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ELECTROLYTIC HYDROGEN EVOLUTION ON NON-UNIFORM SURFACE

An Explanation to Tafel Equation

By

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The possibility suggested by TAFEL, of explaining the TAFEL equation on the basis of non-uniform surface has been discussed. The TAFEL equation has been shown to follow from the premise of the non-uniform surface consisting of physically different sites distributed uniformly over a range of adsorption energy but not from that of sites exponentially distributed over the range. It has been pointed out that this explanation is formally congruent with that given by HORIUTI *et al.* which is alternatively based on the uniform surface but allowed for repulsive potentials among adsorbed hydrogen atoms.

Introduction

The rate of hydrogen evolution on many electrode metals is known to satisfy the TAFEL equation, *i.e.*,

$$i = i_0 \exp(-\alpha F\eta/RT), \qquad (1)$$

where η is the overpotential, i_0 and α are constants independent of overpotential. The α has been found for most of electrodes nearly 1/2 independent of temperature. Various theories have been proposed, to explain this law, which are all based, so far as the present author knows, on the assumption of a uniform surface of electrodes.

TAFEL[1] has expressed the rate of the evolution reaction, under the assumption of the rate-determining recombination of hydrogen atoms liberted on the electrode surface by rapid neutralization of hydrogen ions in the solution, as

$$i = k^2\theta, \qquad (2)$$

where θ is the population of hydrogen atoms on the electrode surface and k the rate constant. Assuming further that the free energy of the hydrogen atoms equals, apart from additive constants, to $RT\log\theta$ by analogy of the three dimensional ideal gas on the one hand and to the free energy $-F\eta$ of the

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1) TAFEL, Z. physik. Chem. **50**, 641 (1905).

system, consisting of a hydrogen ion in the electrolyte and metal electron in the electrode on account of the practical equilibrium with hydrogen atom on the electrode surface attained by rapid neutralization, on the other hand, TAFEL arrived at $\alpha=2$ intead of $\alpha=1/2$.

This reasoning of TAFEL is based on the supposition of a uniform surface of electrode, which accomodates every atom equally. The explanation of the TAFEL equation along this line has been accomplished by HORIUTI *et al.*[2] by allowing for the interactions between adsorbed hydrogen atoms on the basis of statistical mechanical theory of reaction.

TAFEL himself ascribed on the other hand plausibly the above difficulty he encountered with to a non-uniform surface structure, although he gave no consistent account to his empirical relation on this basis. The latter alternative procedure of explaining the TAFEL's law will be pursued and discussed in comparison with the former one in the present article.

Formulation of the Rate of Hydrogen Evolution on the Non-uniform Surface.

We suppose an electrode whose surface sites are not physically uniform but distributed in such a way as the fraction of surface sites having adsorption energies between ε and $\varepsilon+d\varepsilon$ is given by $f_\varepsilon d\varepsilon$, where f_ε is a function of ε. Denoting the coverage of the latter surface sites by θ_ε, the population of hydrogen atoms or the overall coverage θ by adsorbed hydrogen atoms is expressed as

$$\theta = \int_{\varepsilon_l}^{\varepsilon_m} f_\varepsilon \theta_\varepsilon d\varepsilon \,. \tag{3}$$

The rate constant k in (2) is now expressed with special reference to sites of adsorption energy ε as

$$k_\varepsilon = k_0 \exp(-\varepsilon^*/RT), \tag{4}$$

where ε^* is the appropriate activation energy. The overall rate of the reaction on the non-uniform surface is now

$$i = \int_{\varepsilon_l}^{\varepsilon_m} f_\varepsilon k_\varepsilon \theta_\varepsilon^2 d\varepsilon \,. \tag{5}$$

The θ_ε, k_ε and f_ε must now be given as functions of ε and hence of η in order to arrive at the theoretical expression of $i=i(\eta)$.

