



Title	ELECTROLYTIC HYDROGEN EVOLUTION ON NON-UNIFORM SURFACE : An Explanation to Tafel Equation
Author(s)	KEII, Tominaga
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 7(2), 99-105
Issue Date	1959-11
Doc URL	<a href="http://hdl.handle.net/2115/24700">http://hdl.handle.net/2115/24700</a>
Type	bulletin (article)
File Information	7(2)_P99-105.pdf



[Instructions for use](#)

# ELECTROLYTIC HYDROGEN EVOLUTION ON NON-UNIFORM SURFACE

## An Explanation to Tafel Equation

By

Tominaga KEI<sup>\*</sup>

(Received October 26, 1959)

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.*,

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

where  $\eta$  is the overpotential,  $i_0$  and  $\alpha$  are constants independent of overpotential. The  $\alpha$  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<sup>1</sup>) 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

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

where  $\theta$  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

<sup>\*</sup>) Tokyo Institute of Technology, Meguro, Tokyo.

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  $\alpha=2$  instead of  $\alpha=1/2$ .

This reasoning of TAFEL is based on the supposition of a uniform surface of electrode, which accommodates every atom equally. The explanation of the TAFEL equation along this line has been accomplished by HORIUTI *et al.*<sup>2)</sup> 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  $\epsilon$  and  $\epsilon+d\epsilon$  is given by  $f_\epsilon d\epsilon$ , where  $f_\epsilon$  is a function of  $\epsilon$ . Denoting the coverage of the latter surface sites by  $\theta_\epsilon$ , the population of hydrogen atoms or the overall coverage  $\theta$  by adsorbed hydrogen atoms is expressed as

$$\theta = \int_{\epsilon_l}^{\epsilon_m} f_\epsilon \theta_\epsilon d\epsilon . \quad (3)$$

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

$$k_\epsilon = k_0 \exp(-\epsilon^*/RT), \quad (4)$$

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

$$i = \int_{\epsilon_l}^{\epsilon_m} f_\epsilon k_\epsilon \theta_\epsilon^2 d\epsilon . \quad (5)$$

The  $\theta_\epsilon$ ,  $k_\epsilon$  and  $f_\epsilon$  must now be given as functions of  $\epsilon$  and hence of  $\eta$  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).

### Electrolytic Hydrogen Evolution on Nonuniform Surface

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

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

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

$$\mu = RT \log(P/k_B T Q_0), \quad (7)$$

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

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

$$\epsilon^* = \epsilon_i^* + 2\beta(\epsilon - \epsilon_i), \quad (8)$$

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

$$k_\epsilon = k'_0 \exp(-2\beta\epsilon/RT), \quad (9)$$

where

$$k'_0 = k_0 \exp\left\{-(\epsilon_i^* - 2\beta\epsilon_i)/RT\right\}.$$

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

$$f_\epsilon = 1/u \quad (10)$$

and the other is that of an exponential distribution as

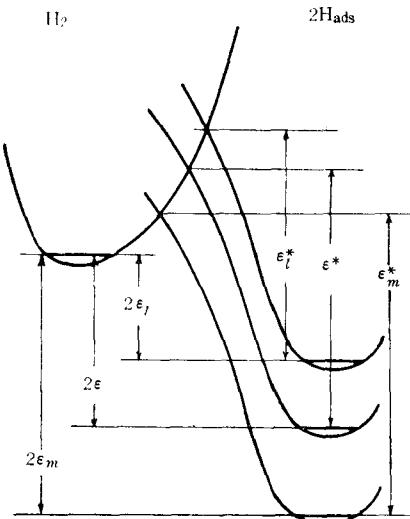


Fig. 1. Potential energy curves involved in the recombination of two adsorbed hydrogen atoms.

3) HORIUTI and POLANYI, *Acta Physicochim. URSS* **2**, 505 (1935).

4) BOCKRIS, *Electrochemistry*, Butterworths Sci. Pub. (1954).

$$f_\epsilon = C \exp(-\gamma \epsilon), \quad (11)$$

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

$$\int_{\epsilon_i}^{\epsilon_m} f_\epsilon d\epsilon = 1. \quad (12)$$

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

$$\theta = \frac{RT}{u} \log \left\{ \frac{1 + \exp(\epsilon_m - \epsilon_{II})/RT}{1 + \exp(\epsilon_i - \epsilon_{II})/RT} \right\}, \quad (13)$$

where

$$-\epsilon_{II} = \frac{1}{2} \mu + RT \log q_0 - F\eta. \quad (14)$$

Eq. (13) is written approximately in the case when  $\epsilon_i \ll \epsilon_{II} \ll \epsilon_m$ , as

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

where  $u = (\epsilon_m - \epsilon_i)$  according to (12).

