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Author(s)	KITA, Hideaki; NOMURA, Okio
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HEAT OF ACTIVATION AND PRE-EXPONENTIAL FACTOR OF THE HYDROGEN EVOLUTION REACTION ON NICKEL IN ALKALINE SOLUTION

By

Hideaki KITA and Okio NOMURA

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Abstract

The present paper is concerned with theoretical and experimental determinations of the heat of activation, ΔH^* , of the hydrogen evolution reaction on nickel and hence the experimental verification of the theoretical value of the pre-exponential factor, B , previously calculated at $\log_{10} B = 6.8 \sim 6.9^{21)}$ on the basis of the catalytic mechanism, taking into account repulsive interactions among hydrogen adatoms and between the hydrogen adatoms and the critical complex by the proportional approximation.

Calculation of ΔH^* on the same basis shows that ΔH^* is almost constant and 18.5 Kcal mol⁻¹ in the range of overvoltage from 120 to 600 mV, where TAFEL law holds.

Experiments were carried out on spherical nickel electrode (0.01 cm²) in 4.96 ± 0.09 N NaOH solution at various temperatures ranging from 4 to 45°C by the galvanostatic method with current densities from 10⁻³ to 10² A cm.⁻² The values of ΔH^* and $\log_{10} B$ thus obtained experimentally, are 15.7 ± 2.9 Kcal mol⁻¹ and 6.7 ± 2.2 in good agreement with the theoretical ones.

These coincidences support our previous conclusion²⁴⁾ that the hydrogen evolution reaction proceeds through the catalytic mechanism on nickel in alkaline solution.

Introduction

HORIUTI *et al.*¹⁾ studied hydrogen evolution reaction,



on various metals, where H^+ is the proton attached to the BRÖNSTED base, H_2O or OH^- and e^- is a metal electron respectively. They have concluded²⁾³⁾ that the reaction (1) on nickel proceeds through the catalytic mechanism, where a discharge step of H^+ yielding hydrogen adatom H(a) ;



is followed by the rate-determining recombination of H(a)'s ;



the notation $\xrightarrow{\Delta}$ referring to the rate-determining step. Recently, one of the present authors and YAMAZAKI⁽⁴⁾ studied the reaction on nickel in 0.95 or 4.73 N NaOH solution at 22°C and observed the saturation current at *ca.* 10^2 A cm^{-2} , which is in agreement with the theoretical estimation by HORIUTI⁽³⁾ on the basis of the catalytic mechanism, taking into account repulsive interactions among hydrogen adatoms as well as between the adatoms and the critical complex. ENYO, HOSHI and one of the present authors⁽⁵⁾ also examined the exchange reaction between pure deuterium and aqueous alkaline solutions on nickel at various pH's, deuterium pressures and temperatures ranging from 0 to 50°C. They found negligible pH-effect upon the rate as well as the heat of activation of the exchange reaction. These experimental results, *i.e.* the existence of saturation current and the absence of pH-effect can be interpreted only by the catalytic mechanism as discussed earlier.⁽⁴⁾⁽⁵⁾ MATSUDA and OHMORI⁽⁶⁾ supported this view by the experimental results that the hydrogen overvoltage remains practically constant independent of pH and that the analysis of the galvanostatic transients leads to large value of the differential capacity of electrode depending on the overvoltage.

The reaction (1) on nickel has been studied by a number of other workers,⁷⁻¹⁹⁾ as reviewed briefly below.

LUKOVZEV, LEVINA and FRUMKIN⁽⁸⁾ observed pH- and neutral salt-effects on the overvoltage and attributed the overvoltage to the discharge step (2). Later FRUMKIN⁽⁹⁾ suggested that the step (2) is rate-determining on the greater part of the surface, while the recombination step (3) is rate-determining on a small part of the surface. BOCKRIS and POTTER⁽¹⁰⁾ and BOCKRIS and AZZAM⁽¹¹⁾ concluded that the most probable mechanism is that of the rate-determining discharge step followed by the recombination step, from their results on the stoichiometric number of rate-determining step found two⁽¹⁰⁾ and from their observation on the TAFEL plot extended to higher current densities.⁽¹¹⁾ DEVANATHAN and SELVARATNAM⁽¹³⁾ determined the hydrogen coverage experimentally as a function of cathodic current density and recently BOCKRIS and SRINIVASAN⁽¹⁹⁾ observed H-T separation factor in 0.5 N NaOH solution, arriving at the same conclusion. PIONTELLI, BICELLI and VECCHIA⁽¹²⁾ observed the hydrogen evolution reaction on different crystal planes of nickel single crystal. CONWAY⁽¹⁴⁾ observed the reaction both in 0.1 N HCl and 0.1 N DCl solution. CONWAY, BEATTY and DE MAINE⁽¹⁵⁾ examined the kinetics of the hydrogen

evolution reaction on a series of copper-nickel alloys of different compositions and tried to determine the trends of the kinetic parameters such as exchange current density, TAFEL constant and the heat of activation with the electronic configuration of the alloys. They stated that this trend is consistent with that expected from the so-called atom-ion desorption mechanism, where the step (2) is followed by the following rate-determining step;



