



Title	ON THE LAW OF EYRING ET AL. ON HYDROGEN ELECTRODE REACTIONS
Author(s)	HORIUTI, Juro; KEII, Tominaga; EN'YO, Michio; FUKUDA, Michiko
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 5(1), 40-54
Issue Date	1957-09
Doc URL	http://hdl.handle.net/2115/24658
Type	bulletin (article)
File Information	5(1)_P40-54.pdf



[Instructions for use](#)

ON THE LAW OF EYRING ET AL. ON HYDROGEN ELECTRODE REACTIONS

By

Juro HORIUTI, Tominaga KEI, Michio EN'YO
and Michiko FUKUDA^{*)}

(Received June 30, 1957)

EYRING, GLASSTONE and LAIDLER¹⁾ have found that the factor B of the equation

$$i_0 = B \exp(-\Delta H^*/RT) \quad (1)$$

is approximately of the common order of magnitude, i.e., 10^2 for different electrode materials and aqueous solutions as determined from the exchange current i_0 and the heat of activation ΔH^* given by BOWDEN and AGAR.²⁾ These authors suggest on the ground of this law that the rate-determining step of these hydrogen electrode reactions consists in the proton transfer from water molecule to the electrode, attributing the common factor to the common constituent i.e., water of the aqueous solutions.

It is shown in the first place in the present work that this law holds for hydrogen electrode reaction in non-aqueous solution as well or even for such process of conversion of hydrogen at overall equilibrium as traced out by the parahydrogen conversion or by means of hydrogen isotope i.e., not only in the presence of aqueous solution but also in the presence of non-aqueous solution or even in its absence.

In the second place it is shown, investigating B according to the generalized statistical mechanical theory of reaction rate developed by one of the present authors³⁾ that the above result is quantitatively accounted for on the basis of the catalytic or electrochemical me-

^{*)} J. H. and T. K.; Research Institute for Catalysis, Hokkaido University.

M. E.; John Harrison Laboratory of Chemistry, University of Pennsylvania (on leave from Research Institute for Catalysis, Hokkaido University).

M. F.; Department of Chemistry, Faculty of Science, Hokkaido University.

chanism^{4)5)6)*)} but not of other mechanisms inclusive of that advanced by EYRING *et al.* It is further concluded that B decreases with decreasing hydrogen pressure and with increasing temperature, although the present accuracy of the B -determination is not sufficient to check the theoretical conclusion.

§ 1. $\log B$ from Different Experimental Results

Table 1 shows B -values calculated according to (1) from different sources in the column *obs.*

Row III shows the result⁷⁾ of the catalyzed exchange reaction between deuterium shifted hydrogen and ordinary water at the liquid state in the presence of nickel wire; i_0 is twice the elementary charge times the number of hydrogen molecules undergoing the process of conversion traced by deuterium per unit area of the nickel wire calculated as

$$i_0 = \left(\frac{2Fk_e}{3600 \times 22400} \right) \left(\frac{273}{T} \right) \left(\frac{P}{760} \right),$$

where F is the FARADAY constant and P the partial pressure of hydrogen; $k_e = (V/St) \ln(D_0/D_t)$ is the volume of hydrogen, at the very condition of the experiment, undergoing the process per unit area per unit time, where V is the volume of the reaction vessel, S the area of the nickel wire, and t the time and D_t or D_0 the atomic fraction of deuterium in hydrogen at time t or $t=0$ respectively. The value of k_e is 0.073 cm hr^{-1} at 100°C , $P=431 \text{ mm Hg}$ or 0.017 cm hr^{-1} at 70°C , $P=387 \text{ mm Hg}$ as given by HIROTA and HORIUTI,⁴⁾ and hence $\Delta H^* = RT^2(d \ln k_e/dT) - RT = 12.6 \text{ kcal}$ according to the above equation of i_0 .

Row IV shows the result of the catalyzed hydrogen-ammonia exchange reaction on nickel wire in the absence of liquid phase as observed by HORIUTI and SUZUKI.⁸⁾ In this experiment the atomic fraction of deuterium in ammonia has been kept practically at unity throughout, whereas that of hydrogen of 1 atm partial pressure, initially practically zero, has been increased by the exchange up to within a few percent. The latter increase must hence practically equal

*) The mechanism of the process traced by the parahydrogen conversion or by means of the hydrogen isotope will here be included in the catalytic mechanism, which is originally that of the hydrogen electrode reactions governed by the recombination of hydrogen atoms formed preliminarily by the discharge of hydrogen ions, provided that the above process is governed by the same step.

TABLE 1.

