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ON THE LAW OF LAIDLER, GLASSTONE AND EYRING

I. Derivation from the Catalytic Mechanism of Hydrogen Electrode Reaction

By

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Summary

The law of LAIDLER, GLASSTONE and EYRING¹⁾ states that

$$\log_{10} B \equiv \log_{10} i_0 + Td \log_{10} i_0 / dT$$

has approximately a common value 3 ± 2 for different hydrogen electrodes, where i_0 is the exchange current density. The $\log_{10} B$ is derived in the present paper with reference to the catalytic mechanism of the reaction on nickel, in which the rate of hydrogen electrode reaction is governed by the recombination of hydrogen adatoms on the electrode surface formed by neutralization of hydrogen ion. The law was similarly theoretically dealt with in a previous paper²⁾ but the theoretical value deduced²⁾ was exact only for a sparse coverage of electrode surface with hydrogen adatom, whereas no experimental data to be compared directly with it were presented²⁾.

The i_0 in the above equation is experimentally determined by extrapolation of cathodic current density to zero overvoltage by means of the TAFEL law³⁾, which holds, as revealed by recent investigation⁴⁾, at fairly large covered fraction θ greater than 0.5.

In the present paper, $\log_{10} B$ determined as above from the extrapolation of i for $\theta > 0.5$ at $\eta = 0$ is theoretically deduced from the catalytic mechanism on nickel on the one hand and the corresponding experimental values are derived from the results of BOCKRIS and POTTER¹³⁾ on the other hand.

The theoretical values thus obtained are found to be slightly greater than the highest of the widely fluctuating experimental values derived from the results of BOCKRIS and POTTER¹³⁾ and fairly larger than the above common value 3 ± 2 which is plausibly attributed to the deficiency of the proportional approximation resorted to in the present theoretical calculation for the repulsive interactions between unbonded hydrogen atoms.

Introduction

LAIDLER, GLASSTONE and EYRING¹⁾ found that

$$\log_{10} B \equiv \log_{10} i_0 + Td \log_{10} i_0 / dT \quad (1)$$

has approximately a common value 3 ± 2 for different hydrogen electrodes in

aqueous solution, where i_0 is the so-called exchange current density. These authors¹⁾ attributed the common value of $\log_{10} B$ to the commonly existent substance, *i.e.* water, as involved in the reaction and proposed an appropriate mechanism.

HORIUTI, KEII, ENYO and FUKUDA²⁾ have later shown that approximately the same common value of $\log_{10} B$ is obtained from hydrogen electrode reaction in nonaqueous electrolyte and even from H_2 - ND_3 exchange and parahydrogen conversion on nickel, expressing their rates formally by current densities associating two elementary charges with every hydrogen molecule involved in the heterogeneous reactions. They have calculated²⁾ theoretically on the other hand the values of B , which are in tolerable agreement with experimental results. In case of hydrogen electrode reaction, the theoretical values of B have been deduced both from the catalytic as well as the electrochemical mechanism^{2)*}. The experimental results and their theoretical interpretation²⁾ indicated that the law of LAIDLER *et al.*¹⁾ is rather the characteristic of such reactions as the initial or final system of the rate-determining step consists of hydrogen molecule or molecules alone. Their theoretical calculations in case of the catalytic mechanism are on the other hand exact only when the electrode surface is sparsely covered, whereas recent investigation^{3,4)} has shown that the covered fraction amounts to around 0.7, over the range of overvoltage, where the TAFEL law⁵⁾ is closely obeyed but not at extremely high or low coverage. The TAFEL law⁵⁾ is, as well-known, a linear relation observed at constant temperature between the logarithm of the cathodic current density i and the overvoltage η or the cathodic polarization, *i.e.*

$$\log_{10} i = \frac{\tau F \eta}{2.30 RT} + \text{constant}, \quad (2)$$

where τ is the TAFEL constant independent of temperature and overvoltage, F the Faraday and R the gas constant. The i_0 in (1) is now i extrapolated according to (2) at $\eta=0$, *i.e.*

$$\log_{10} i_0 = \log_{10} i - \eta \left(\frac{\partial \log_{10} i}{\partial \eta} \right)_T \quad (3)$$

from the range of η , where the TAFEL law holds.