HUO and ROSENBERG¹⁶⁾ also studied the reaction on several compounds of nickel with elements from groups IVB, VB and VIB of the Periodic Table to investigate the influence of crystal environment on electrochemical properties of a transition metal atom on the surface. MAKRIDES¹⁷⁾ placed emphasis on surface states of nickel electrodes, which were prepared by different pretreatments, concluding that the discharge step (2) is rate-determining only on fresh surface ("initial" state) which has a high affinity for hydrogen adatom. Anodic-cathodic cycling produced a steady state of surface for which the exchange rates of the discharge and the recombination steps were approximately equal. WEININGER and BREITER¹⁸⁾ suggested that the hydrogen evolution from 4 N NaOH solution, is controlled by the discharge step of water molecules between 100 and 300 mV of overvoltage, where the relatively small values of capacity were observed.

Most of the works reviewed above where the slow discharge mechanism is concluded as operative, do not take the repulsive interactions among hydrogen atoms on the electrode surface into account, which essentially affect the aspects of hydrogen electrode reaction.²⁰⁾ HORIUTI and one of the present authors²¹⁾ have thus theoretically deduced the value of

$$\log_{10} B \equiv \log_{10} i_0 + \Delta H^* / 2.303 RT \quad (5. a)$$

to be 6.8~6.9 for hydrogen electrode of nickel on the basis of the catalytic mechanism allowing for the repulsive interactions, where i_0 is the exchange current density and ΔH^* the heat of activation, *i.e.*

$$\Delta H^* = RT^2 \frac{\partial \ln i_0}{\partial T}, \quad (5. b)$$

the partial differentiation referring to constant pressure. The present paper is concerned with the theoretical determination of ΔH^* on the same basis and the experimental determination of ΔH^* to be compared with the theoretical one, hence the experimental verification of the theoretical value of $\log_{10} B$.

§ 1. Formulation of the Heat of Activation

The theoretical formulation of the heat of activation, ΔH^* is based on the assumptions used previously²⁾³⁾²¹⁾ that the seat, σ^* , of the critical complex consists of two adjacent physically identical sites, σ 's, of hydrogen adatoms and that the repulsive potential of hydrogen adatom or critical complex due to surrounding adatoms is proportional to the covered fraction, θ , of electrode surface with H(a). The latter assumption is called proportional approximation.

The forward rate, v_+ , of a steady reaction with rate-determining step is in general given by the theory of reaction rate developed by HORIUTI²²⁾ as

$$v_+ = \frac{kT}{h} \frac{1}{\nu} \frac{\exp(-\mu^*/RT)}{\exp(-\mu^I/RT)}, \quad (6)$$

where ν is the stoichiometric number²³⁾, μ^* or μ^I is the chemical potential of critical complex or initial system respectively of the rate-determining step and k , T , h and R are of usual meanings. Taking now the step (3) as rate-determining in accordance with the catalytic mechanism, we have

$$I = 2H(a), \quad \nu = 1.$$

Since every forward act of the steady reaction transfers two elementary charges, the current density is given from Eq. (6) as

$$i_+ = 2\varepsilon \frac{kT}{hA} \frac{\exp(-\mu^*/RT)}{\exp(-\mu^{2H(a)}/RT)}, \quad (7)$$

where A is the surface area of the electrode and ε is the elementary charge. We have on account of the premised partial equilibrium of the step (2)

$$\mu^{H(a)} = \mu^{H^+} + \mu^{e^-},$$

where μ^{H^+} or μ^{e^-} is the chemical potential of H^+ or e^- respectively. The μ^{e^-} is on the other hand given in terms of the observable quantity, *i.e.* over-voltage η as

$$F\eta = \mu^{e^-} - \mu_{eq}^{e^-},$$

where $\mu_{eq}^{e^-}$ is the chemical potential of e^- of the reversible hydrogen electrode. The $\mu_{eq}^{e^-}$ is related to the chemical potential, μ^{H_2} , of hydrogen gas as

$$\mu^{H_2} = 2\mu^{H^+} + 2\mu_{eq}^{e^-}.$$

From the above three equations we have

$$2\mu^{H(a)} = \mu^{H_2} + 2F\eta. \quad (8)$$

The current density is now expressed from Eqs. (7) and (8) as,

$$i_+ = 2\varepsilon \frac{kT}{hA} \exp(-\mu^*/RT) \exp\{(\mu^{\text{H}_2} + 2F\eta)/RT\}. \quad (9)$$