No.	Reactions	Electrode or catalysts	Hydrogen pressure <i>P</i> mmHg	Electrolytes or additions	<i>t</i> °C	log ₁₀ <i>i</i> ₀ (amp cm ⁻²)	ΔH^* kcal	log ₁₀ <i>B</i>				Ref.
								obs.	$\nu = m = 1$	$\nu = m = 2$	$\nu = 1 \ m = 2/3$	
I	Hydrogen electrode reaction in aq. soln.	Hg	760	0.1N HCl aq.	20	- 12.0	21.1	3.7	2.9	6.0		a
		Hg		0.1N HCl aq.	20	- 12.1	21.7	4.0				b
II	Hydrogen electrode reactions in non- aq. soln.	Hg	760	36 mole % CH ₃ OH aq.	20	- 12.0	23.2	5.2				a
		Hg		CH ₃ OH	20	- 11.7	19.7	2.9				a
		Hg		CH ₃ OH	20	- 11.4	20.6	3.9				c
		Hg		CH ₃ OH	-88	- 15.3	20.6	3.8	3.2	5.1		c
III	H ₂ -H ₂ O exchange	Ni-wire	431	H ₂ O	100	- 4.14	12.6	3.2	2.5 (0.08)	5.8 (-0.02)	1.3 (-0.02)	d
			387		70	- 4.78	12.6	3.2	2.5 (0.06)	5.8 (-0.04)	-1.2 (-0.04)	d
IV	H ₂ -NH ₃ exchange	Ni-wire (reduced in H ₂ 42 hr 300 °C)	760	ND ₃ gaseous	25	- 6.55	11.4	1.8	2.9 (0.02)	5.9 (-0.07)	-0.6 (-0.07)	e
		Ni-wire (reduced in H ₂ 12 hr 280°C)			31	- 6.27	11.4	1.9	2.9 (0.06)	5.9 (-0.06)	-0.6 (-0.06)	e
V	Para-H ₂ conversion	Ni-wire	100	none	125	- 0.57	4.77	2.0	1.8 (0.12)		-2.4 (-0.01)	f

a) BOCKRIS and PARSONS, Trans. Faraday Soc. 45, 916 (1949).

b) POST and HISKEY, J. Am. Chem. Soc. 72, 4203 (1950).

c) BOCKRIS PARSONS, and ROSENBERG, Trans. Faraday Soc. 47, 766 (1951).

d) HIROTA and HORIUTI, Sci. Pap. Inst. Phys. Chem. Res. Tokio 30, 151 (1936).

e) HORIUTI and SUZUKI, Shokubai (Catalyst) No. 4 (1948) (in Japanese).

f) FARKAS, Orthohydrogen, Parahydrogen and Heavy Hydrogen p. 99 (1935).

the fraction of protium of hydrogen having undergone the process; the rate of hydrogen undergoing the process is thus given by multiplying the increasing rate \dot{D} hr⁻¹ of the fraction by the quantity of hydrogen present in the reaction vessel and hence i_0 appropriate to the process as

$$i = (\dot{D}/3600)(V/22400)(2F/S)(273/T),$$

where $V=332$ or 350 cc is the volume of the reaction vessel and $S=1150$ or 860 cm² the surface area of the catalyst. The $\Delta H^* = RT^2 (d \log i_0/dT) = 11.4$ kcal was calculated from the observed temperature variation of D according to the above equation.

Row V shows $\log_{10} B$ obs. derived from the result of catalyzed parahydrogen conversion at 100 mm Hg hydrogen pressure in the presence of nickel.¹⁰ The fraction of hydrogen undergoing the process traced by parahydrogen per unit time is given as

$$k_p = \frac{1}{t} \ln \frac{C_0 - C_\infty}{C_t - C_\infty}$$

where C_t , C_0 or C_∞ is the concentration of parahydrogen at time t , $t=0$ or $t=\infty$ respectively. The appropriate i_0 is calculated similarly as above by multiplying the increasing rate k_p of the fraction by the quantity of hydrogen present and electricity formally associated with as

$$i_0 = \frac{k_p}{S} V(2F/22400)(P/760)(273/T),$$

where $V=500$ cc or $S=0.5$ cm² is the volume of the reaction vessel or the surface area of the nickel catalyst used as given by FARKAS.¹⁰ $\Delta H^* = 4.77$ kcal is calculated according to the above equation from the temperature coefficient of k_p given by FARKAS.¹⁰

It is seen from Table 1 that the values of $\log_{10} B$ obs. is tolerably constant throughout the different processes of hydrogen, and that the constancy of $\log_{10} B$ -values has little to do with the presence of water. What is common to all these cases inclusive of the data, on which EYRING *et al.* based their law, is that they deal with the heterogeneous reactions of hydrogen. It is theoretically shown in next sections that the value of $\log_{10} B$ must be actually common to all these cases around 1 atm hydrogen pressure and room temperature, if the complex^{*)} of the rate-determining step is as a whole derivable from one hydrogen

*) The complex will here refer to the common constituent of the initial, final or critical complex of a step, which are only different from each other in configuration.

molecule like in the case of the catalytic or electrochemical mechanism^{*)}, and the appropriate critical complex is confined in a narrow space of the molecular dimension.