Assuming that the hydrogen atoms adsorbed on the sites with the same

2) OKAMOTO, HORIUTI and HIROTA, Sci. Pap. I. P. C. R. Tokio. **29**, 223 (1936).

adsorption energy compose an ideal localized monolayer, the coverage θ_ε is given by a LANGMUIR type isotherm, *i.e.*

$$\frac{\theta_\varepsilon}{1-\theta_\varepsilon} = q_0 \exp\left(\frac{\varepsilon + \frac{1}{2}\mu - F\eta}{RT}\right), \tag{6}$$

where q_0 is the partition function of an adsorbed hydrogen atom, and μ the chemical potential of hydrogen molecule, *i. e.*

$$\mu = RT \log (P/k_B T Q_0), \tag{7}$$

where P is the pressure, Q_0 the partition funcion of hydrogen molecule and k_B the BOLTZMANN constant.

The plausible expression for k_ε may be given, according to the rule of HORIUTI and POLANYI[3], which has been of frequent use in the field of electrode kinetics[4]. The rule states with regard to the present particular case that the increase $\Delta\varepsilon$ in the adsorption energy or that $-2\Delta\varepsilon$ in energy of the initial state of the recombination is accompanied by a proportional decrease $\beta \cdot 2\Delta\varepsilon$ in the activation energy, where β is a constant positive proper fraction. The activation energy ε^* on the site with the adsorption energy ε is now given, according to the above rule, as

$$\varepsilon^* = \varepsilon_l^* + 2\beta(\varepsilon - \varepsilon_l), \tag{8}$$

denoting the minimum activation energy on the sites with the minimum adsorption energy ε_l by ε_l^*, and writing $\varepsilon - \varepsilon_l$ for $\Delta\varepsilon$ (Fig. 1). It follows from (4) and (8)

$$k_\varepsilon = k_0' \exp(-2\beta\varepsilon/RT), \tag{9}$$

where

$$k_0' = k_0 \exp\left\{-(\varepsilon_l^* - 2\beta\varepsilon_l)/RT\right\}.$$

The forms of the distribution function of non-uniform surface have frequently discussed. One is that of a uniform distribution as

$$f_\varepsilon = 1/u \tag{10}$$

and the other is that of an exponential distribution as

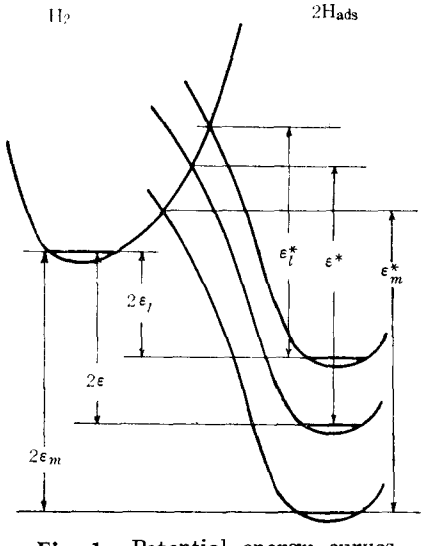

Fig. 1. Potential energy curves involved in the recombination of two adsorbed bydrogen atoms.

3) HORIUTI and POLANYI, Acta Physicochim. URSS **2**, 505 (1935).
4) BOCKRIS, *Electrochemistry*, Butterworths Sci. Pub. (1954).

$$f_\varepsilon = C\exp(-\gamma\varepsilon), \tag{11}$$

where u, C and γ are constants which may be determined by the condition of normalization, *i.e.*

$$\int_{\varepsilon_l}^{\varepsilon_m} f_\varepsilon d\varepsilon = 1 . \tag{12}$$

Integration (3) is carried out for the distribution function (10) according to (6), as

$$\theta = \frac{RT}{u}\log\left\{\frac{1+\exp(\varepsilon_m-\varepsilon_{II})/RT}{1+\exp(\varepsilon_l-\varepsilon_{II})/RT}\right\}, \tag{13}$$

where

$$-\varepsilon_{II} = \frac{1}{2}\mu + RT\log q_0 - F\eta . \tag{14}$$

Eq. (13) is written approximatly in the case when $\varepsilon_l \ll \varepsilon_{II} \ll \varepsilon_m$, as

$$\theta \doteq \frac{1}{u}\left(\varepsilon_m + \frac{1}{2}\mu + RT\log q_0 - F\eta\right) \tag{15}$$

where $u=(\varepsilon_m-\varepsilon_l)$ according to (12).