The approximation implied in (15) is however equivalent to that of the ROGINSKY's method<sup>5),6)</sup>, *i.e.* that of putting  $\theta_\epsilon$  unity or zero according as  $\epsilon$  is above or below  $\epsilon_{II}$ , which leads to the equation identical with (15), *i.e.*

$$\theta \doteq \int_{\epsilon_{II}}^{\epsilon_m} f_\epsilon d\epsilon = \frac{\epsilon_m - \epsilon_{II}}{u}. \quad (16)$$

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

$$i = \int_{\epsilon_i}^{\epsilon_m} f_\epsilon k_\epsilon \theta_\epsilon^2 d\epsilon \doteq \int_{\epsilon_{II}}^{\epsilon_m} f_\epsilon k_\epsilon d\epsilon.$$

Substituting  $k_\epsilon$  from (9) and  $f_\epsilon$  from (10) into the above equation, we have

$$i = \frac{k'_0 RT}{2\beta u} \exp\left(-\frac{2\beta\epsilon_{II}}{RT}\right) \cdot \left[ 1 - \exp\left\{-\frac{2\beta(\epsilon_m - \epsilon_{II})}{RT}\right\} \right],$$

hence according to (14) and (7)

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

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).

*Electrolytic Hydrogen Evolution on Nonuniform Surface*

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

$$k' = \frac{k'_0 RT q_0^{2\beta}}{2\beta u (k_B T Q_0)^\beta} \quad (18)$$

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<sup>7)</sup> with regard to the analysis of the adsorption data of W-H<sub>2</sub> system observed by FRANKENBURG<sup>8)</sup>. We have, carrying out the integration according to the method ROGINSKY

$$\begin{aligned} \theta &\doteq \frac{C}{r} [1 - \exp\{-r(\epsilon_m - \epsilon_{II})\}] \exp(-r\epsilon_{II}) \\ &\doteq \frac{C}{r} \left( \sqrt{\frac{P}{k_B T Q_0}} q_0 \right)^{r RT} \exp(-rF\eta) \end{aligned} \quad (19)$$

and

$$\begin{aligned} i &= k'_0 C \int_{\epsilon_{II}}^{\epsilon_m} \exp\left(-r + \frac{2\beta}{RT}\right) \epsilon \cdot d\epsilon \\ &\doteq \frac{k'_0 CRT}{r RT + 2\beta} \left( \sqrt{\frac{P}{k_B T Q_0}} q_0 \right)^{(r RT + 2\beta)} \exp\left\{-\frac{(r RT + 2\beta) F\eta}{RT}\right\}, \end{aligned} \quad (20)$$

ignoring such terms as  $\exp\{-r(\epsilon_m - \epsilon_{II})\}$  as before. The TAFEL constant  $\alpha$  is now given as

$$\alpha = r RT + 2\beta \quad (21)$$

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  $f_\epsilon = C \exp(-r'\epsilon/RT)$  instead, which leads however to the temperature independent exponent  $(r' + 2\beta)/2$  to  $P$  in the expression of  $\theta$ , *i.e.* such constant of Freundlich isotherm in derivation from the observed one such as  $r''RT$ , where  $r''$  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.*<sup>2)</sup>

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  $\theta$ , leading to the equation

$$i = K(1-\theta)^2 \exp \left\{ -\frac{\epsilon_0^* + u^*\theta - \mu + 2F\eta}{RT} \right\}, \quad (22)$$

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,  $\epsilon_0^*$  the energy of the complex at  $\theta=0$  and  $u^*$  the proportionality constant of the repulsive potential  $u^*\theta$  of the complex. The coverage  $\theta$  is given on the other hand as

$$\frac{\theta}{1-\theta} = q_0 \exp \left( \frac{\epsilon_0 - u\theta + \frac{1}{2}\mu - F\eta}{RT} \right) \quad (23)$$

where  $u$  is the proportionality constant of the repulsive potential  $u\theta$  of an adsorbed hydrogen atom and  $\epsilon_0$  is the value of  $\epsilon$  at  $\theta=0$ . Substituting  $(1-\theta)$  from (23) into (22), we have

$$i = K'\theta^2 \exp \left\{ -\frac{\epsilon_0^* + 2\epsilon_0 - (2u - u^*)\theta}{RT} \right\}, \quad (24)$$

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

$$\frac{\theta}{1-\theta} \approx \text{const.} = q_0 \exp \left( \frac{\epsilon_0 + \frac{1}{2}\mu - u\theta - F\mu}{RT} \right) \quad (25)$$

or, as  $u=\text{constant}$  for one and the same hydrogen electrode,

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

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

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

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

### *Electrolytic Hydrogen Evolution on Nonuniform Surface*

of which the uniform surface, of crystal consists<sup>9</sup>. The latter result reproduces the TAFEL's equation in accordance with the above equation fitting the coefficient of  $-F/RT\gamma$  just to  $\alpha=1/2$  on the one hand and fixes the ratio  $\beta$  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  $\epsilon$  in the former being identically created by increase of repulsive potential with increasing coverage in the latter.

#### **Acknowledgement**

The present author wishes to express his sincere thanks to Professor Juro HORIUTI for his kind interests and valuable discussions on the present work.

---

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