We will treat i_0 in the present work as a physical quantity defined by (3) rather than as an idealistic exchange current density and deduce B -value theoretically from i_0 as defined by (3). The $\log_{10} B$ is thus according to (1) and (3)

*) The rate is governed by the recombination of hydrogen adatom formed by neutralization of hydrogen ion in case of the catalytic mechanism and by neutralization of adsorbed hydrogen molecule-ion in case of the electrochemical mechanism; *cf.* Refs. 6) and 7).

$$\log_{10} B = \log_{10} i + T \left(\frac{\partial \log_{10} i}{\partial T} \right)_{\eta} - \eta \left(\frac{\partial \log_{10} i}{\partial \eta} \right)_{T} - T \eta \frac{\partial^2 \log_{10} i}{\partial T \partial \eta}. \quad (4)$$

We see immediately that the last two terms of the above equation cancel each other, provided that (2) holds exactly, leaving an expression of $\log_{10} B$ consisting of the first two terms which has been used in the previous work²⁾. The $\log_{10} B$ expressed by (4) is now theoretically evaluated according to the catalytic mechanism over the range of η , where the TAFEL law has been found to be obeyed most closely^{3,4)}, resorting to a recent consistent method of proportional approximation⁴⁾.

§ 1. Rate Equation of the Catalytic Mechanism

The rate of hydrogen electrode reaction



is governed, in case of the catalytic mechanism^{6,7)}, by the recombination



of hydrogen adatoms H(a) on the electrode surface, which are formed by the neutralization of hydrogen ion H^+ by metal electron e.

The present theoretical derivation of B is based on the assumptions that the seat σ^* of the critical complex of rate-determining step (5. b) consists of adjacent two of physically identical sites of hydrogen adatom on each lattice plane and that the additional potential of H(a) or of constituent hydrogen atom of the critical complex of (5. b) due to repulsion of surrounding H(a)'s is proportional to the covered fraction θ of electrode surface with H(a) *i. e.* the proportional approximation.

The i in (4) is theoretically formulated as follows. Since every forward or backward act of the rate-determining step conveys two elementary charges into the electrode or reversely at the steady state respectively, the observed current density i is the excess of the forward unidirectional current density i_+ over the backward unidirectional one i_- , respectively associated with the forward and the backward unidirectional rates v_+ and v_- of (5. a) per unit area, *i. e.*

$$i_+ = 2\varepsilon v_+, \quad i_- = 2\varepsilon v_-,$$

where ε is the elementary charge. The forward and the backward rates of an elementary reaction are given by the generalized theory of reaction rate^{8)*} as $v_+ = (kT/h) \exp \{(\mu^I - \mu^*)/RT\}$ and $v_- = (kT/h) \exp \{(\mu^F - \mu^*)/RT\}$, hence

*) Cf. Eqs. (8. 12), (24.1 \bar{v}) and (26.1 \bar{v}) of Ref. 8).

$$i_+ = 2\varepsilon \frac{kT}{h} \exp\left(\frac{\mu^I - \mu^*}{RT}\right), \quad i_- = 2\varepsilon \frac{kT}{h} \exp\left(\frac{\mu^F - \mu^*}{RT}\right), \quad (6. a), (6. b)$$

assuming the transmission coefficient unity, where μ^* , μ^I and μ^F are the chemical potentials respectively of the critical complex, initial system and final system of the rate-determining step (5. b), k the BOLTZMANN constant and h the PLANCK constant.

The ratio i_+/i_- is now according to (6)

$$i_+/i_- = \exp\left(\frac{\mu^I - \mu^F}{RT}\right)$$

or since^{*)}

$$\mu^I - \mu^F = 2F\eta, \quad (7)$$

we have

$$i_+/i_- = \exp\left(\frac{2F\eta}{RT}\right),$$

and in consequence $i_+/i_- > 100$ for $\eta > 59$ mV. at 25°C. It follows that the directly observed current density $i = i_+ - i_-$ equals practically i_+ at the higher overvoltage, hence that the TAFEL law states practically the linear relation between $\log_{10} i_+$ and η at higher overvoltage. The i_0 determined by (3) equals in consequence physically the exchange current density, provided that the linear relation between $\log_{10} i_+$ and η holds down to $\eta = 0$, which is not however assured.