The approximation implied in (15) is however equivalent to that of the ROGINSKY's method[5),6)], *i.e.* that of putting θ_ε unity or zero according as ε is above or below ε_{II}, which leads to the equation identical with (15), *i.e.*

$$\theta \doteq \int_{\varepsilon_{II}}^{\varepsilon_m} f_\varepsilon d\varepsilon = \frac{\varepsilon_m-\varepsilon_{II}}{u} . \tag{16}$$

The ROGINSKY's method of approximation may be extended to θ_ε^2 even the more exactly, as it varies more accurately than θ_ε does, *i.e.* to the integration of (5) with reference to (9), as

$$i = \int_{\varepsilon_l}^{\varepsilon_m} f_\varepsilon k_\varepsilon \theta_\varepsilon^2 d\varepsilon \doteq \int_{\varepsilon_{II}}^{\varepsilon_m} f_\varepsilon k_\varepsilon d\varepsilon .$$

Substituting k_ε from (9) and f_ε from (10) into the above equation, we have

$$i = \frac{k_0' RT}{2\beta u}\exp\left(-\frac{2\beta\varepsilon_{II}}{RT}\right)\cdot\left[1-\exp\left\{-\frac{2\beta(\varepsilon_m-\varepsilon_{II})}{RT}\right\}\right],$$

hence according to (14) and (7)

$$i \doteq k' P^\beta \exp\left(-\frac{2\beta F\eta}{RT}\right), \tag{17}$$

5) ROGINSKY, *Adsorption and Catalysis on Nonuniform Surfaces*, Academy of Science, USSR (1948); TAPLIN *et al.*, *Advance in Catalysis*, **5**, 217 (1953).

6) KEII, *Shokubai* (Catalyst), No. 13, 29 (1956).

ignoring $\exp\{-2\beta(\varepsilon_m-\varepsilon_{II})/RT\}$ compared with unity on the ground that $\varepsilon_m \gg \varepsilon_{II}$, where

$$k' = \frac{k_0' RT q_0^{2\beta}}{2\beta u (k_B T Q_0)^{\beta}} \tag{18}$$

is constant at constant temperature. Eq. (17) agrees with the TAFEL equation provided that $2\beta = \alpha$, which will further be discussed in the next section.

The above procedure is now alternatively followed with the distribution function (11), discussed by HALSEY and TAYLOR[7] with regard to the analysis of the adsorption data of W-H_2 system observed by FRANKENBURG[8]. We have, carrying out the integration according to the of method ROGINSKY

$$\begin{aligned}\theta &\doteq \frac{C}{\gamma}\left[1-\exp\left\{-\gamma(\varepsilon_m-\varepsilon_{II})\right\}\right]\exp(-\gamma\varepsilon_{II}) \\ &\doteq \frac{C}{\gamma}\left(\sqrt{\frac{P}{k_B T Q_0}}q_0\right)^{\gamma RT}\exp(-\gamma F\eta)\end{aligned} \tag{19}$$

and

$$\begin{aligned}i &= k_0' C\int_{\varepsilon_{II}}^{\varepsilon_m}\exp\left(-\gamma+\frac{2\beta}{RT}\right)\varepsilon\cdot d\varepsilon \\ &\doteq \frac{k_0' CRT}{\gamma RT+2\beta}\left(\sqrt{\frac{P}{k_B T Q_0}}q_0\right)^{(\gamma RT+2\beta)}\exp\left\{-\frac{(\gamma RT+2\beta)F\eta}{RT}\right\},\end{aligned} \tag{20}$$

ignoring such terms as $\exp\{-\gamma(\varepsilon_m-\varepsilon_{II})\}$ as before. The TAFEL constant a is now given as

$$a = \gamma RT+2\beta \tag{21}$$

from the comparison of (20) with (1), is however incompatible with the observed independence of TAFEL's constant on temperature. This objection is evadable by putting $f_\varepsilon = C\exp(-\gamma'\varepsilon/RT)$ intead, which leads however to the temperature independent exponent $(\gamma'+2\beta)/2$ to P in the expression of θ, *i.e.* such constant of Freundlich isotherm in derivation from the observed one such as $\gamma'' RT$, where γ'' is another constant. The exponential distribution (11) is thus inconsistent with the observations.

