The Mechanism of the Hydrogen Electrode Process. I. The Catalytic Mechanism.

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The elementary reaction underlying to the hydrogen electrode process such as the evolution of hydrogen at cathode or the consumption at anode may generally be formulated in the form,

$$2H^{+}B + 2\ominus \rightleftarrows H_2 + 2B ,$$

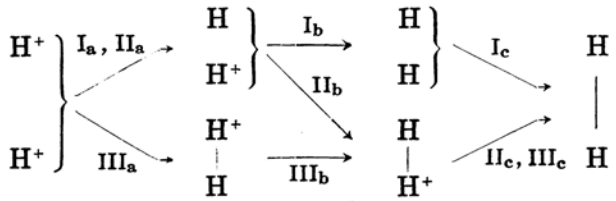
where B is the base of generalised sense due to Brönsted[1] and $\ominus$ the metal electron.

In the case when the two opposed processes are balanced we are dealing with the reversible hydrogen electrode. In the latter case hydrogen gas and the solution are catalytically interchanging their hydrogen atoms by way of the hydrogen electrode process. If further this is the only possibility of interchanging hydrogen atoms, the isotopic interchange reaction is simply a special case of the hydrogen electrode process, and we are enabled to observe the rate of electrode process in each direction at equilibrium by labelling it with a hydrogen isotope.

(1) Brönsted, *Rec. trav. chim.*, **42** (1923), 718.

The elementary process in question may take place through various possible intermediate states and any reaction step between successive intermediate states may possibly govern the rate, thus giving rise to various mechanisms.

Remembering that the elementary process of interest includes three acts i.e. neutralizations of two protons and the combination of them, all possible sequences of intermediate states can be schematically expressed as follows:



where parentheses show two protons (or a hydrogen atom and a proton) which are statistically independent of each other and dashes two such ones combined somehow with each other.

I shows the sequence of intermediate states—to be called "reaction path" hereafter—in which two protons are independently neutralised and subsequently combined with each other to form a hydrogen molecule, II that in which one of protons is neutralised, combined with the second one to form a hydrogen molecule ion, the latter being subsequently neutralised to form a hydrogen molecule and III that in which two protons are combined with each other and are neutralised one after another to form a hydrogen molecule.

Any transitions from an intermediate state to another can possibly be the rate determining step thus giving rise to different mechanisms. In usual attempts to find out the mechanism it was customary to restrict oneself to the reaction path I and to pick up the rate determining step from the two alternatives (I_a and I_b are identical) with a hope that a single mechanism thus found might rule over all hydrogen electrode processes.

Tafel[2] in old days considered that I_c was the rate determining step. This concept has found a considerable support in experiments of Bonhoeffer,[3] who has found that the series of catalytic activity of several metals for the recombination of active hydrogen ran parallel with that of cathodic overvoltage.

(2) Tafel, *Z. physik. Chem.*, **50** (1905), 641.
(3) Bonhoeffer, *Z. physik. Chem.*, **113** (1924), 199.

Le Blanc[4] maintained against the former that it was the neutralisation of proton which governed the rate. This was later supported by Volmer[5] and Frumkin,[6] who on the basis of this mechanism accounted for the well known Tafel's empirical relation between cathodic current i and overvoltage η,

$$\log i = -\frac{\alpha F \eta}{RT} + \text{constant, where } 0 < \alpha < 1 .$$

On the basis of the same mechanism but in language of wave mechanics Gurney[7] and Fowler[8] have also arrived at the explanation of the interesting empirical relation. In use of heavy hydrogen Horiuti and Polanyi[9] have later found that hydrogen gas and water were catalytically interchanging their hydrogen atoms in the presence of platinum black and that the interchange rates were appreciably affected by the hydrogen ion concentration and by addition of salts. The result of experiments seemed to direct to the fact that the rate determining reaction was associated with the change of electric charge of the elementary system since the change of concentrations of hydrogen ions and salts was known to affect the potential across the double layer at the interface where reactants were situated. This being however only compatible with I_a (or I_b) as the rate determining step, the claimed mechanism for the hydrogen electrode process seemed for some time convincing so far as one adheres to the customary manner of treating the mechanism.