The chemical potential of the critical complex has been developed for the present case by HORIUTI¹⁾²⁾²¹⁾²²⁾ as

$$\mu^* = -RT \ln N^* \cdot \theta_{(0)}^* \cdot q^*,$$

where N^* is the total number of seat, σ^* , for the critical complex, $\theta_{(0)}^*$ the probability of σ^* being unoccupied and q^* the BOLTZMANN factor of the reversible work*) required to bring up the constituent hydrogen atoms of the critical complex from their standard state into a definite σ^* kept preliminarily unoccupied with certainty, to construct the critical complex there. The factor q^* can be expressed in accordance with the proportional approximation as

$$q^* = q_0^* \exp(-u^*\theta/RT),$$

where θ is the covered fraction of electrode surface (of sites σ 's) with hydrogen adatoms, u^* is the repulsive potential per mol of critical complex due to surrounding hydrogen adatoms at $\theta = 1$ and q_0^* is the value of q^* at $\theta = 0$ respectively. The factor q_0^* has been expressed²⁾ allowing for the five normal modes of vibration of the critical complex as

$$q_0^* = \exp\left(-\frac{E_0^*}{RT}\right) \prod_{i=1}^5 \left\{1 - \exp\left(-\frac{h\nu_i^*}{kT}\right)\right\}^{-1},$$

where E_0^* is the ground state energy per mol of the critical complex and ν_i^* the frequency of its i -th normal mode of vibration. The rate of hydrogen evolution reaction is thus finally expressed according to the above three equations and Eq. (9) as

$$i_+ = 2\varepsilon \frac{kT}{h} N_1^* \theta_{(0)}^* \cdot \exp\left(-\frac{E_0^* + u^*\theta}{RT}\right) \prod_{i=1}^5 \left\{1 - \exp\left(-\frac{h\nu_i^*}{kT}\right)\right\}^{-1} \cdot \exp\left(\frac{\mu^{\text{H}_2} + 2F\eta}{RT}\right), \quad (10)$$

where

$$N_1^* = N^*/A.$$

The theoretical expression for ΔH^* is now readily deduced according to Eq. (5. b), where i_0 is the exchange current density evaluated experimentally by extrapolating $\log_{10} i_+ \sim \eta$ plot to $\eta = 0$, hence as

$$\log_{10} i_0 = \log_{10} i_+ - \eta (\partial \log_{10} i_+ / \partial \eta)_T \quad (11)$$

*) The work done keeping the assembly in statistical mechanical equilibrium in its every stage.

from the range of η , where the TAFEL law²⁴⁾ holds. Substituting $\log_{10} i_+$ from Eq. (10) into Eq. (11) and $\log_{10} i_0$ thus expressed into Eq. (5. b), we have

$$\begin{aligned} \Delta H^* = & RT + RT^2 \left(\frac{\partial \ln \theta_{(0)}^*}{\partial T} \right)_{\eta} - u^* \left\{ T \left(\frac{\partial \theta}{\partial T} \right)_{\eta} - \theta \right\} \\ & + RT^2 \left[\frac{\partial}{\partial T} \ln \exp \left(-\frac{E_0^*}{RT} \right) \prod_{i=1}^5 \left\{ 1 - \exp \left(-\frac{h\nu_i^*}{kT} \right) \right\}^{-1} \right] - (T\bar{S}^{H_2} + \mu^{H_2}) \\ & - \eta RT^2 \frac{\partial^2 \ln \theta_{(0)}^*}{\partial \eta \partial T} + u^* \eta \left\{ T \frac{\partial^2 \theta}{\partial \eta \partial T} - \left(\frac{\partial \theta}{\partial \eta} \right)_T \right\}. \end{aligned} \quad (12)$$

Each term of the above equation and hence ΔH^* is now evaluated in the next section.

§ 2. Theoretical Value of the Heat of Activation

The probability, $\theta_{(0)}^*$, of σ^* being unoccupied has been formulated on the basis of the proportional approximation as²⁵⁾

$$\theta_{(0)}^* = (1 + 2\beta + \xi\beta^2)^{-1*}), \quad (13)$$

where

$$\beta = r \exp \left\{ -(u - u_i)\theta/RT \right\}, \quad (14. a)$$

$$r = q_0^{H(a)}/\exp(-\mu^{H(a)}/RT), \quad (14. b)$$

$$q_0^{H(a)} = \exp \left(-\frac{E_0^{H(a)}}{RT} \right) \prod_{i=1}^3 \left\{ 1 - \exp \left(-\frac{h\nu_i}{kT} \right) \right\}^{-1}, \quad (14. c)$$

