l}$$

Substituting (5.11) into (3.3) we have

$$\alpha_h = \frac{\dfrac{D_P}{4\pi x_P} + \dfrac{GF^2}{N_A RT}\dfrac{\theta_0(1-\theta_0+u\theta\theta_{H^+})}{1+u\theta(1-\theta)}}{\dfrac{D_P}{4\pi x_P} - \dfrac{D_P}{4\pi}\dfrac{\partial}{\partial E_P}\left(\dfrac{\partial E}{\partial x}\right)_a + \dfrac{GF^2}{N_A RT}\dfrac{\theta_0(1-\theta_0+u\theta\theta_{H^+})}{1+u\theta(1-\theta)}}, \quad (5.12.h)$$

$$\alpha_l = \frac{\dfrac{D_P}{4\pi x_P} - \dfrac{GF^2}{N_A RT}\dfrac{\theta\theta_0}{1+u\theta(1-\theta)}}{\dfrac{D_P}{4\pi x_P} - \dfrac{D_P}{4\pi}\dfrac{\partial}{\partial E_P}\left(\dfrac{\partial E}{\partial x}\right)_a + \dfrac{GF^2}{N_A RT}\dfrac{\theta_0(1-\theta_0+u\theta\theta_{H^+})}{1+u\theta(1-\theta)}}, \quad (5.12.l)$$

or in the particular case when $H^+(a)$ is absent as

$$\alpha_h = \frac{\dfrac{D_P}{4\pi x_P} + \dfrac{GF^2}{N_A RT}\dfrac{\theta_0(1-\theta_0)}{1+u\theta(1-\theta)}}{\dfrac{D_P}{4\pi x_P} - \dfrac{D_P}{4\pi}\dfrac{\partial}{\partial E_P}\left(\dfrac{\partial E}{\partial x}\right)_a + \dfrac{GF^2}{N_A RT}\dfrac{\theta_0(1-\theta_0)}{1+u\theta(1-\theta)}}, \quad (5.13.h)$$

$$\alpha_l = \frac{\dfrac{D_P}{4\pi x_P} - \dfrac{GF^2}{N_A RT}\dfrac{\theta\theta_0}{1+u\theta(1-\theta)}}{\dfrac{D_P}{4\pi x_P} - \dfrac{D_P}{4\pi}\dfrac{\partial}{\partial E_P}\left(\dfrac{\partial E}{\partial x}\right)_a + \dfrac{GF^2}{N_A RT}\dfrac{\theta_0(1-\theta_0)}{1+u\theta(1-\theta)}}. \quad (5.13.l)$$

It can be seen from (5.12) that α_h is a positive proper fraction, while α_l is a positive or negative proper fraction since $\dfrac{D_P}{4\pi}\dfrac{\partial}{\partial E_P}\left(\dfrac{\partial E}{\partial x}\right)_a$ is a negative, *i. e.*,

$$0 < \alpha_h < 1, \quad -1 < \alpha_l < 1. \qquad (5,14.h),\ (5.14.l)$$

The equation (5.8) shows that if E_P-potential is kept constant, *i. e.* $\alpha_h = \alpha_l = 0$, τ takes a value between $2-\alpha$ and $1-\alpha$ depending on the surface coverage of $H_2^+(a)$. Particularly when there is no specific adsorption on the electrode surface and E_P-potential is kept constant τ and γ are simply given as

$$\tau = 2-\alpha, \quad \gamma = -\frac{\alpha}{2-\alpha}. \qquad (5.15.\tau),\ (5.15.\gamma)$$

§ 6. Discussion of τ and γ

The τ, γ, α_h and α_l derived in the preceding section will be discussed here for the special case of SDM and ECM when the electrolyte is uni-uni-valent and of concentration $n=0.1$N, $D=40$, $\overline{D}=10$,*) $x_P=1$A

*) See Appendix.

and $G=10^{15}$, assuming $\alpha=1/2$. The expressions of τ, γ, α_h and α_l in this case are given in table I.