Following consideration would, however, reveal that the usual concept does not suffice to understand general features of the hydrogen electrode process. Since the rate with which the elementary system passes through an intermediate state must be equal or greater than the total reaction rate, any assigned intermediate state imposes an upper limit upon the reaction rate. Topley and Eyring[10] have thus found that the energy of the state of neutral atoms on the reaction path I, if they were free ones wandering about in the solution as supposed by Fowler[8] and Gurney,[7] was too high for a reasonable magnitude of the reaction rate. It follows then that metals of large adsorption energy may give rise to the reaction path I by sheltering free atoms at the state of lower energy while such metals of very small adsorption energy as mercury practically blocks up

(4) Le Blanc, "Abhandlungen der deutschen Bunsen-Gesellschaften," No. 3, Halle (1910).
(5) Volmer, *Z. physik. Chem.*, *A*, **150** (1930), 209.
(6) Frumkin, *Z. physik. Chem.*, *A*, **164** (1933), 121.
(7) Gurney, *Proc. Roy. Soc.* (London), A, **134** (1931), 137; **136** (1932), 378.
(8) Fowler, *Trans. Faraday Soc.*, **28** (1932), 368.
(9) Horiuti and Polanyi, *Nature*, **132** (1933), 819, 931; **133** (1934), 142.
(10) Topley and Eyring, *J. Chem. Phys.*, **2** (1934), 222.

the reaction path I. The reaction in this case must have managed another path to pass through, if it has occurred at all.

On the basis of the more basic concept advanced above and of experiments with several different hydrogen electrode processes, the present authors have previously suggested that the step I_c governed the rate of hydrogen electrode process with electrodes of Ni, Cu, Fe, Ag, Au, and Pb (in alkaline solution) and II_c that of Hg, Sn, and Pb (in acidic solution).[11]

The former in which the recombination of two chemisorbed atoms was the rate determining step was called the catalytic mechanism and the latter in which the neutralization of hydrogen molecule ion governed the rate was called the electrochemical mechanism.[12]

These assignments of mechanisms have since been confirmed from various angles in this laboratory. Experimental confirmations were given to conclusions on the behavior of the hydrogen electrode process derived from respective mechanisms. Some quantitative conclusions have thus been derived on respective rates of the governing reactions by virtue of the statistical mechanical method, which could nicely account for behaviors of hydrogen electrode processes.[13][14] Tafel's empirical relation was thus quantitatively accounted for in both cases of mechanisms with special reference to the mutual interaction of hydrogen atoms and protons situated on the surface of the catalyst.

It is the object of the present paper to put forward some of our recent experimental evidences for the catalytic mechanism with special reference to nickel electrode. Experimental evidences for the electrochemical mechanism will be presented in a separate paper by Hirota in conjunction with one of the present authors.

Under the assumption that the adsorbed hydrogen atoms are practically non-polar and that the hydrogen electrode processes comprise the isotopic interchange reaction in the above sense, conclusions will be derived from the catalytic mechanism and confirmed by experiments in the following three cases.

(1) The rate determining step of the catalytic mechanism being the transition between neutral states i.e. chemisorbed hydrogen atoms

(11) Horiuti and Okamoto, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **28** (1936), 231.

(12) According to the recent study of Ikusima in this laboratory it is very probable that the electrochemical mechanism is operative on the hydrogen electrode of platinum at least in the neighbourhood of the reversible equilibrium. The result will be published in a near future.

(13) G. Okamoto, J. Horiuti, and K. Hirota, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **29** (1936), 223.

(14) Hirota and Horiuti, to be published in a near future.

and hydrogen molecule, the change of electrical potential at the interface cannot affect the reaction rate. It follows that the isotopic interchange rate between heavy hydrogen gas and aqueous solution will be insensitive to the change of hydrogen ion concentration or to the addition of salts contrary to the case of a platinum catalyst for which the rate with N/10 HCl solution was found 100 times as large as that with 1 N KOH + 1 N KCl solution according to a recent result of Ikusima.[15]

This conclusion was experimentally investigated by the following procedure. 4% shifted hydrogen gas of 104 mm. pressure was shaken with several different aqueous solution in a suitable vessel in the presence of annealed nickel wire of 0.1 mm. diameter and of 3300 m. length at 100°C.

The following table shows the results of experiments carried out with one and the same catalyst changing the solution from time to time, the interchange reaction rate being expressed by the first order rate, $k=\frac{1}{t}\log\frac{x_0}{x_t}$, where x_0 and x_t are atomic fractions of deuterium in hydrogen gas respectively before and after the reaction and t time of

Catalysed interchange reaction with different solutions at 100°C.