and

$$\xi = \exp(-u_i/RT), \quad (14. d)$$

*) The probability $\theta_{(0)}^*$ is defined as

$$\theta_{(0)}^* = \Omega C_{\sigma^*_{(0)}} / \Omega C$$

in terms of partition functions $\Omega C_{\sigma^*_{(0)}}$ and ΩC respectively of $C_{\sigma^*_{(0)}}$ and C , where $C_{\sigma^*_{(0)}}$ is the whole assembly in question subject to the specification that a definite σ^* on the electrode surface is unoccupied with certainty and C is the same assembly subject to none of such specification. ΩC is expressed with special reference to the σ^* as

$$\Omega C = \Omega C_{\sigma^*_{(0)}} + 2\Omega C_{\sigma^*_{(H)}} + \Omega C_{\sigma^*_{(2H)}}$$

according to the properties of partition function, where $\Omega C_{\sigma^*_{(H)}}$ is the partition function of the assembly $C_{\sigma^*_{(H)}}$ with either of the constituent σ 's of σ^* occupied by one hydrogen adatom and $\Omega C_{\sigma^*_{(2H)}}$ is that of $C_{\sigma^*_{(2H)}}$ with both the σ 's occupied by hydrogen adatoms respectively. Eq. (13) is readily derived from the above two equations, where the factor β in Eq. (13) is the ratio of $\Omega C_{\sigma^*_{(H)}}$ to $\Omega C_{\sigma^*_{(0)}}$ and $\xi\beta^2$ is that of $\Omega C_{\sigma^*_{(2H)}}$ to $\Omega C_{\sigma^*_{(0)}}$.

u being the repulsive potential of an adatom due to surrounding adatoms at $\theta=1$, u_1 the repulsive potential between the two adatoms on the constituent sites of σ^* , $E_0^{H(a)}$ the ground state energy per mol of the hydrogen adatom and ν_i the frequency of i -th normal mode of vibration respectively.

Hydrogen isotherm has been derived on the same basis^{(25)*} as

$$\frac{\theta}{1-\theta} = \beta \frac{1+\xi\beta}{1+\beta} \quad (15)$$

The chemical potential, μ^{H_2} , of gaseous hydrogen molecule is statistical mechanically developed as

$$\mu^{H_2} = -RT \ln \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{4\pi^2 IkT}{h^2} / N^{H_2}$$

with good approximation, identifying its vibrational partition function with unity, where m or I is the mass or the moment of inertia respectively of hydrogen molecule and N^{H_2} the number of hydrogen molecules per cm^3 . The latter factor N^{H_2} is given in terms of hydrogen pressure P^{H_2} in mmHg as

$$N^{H_2} = 1.360 \times 980.5 \cdot P^{H_2} / kT.$$

We have from the above two equations and Eqs. (8), (14. b) and (14. c)

$$r = \frac{(1.360 \times 980.5 \cdot P^{H_2} / kT)^{1/2} \cdot \exp\{(F\eta - E_0^{H(a)}) / RT\}}{(2\pi mkT)^{3/2} \cdot 4\pi^2 IkT / h^5 \}^{1/2} \cdot \prod_{i=1}^3 \{1 - \exp(-h\nu_i / kT)\}} \quad (16)$$

Now, using Eqs. (13) to (16), each term except first and fifth ones on the right hand side of Eq. (12) is developed as follows.

Second term;

$$-RT^2 \theta_{(0)}^* \left\{ 2\beta(1+\xi\beta) \left(\frac{\partial \ln \beta}{\partial T} \right)_\eta + \xi\beta^2 \frac{u_1}{RT^2} \right\},$$

) The covered fraction, θ , of electrode surface with hydrogen adatoms is now defined with special reference to σ^ for the sake of expedient calculation as

$$\theta = \Omega C_{\sigma_1(H)} / \Omega C,$$

where $\Omega C_{\sigma_1(H)}$ is the partition function of the assembly $C_{\sigma_1(H)}$ subject to the specification that one of the two constituent sites of σ^* , i.e. σ_1 is occupied by a hydrogen adatom with certainty, hence expressed as

$$\Omega C_{\sigma_1(H)} = \Omega C_{\sigma^*_{(0)}} (\beta + \xi\beta^2).$$

We have from the above two equations and the expression for ΩC given in the footnote

*) on page 112

$$\theta = \beta(1+\xi\beta) / (1+2\beta+\xi\beta^2)$$

and hence Eq. (15).