TABLE I. The τ, γ, α_h and α_l in SDM and ECM

SDM	$\tau = (1-\alpha)+\dfrac{\alpha-\theta+u\theta_{\mathrm{H}}\{(1-\theta_{\mathrm{H}})\alpha-\theta\}}{1+u\theta_{\mathrm{H}}(1-\theta_{\mathrm{H}})}\alpha_l$ $\gamma = -\dfrac{1}{\tau}\dfrac{\alpha-\theta+u\theta_{\mathrm{H}}\{(1-\theta_{\mathrm{H}})\alpha-\theta\}}{1+u\theta_{\mathrm{H}}(1-\theta_{\mathrm{H}})}(1-\alpha_h)$ $\alpha_h = \dfrac{1+\dfrac{143\,\theta\,(1-\theta+u\theta_{\mathrm{H}}\theta_0)}{1+u\theta_{\mathrm{H}}(1-\theta_{\mathrm{H}})}}{1+0.2\cosh\dfrac{FE_{\mathrm{P}}}{2RT}+\dfrac{143\,\theta\,(1-\theta+u\theta_{\mathrm{H}}\theta_0)}{1+u\theta_{\mathrm{H}}(1-\theta_{\mathrm{H}})}}$ $\alpha_l = \dfrac{1}{1+0.2\cosh\dfrac{FE_{\mathrm{P}}}{2RT}+\dfrac{143\,\theta\,(1-\theta+u\theta_{\mathrm{H}}\theta_0)}{1+u\theta_{\mathrm{H}}(1-\theta_{\mathrm{H}})}}$
ECM	$\tau = 2(1-\alpha)+\dfrac{\alpha-\theta}{1+u\theta(1-\theta)}+\dfrac{\alpha+\theta_0-1+(\alpha-1)u\theta\theta_{\mathrm{H}^+}}{1+u\theta(1-\theta)}\alpha_l$ $\gamma = -\dfrac{1}{\tau}\dfrac{\alpha+\theta_0-1+(\alpha-1)u\theta\theta_{\mathrm{H}^+}}{1+u\theta(1-\theta)}(1-\alpha_h)$ $\alpha_h = \dfrac{1+\dfrac{143\,\theta_0(1-\theta_0+u\theta\theta_{\mathrm{H}^+})}{1+u\theta(1-\theta)}}{1+0.2\cosh\dfrac{FE_{\mathrm{P}}}{2RT}+\dfrac{143\,\theta_0(1-\theta_0+u\theta\theta_{\mathrm{H}^+})}{1+u\theta(1-\theta)}}$ $\alpha_l = \dfrac{1-\dfrac{143\,\theta\theta_0}{1+u\theta(1-\theta)}}{1+0.2\cosh\dfrac{FE_{\mathrm{P}}}{2RT}+\dfrac{143\,\theta_0(1-\theta_0+u\theta\theta_{\mathrm{H}^+})}{1+u\theta(1-\theta)}}$

We see from table I with respect to α_h and α_l that:

i) $0<\alpha_h<1,\quad 0<\alpha_l<1$ for SDM, (6.1.S)

$0<\alpha_h<1,\quad -1<\alpha_l<1$ for ECM. (6.1.E)

ii) α_h and α_l tend to zero in either mechanism with increase of $|E_{\mathrm{P}}|$ irrespective of the state of specific adsorption, *i.e.*

$$\alpha_h=\alpha_l\approx 0 \qquad \text{at} \quad |E_{\mathrm{P}}|>400\ \mathrm{mv}. \tag{6.2}$$

iii) when the surface is bare or fully covered with $H^+(a)$ in SDM or with $H_2^+(a)$ in ECM,

$$\alpha_h=\alpha_l\approx 1 \qquad \text{at} \quad |E_{\mathrm{P}}|=0. \tag{6.3}$$