No. of exp.	Solution	Initial D-percent. $100\,x_0$	Final D-percent. $100\,x_t$	Time of shaking t (hr.)	Reaction rate $k\left(=\frac{1}{t}\log_{10}\frac{x_0}{x_t}\right)$
1	Neutral water	4.42	2.15	6.08	0.051
2	,,	,,	2.27	6.30	0.046
3	,,	,,	1.89	7.23	0.051
4	$\frac{N}{1000}$ KOH	,,	1.78	6.17	0.064
5	,,	,,	1.85	6.00	0.063
6	,,	,,	1.85	6.00	0.063
7	$\frac{N}{1000}$ KOH+$\frac{N}{10}$ KCl	,,	2.17	7.70	0.040
8	,,	,,	2.46	6.00	0.043
9	,,	,,	2.43	6.17	0.042
10	$\frac{N}{1000}$ KOH	,,	1.67	5.97	0.070
11	,,	,,	1.93	6.00	0.060
12	,,	,,	1.69	6.38	0.065
13	Neutral water	,,	2.29	6.00	0.048
14	,,	,,	2.01	8.00	0.043

(15) To be published in a near future.

shaking. One sees that experiments Nos. 1, 2, 3, 13, and 14 give good check with the activity of the catalyst. No appreciable variation of reaction rate being observed here contrary to the case of platinum, the conclusion from the mechanism was amply justified by experiments.

(2) From the catalytic mechanism it is expected that the electrode current behaves peculiarly when the electrode potential is suddenly raised or lowered. An experiment which confirmed the above expectation was described in our previous communication[11] and employed as one of the basis of concluding the catalytic mechanism. Here will be presented in a more improved form the experiment and the argument which connect the behavior of electrode current with the mechanism.

Let an anodically polarised hydrogen electrode be at a steady state or an anode at a constant polarization be steadily consuming hydrogen gas to form Brönsted's base[1] giving rise to a constant anodic current. Assuming the catalytic mechanism the state of affairs can be expressed by the following scheme:

$$\frac{1}{2}H_2 \underset{\langle i \rangle}{\overset{(\vec{I})}{\rightleftarrows}} K-H \underset{\langle i \rangle}{\overset{(\vec{\mathfrak{I}})}{\rightleftarrows}} H^+-B + \ominus \qquad (1),$$

where $^1/_2H_2$ denotes gaseous state, K − H chemisorbed state and $H^+ - B$ ionised state. Length of arrows schematically corresponds the relative frequencies of elementary reactions, latters being expressed in terms of electric currents by $\vec{I}$, $\overleftarrow{I}$, $\vec{\mathfrak{I}}$, and $\overleftarrow{\mathfrak{I}}$. Longer arrows above thus correspond to the positive resultant current i and shorter ones on the left to the governing step of the catalytic atomisation. The same thing, when expressed by above quantities, is

$$i = \vec{I}(\theta) - \overleftarrow{I}(\theta) = \vec{\mathfrak{I}}(\theta, \eta) - \overleftarrow{\mathfrak{I}}(\theta, \eta) \qquad (2a),$$

and

$$\vec{I} \ll \vec{\mathfrak{I}} \qquad (2b).$$

$\vec{I}$ and $\overleftarrow{I}$ are independent of the electrode potential because of neutral reactants and resultants but depend in general upon the degree of saturation θ of the catalyst's surface with chemisorbed atoms, while $\vec{\mathfrak{I}}$ and $\overleftarrow{\mathfrak{I}}$ depending in general on the both.

From the above equations we have

$$\frac{\overleftarrow{\mathfrak{I}}}{\vec{\mathfrak{I}}} = 1 - \frac{i}{\vec{\mathfrak{I}}}.$$

But since $i < \vec{I}$, according to (2b),

$$i \ll \vec{\mathfrak{I}} \,.$$

Hence we have

$$\vec{\mathfrak{I}}(\theta_1, \eta_1) \fallingdotseq \overleftarrow{\mathfrak{I}}(\theta_1, \eta_1) \,,$$

which expresses the partial equilibrium between adsorbed state and the ionised state.