The Congruence between HORIUTI's Treatment and the Present One.

The conclusion in the foregoing section will be discussed here in connection with the statistical mechanical treatment by HORIUTI *et. al.*[2]

7) HALSEY and TAYLOR, J. Chem. Phys. **15**, 625 (1947).
8) FRANKENBURG, J. Am. Chem. Soc. **66**, 1827 (1944).

Their treatment premises a uniform surface or physically identical sites but the repulsive potentials of adsorbed hydrogen atoms and of the critical complex, due to surrounding hydrogen atoms, taken respectively proportional to θ, leading to the equation

$$i = K(1-\theta)^2 \exp\left\{-\frac{\varepsilon_0^* + u^*\theta - \mu + 2F\eta}{RT}\right\}, \tag{22}$$

where

$$K = \frac{2F}{N_A}\frac{k_B T}{h} G^* q_0^*,$$

G^* is the number of the reaction sites, q_0^* the partition function of the critical complex, ε_0^* the energy of the complex at $\theta=0$ and u^* the proportionality constant of the repulsive potential $u^*\theta$ of the complex. The coverage θ is given on the other hand as

$$\frac{\theta}{1-\theta} = q_0 \exp\left(\frac{\varepsilon_0 - u\theta + \frac{1}{2}\mu - F\eta}{RT}\right) \tag{23}$$

where u is the proportionality constant of the repulsive potential $u\theta$ of an adsorbed hydrogen atom and ε_0 is the value of ε at $\theta=0$. Substituting $(1-\theta)$ from (23) into (22), we have

$$i = K'\theta^2 \exp\left\{-\frac{\varepsilon_0^* + 2\varepsilon_0 - (2u-u^*)\theta}{RT}\right\}, \tag{24}$$

where $K'=K/q_0^2$. As seen from (23) its left-hand side is approximately constant irrespective of η, provided that u is sufficiently large and θ is close neither to 0 nor 1, *i.e.* as

$$\frac{\theta}{1-\theta} \fallingdotseq \text{const.} = q_0 \exp\left(\frac{\varepsilon_0 + \frac{1}{2}\mu - u\theta - F\mu}{RT}\right) \tag{25}$$

or, as $u=$constant for one and the same hydrogen electrode,

$$\theta = \text{const.} - \left(\frac{F\eta}{u}\right), \tag{26}$$

which corresponds to (15). Substituting θ from (26) into the exponential function of (24) and taking θ^2 in the non-exponential factor constant along with the approximate constancy of the left-hand side of (23), we have

$$i = K'' \exp\left\{-\left(\frac{2u-u^*}{u}\right)\frac{F\eta}{RT}\right\}. \tag{27}$$

Horiuti *et al.* have deduced $u^*/u=1.5$ from the structure of the crystal plane,

of which the uniform surface, of crystal consists[9]. The latter result reproduces the TAFEL's equation in accordance with the above equation fitting the cofficient of $-F/RT\eta$ just to $\alpha=1/2$ on the one hand and fixes the ratio β of the decrease $(2u-u^*)\theta$ of the activation energy to the increase $2u\theta$ of the energy of the initial state as $\beta=(2u-u^*)/2u=0.25$ on the other hand.

It is pointed from the above that the explanation of TAFEL equation in terms of non-uniform surface suggested first by TAFEL himself, is formally congruent with that given by HORIUTI *et al.* on the basis of the uniform surface, classes of sites of different ε in the former being identically created by increase of repulsive potential with increasing coverage in the latter.

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9) HORIUTI, J. Research Inst. Catalysis, 4, 55 (1956).