In SDM in particular we see from (6.2), (6.3) and Table I that:

i) with increase of $|E_P|$, τ tends to 0.5 irrespective of the state of specific adsorption, while γ to a definite value dependent on the state of specific adsorption.

ii) when the surface is bare, we have

$$\tau = 1-\alpha+\alpha\alpha_l, \quad \gamma = -\frac{\alpha}{\tau}(1-\alpha_h),$$

thus according to (6.2) and (6.3)

$\tau = 0.5$, $\gamma = -1$ at $|E_P| > 400$ mv

or

$\tau = 1$, $\gamma = 0$ at $E_P = 0$.

iii) when the surface is fully covered with H^+(a),

$$\tau = (1-\alpha)(1-\alpha_l), \quad \gamma = \frac{1}{\tau}(1-\alpha)(1-\alpha_h)$$

and thus

$\tau = 0.5$, $\gamma = 1$ at $|E_P| > 400$ mv

$\tau = 0$, $\gamma = 1$ at $E_P = 0$.

iv) τ never exceeds 1 thrughout the whole range of θ and E_P.

v) γ changes sign at a certain state of specific adsorption. Extreme cases ii) and iii) are summarized in Table II.

TABLE II. The τ and γ for SDM.

τ			γ		
θ \ E_P	0	$\|E_P\| > 400$	θ \ E_P	0	$\|E_P\| > 400$
0	1	0.5	0	0	−1
1	0	0.5	1	1	1

Table II indicates the change of τ and γ along with the variation of E_P-potential and θ, or the break down of the appropriate linear relation.

In the electrochemical mechanism we see from (6.2), (6.3) and Table I that:

i) τ tends with increase of $|E_P|$ to a definite value $2(1-\alpha)+\frac{\alpha-\theta}{1+u\theta(1-\theta)}$ which lies between 1.5 and 0.5 depending on the magnitude of θ, and γ to a limiting value

$$-\frac{1}{\tau}\frac{\alpha+\theta_0-1+(\alpha-1)u\theta\theta_H}{1+u\theta(1-\theta)}.$$

ii) when the surface is bare $\tau = 2 - \alpha + \alpha\alpha_l$, $\gamma = -\frac{\alpha}{\tau}(1-\alpha_h)$, thus according to (6.2) and (6.3)

$$\tau = 1.5, \quad \gamma = -\frac{1}{3} \qquad \text{at} \quad |E_P| > 400 \text{ mv},$$

$$\tau = 2, \quad \gamma = 0 \qquad \text{at} \quad E_P = 0.$$

iii) when the surface is fully covered with $H_2^+(a)$

$$\tau = (1-\alpha)(1-\alpha_l), \quad \gamma = \frac{1}{\tau}(1-\alpha)(1-\alpha_h)$$

and thus

$$\tau = 0.5, \quad \gamma = 1 \qquad \text{at} \quad |E_P| > 400 \text{ mv}$$

$$\tau = 0, \quad \gamma = 1 \qquad \text{at} \quad E_P = 0.$$

iv) τ never exceeds 2 throughout the whole range of θ and E_P.

v) γ changes sign at a certain state of specific adsorption.

Extreme cases ii) and iii) are summarized in Table III.

TABLE III. The τ and γ for ECM

τ			γ		
θ \ E_P	0	$\lvert E_P \rvert > 400$	θ \ E_P	0	$\lvert E_P \rvert > 400$
0	2	1.5	0	0	$-\frac{1}{3}$
1	0	0.5	1	1	1

Table III indicates the change of τ and γ along with the variation of E_P-potential and θ, or the break down of the appropriate linear relation as in the case of SDM.

The most striking difference between the slow discharge and the electrochemical mechanism is that:

> the TAFEL's constant is fixed at 0.5 irrespective of the state of specific adsorption in large $|E_P|$ in the slow discharge mechanism, while in the electrochemical mechanism the TAFEL's constant varies from 1.5 to 0.5 depending on the state of specific adsorption, in spite of α being fixed constant at 0.5.