§ 2. Investigation of $\log B$

The $\log_{10} B$ defined above is investigated closer below as required for its theoretical evaluation.

The exchange current i_0 of the hydrogen electrode reaction is, as a matter of fact, extrapolated from the directly observed cathodic current i at sufficiently low overpotential^{**)}, where i is practically identifiable with the forward current, according to the TAFEL empirical relation valid in the latter region

$$\ln i = -\frac{\alpha F \eta}{RT} + \text{const.}, \quad \alpha \approx 0.5, \quad (2)$$

as

$$i_0 = i \exp\left(\frac{\alpha F \eta}{RT}\right) \quad (3)$$

The $\log_{10} B$ -value is given in accordance with (1) and (3) as

$$\log_{10} B = \log_{10} i_0 + T \frac{d \log_{10} i_0}{dT} = \log_{10} i + T \left(\frac{\partial \log_{10} i}{\partial T} \right).$$

The above expression of $\log_{10} B$ may further be generalized: we have according to the definition of η ^{**)}

$$-F\eta = \mu^\epsilon - \mu_e^\epsilon,$$

where μ^ϵ or μ_e^ϵ is the chemical potential of metal electron ϵ in the test or the reversible hydrogen electrode respectively, which are surrounded by common hydrogen atmosphere and hydrogen ion H^+ of chemical potentials μ^{H_2} and μ^{H^+} respectively. Eliminating μ_e^ϵ from the above equation and the relation

*) The complex of the rate-determining step $2H(a) \rightarrow H_2$ or $H_2^+(a) + \epsilon \rightarrow H_2$ [$H(a)$: adsorbed hydrogen atom, $H_2^+(a)$: adsorbed hydrogen molecule-ion, ϵ : metal electron] respectively of the catalytic or electrochemical mechanism is derivable as a whole from one hydrogen molecule, whereas two complexes of the rate-determining step $H^+ + \epsilon \rightarrow H(a)$ of the slow discharge or the proton transfer mechanism are formed from one hydrogen molecule.

**) Overpotential η means here the electrode potential of the test electrode referred to the reversible hydrogen electrode at the same condition.

$$\mu^{\text{H}_2} = 2\mu^{\text{H}^+} + 2\mu^{\text{e}}$$

valid to the reversible hydrogen electrode, we have

$$\mu^{\text{H}_2} - 2(\mu^{\text{H}^+} + \mu^{\text{e}}) = 2F\eta = \Delta F, \quad (4)$$

i.e., $2F\eta$ gives the free energy increment ΔF associated with the reaction



The $\log_{10} B$ is now expressed as

$$\log_{10} B = \log_{10} i + T \left(\frac{\partial \log_{10} i}{\partial T} \right)_{\Delta F}, \quad (6)$$

i.e., in a general form aside from the forward reaction rate given formally in terms of the associated current density.

Eq. (6) covers, besides hydrogen electrode reactions, the other processes of hydrogen traced isotopically or by parahydrogen conversion as the special case, when $\Delta F=0$, i.e., at the overall equilibrium.

§ 3. Statistical-Mechanical Theory of $\log B$

The value of $\log_{10} B$ will now be theoretically developed with regard to the generalization in the foregoing section.

The i in (6) is generally given as^{*)}

$$i = \frac{2F}{\nu N_A} \frac{kT}{h} \exp \left(\frac{\mu^{\text{I}} - \mu^*}{RT} \right) \quad (7)$$

provided that two elementary charges are associated with every overall reaction as in the case of hydrogen electrode reaction: ν is the stoichiometric number of the rate-determining step r , N_A the AVOGADRO number, k or h the BOLZMANN or the PLANCK constant and μ^{I} or μ^* the chemical potential of the initial or the critical complex of r respectively.

The μ^* of a heterogeneous step is expressed^{**)} as

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

where G^* is the number of surface sites σ^* for the critical complex per unit area, $\theta_{\sigma^*(0)}$ the probability of σ^* being at the unoccupied state $\sigma^*(0)$ and q^* the BOLZMANN factor of the reversible work required to

*) The equation is obtained from Eqs. (8.12), (24.1. \bar{v}) and (26.1. \bar{v}) of Ref. 3.

**) Cf. Ref. 3, § 24 and Eq. (8.12).

set up a critical complex in a definite $\sigma^*(0)$.