The $\log_{10} B$ is now formulated over the range of η , where the TAFEL law is most closely obeyed and i practically equals i_+ as follows. The μ^* in (6. a) is expressed according to the generalized theory of reaction rate^{*)**)} as

$$\mu^* = -RT \ln G^* \Theta_{\sigma^*(0)} q^*, \quad (8)$$

where G^* is the number of sites σ^* for the critical complex per unit area, $\Theta_{\sigma^*(0)}$ the probability of σ^* being free to admit a critical complex and q^* the

*) Every forward act of the overall reaction (5. a) is completed by twice the neutralization $H^+ + e \rightarrow H(a)$ and once the rate-determining step (5. b). The overall reaction being dammed up by the latter, according to the catalytic mechanism, the free energy decrease $-\Delta F = 2\mu^{H^+} + 2\mu^e - \mu^H$, per mol occurrence of the overall reaction (5. a) equals practically $\mu^I - \mu^F$ of the rate-determining step, where μ^{H^+} etc. are chemical potentials of H^+ etc. respectively. The $-\Delta F$ is zero in equilibrium, where $2\mu^{H^+} + 2\mu_{e_0}^e = \mu^H$, $\mu_{e_0}^e$ being the appropriate particular value of μ^e . It follows from the last two equations $-\Delta F = 2(\mu^e - \mu_{e_0}^e)$, hence (7) in the text, since $-\Delta F$ equals practically $\mu^I - \mu^F$ of the rate-determining step as mentioned above, while $\mu^e - \mu_{e_0}^e$ is $F\eta$ by definition.

***) Cf. §24 and Eq. (8.12) of Ref. 8).

BOLTZMANN factor of the reversible work required to bring up the constituents of the critical complex from their respective standard states into a definite σ^* kept preliminarily free to admit them with certainty to construct the critical complex there.

The q^* in (8) for the catalytic mechanism is expressed in accordance with the proportional approximation as

$$q^* = q_0^* \exp(-u^*\theta/RT), \quad (9)$$

where θ is the covered fraction of the electrode surface by hydrogen adatoms, q_0^* the value of q^* at $\theta=0$ and u^* is the additional potential per mol of the critical complex due to the repulsion of surrounding adatoms at $\theta=1$. The q_0^* is expressed allowing for the five normal modes of vibration of the critical complex as^{*)}

$$q_0^* = \exp\left(-\frac{E_0^*}{RT}\right) \prod_{i=1}^5 \left\{1 - \exp\left(-\frac{h\nu_i^*}{kT}\right)\right\}^{-1}, \quad (10)$$

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 μ^I in (6. a) is expressed by (7), noting that $F \equiv H_2$ in accordance with (5. b), as

$$\mu^I = \mu^{H_2} + 2F\eta, \quad (11)$$

where μ^{H_2} is the chemical potential of hydrogen around the electrode, hence

$$(\partial\mu^I/\partial T)_\eta = d\mu^{H_2}/dT = -\bar{S}^{H_2} \quad (12. a)$$

and

$$\partial^2\mu^I/\partial T\partial\eta = 0, \quad (12. b)$$

where \bar{S}^{H_2} is the partial molar entropy or the entropy of 1 mol pure hydrogen gas at its partial pressure and temperature in the assembly^{**)} in question.

Substituting μ^* and μ^I respectively from (8) and (11) into (6. a) identifying i_+ with i , we have according to (4) with reference to (9) and (12)

$$\begin{aligned} \log_{10} B = \log_{10} B_0 + \left(\frac{\partial T \log_{10} \Theta_{\sigma^*(0)}}{\partial T}\right)_\eta - \frac{u^*}{2.30R} \left(\frac{\partial \theta}{\partial T}\right)_\eta \\ + \frac{u^*\eta}{2.30R} \frac{\partial^2 \theta}{\partial \eta \partial T} - \eta \frac{\partial^2 T \log_{10} \Theta_{\sigma^*(0)}}{\partial \eta \partial T}, \end{aligned} \quad (13. a)$$

) The q_0^ here is identical with q_p^{*d} given by Eq. (23) of Ref. 7), E_0^* here being equal to $\epsilon_{H_2} + \frac{1}{2} \sum h\nu_i$ there ⁷⁾ multiplied by the AVOGADRO number.