If one changes η_1 suddenly to another value η_2 a new steady state is to be attained, being characterised by

$$\vec{\mathfrak{I}}(\theta_2, \eta_2) \fallingdotseq \overleftarrow{\mathfrak{I}}(\theta_2, \eta_2) \,.$$

θ_1 must now be readjusted to a new value θ_2 by removing or adding some hydrogen atoms to the chemisorbed state in order to attain the new steady state.

Since however,

$$\vec{I} > \overleftarrow{I} \,,$$

we have by Eq.(2b)

$$\overleftarrow{I} \ll \vec{\mathfrak{I}} \,,$$

and by Eq.(2a)

$$\vec{I} \ll \overleftarrow{\mathfrak{I}} \,,$$

which show that the excess or the defect of θ is readjusted almost exclusively through ionization or neutralization respectively. Since latter acts are associated with the transposition of electricity, the sudden change of the electrode current thus inserts and additional current to the steady value.

Fig. 1a shows the expected behavior of the anodic current when the electrode potential is suddenly raised. By a similar reasoning it is inferred for the case when the ionization governs the rate that the sudden change of the electrode potential will result merely in an abrupt change of steady current as shown in Fig. 1b without the initial peak as in the case of 1a.

For the experimental confirmation of the above conclusions a hydrogen electrode was constructed with a thin nickel wire A of 0.1 mm. diameter and of 67 m. length (200 cm.^{2} of apparent area) which was sealed in a glass vessel of 170 c.c. capacity as shown in Fig. 2 together with 110 c.c. of N/10 KOH solution and hydrogen gas of 580 mm. Hg pressure.

The vessel was shaken lengthwise to assure a dissolution equilibrium and the hydrogen electrode of nickel was polarised against a platinised

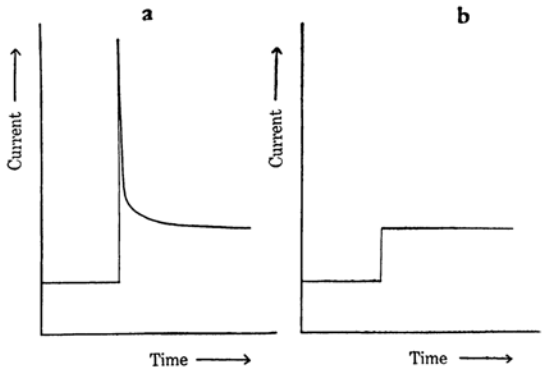


Fig. 1

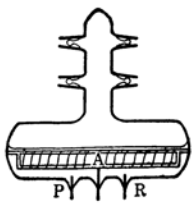


Fig. 2

platinum wire P sealed in the vessel. Anodic and cathodic polarization were determined against a reference electrode R.

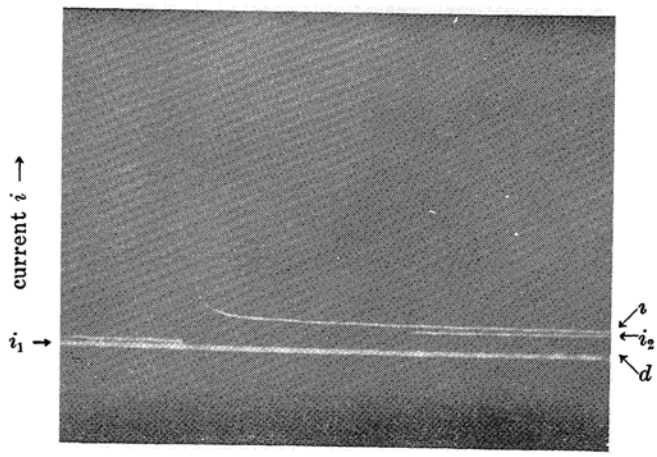
Over the whole range of electrode current (<0.2 microamp. cm.$^{-2}$) observed in the present experiment, the cathodic overvoltage was found to be negligible compared to the anodic one. This affords a sound basis to attribute observed aspects of current to the reaction at the anode. Moreover the diffusion of hydrogen gas toward the anode cannot be the governing process, for if it were the case, the thickness of the layer of solution adhered on the surface of the catalyst computed from the observed current, solubility of hydrogen gas and from the diffusion constant (10^{-5} cm.^{2}/sec.) amounts to the order of magnitude of 10 m., which is apparently impossible in our case. The genuine reaction rate at the anode in question could thus be observed by following the electrolytic current of the cell.