The $\log_{10} B$ is given according to (6), (7) and (8) as

$$\log_{10} B = \log_{10} B_0 + \theta_T, \quad (9. B)$$

where

$$\log_{10} B_0 = \log_{10} \left(\frac{2F}{\nu N_A} \frac{kT}{h} G^* \right) + \frac{1}{2.3} + \frac{1}{2.3R} \left(\frac{\partial \mu^I}{\partial T} \right)_{\Delta F} + \left(\frac{\partial T \log_{10} q^*}{\partial T} \right)_{\Delta F}, \quad (9. B_0)$$

$$\theta_T = \left(\frac{\partial T \log_{10} \theta_{\sigma^*(0)}}{\partial T} \right)_{\Delta F}. \quad (9. \theta)$$

The $\log_{10} B_0$ gives the value of $\log_{10} B$ in the particular case, when $\theta_{\sigma^*(0)}=1$ and in consequence $\theta_T=0$ i.e., when σ^* is unoccupied with certain.

In the other particular case when $\theta_{\sigma^*(0)} \ll 1$, σ^* being occupied nearly with certain by the initial complex I of the rate-determining step, θ_T is developed according to the general relation^{*}

$$\frac{\theta_{\sigma^*(I)}}{\theta_{\sigma^*(0)}} = q^I \exp \left(\frac{\mu^I}{RT} \right), \quad (10)$$

where q^I is the BOLTZMANN factor of the reversible work required to set up I in a definite $\sigma^*(0)$ and $\theta_{\sigma^*(I)}$ the probability of σ^* being occupied by I^{**}.

We have thus according to (9) and (10) for the value $\log_{10} B_1$ of $\log_{10} B$ at $\theta_{\sigma^*(I)}=1$

$$\log_{10} B_1 = \log_{10} \left(\frac{2F}{\nu N_A} \frac{kT}{h} G^* \right) + \frac{1}{2.3} + \left(\frac{\partial T \log_{10} (q^*/q^I)}{\partial T} \right)_{\Delta F}. \quad (11)$$

The reversible work $-RT \ln q^*$ or $-RT \ln q^I$ may be taken approximately constant independent of temperature at not very high temperature, where the probability of excited levels is but small because of the large vibrational frequencies of the critical or the initial complex confined in a narrow space of molecular dimension. We have thus $(\partial T \log_{10} q^*/\partial T)_{\Delta F} \simeq 0$, $(\partial T \log_{10} q^I/\partial T)_{\Delta F} \simeq 0$ and hence from (11) and (9. B_0)

^{*}) The equation is readily obtained from Eqs. (8. 12) and (5. 1) of Ref. 3.

^{**}) Cf. § 5, Ref. 3.

$$\log_{10} B_1 = \log_{10} \left(\frac{2F'}{\nu N_A} \frac{kT}{h} G^* \right) + \frac{1}{2.3} \quad (12. B_1)$$

$$\log_{10} B_0 = \log_{10} B_1 + \frac{1}{2.3 R} \left(\frac{\partial \mu^I}{\partial T} \right)_{\Delta F}. \quad (12. B_0)$$

The $\log_{10} B_1$ is numerically given by (12. B_1) as

$$\log_{10} B_1 = 9.70 - \log_{10} \nu + \log_{10} \frac{T}{298} \quad (13)$$

for $G^* = 10^{15}$ where the numerical term on the right is the value of $\log_{10} B_1$ at $\nu=1$ and 25°C .

The $\log_{10} B$ is now settled by evaluating $(\partial \mu^I / \partial T)_{\Delta F}$ and Θ_T .

§ 4. Evaluation of $(\partial \mu^I / \partial T)_{\Delta F}$

The I is $\text{H}^+ + \epsilon$ for the slow discharge mechanism of hydrogen electrode reaction (5) and hence according to (4)

$$\mu^I \equiv \mu^{\text{H}^+} + \mu^\epsilon = \frac{1}{2} \mu^{\text{H}_2} - \frac{1}{2} \Delta F,$$

we have on the other hand

$$\mu^I = \mu^{\text{H}_2} - \Delta F$$

for the electrochemical or the catalytic mechanism of the hydrogen electrode reaction, when the respective initial complex $\text{H}_2^+(a) + \epsilon$ or $2\text{H}(a)$ is in partial equilibrium*) with the left $2\text{H}^+ + 2\epsilon$ of hydrogen electrode reaction (5), as



or



where $\text{H}_2^+(a)$ or $\text{H}(a)$ is hydrogen molecule-ion or hydrogen atom respectively adsorbed on the electrode. The latter expression of μ^I gives simultaneously that of the catalytic mechanism of the isotopic exchange or the parahydrogen conversion as its particular case, when $\Delta F=0$. We have further $\mu^I = \frac{3}{2} \mu^{\text{H}_2}$ for the COUPER and ELEY's mechanism¹⁰⁾ at-

*) We will call a rate-determining step r to exist, if the steady rate of the overall reaction is sufficiently approximated by means of the assumption, that the constituent steps other than r are practically in equilibrium, i. e., in partial equilibrium.

tributed to the parahydrogen conversion, where I consists of a hydrogen molecule and an adsorbed hydrogen atom in equilibrium with hydrogen molecules.