***) The assembly means here a macroscopic system in which the hydrogen electrode reaction in question is going on.

where

$$\log_{10} B_0 = \log_{10} 2\varepsilon \frac{kT}{h} G^* + \frac{1}{2.30} + \frac{dT \log_{10} q_0^*}{dT} - \frac{\bar{S}^{\text{H}_2}}{2.30R} \quad (13. b)$$

is the value of $\log_{10} B$ at $\theta=0$, in which case all the other terms on the right of (13. a) vanish; the first three terms or the last two terms on the right of (13. a) arise respectively from the first two or the last two terms on the right of (4).

The first term on the right of (13. b) is calculated at 9.73 for $G^* = 10^{15} \text{ cm}^{-2}$ at 25°C . The third term in (13. b) is evaluated according to (10) on the base of calculated wave numbers⁷⁾ 936, 687, 1704, 368 and 626 cm^{-1} of the five normal vibrations of the critical complex, as

$$\frac{dT \log_{10} q_0^*}{dT} = 0.425, \quad 25^\circ\text{C}.$$

The last term of (13. b) is determined from the \bar{S}^{H_2} -value⁹⁾,

$$\bar{S}^{\text{H}_2} = 31.211 \text{ cal/deg}, \quad 25^\circ\text{C}, \quad 760 \text{ mmHg},$$

admitting that the hydrogen electrode in question is surrounded by hydrogen of 760 mmHg partial pressure. The numerical value of $\log_{10} B_0$ at 25°C is now

$$\log_{10} B_0 = 3.33, \quad 25^\circ\text{C}. \quad (14)$$

Other terms in (13. a) are developed and evaluated at a few prescribed values of θ over its range, where the TAFEL law holds good, in subsequent sections.

$$\S 2. \quad \left(\frac{\partial T \log_{10} \theta_{\sigma^*(0)}}{\partial T} \right)_v \quad \text{and} \quad \frac{u^*}{2.30R} \left(\frac{\partial \theta}{\partial T} \right)_v$$

In a previous work⁷⁾ the $\theta_{\sigma^*(0)}$ was equated to $(1-\theta)^2$, which is not exact, insofar as the repulsive interaction between H(a)'s is taken into account⁷⁾, inasmuch as the probabilities of the two sites constituting σ^* being respectively occupied or unoccupied are not then independent of each other. In a later work³⁾, the interaction in question has been taken into account in calculating $\theta_{\sigma^*(0)}$, but the probability of the one, σ_1 , of the two constituent sites of σ^* being unoccupied has then been calculated assuming that the repulsive potential due to an adatom on the other constituent site σ_2 is $u_1\theta$, where u_1 is the repulsive potential between the two adatoms respectively on the two constituent sites, whereas the unoccupied probability of σ_2 with σ_1 unoccupied was calculated for the definite vacancy of σ_1 . The two physically identical sites have now been consistently equally treated in formulating $\theta_{\sigma^*(0)}$ in a later paper⁴⁾, although

based on the proportional approximation as yet. The $\Theta_{\sigma^*(0)}$ is thus expressed by the latter approximation⁴⁾, as

$$\Theta_{\sigma^*(0)} = (1 + 2\beta + \xi\beta^2)^{-1}, \quad (15)$$

where

$$\beta = \gamma \exp \left\{ -(u - u_1)\theta / RT \right\}, \quad (16. a)$$

$$\gamma = q_0^H / p^H, \quad (16. b)$$

$$\xi = \exp(-u_1/RT), \quad (16. c)$$

u is the additional potential of an adatom due to the repulsion of surrounding adatoms at $\theta=1$, hence $(u-u_1)\theta$ the additional potential per mol of H(a) inside σ^* due to the repulsion of adatoms outside σ^* in accordance with the proportional approximation, q_0^H is the BOLTZMANN factor of the reversible work required to bring up a hydrogen atom from its standard state to a definite, preliminarily evacuated site of adsorption in the absence of surrounding hydrogen adatoms and p^H the BOLTZMANN factor of the chemical potential of hydrogen adatom, hence γ is according to (16. b) that of the reversible work required to bring up a hydrogen adatom onto a definite, preliminarily evacuated site from anywhere else in the assembly in the absence of interaction with surrounding adatoms. The u and u_1 have been evaluated as^{3,4)}

$$u = 25 \text{ Kcal/mol}, \quad u_1 = 1.38 \text{ Kcal/mol}. \quad (17. a), (17. b)$$