Third term;

$$-u^* \theta \left[(1-\theta) T \left\{ \varphi \left(\frac{\partial \ln \beta}{\partial T} \right)_\eta + \frac{\xi \beta}{1+\xi \beta} \frac{u_1}{RT^2} \right\} - 1 \right],$$

where

$$\varphi \equiv \frac{1}{1+\beta} + \frac{\xi \beta}{1+\xi \beta}$$

Fourth term;

$$E_0^* + N_A \sum_{i=1}^5 h\nu_i^* / \{ \exp(h\nu_i^*/kT) - 1 \}$$

Sixth term;

$$\eta RT^2 \cdot 2\beta \{ \theta_{(0)}^* \}^2 \left[\left(\frac{\partial \ln \beta}{\partial \eta} \right)_r \left\{ (1+2\xi\beta + \xi\beta^2) \left(\frac{\partial \ln \beta}{\partial T} \right)_\eta \right. \right. \\ \left. \left. + \xi\beta(1+\beta) \frac{u_1}{RT^2} - \frac{1+\xi\beta}{T \cdot \theta_{(0)}^*} \right\} - \frac{(1+\xi\beta)(u-u_1)}{\theta_{(0)}^* \cdot RT} \frac{\partial \theta}{\partial \eta \partial T} \right]$$

Seventh term;

$$\frac{u^* \eta F}{RT} \left[\frac{T \frac{1-2\theta}{\theta^2(1-\theta)^2} \left(\frac{\partial \theta}{\partial T} \right)_\eta \cdot \varphi + \frac{1}{\theta(1-\theta)} \left\{ \phi \left(\frac{\partial \ln \beta}{\partial T} \right)_\eta T - \varphi + \frac{\xi \beta}{(1+\xi \beta)^2} \frac{u_1}{RT} \right\}}{\left\{ \frac{1}{\theta(1-\theta)} + \frac{u-u_1}{RT} \varphi \right\}^2} \right. \\ \left. - \frac{\varphi}{\left\{ \frac{1}{\theta(1-\theta)} + \frac{u-u_1}{RT} \varphi \right\}} \right],$$

where

$$\phi \equiv \frac{\xi \beta}{(1+\xi \beta)^2} - \frac{\beta}{(1+\beta)^2}.$$

Using above five equations and Eq. (12), ΔH^* is calculated using the numerical values given below at 25°C, 760 mmHg H_2 ;

$$u^*, u_1 \text{ and } u; 35, 1.38 \text{ and } 25 \text{ Kcal mol}^{-1 \text{ 3)}})$$

$$E_0^* \text{ and } E_0^{H(a)}; \frac{5}{2} RT^{3)} \text{ and } -12.3^{25)} \text{ Kcal mol}^{-1 \text{ 3)}})$$

$$\nu_i^*; 936, 687, 1704, 368, 626 \text{ cm}^{-1 \text{ 2)}})$$

$$\nu_i; 417, 479, 1900 \text{ cm}^{-1 \text{ 2)}})$$

$$N_1^*; 10^{15} \text{ cm}^{-2 \text{ 2)}})$$

$$m \text{ and } I; 2.016/6.025 \times 10^{23} \text{ gm and } 4.664 \times 10^{-41} \text{ gm cm}^2 \text{ 27)})$$

$$\bar{S}^{H_2}; 31.211 \text{ cal deg.}^{-1 \text{ 28)}})$$

Results are shown in Table I and Fig. 1.

TABLE 1. Theoretical values of ΔH^* at various overvoltages on nickel at 25°C

$\frac{\eta \text{ (mV)}}{59.1}$	θ	Values of each term of Eq. (12) in Kcal mol ⁻¹							ΔH^* Kcal mol ⁻¹
		1st	2nd	3rd	4th	5th	6th	7th	
2	0.467		1.055	21.416			-0.553	-3.382	18.97
4	0.563		1.600	24.869			-0.966	-7.174	18.76
6	0.660	0.593	2.001	28.586	1.893	-2.056	-1.037	-11.414	18.57
8	0.757		2.366	32.391			-1.711	-15.061	18.42
10	0.853		2.990	36.012			-4.691	-16.936	17.81
12	0.941		4.868	38.709			-21.553	-8.664	13.79

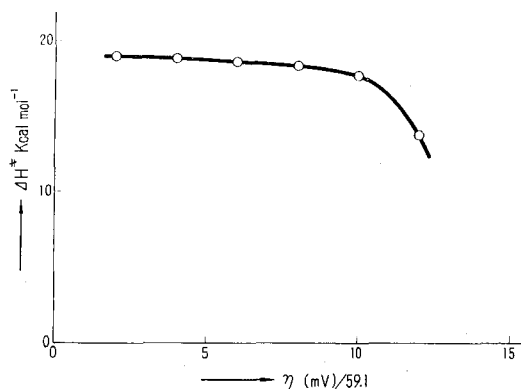


Fig. 1. Theoretical value of ΔH^* as a function of overvoltage on nickel at 25°C.

It is thus shown that the heat of activation of hydrogen evolution reaction on nickel remains almost constant at 18.5 Kcal mol⁻¹ in the range of 120~600 mV of η . At higher overvoltages than 600 mV, however, ΔH^* decreases and finally reaches the value of ca. 10 Kcal mol⁻¹ at $\theta=1$, which was previously calculated by HORIUTI.³⁾

§ 3. Experimental

The heat of activation is experimentally determined as follows.