Actually the hydrogen electrode was kept at a fixed anodic polarization until a steady state was reached. The polarization was now suddenly raised by a small amount, the instantaneous current being followed by means of an oscillograph. Details of the experimental procedures and results are described in papers from this laboratory.[16]

The oscillograph record shows one of typical results of our observation. One sees that the theoretical conclusion is fully confirmed by the experiment.

(3) In the catalytic mechanism the rate of the electrode process at the steady state is governed by that of catalytic dissociation of hydrogen

(16) Okamoto, *J. Faculty Sci., Hokkaido Imp. Univ.*, Ser. III, Vol. II, No. 3 (1938), 116; Okamoto and Iijima, *Bull. Inst. Phys. Chem. Research* (Tokyo), **16** (1937), 1426 (printed in Japanese).



Temperature: 26°C.
Pressure: 580 mm. Hg.
η_1: 0.0114 volt.
η_2: 0.0226 volt.
i : instantaneous current.
i_1: initial steady current at η_1.
i_2: new steady current at η_2.
d: zero line.

Fig. 3. Oscillograph record.

molecules or of its reversed process. By formulating the latter at a given condition one could obtain an expression for the electrode current. Along this line Hirota in conjunction with present authors[13] arrived at the following expressions for the reaction rates in respective directions:

Catalytic atomization, $$\vec{v} = KGe^{-\frac{\varepsilon^*_{H_2}}{RT}}\frac{n}{Q_{H_2}} \qquad (3a),$$

Catalytic recombination, $$\overleftarrow{v} = KGe^{-\frac{\varepsilon^*_{H_2}}{RT}}\frac{1}{P^2} \qquad (3b),$$

where G is the number of adjacent pairs of metal atoms per unit area at which the catalytic atomization or the recombination takes place, $\varepsilon^*_{H_2}$ minimum potential energy of HH at the activated state, n the number of hydrogen molecules per unit volume and

$$Q_{H_2} = \frac{(2\pi mkT)^{\frac{3}{2}}\,2\pi^2 IkT}{h^5 \sinh\frac{h\nu_{H_2}}{2kT}} \cdot e^{-\frac{\varepsilon_{H_2}}{RT}} \quad \text{(State sum of a hydrogen molecule)},$$

$$K = \frac{kT}{h}(1-\theta)^2 e^{-\frac{u^*\theta}{RT}} \sum_{j}^{1-5} \frac{1}{2}\left(\sinh\frac{h\nu^*_{H_2,\,j}}{2kT}\right)^{-1}, \quad \frac{1-\theta}{\theta} = \frac{\sqrt{Q_{H_2}}}{n} \cdot e^{\frac{F(\eta-\eta_0)}{RT}},$$

$$q = e^{-\frac{\varepsilon_H + u\theta}{RT}} \sum_{j}^{1-3} \frac{1}{2}\left(\sinh \frac{h\nu_{H,j}}{2kT}\right)^{-1}, \qquad \text{and} \qquad P = \sqrt{\frac{Q_{H_2}}{n}} \cdot e^{\frac{F(\eta-\eta_0)}{RT}}.$$

Other notations have following meanings: θ: degree of saturation of chemisorbed atoms. $\varepsilon_{H_2} = -109.12$ kcal.[17]: potential energy of hydrogen molecule at the equilibrium position. $\varepsilon_H = -60$ kcal.[18]: heat of adsorption of a hydrogen atom. η: electrode potential. η_0: potential of reversible hydrogen electrode. $\nu^*_{H_2,j} = 936, 687, 1704, 368, 626$ (cm.$^{-1}$)[13]: normal vibrational frequencies of HH at the activated state. $\nu_{H,j} = 417, 479, 1900$ (cm.$^{-1}$)[13]: normal vibrational frequencies of H at the adsorbed state. $\nu_{H_2} = 4417.2$ (cm.$^{-1}$)[17]: harmonic frequency of a hydrogen molecule. $I = 4.65 \times 10^{-41}$ (g. cm.^{2})[17]: moment of inertia of hydrogen molecule. $u = 5.65$ kcal.[11]: repulsive potential of an adsorbed hydrogen atom due to surrounding ones at $\theta = 1$. $u^* = 6.70$ kcal.[13]: repulsive potential of HH at the activated state due to the surrounding chemisorbed atoms at $\theta = 1$.