The q_0^H is derived according to the above definition similarly as (10), as^{7,10,11,*)}

$$q_0^H = \exp \left(-\frac{E_0^H}{RT} \right) \prod_{j=1}^3 \left\{ 1 - \exp \left(\frac{-h\nu_j}{kT} \right) \right\}^{-1}, \quad (18. a)$$

where E_0^H is the ground state energy of hydrogen adatom as referred to the ground state energy of hydrogen molecule, and ν_j 's are the frequencies of normal vibration of the adatom, the appropriate wave numbers $\tilde{\nu}_j$ being⁷⁾

$$\tilde{\nu}_j = 417, 479 \text{ and } 1900 \text{ cm}^{-1}. \quad (18. b)$$

The above definition of p^H leads on the other hand readily to the equation

$$\mu^1 = -2RT \ln p^H, \quad (19)$$

inasmuch as the initial system I of the rate-determining step (5. b) consists of two statistically independent hydrogen adatoms.

The term $(\partial T \log_{10} \Theta_{\sigma^*(0)} / \partial T)_T$ in (13. a) is now developed according to (15) as

*) Cf. footnote *) on p. 63 of Ref. 10) or § 2 of Ref. 11).

$$(\partial T \log_{10} \Theta_{\sigma^*(0)} / \partial T)_\gamma = \log_{10} \Theta_{\sigma^*(0)} - T \Theta_{\sigma^*(0)} \left\{ 2\beta(1 + \xi\beta) (\partial \log_{10} \beta / \partial T)_\gamma + \xi\beta^2 d \log_{10} \xi / dT \right\}. \quad (20. a)$$

The $T d \log_{10} \xi / dT$ in (20. a) is readily determined by (16. c) as

$$T d \log_{10} \xi / dT = u_1 / 2.30 RT. \quad (20. b)$$

The β and its temperature derivative in (20. a) are now determined from the adsorption isotherm⁴⁾

$$\frac{\theta}{1-\theta} = \beta \frac{1 + \beta\xi}{1 + \beta}, \quad (21)$$

which is derived⁴⁾ dealing equally with two constituent sites of σ^* consistently as mentioned above. Eq. (21) determines β for any prescribed value of θ with reference to (16. c) and (17. b). Differential coefficients $(\partial \ln \beta / \partial T)_\gamma$ in (20. a) and $(\partial \theta / \partial T)_\gamma$ in (13. a) are determined as roots of equations obtained by differentiating (21) and (16. a), *i. e.*

$$\frac{(\partial \theta / \partial T)_\gamma}{\theta(1-\theta)} = \left(\frac{\partial \ln \beta}{\partial T} \right)_\gamma \varphi + \frac{\xi\beta}{1 + \xi\beta} \frac{u_1}{RT^2} \quad (22. a)$$

and

$$\ln \beta + T \left(\frac{\partial \ln \beta}{\partial T} \right)_\gamma = \left(\frac{\partial T \ln \gamma}{\partial T} \right)_\gamma - \frac{u - u_1}{R} \left(\frac{\partial \theta}{\partial T} \right)_\gamma, \quad (22. b)$$

where

$$\varphi = \frac{1}{1 + \beta} + \frac{\xi\beta}{1 + \xi\beta}, \quad (22. c)$$

as

$$\left(\frac{\partial \ln \beta}{\partial T} \right)_\gamma = \frac{\frac{1}{\theta(1-\theta)} \left\{ -\frac{\ln \beta}{T} + \left(\frac{\partial T \ln \gamma}{T \partial T} \right)_\gamma \right\} - \frac{\xi\beta}{1 + \xi\beta} \frac{u_1}{RT^2} \frac{u - u_1}{RT}}{\frac{1}{\theta(1-\theta)} + \frac{u - u_1}{RT} \varphi} \quad (23. a)$$

and

$$\left(\frac{\partial \theta}{\partial T} \right)_\gamma = \frac{\left\{ -\frac{\ln \beta}{T} + \left(\frac{\partial T \ln \gamma}{T \partial T} \right)_\gamma \right\} \varphi + \frac{\xi\beta}{1 + \xi\beta} \frac{u_1}{RT^2}}{\frac{1}{\theta(1-\theta)} + \frac{u - u_1}{RT} \varphi}. \quad (23. b)$$