The $(\partial\mu^I/\partial T)_{\Delta F}$ is now given throughout the above cases as

$$\left(\frac{\partial\mu^I}{\partial T}\right)_{\Delta F} = \frac{1}{m} \left(\frac{\partial\mu^{H_2}}{\partial T}\right)_{\Delta F}, \quad (15)$$

where m is 2 for the slow discharge mechanism, 1 both for the electrochemical and the catalytic mechanism and 2/3 for the COUPER and ELEY's mechanism, ν being in the respective cases 2, 1 and 1 referred to one hydrogen molecule undergoing the process. The proton transfer mechanism of EYRING *et al.* belongs to the case $\nu=m=2$.

The $(\partial\mu^{H_2}/\partial T)_{\Delta F}$ is now the negative partial molal entropy of hydrogen gas given numerically as

$$-\left(\frac{\partial\mu^{H_2}}{\partial T}\right)_{\Delta F} = \bar{S}_1^{H_2} + \frac{7}{2} R \ln \frac{T}{298} + R \ln \frac{760}{P_{\text{mm Hg}}}. \quad (16. a)$$

where

$$\bar{S}_1^{H_2} = 31.211 \text{ cal/deg}, \quad 25^\circ\text{C}, 1 \text{ atm}^{11)} \quad (16. b)$$

is the partial molal entropy of hydrogen gas at the specified state. The $\log_{10} B_0$ is now according to (12, B_0) and (16)

$$\log_{10} B_0 = \log_{10} B_1 - \frac{6.83}{m} - \frac{7}{2m} \log_{10} \frac{T}{298} + \frac{1}{m} \log_{10} \frac{P_{\text{mm Hg}}}{760}. \quad (17)$$

It might be mentioned that $(\partial\mu^I/\partial T)_{\Delta F}$ is expressed as (15) in terms of a mere number m only in the particular case when a set of stable molecules yields just a definite number of I without surplus or defect, as $\frac{3}{2}H_2$ just provides I of the COUPER and ELEY mechanism.¹⁰⁾ In general the left L of the chemical equation of the overall reaction yields,¹²⁾ through steps other than the rate-determining one, ν pieces of I and simultaneously the surplus W, including the defect, if any, algebraically with minus sign. Since the steps other than the rate-determining one are in partial equilibrium^{*)}, the resultant partial reaction $L = \nu I + W$ must be too and hence we have

$$\mu^I = \frac{\mu^L - \mu^W}{\nu}.$$

*) Cf. footnote *) on p. 47.

Writing for example the chemical equation of the process traced by parahydrogen conversion as $H_2=H_2$, we see that W for the COUPER-ELEY mechanism is $-H(a)$, i. e., a defect, whereas none for the electrochemical or the catalytic mechanism.

The ν - and m -values are summarized in Table 2.

TABLE 2.

Mechanism	ν	m
Electrochemical, Catalytic	1	1
Slow discharge, Proton transfer	2	2
COUPER-ELEY	1	2/3

§ 5. Evaluation of θ_T

The $\log_{10} B$ is now numerically determined according to (9. B), (17) and (13) by evaluating θ_T of (9. θ).

The detailed calculation has been conducted in the case of the catalytic mechanism by the equation

$$\theta_{\sigma^*(0)} = (1-\theta)^2 / \{1 + \theta(e^{u_i \theta / RT} - 1)\} \quad (18. a)$$

derived⁽⁶⁾ recently, where θ denotes the fraction of the electrode surface covered by $H(a)$ and u_i the interaction potential between two $H(a)$ situated in the same σ^* , which consists of an adjacent pair of adsorption sites of $H(a)$. The θ is given^{(5)(6)*)} as

$$\frac{\theta}{1-\theta} = \exp \left(\frac{-\epsilon_0 - u\theta + \frac{\mu^{H_2}}{2}}{RT} \right) \quad (18. b)$$

in the present applications of the catalytic mechanism in Table 1, when the chemisorbed hydrogen atoms happen to be in equilibrium with hydrogen molecules and hence $2\mu^{H(a)} = \mu^{H_2}$, where $\mu^{H(a)}$ is the chemical potential of $H(a)$, u the potential of repulsion upon an adsorbed hydrogen atom exerted by its all neighbours at $\theta=1$, and ϵ_0 the height

*) The equation is derived by expressing $\mu^{H(a)}$ according to Eqs. (5.1) and (8.12) of Ref. 3 as $\mu^{H(a)} = RT \ln \frac{\theta}{1-\theta} - RT \ln q^{H(a)}$, the reversible work $-RT \ln q^{H(a)}$ as $\epsilon_0 + u\theta$ and equating $\mu^{H(a)}$ thus obtained to $\mu^{H_2}/2$.

of the lowest energy level of adsorbed hydrogen atom at $\theta=0$ referred to that of hydrogen molecule.