Detailled discussions of τ and γ with reference to experimental results will be given in later papers.

Summary

The TAFEL's constant τ and the coefficient γ of dependence of overvoltage on hydrogen ion concentration in the hydrogen evolution reaction were derived for the slow discharge mechanism (SDM) and the electrochemical mechanism (ECM) from the steady current equation on the base of the theory of hydrogen intermediates (Ref. 17) assuming the rule $\delta\varepsilon^* = \alpha\delta\varepsilon^{\mathrm{I}}$ (Ref. 19), where $\delta\varepsilon^*$ is the increment of the energy ε^* of the critical complex of the rate-determining step, $\delta\varepsilon^{\mathrm{I}}$ the increment of the energy ε^{I} of the initial complex I situated in the same site as that of the critical complex, and α a constant near 0.5.

The τ and γ were shown strongly dependent on the state of specific adsorption (SSA) on the electrode surface and electrostatic potential E_{P} at the adsorption layer, *i. e.*

i) for SDM in the neighbourhood of $E_{\mathrm{P}}=0$, τ lies between 0 and 1 depending on SSA and γ is practically zero irrespective of SSA, while with increase of $|E_{\mathrm{P}}|$, τ tends to 0.5 irrespective of SSA and γ to a value between -1 and 1 depending on SSA.

ii) for ECM in the neighbourhood of $E_{\mathrm{P}}=0$, τ lies between 2 and 0 depending on SSA and γ is practically zero irrespective of SSA, while with increase of $|E_{\mathrm{P}}|$, τ tends to a definite value between 1.5 and 0.5, whereas γ to a value between $-1/3$ and 1 both depending on SSA.

It was emphasized as the conclusion that τ of SDM can neither exceed 1 throughout whole region of polarization nor deviate from $1-\alpha$ at large $|E_{\mathrm{P}}|$.

The deviation of the TAFEL's constant from classical kinetic values, *i. e.*, 0.5 (SDM) and 1.5 (ECM), or the deviation from the TAFEL's linear relation, or the appearance of a break on $\log i, \eta$-curve and miscellaneous dependency observed of overvoltage on the hydrogen ion concentration were shown to be explained on account of the change of SSA and E_{P}.

Appendix

Derivation of α_h and α_l

The derivation of α_h and α_l in the original work[17] is summarized in what follows so far as connected with the inference of the present paper.

According to our model illustrated in Fig. 1 the electric displacement ϑ and the charge density ρ should satisfy the one-dimensional POISSON equation

$$\frac{d\vartheta}{dx} = \rho \,, \tag{i}$$

where $\vartheta = -D/4\pi \cdot dE/dx$, D is dielectric constant and the electrostatic potential E is taken zero at $x=\infty$.

The charge density s on P-plane is obtained by integrating (i) as

$$\vartheta_a - \vartheta_i = \lim_{t\to 0} \int_{x_P - t}^{x_P + t} \rho dx = s \,, \tag{ii}$$

where x_P is the distance between C and P, suffix a or i denotes just outside or inside P respectively,

$$\vartheta_a = -\frac{D_P}{4\pi}\left(\frac{\partial E}{\partial x}\right)_a \tag{iii}$$

$$\left(\frac{\partial E}{\partial x}\right)_a = \pm \frac{1}{D_P}\sqrt{-8\pi\int_0^{E_P}\rho D dE} \tag{iv}$$

plus or minus sign being respectively relevant to negative or positive E or E_P,

$$\vartheta_i = -\frac{D_P}{4\pi}\left(\frac{\partial E}{\partial x}\right)_i = -\frac{D_P}{4\pi}(E_P - E_C) \tag{v}$$

E_P and E_C being electrostatic potential of P and C respectively, and D_P is the dielectric constant between C and P inclusive of just outside P. We have from (ii), (iii) and (v)

$$\frac{D_P}{4\pi x_P}(E_P - E_C) - \frac{D_P}{4\pi}\left(\frac{\partial E}{\partial x}\right)_a = s \,. \tag{vi}$$