The $(\partial T \ln \gamma / \partial T)_\gamma$ in (23) is evaluated as follows. The γ is expressed by

eliminating μ^I , q_0^H and p^H from (11), (16. b), (18. a) and (19) as

$$\gamma = \exp\left(\frac{F\eta - E_0^H}{RT}\right) \exp\left(\frac{\mu^{H_2}}{2RT}\right) \prod_{j=1}^3 \left\{1 - \exp\left(-\frac{h\nu_j}{kT}\right)\right\}^{-1}.$$

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

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

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 the number of hydrogen molecule per cm^3 . The N is given in terms of hydrogen pressure P in mmHg as

$$N = 1.360 \times 980.5 P/kT.$$

We have from the last three equations

$$\gamma = \frac{\sqrt{\frac{1.360 \times 980.5 \cdot P}{kT}} \exp\left(\frac{F\eta - E_0^H}{RT}\right)}{\sqrt{\frac{(2\pi mkT)^{3/2}}{h^3} \frac{4\pi^2 IkT}{h^2}} \prod_{j=1}^3 \left\{1 - \exp\left(-\frac{h\nu_j}{kT}\right)\right\}}, \quad (24. a)$$

hence

$$\begin{aligned} (\partial T \ln \gamma / \partial T)_\eta &= \frac{1}{2} \ln \frac{1.360 \times 980.5 \cdot P \cdot h^5}{(2\pi mkT)^{3/2} 4\pi^2 I (kT)^2} - \frac{7}{4} \\ &\quad - \sum_{j=1}^3 \ln \left\{1 - \exp\left(-\frac{h\nu_j}{kT}\right)\right\} + \sum_{j=1}^3 \frac{h\nu_j/kT}{\exp(h\nu_j/kT) - 1}. \end{aligned} \quad (24. b)$$

Numerically we have for $m = 2.016/6.025 \times 10^{23}$ and $I = 4.664 \times 10^{-41} \text{ gm cm}^2$ ¹²⁾

$$\gamma = 2.909 \times 10^{-3} \exp\left(\frac{F\eta - E_0^H}{RT}\right), \quad 25^\circ\text{C}, \quad P = 760 \text{ mmHg} \quad (25. a)$$

and

$$dT \ln \gamma / dT = -7.00, \quad 25^\circ\text{C}, \quad (25. b)$$

irrespective of η and E_0^H .

The β is now calculated by (21), (16. c) and (17. b) for the three values 0.6, 0.7 and 0.8 of θ , where the TAFEL law is most precisely reproduced by

^{*}) The BOLTZMANN factor p^{H_2} of chemical potential μ^{H_2} of hydrogen molecule is expressed as $p^{H_2} = Q^{H_2}/N$, where Q^{H_2} is the partition function of a single hydrogen molecule per unit volume; cf. e. g. Eq. (5.5) of Ref. 8).

the present approximation^{3,4)*}, hence γ by (16. a) and (17), η by (25. a) for

$$E_0^H = -12.3 \text{ Kcal}^{10)},$$

$(\partial\theta/\partial T)_\gamma$ by (23. b), (22. c), (17) and (25. b), and $(\partial \ln \beta/\partial T)_\gamma$ by (23. a) respectively at 25°C as shown in Table 1. The values of $(u^*/2.30 R)(\partial\theta/\partial T)_\gamma$ given in the same Table are computed for the value of u^*

$$u^* = 35 \text{ Kcal/mol} \quad (26)$$

as deduced from the result of the above mentioned work^{4)*}.

§ 3. $\partial^2\theta/\partial\eta\partial T$ and $\eta \partial^2 T \log_{10} \theta_{s^*(0)}/\partial\eta\partial T$