Using the values $u=25$ kcal, $u_1=1.4$ kcal, $\epsilon_0=-11$ kcal derived⁶⁾ from the experimental results of KWAN¹³⁾ and the statistical mechanical value of μ^{H_2}

$$\mu^{\text{H}_2} = -7250^{*)} + \frac{7}{2} RT \log \frac{298}{T} + RT \log \frac{P}{760} \text{ cal}$$

θ and θ_r are evaluated according to (18) and (9. θ) as

TABLE 3.

$T^\circ\text{C}$	$P\text{mmHg}$	θ	θ_r
25	760	0.314	0.023
31	760	0.311	0.027
70	387	0.283	0.062
100	431	0.269	0.079
125	100	0.236	0.124

and the resultant values of $\log B_{10}$ calculated by (9. B), (17) and (13) are given under " $\nu=m=1$ " in Row III, IV and V of Table 1.

The process of hydrogen conversion traced by deuterium exchange may possibly be governed by some act of single H(a), in which case $\nu=m=2$ and

$$\theta_{\sigma\kappa_0} = 1 - \theta \quad (19)$$

where θ is the fraction of the catalyst's surface covered by H(a), Eq. (19) may also be taken valid for the COUPER and ELEY's mechanism of parahydrogen conversion, where $\nu=1$, $m=2/3$. The appropriate value of θ_r is calculated according to (9. θ), (19) and (18. b) using the data of u and ϵ_0 given above and henceforth $\log_{10} B$ is worked out according to (9. B), (17) and (13) as shown under the column " $\nu=1$, $m=2$ " in Row III and IV for the exchange reactions or under " $\nu=1$, $m=2/3$ " in Row V for the parahydrogen conversion in Table 1.

The contribution of θ_r in all the above cases are shown in paren-

*) The value of μ^{H_2} at 25°C and 760 mmHg calculated according to the expression $\mu^{\text{H}_2} = RT \ln N^{\text{H}_2} - RT \ln \frac{(2\pi m^{\text{H}_2} kT)^{3/2}}{h^3} \frac{4\pi^3 I^{\text{H}_2} kT}{h^2}$, where N^{H_2} is the concentration, m^{H_2} the mass and $I^{\text{H}_2}=4.66 \times 10^{-40}$ gm cm² the moment of inertia respectively of hydrogen molecule.

theses respectively next to the relevant values of $\log_{10} B$; they are appreciably small, perhaps, quite within the errors of experimental determination of $\log_{10} B$.

In the case of hydrogen electrode reaction, when i is extrapolated from the range of η , where the TAFEL's relation holds, it is consistent to calculate $\log_{10} B$ theoretically according to (6) for the appropriate value of ΔF ; as $\log_{10} B_0$ does not depend on ΔF as seen from (12. B_1) and (17), the dependence of $\log_{10} B$, if any, is according to (9. B) solely due to θ_T .

Experimental values of $\log_{10} B$ of hydrogen electrode reaction given in Table 1 are all those of mercury, for which the electrochemical mechanism is valid.¹⁴⁾ It has been shown in the previous work¹⁴⁾ for the latter case, that the occupant of σ^* is practically $H_2^+(a)$ alone over the region where the TAFEL law holds, and that the appropriate value of $\theta_{\sigma^*(H_2^+)} = 1 - \theta_{\sigma^*(H)}$ is comparable with but less than unity.

The θ_T is now estimated below on these bases, assuming, besides, that the $H_2^+(a)$ alone compose the HELMHOLTZ double layer, i.e., as

$$1 - \theta_{\sigma^*(H)} = \theta_{\sigma^*(H_2^+)} = CEN_A/G^*F, \quad (20)$$

where C is the capacity of the double layer, E the electrostatic potential in the bulk of the solution referred to the electrode, N_A the AVOGADRO number, F the FARADAY constant and G^* the number of σ^* . The E is expressed according to the definition as

$$E = -\eta + E_{O-H_2}, \quad (21)$$

where E_{O-H_2} is the potential of the electrode which has no potential difference from an solution, taken sometimes as realized with the electrode at the electrocapillary maximum, referred to the reversible hydrogen electrode and $-\eta$ by definition the potential of the latter minus that of the test electrode.