The E_C is expressed in terms of l, h and the work function λ of the electrode as*)

$$E_C = \frac{1}{F}(h-l) - \lambda \tag{vii}$$

and hence (vi) is expressed as

$$\left\{E_P - \frac{1}{F}(h-l) + \lambda\right\} - x_P\left(\frac{\partial E}{\partial x}\right)_a = \frac{4\pi x_P}{D_P} s \,. \tag{viii}$$

*) The μ^e is expressed as $\mu^e = -F\lambda - FE_C$ or we have in the text according to (2. 9. *l*).

Assuming now λ constant for a definite electrode, E_{P} is given by (viii) as a function of l and h, because $\left(\frac{\partial E}{\partial x}\right)_a$ is a function of E_{P} by (iv), while s is given by the surface coverages of charged hydrogen intermediates on P-plane which are given in accordance with (2.10), (3.1) and (4.11) or (5.10) as functions of l, h and E_{P}. Taking total differentials of (viii)

$$\left\{\left(\frac{\partial E_{\mathrm{P}}}{\partial h}\right)_l \delta h + \left(\frac{\partial E_{\mathrm{P}}}{\partial l}\right)_h \delta l - \frac{1}{F}(\delta h - \delta l)\right\} - x_{\mathrm{P}} \frac{\partial}{\partial E_{\mathrm{P}}}\left(\frac{\partial E}{\partial x}\right)_a \left\{\left(\frac{\partial E_{\mathrm{P}}}{\partial h}\right)_l \delta h + \left(\frac{\partial E_{\mathrm{P}}}{\partial l}\right)_h \delta l\right\} = \frac{4\pi x_{\mathrm{P}}}{D_{\mathrm{P}}}\left[\left(\frac{\partial s}{\partial E_{\mathrm{P}}}\right)_{h,l}\left\{\left(\frac{\partial E}{\partial h}\right)_l \delta h + \left(\frac{\partial E_{\mathrm{P}}}{\partial l}\right)_h \delta l\right\} + \left(\frac{\partial s}{\partial h}\right)_{l,E_{\mathrm{P}}} \delta h + \left(\frac{\partial s}{\partial l}\right)_{h,E_{\mathrm{P}}} \delta l\right], \tag{ix}$$

we have

$$\alpha_h \equiv \left(\frac{\partial F E_{\mathrm{P}}}{\partial h}\right)_l = \frac{\dfrac{D_{\mathrm{P}}}{4\pi x_{\mathrm{P}}} + F\left(\dfrac{\partial s}{\partial h}\right)_{l,E_{\mathrm{P}}}}{\dfrac{D_{\mathrm{P}}}{4\pi x_{\mathrm{P}}} - \dfrac{D_{\mathrm{P}}}{4\pi}\dfrac{\partial}{\partial E_{\mathrm{P}}}\left(\dfrac{\partial E}{\partial x}\right)_a - \left(\dfrac{\partial s}{\partial E_{\mathrm{P}}}\right)_{h,l}} \tag{x}$$

$$\alpha_l \equiv -\left(\frac{\partial F E_{\mathrm{P}}}{\partial l}\right)_h = \frac{\dfrac{D_{\mathrm{P}}}{4\pi x_{\mathrm{P}}} - F\left(\dfrac{\partial s}{\partial l}\right)_{h,E_{\mathrm{P}}}}{\dfrac{D_{\mathrm{P}}}{4\pi x_{\mathrm{P}}} - \dfrac{D_{\mathrm{P}}}{4\pi}\dfrac{\partial}{\partial E_{\mathrm{P}}}\left(\dfrac{\partial E}{\partial x}\right)_a - \left(\dfrac{\partial s}{\partial E_{\mathrm{P}}}\right)_{h,l}} \tag{xi}$$