As in the previous work⁴⁾, a series of constant currents is applied to the electrode immersed in alkaline solution and the current-potential curve is observed as a function of temperature. Experimental methods are similar to those used by BOCKRIS *et al.*²⁹⁾³⁰⁾ and by one of the present authors.⁴⁾

The apparatus

The apparatus comprises purification units for gases, device for preparing electrode, cell, air thermostat, pulse generator and recorder of potential of electrode.

Hydrogen from cylinder was purified through a train consisting of columns of silicagel, soda lime, platinum asbestos heated at about 350°C, silicagel and three liquid N₂ cooled traps, the first two of them containing tablets of active carbon. He-gas was purified similarly as hydrogen but using copper heated at about 600°C instead of the platinum asbestos. Water was distilled from alkaline KMnO₄ solution. Conductivity of the water thus obtained was about 10⁻⁶ mhos cm⁻¹ (called conductivity water in what follows).

Electrolyte solutions were prepared from special grade of NaOH, KANTO Chem. Co., Tokyo and kept in a flask attached to the apparatus in atmosphere of the purified hydrogen.

Test electrodes were nickel spheres prepared by melting thin wire of 99.99% purity drawn from JOHNSON, MATHEY & Co, (0.1 mm dia., 1.3 cm length) in the purified He, the surface of wire having been preliminarily freed from oxide by reduction in the purified hydrogen at elevated temperature. The sphere was sealed into thin walled glass bulb with the same sample of hydrogen in order to prevent a contact of the surface with air. Surface area was about 0.01 cm.² Counter electrode was a cylindrical net of platinized platinum and cathode used in pre-electrolysis was a blank platinum wire. Reference electrode and anode in pre-electrolysis were platinized platinum foils.

The cell consisted of reference, main and anode compartments which were connected with each other by sintered glass disks. The main compartment held six glass pipes sliding up and down through slip joints in the top of the cap. The counter electrode and the cathode used in pre-electrolysis were sealed into the glass pipes at their ends and four glass bulbs, each containing a test electrode inside were sealed with the rest of the glass pipes.

The air thermostat which accommodated the cell controlled the temperatures ranging from 0°C to 50°C constant within ±0.05°C. A water thermostat might not be used owing to the electrical leaks thereby involved.

The pulse generator was the same as that used before⁴⁾ and similar to that used by MEHL, DEVANATHAN and BOCKRIS.³¹⁾ Rise time of the pulses was less than 2μ sec in the range of current from *ca.* 1 mA to 1 A but apt to increase with decrease of current. It was however less than msec even at the lowest current of 10 μA used.

Galyanostatic transients, *i.e.* potential changes with time were recorded on the screen of the cathode ray oscilloscope (Synchroscope SS 5302, Preamp. SP-15H-A, IWASAKI Communication Apparatus Co., Ltd., Tokyo).

Procedure

Before every series of measurements, the cell and the glass pipes with the glass bulbs at their ends, each containing the test electrode inside were cleaned overnight with a mixture of concentrated nitric and sulphuric acids and the counter and the reference electrodes were freshly platinized. They were washed thoroughly with the conductivity water, with special care to remove traces of acids from the sintered glass disks. Mounting six glass pipes by their upper cylindrical part on the cap of the cell and filling up the conductivity water, the cell was set in the air thermostat. A few hours later, the water in the cell was pushed out and

the electrolyte solution introduced from the storage flask by pressure of the purified hydrogen. The solution first introduced was discarded after being transferred several times from one to another among three compartments in order to replace water remaining in the cell with the solution. The solution of *ca.* 100 cc was then introduced. Raising the temperature of the air thermostat above the highest temperature in a series of experiments at least by 5°C, the pre-electrolysis was started with bubbling of hydrogen for 2~3 days with current of 10~20 mA. After the pre-electrolysis, one of the glass bulbs was slid down and fractured by glass bar attached to the main compartment. The sphere thus exposed was then positioned at the tip of LUGGIN capillary which was centered inside the cylindrical counter electrode. After the temperature was controlled as desired, pulses of a constant current were applied between the counter and the spherical test electrodes, while the resulting transients on the screen of oscilloscope were photographed on film (Neopan SSS, FUJI Photo Film Co. Ltd.) with a camera (CANON RM. F, 1.2). The potential was always referred to that of the reversible hydrogen electrode in the same solution and hydrogen atmosphere. The current applied in a series of measurements was usually successively increased in the range of 10^{-3} to 10^2 A cm⁻² and this increase was occasionally repeated a few times in some series. At high current densities, the duration of the pulses was kept short enough to prevent heating effect and concentration change near the electrode.⁵⁾ The similar series of measurements were carried out at other temperatures, ranging from 4 to 45°C. Solutions were titrated with standard HCl (1.0 N) solution after every series. The glass used was the borosilicate glass called HARIO of SHIBATA & Co., Tokyo. Taps used were all greaseless in order to prevent any contamination by organic substances.