Steady anodic current i is now expressed by

$$i = 2\epsilon KG e^{-\frac{\varepsilon^*_{H_2}}{RT}}\left(\frac{n}{Q_{H_2}} - \frac{1}{P^2}\right) \qquad (4),$$

where ϵ is the elementary charge, two charges being conveyed by one act at catalytic atomisation or recombination.

Eqs. (3a) and (3b) could be checked respectively by observations of individual rates of atomisation and the recombination labelled by deuterium while (4) by direct observations of anodic currents. But since estimations of $\varepsilon^*_{H_2}$ and G are associated with a considerable inaccuracy, the experimental confirmation was made other way round in the present work i.e. G was inversely calculated from experimental data of the anodic current as well as from those of the isotopic interchange reaction and two values thus obtained were compared with each other and with Z, the number of available metal atoms per unit area for the chemisorption of hydrogen atoms. G from two sources should coincide with each other and be of the same order of magnitude with Z whichever lattice plane of the electrode were active, so far as the catalytic mechanism were actually operative.

(17) Jeppesen, *Phys. Rev.*, **44** (1933), 195.
(18) Horiuti and Polanyi, *Acta Physicochim. U.R.S.S.*, **2** (1935), 505.

Evaluating K, n/Q_{H_2} and P by data given above G could be determined from observations of the absolute value and of its temperature coefficient of the anodic current or of the interchange reaction rate. Details of the experiments are given in a separate paper from this laboratory.[16]

The results were

$$G = 4 \times 10^{12} \quad \text{from the anodic current,}$$

$$G = 2 \times 10^{12} \quad \text{from the interchange reaction.}$$

Z was, on the other hand, obtained from the following quantitative analysis of the result of experiments (2).

The instantaneous current i or the excess of the rate of ionization of chemisorbed hydrogen atoms over that of neutralization will be assumed to vary linearly with θ,

or

$$i = \epsilon Zk\theta + \text{const.},$$

where ϵ is the elementary charge and k a proportionality constant. Denoting with i_2 and θ_2 corresponding quantities at the steady state reached some time after the raise of the anodic polarization, the above equation is

$$i - i_2 = \epsilon Zk(\theta - \theta_2) \qquad (5).$$

On the other hand the time rate, $-Z\frac{d\theta}{dt}$, of the decrease of chemisorbed atoms can similarly be expressed by

$$-Z\frac{d\theta}{dt} = Zk(\theta - \theta_2) - \{v(\theta) - v(\theta_2)\} \qquad (6),$$

where $v(\theta)$ is the supply of chemisorbed atoms due to the excess of the rate of the catalytic atomization of hydrogen molecules over that of recombination. Neglecting the second member on the right,[19] Eq.(6) is integrated in the form,

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(19) $\varepsilon v(\theta_1)$ and $\varepsilon v(\theta_2)$ are steady currents respectively before and after the polarization was raised. According to Eq.(4) however the rate of the catalytic atomization varies monotonously from $v(\theta_1)$ to $v(\theta_2)$ along with the decrease of θ or $v(\theta_1) < v(\theta) < v(\theta_2)$. It follows then that $v(\theta_2) - v(\theta)$, which is smaller than $v(\theta_2) - v(\theta_1)$, can be neglected in comparison with $zk(\theta - \theta_2)$, since as seen from the oscillograph record, the total variation of the steady current $i_2 - i_1 = \varepsilon\{v(\theta_2) - v(\theta_1)\}$ is only a small fraction of $i - i_2$, or of $\varepsilon zk(\theta - \theta_2)$ by Eq.(5), at earlier stage immediately after the sudden raise of the anodic potential.

$$\log \frac{\theta - \theta_2}{\theta_1 - \theta_2} = -kt ,$$

time of switching being the origin of t.

By Eq.(5) we have

$$\log \frac{i - i_2}{i_0 - i_2} = -kt \qquad (7),$$

where

$$i_0 - i_2 = \epsilon Z k(\theta_1 - \theta_2) \qquad (8),$$

i_0 being the big initial current at $t = 0$.

Observed current was now analysed[20] according to Eq.(7) evaluating i_0 and k. From Eq.(8) we have immediately

$$Z = 2 \times 10^{12} ,$$

which is concordant with the forgoing two values of G affording another experimental support to the catalytic mechanism.

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(20) According to a more detailed analysis, $i - i_2$ at the later stage is due to the outward diffusion of occluded hydrogen atoms in the metal. Cf. Reference (16).