The θ_T is now according to (9. θ), (4) and (20)

$$\begin{aligned} \theta_T = & \left(\frac{\partial T \log_{10} \theta_{\sigma^*(H_2^+)}}{\partial T} \right)_\eta = \log_{10} (1 - \theta_{\sigma^*(H_2^+)}) \\ & - \frac{1}{2.3} \frac{\theta_{\sigma^*(H_2^+)}}{1 - \theta_{\sigma^*(H_2^+)}} \left\{ \left(\frac{\partial \ln C}{\partial \ln T} \right)_\eta + \left(\frac{\partial \ln E}{\partial \ln T} \right)_\eta \right\}. \end{aligned} \quad (22)$$

The $(\partial \ln C / \partial \ln T)_\eta$ in the above equation is identified with $d \ln D / d \ln T = -1.343^{15)}$ in accordance with the expression $C = D/4\pi d$ of the capacity of the double layer, where D is the dielectric constant and d the thick-

ness of the double layer, i.e., as

$$\left(\frac{\partial \ln C}{\partial \ln T}\right)_\eta = \frac{d \ln D}{d \ln T} = -1.343, \quad 20^\circ\text{C}. \quad (23)$$

Writing $E_{\text{O-H}_2}$ as

$$E_{\text{O-H}_2} = E_{\text{O-C}} + E_{\text{C-H}_2}, \quad (24)$$

where $E_{\text{O-C}}$ is the potential of the electrode of no potential difference from the solution referred to the normal calomel electrode and $E_{\text{C-H}_2}$ the potential of the latter calomel electrode referred to the reversible hydrogen electrode, we have

$$(\partial \ln E / \partial \ln T)_\eta = -0.133 \quad (25)$$

for $\eta = -0.9$, where the TAFEL's relation is experimentally known to hold, from (21), (24) and the known values,

$$\begin{aligned} E_{\text{O-C}} &= -0.56 \text{ volt}, & dE_{\text{O-C}}/dT &= -0.00007 \text{ volt/deg.}^{16)} \\ E_{\text{C-H}_2} &= +0.34 \text{ volt}, & dE_{\text{C-H}_2}/dT &= -0.00024 \text{ volt/deg.}^{17)} \end{aligned} \quad (26)$$

The θ_T is now according to (22), (23) and (25)

$$\theta_T = -0.30 + \frac{1}{2.3} (1.343 + 0.133) = 0.34$$

for $\theta_{\sigma^*(\text{H}_2^+)} = 0.5$, around which the TAFEL law has been shown valid.¹⁴⁾

The value of $d \ln D / d \ln T$ given by (23) corresponds however to the macroscopic dielectric constant $D=80$ of water. D must approach the saturation value i.e., that of the optical polarizability¹⁸⁾ in the neighbourhood of ions and hence the effective value of D of the double layer must do similarly with increasing population of ions there. The capacity is calculated on the basis of the thickness 1.5 \AA of the double layer as $480 \mu\text{F}$ or $10 \mu\text{F}$ according as D is taken as the macroscopic value 80 or as the optical value 1.7^*). In agreement with the theoretical result, the capacity of hydrogen electrode decreases, as observed, from several hundred microfarads at lower value of $-\eta$, to a few ten microfarads¹⁹⁾ at its higher value, where the TAFEL law holds. As the optical dielectric constant should have no temperature coefficient, we should expect on these grounds that $d \ln D / d \ln T$ is more or less smaller than the macroscopic value -1.343 used above and in

*) The optical value of D is taken as the square of the refractive index of water 1.3, which is extrapolated from experimental data for visible and ultraviolet lines to infinite frequency according to KETTELER-HELMHOLTZ's dispersion formula.

consequence that θ_T is smaller than that given by (22).

The value of $(\partial \ln E / \partial \ln T)_T$ may deviate in the actual case from that given by (25) along with the insufficient validity of the HELMHOLTZ double layer but we might safely expect that the deviation would be at most of the same order of magnitude as its own value of (25), whose contribution to θ_T is only 0.06 according to (22) and (25); the deviation, if any, would not make much difference. The same would be the case with the unreliability associated with the "absolute potential" E_{O-C} and its temperature coefficient, whose contribution to θ_T is, according to (21), (24), (26) and (22), only 0.013.

Summing up θ_T should amount only to a few tenth over the region of polarization, to which the value of $\log_{10} B$ is essentially relevant as mentioned above, in the case of the electrochemical mechanism of the hydrogen electrode of mercury, whereas in the other cases θ_T rarely exceeds 0.1 as shown in Table 1. This account for the observed constancy of $\log_{10} B$ given by (9. *B*) as being essentially due to that of $\log_{10} B_0$. Eq. (17) and (13) state now approximately identifying $\log_{10} B_0$ with $\log_{10} B$ that the latter decreases with decreasing pressure and increasing temperature as stated in the introduction, provided that $m < 3.5$.