The last two terms of (13. a) are evaluated first by determining $\partial^2\theta/\partial\eta\partial T$ as follows. We have by differentiating (23. b) with respect to γ

$$\begin{aligned} T \frac{\partial^2\theta}{\partial\eta\partial T} = & \left[\left\{ -\varphi + \alpha\phi + \frac{u_1}{RT} \frac{\xi\beta}{(1+\xi\beta)^2} \right\} / \theta(1-\theta) \right. \\ & + \left\{ \alpha\varphi + \frac{\xi\beta}{1+\xi\beta} \frac{u_1}{RT} \right\} \frac{1-2\theta}{\theta(1-\theta)} \varphi - \frac{u-u_1}{RT} \varphi^2 \\ & \left. + \frac{(u-u_1)u_1}{(RT)^2} \frac{\xi\beta}{1+\xi\beta} \left(\frac{\varphi}{1+\xi\beta} - \phi \right) \right] \left(\frac{\partial \ln \beta}{\partial \eta} \right)_r / \left\{ \frac{1}{\theta(1-\theta)} + \frac{u-u_1}{RT} \varphi \right\}^2, \end{aligned} \quad (27)$$

where

$$\alpha = -\ln \beta + (\partial T \ln \gamma / \partial T)_\gamma \quad (28. \alpha)$$

and

$$\phi = \frac{\xi\beta}{(1+\xi\beta)^2} - \frac{\beta}{(1+\beta)^2}, \quad (28. \phi)$$

noting that

$$\frac{\partial^2 T \ln \gamma}{\partial \eta \partial T} = 0 \quad (29)$$

according to (24. a). The φ , α and ϕ in (27) are evaluated by (22. c), (28) and (25. b), whereas $(\partial \ln \beta / \partial \eta)_r$ in the same equation is determined as follows. We

) The value of $2u-u^$ is deduced in Ref. 4) conversely from a constant value 0.52 of $\tau = (RT/F)(\partial \ln i / \partial \eta)_r$ according to (2) by (6. a), (8), (9), (10), (11), (15), (16), (21) and (24. a) and found almost stationary at 15 Kcal/mol over the range 0.6-0.8 of θ . This means conversely that the TAFEL law is most precisely obeyed over the latter range of θ . The value of u^* in the text follows from the above stationary value of $2u-u^*$ and (17. a).

have from (16. a) and (24. a)

$$\left(\frac{\partial \ln \beta}{\partial \eta}\right)_r = \frac{F}{RT} - \frac{u-u_1}{RT} \left(\frac{\partial \theta}{\partial \eta}\right)_r$$

and from (21) with reference to (22. c)

$$\frac{(\partial \theta / \partial \eta)_r}{\theta(1-\theta)\varphi} = \left(\frac{\partial \ln \beta}{\partial \eta}\right)_r,$$

hence from the above two equations

$$\left(\frac{\partial \theta}{\partial \eta}\right)_r = \frac{F}{RT} \left/ \left\{ \frac{1}{\theta(1-\theta)\varphi} + \frac{u-u_1}{RT} \right\} \right. \quad (30. a)$$

and

$$\left(\frac{\partial \ln \beta}{\partial \eta}\right)_r = \frac{F}{RT} \left/ \left\{ 1 + \frac{(u-u_1)\theta(1-\theta)\varphi}{RT} \right\} \right. \quad (30. b)$$

The values of $(\partial \ln \beta / \partial \eta)_r$ are calculated by (30. b) and (22. c) as shown in Table 1. Substituting $(\partial \ln \beta / \partial \eta)_r$ from (30. b) into (27), we have

$$\begin{aligned} \frac{\partial^2 \theta}{F \partial \eta \partial T} = & \left[\left\{ \alpha \varphi - \varphi + \frac{u_1}{RT} \frac{\xi \beta}{(1+\xi \beta)^2} \right\} / \theta(1-\theta) \right. \\ & + \left\{ \alpha \varphi + \frac{\xi \beta}{1+\xi \beta} \frac{u_1}{RT} \right\} \frac{1-2\theta}{\theta(1-\theta)} \varphi - \frac{u-u_1}{RT} \varphi^2 \\ & \left. + \frac{(u-u_1)u_1}{(RT)^2} \frac{\xi \beta}{1+\xi \beta} \left(\frac{\varphi}{1+\xi \beta} - \phi \right) \right] \theta^2 (1-\theta)^2 / RT^2 \left\{ 1 + \frac{(u-u_1)\theta(1-\theta)\varphi}{RT} \right\}^3. \end{aligned} \quad (31)$$

The $\partial^2 \theta / \partial \eta \partial T$ is now calculated by (31) referring to (22. c), (28), (16. c) and (17), hence the value of the second last term in (13. a) by (26) as shown in Table 1.