§ 4. Results

Overvoltage, η , is determined from observed steady potential in transients by subtracting the potential due to solution resistance (IR drop) between the tip of LUGGIN capillary and the spherical electrode. The IR drop is obtained from the initial jump of potential at the very beginning of transient, which was proportional to the applied current as expected.

Hysteresis of the $\log_{10} i_+ \sim \eta$ relation with respect to temperature

In a series of measurements, $\log_{10} i_+ \sim \eta$ relation is observed repeatedly on the same electrode by changing temperature in a cyclic manner between two temperatures in order to control whether the measurements are reproducible. It is found that an amount of shift of the relation due to the temperature change gets smaller with the repetition of the cycle as shown in Fig. 2 by 20~50 mV, which exceeds appreciably experimental error of ~10 mV.

This tendency reveals itself irrespective as to whether the measurements are started from higher or lower temperature as well as whether 1 to 12 hours elapsed between two successive measurements or not. Each measurement recorded below is that conducted on a virgin electrode at every temperature.

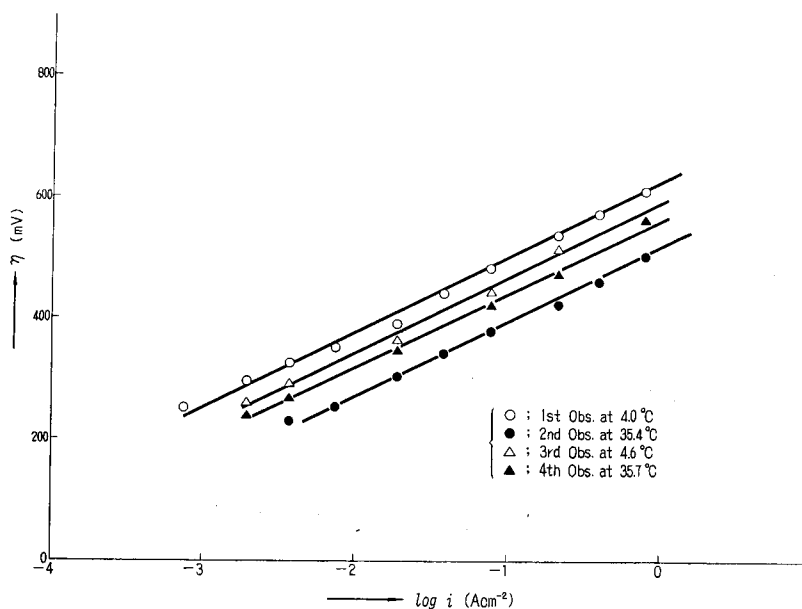


Fig. 2. Successive observations of $\log_{10} i_+ \sim \eta$ relation on nickel in 5.04 N NaOH aqueous solution.

○ represents the observation in the first series of measurements at 4.0°C on the virgin electrode (surface area, $1.11 \times 10^{-2} \text{ cm}^2$). ●, △ or ▲ represents respectively that in the second (35.4°C), third (4.6°C) or fourth (35.7°C) ones on the same electrode in the same solution.

TABLE 2. Observed values of i_0 and slope of $\log_{10} i_+ \sim \eta$ plot

No.	Conc. of NaOH, N	Temp., °C	i_0 , A cm ⁻²	Slope, mV
2	4.27	4.1	$2.24 \cdot 10^{-6}$	104
4	4.58	5.0	$1.24 \cdot 10^{-6}$	112
5	4.51	4.0	$5.03 \cdot 10^{-6}$	124
7	4.66	4.4	$1.58 \cdot 10^{-6}$	105
8	5.46	4.1	$5.74 \cdot 10^{-7}$	119
10	5.04	4.0	$7.05 \cdot 10^{-6}$	120
12	5.02	38.1	$1.33 \cdot 10^{-4}$	122
13	5.78	34.8	$1.99 \cdot 10^{-5}$	107
15	5.52	37.8	$2.45 \cdot 10^{-5}$	105
17	4.91	36.5	$2.50 \cdot 10^{-5}$	116
19	5.29	43.0	$2.81 \cdot 10^{-5}$	112
20	4.87	45.0	$2.17 \cdot 10^{-4}$	131