As seen from (iv) $(\partial E/\partial x)_a$ decreases with increase of E_{P} irrespective of its sign, *i. e.*

$$\frac{\partial}{\partial E_{\mathrm{P}}}\left(\frac{\partial E}{\partial x}\right)_a < 0 \ . \tag{xii}$$

Particularly for the uni-uni-valent electrolyte (iv) is integrated as

$$\frac{D_{\mathrm{P}}}{4\pi}\left(\frac{\partial E}{\partial x}\right)_a = \sqrt{\frac{n\bar{D}RT}{2\pi}}\left\{e^{-\frac{FE_{\mathrm{P}}}{2RT}} - e^{\frac{FE_{\mathrm{P}}}{2RT}}\right\} \tag{xiii}$$

$$\frac{D_{\mathrm{P}}}{4\pi}\frac{\partial}{\partial E_{\mathrm{P}}}\left(\frac{\partial E}{\partial x}\right)_a = -F\sqrt{\frac{n\bar{D}}{8\pi RT}}\left(e^{-\frac{FE_{\mathrm{P}}}{2RT}} + e^{\frac{FE_{\mathrm{P}}}{2RT}}\right) \tag{xiv}$$

where $\bar{D} = \int_0^{E_{\mathrm{P}}} D\rho\, dE \Big/ \int_0^{E_{\mathrm{P}}} \rho\, dE$.

References

1) A. MITSUYA, this Journal **4**, 228 (1956).
2) J. O'M. BOCKRIS, I. A. AMMAR and A. K. M. HUQ, J. Phys. Chem. **61**, 879 (1957).
3) J. P. HOARE and S. SCHULDINER, J. Phys. Chem. **62**, 229 (1958).
4) S. SCHULDINER, J. Electrochem. Soc. **99**, 488 (1952).
5) St. G. CHRISTOV and N. A. PANGAROV, Z. Elektrochem. Ber. Bunsenges. physik. Chem. **61**, 113 (1958).
6) J. O'M. BOCKRIS and E. C. POTTER, J. Chem. Phys. **20**, 614 (1952).
7) S. SCHULDINER, J. Electrochem. Soc. **104**, 319 (1957).
8) J. HORIUTI, this Journal **1**, 18 (1948-51).
9) J. HORIUTI, *ibid.* **4**, 55 (1956).
10) J. HORIUTI, T. KEII and K. HIROTA, *ibid.* **2**, 1 (1951).
11) P. LUKOVTSEV and S. LEVINA, J. phys. Chem. USSR **21**, 599 (1947).
12) A. N. FRUMKIN, Acta Physicochim, USSR **11**, 21 (1939).
13) A. FRUMKIN, J. Phys. Chem. USSR **24**, 244 (1950);
A. Frumkin, Disc. Faraday Soc. **1**, 57 (1947);
S. Jofa and A. Frumkin, Acta Physicochim. USSR **18**, 183 (1943);
V. Bagozky, Compt. Rend. Acad. Sc. USSR **58**, 1387 (1947);
V. Bagozky, J. Phys. Chem. USSR **22**, 1466 (1948);
V. Bagozky and I. Jablokova, J. Phys. Chem. USSR **23**, 413 (1949).
14) A. N. FRUMKIN, Z.physik. Chem. A **164**, 121 (1933).
15) R. PARSONS, Trans. Faraday Soc. **47**, 1332 (1951).
16) J. O'M. BOCKRIS, *Modern Aspects of Electrochemistry*, Butterworths Sci. Pub. London, 1954, p. 180.
17) J. HORIUTI, this Journal **3**. 52 (1954), Proc. IInd International Congress, Surface Activity 280 (1957).
18) J. HORIUTI and G. OKAMOTO, Sci. Pap. Inst. Phys. Tokio **28**, 231 (1936).
19) J. HORIUTI and M. POLANYI, Acta Physicochim. USSR **2**, 505 (1935).