The last term of (13. a) is evaluated by differentiating (20. a) written in the form

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

with respect to η as

$$\begin{aligned} -\frac{\partial^2 T \ln \Theta_{\sigma^*(0)}}{\partial \eta \partial T} = & 2\beta \Theta_{\sigma^*(0)} \left[\left\{ T \left(\frac{\partial \ln \beta}{\partial T} \right) \right\}_\eta (1+2\xi\beta+\xi\beta^2) \right. \\ & \left. + \xi\beta(1+\beta) \frac{u_1}{RT} \right] \left(\frac{\partial \ln \beta}{\partial \eta} \right)_r - (1+\xi\beta) \frac{u-u_1}{R\Theta_{\sigma^*(0)}} \frac{\partial^2 \theta}{\partial \eta \partial T}. \end{aligned} \quad (32)$$

Table 1 shows the values of the last term of (13. a) calculated by (32) using (15),

TABLE 1. Calculated Values at 25°C and 760mmHg Hydrogen Partial Pressure Around the Electrode

θ	0.600	0.700	0.800
β	7.256	15.26	32.08
η	0.2817	0.4032	0.5247
$(\partial\theta/\partial T)_\eta$	$-5.05 \cdot 10^{-4}$	$-5.42 \cdot 10^{-4}$	$-5.77 \cdot 10^{-2}$
$(\partial \ln \beta/\partial T)_\eta$	$-0.998 \cdot 10^{-2}$	$-1.10 \cdot 10^{-2}$	$-1.21 \cdot 10^{-2}$
$(\partial \ln \beta/\partial \eta)_T$	6.36	5.97	6.46
$\left(\frac{\partial T \log_{10} \theta_{\sigma^*(0)}}{\partial T}\right)_\eta$	-0.0162	-0.163	-0.326
$-\frac{u^*}{2.30 R} \left(\frac{\partial \theta}{\partial T}\right)_\eta$	3.82	4.15	4.412
$\frac{u^* \eta}{2.30 R} \frac{\partial^2 \theta}{\partial \eta \partial T}$	-0.555	-0.985	-0.942
$-\eta \frac{\partial^2 T \log_{10} \theta_{\sigma^*(0)}}{\partial \eta \partial T}$	0.215	0.593	0.510
$\log_{10} B$ calc.	6.84	6.92	6.98

(16. c), (17), the values of $\partial^2\theta/\partial\eta\partial T$ calculated above and those of $(\partial \ln \beta/\partial T)_\eta$, β and $(\partial \ln \beta/\partial \eta)_T$ given in the same Table.

§ 4. Comparison with Experiment

BOCKRIS and POTTER¹³⁾ have observed the TAFEL lines on nickel electrode in HCl_{aq} as well as in NaOH_{aq} at different concentrations and deduced from their experimental results i_0 and $\Delta H_0^* = RT^2 d \ln i_0/dT$. The $\log_{10} B$ calculated from their data of i_0 and ΔH_0^* fluctuates between 6.5 and -3.0 . The determination of ΔH_0^* and in consequence of B would probably be associated with a considerable error in case of this sort of electrode, where the observation of TAFEL line is not very reproducible. It may be mentioned in this connection, that the experimental value of $\log_{10} B$ lies between 2.9 and 5.2²⁾ in case of hydrogen electrode of mercury, where the electrode surface is readily kept clean and the observation of TAFEL line may be fairly reproducible. Accurate observation on clean surface of nickel is desirable for a reasonable check of the theoretical values.

We see from Table 1 that just a little is contributed to $\log_{10} B$ by the last two terms of (13. a), hence by those of (4), which allow for the effect of deviation from the TAFEL law on B -value. We see on the other hand a con-

siderable positive contribution to the theoretical value of $\log_{10} B$ is made by the third term $-(u^*/2.30R)(\partial\theta/\partial T)_v$ of (13.a), which has been left out in the previous paper³⁾ rendering the calculated value of B even slightly larger than the highest of the fluctuating experimental values and fairly larger than the common value 3 ± 2 . It has been shown in a previous paper¹⁰⁾ that the proportional approximation resorted to in the present calculation gives adsorption isotherms appreciably deviating from those of higher approximations, which are nearly coincident with each other.

The calculation of B by higher approximations is in progress in this laboratory.

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