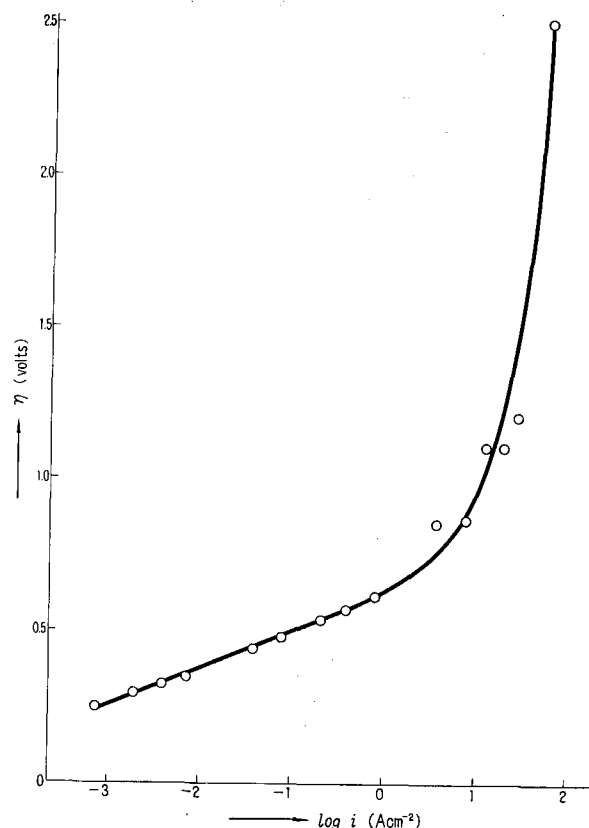


Fig. 3. Typical $\log_{10} i_+ \sim \eta$ plot on nickel in alkaline solution.
Conc. of NaOH; 5.04 N, Temp; 4.0°C, Surface area; $1.11 \times 10^{-2} \text{ cm}^2$.

$\log_{10} i_+ \sim \eta$ plot

The $\log_{10} i_+ \sim \eta$ plot in a wide range of current density reproduces the one reported previously⁴⁾, thus showing the saturation current at about 10^2 A cm^{-2} (Fig. 3), which is a characteristic criterion for the catalytic mechanism as mentioned in the Introduction. At current densities lower than 1 A cm^{-2} , the linear relation between them as called TAFEL law is established, of which slope and exchange current density, i_0 , obtained extrapolating the relation to $\eta=0$, are given in Table 2.

The electrodes which happened to give a few hundred millivolts of rest potential were discarded, being found to reveal an extraordinary $\log_{10} i_+ \sim \eta$ relation. Magnitude of the slope is not temperature dependent within an experimental error as seen in Table 2.

Heat of activation and pre-exponential factor

The heat of activation and $\log_{10} B$ are now determined from the experimental results in Table 2 according to Eqs. (5. a) and (5. b) by the method of least squares as shown in Table 3.

TABLE 3. Comparison of the experimental values of ΔH^* and $\log_{10} B$ with the theoretical ones.

	Obs.	Calc.
Conc. of NaOH	4.96 ± 0.09 N	
Temp.	$4 \sim 45^\circ\text{C}$	
ΔH^* (Kcal mol ⁻¹)	15.7 ± 2.9	18.5
$\log_{10} B$	6.7 ± 2.2	$6.8 \sim 6.9$

The heat of activation thus obtained for the range of η , where the TAFEL law holds, is in good agreement with the theoretical one calculated in §2 within the experimental error. The heat of activation of the saturation current has been theoretically estimated by HORIUTI³⁾ as *ca.* 10 Kcal mol⁻¹. The observation of the saturation current is not, however, accurate enough to determine the relevant heat of activation. The theoretical value of $\log_{10} B$ has been estimated by HORIUTI and one of the present authors by the same approximation with that used in this work as $\log_{10} B = 6.8 \sim 6.9^{21)}$, which agrees excellently with experimental value in Table 3.

Conclusive Remarks

(1) Hydrogen evolution reaction on nickel in 4.96 ± 0.09 N NaOH solution was observed at various temperatures with the results that $\Delta H^* = 15.7 \pm 2.9$ Kcal mol⁻¹ and $\log_{10} B = 6.7 \pm 2.2$ over the range of η , where the TAFEL law holds. The slope of the $\log_{10} i_+ \sim \eta$ relation was found temperature independent.

(2) The heat of activation was calculated theoretically on the basis of the catalytic mechanism, taking into account the repulsive interactions among hydrogen adatoms and between hydrogen adatoms and critical complex by the proportional approximation, with the result that $\Delta H^* = 18.5$ Kcal mol⁻¹ in the range of η from 120 to 600 mV, where the TAFEL law holds and then decreases with further increase of η to the limiting value of *ca.* 10 Kcal mol^{-1, 3)} which corresponds to that of the saturation current.

(3) The catalytic mechanism of the hydrogen electrode reaction on nickel was confirmed by the coincidence between the experimental and the theoretical values of ΔH^* as well as those of $\log_{10} B$.

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