Table 1 shows $\log_{10} B_0$ values in place of $\log_{10} B$ neglecting θ_T in the case of the hydrogen electrode of mercury in Row I and II respectively under the column " $\nu = m = 1$ " for the electrochemical mechanism and " $\nu = m = 2$ " for the slow discharge mechanism inclusive of the proton transfer mechanism.

We see from the Table that only the electrochemical and the catalytic mechanism are capable of accounting for the observed values of $\log_{10} B$ satisfactorily.

§ 6. Concluding Remarks

It has been shown by the investigation of experimental data that there is no ground to attribute the law found by EYRING *et al.*¹⁾ to the water molecule playing the leading part in the hydrogen electrode reaction. Theoretical consideration has revealed on the other hand that the law holds to the catalytic and the electrochemical mechanism, only, for which $\nu = m = 1$ and the critical complex is confined in a narrow space σ^* of molecular dimension, provided that the number of σ^* is of order of 10^{15} cm.^{-2} . The above theoretical conclusion denies the me-

chanism of EYRING *et al.* itself proposed on the ground of the law.

As seen from (9.B) and (12), the decisive part is played in the theoretical value of $\log_{10} B$ by the entropy of the initial complex I of the rate-determining step. The I and hence the rate-determining step itself may be diagnosed by the comparison of observed $\log_{10} B$ -value with its theoretical value.

So far we have fixed G^* at 10^{15} . When θ_T is negligible as in most of cases, (9.B), (12.B₀) and (15) provide a linear relation between $\log_{10} B$ and $(\partial\mu^{H_2}/\partial T)_{\Delta F}$, i. e.,

$$\log_{10} B = \log_{10} B_1 + \frac{1}{2.3 mR} \left(\frac{\partial\mu^{H_2}}{\partial T} \right)_{\Delta F}.$$

Sufficient data will decide G^* in the constant term $\log_{10} B_1$ as well as m in the coefficient of $(\partial\mu^{H_2}/\partial T)_{\Delta F}$ from the linear relation.

References

- 1) EYRING, GLASSTONE and LAIDLER, J. Chem. Phys. **7**, 1053 (1939).
- 2) BOWDEN and AGAR, Ann. Rep. Chem. Soc. **35**, 90 (1938).
- 3) HORIUTI, J. Research Inst. Catalysis **1**, 8 (1948).
- 4) HORIUTI and OKAMOTO, Sci. Pap. Inst. Phys. Chem. Res. Tokio **28**, 231 (1936); Bull. Chem. Soc. Japan **13**, 216 (1938).
HORIUTI and IKUSIMA, Proc. Imp. Acad. Tokio **15**, 39 (1939).
HORIUTI, Sci. Pap. Inst. Phys. Chem. Res. Tokio **37**, 274 (1940).
- 5) OKAMOTO, HORIUTI and HIROTA, Sci. Pap. Inst. Phys. Chem. Res. Tokio **29**, 223 (1936).
- 6) HORIUTI, J. Research Inst. Catalysis **4**, 55 (1956).
- 7) HIROTA and HORIUTI, Sci. Pap. Inst. Phys. Chem. Res. Tokio **30**, 151 (1936).
- 8) HORIUTI and SUZUKI, Shokubai (Catalyst) **4**, 1 (1948) (in Japanese).
- 9) FARKAS, *Orthohydrogen, Parahydrogen and Heavy Hydrogen*, p. 99 (Cambridge Univ. Press, 1935).
- 10) COUPER and ELEY, Discussion, Faraday Soc. **8**, 172 (1957).
- 11) *Selected Values of Chemical Thermodynamic Properties*, Circular of The National Bureau of Standards 500, p. 9 (1952).
- 12) HORIUTI, *Advances in Catalysis*, Vol. **9**, in the press.
- 13) KWAN, J. Research Inst. Catalysis **1**, 81 (1949).
- 14) HORIUTI, KEI and HIROTA, *ibid.* **2**, 1 (1951).
- 15) HARNED and OWEN, *The Physical Chemistry of Electrolytic Solutions*, 2nd ed., p. 118 (1950).
- 16) GRAHAM, LARSEN and POTH, J. Am. Chem. Soc. **71**, 2978 (1949).
- 17) BUTLER, *The Fundamentals of Chemical Thermodynamics*, p. 154 (1939).
- 18) WEBB, J. Am. Chem. Soc. **48**, 2589 (1926).
- 19) DOLIN and ERSHLER, Acta Physicochim. USSR **13**, 747 (1941).