STOICHIOMETRIC NUMBER OF THE HYDROGEN ELECTRODE PROCESS ON NICKEL:
COMMENT ON A PAPER OF BOCKRIS AND POTTER

By

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§ 1. Introduction

One of the present authors and his collaborators\(^3\) put forward the dual theory of the hydrogen electrode process,

\[
2H^+ + 2e = H_2
\]

i.e. that the reaction proceeds alternatively, depending on the electrode material and the electrolyte, either through the sequence of steps,

\[
H^+ + e \rightarrow H(a), \quad 2H(a) \rightarrow H_2
\]

(2. a), (2. b)

with the rate governed by (2. b) or through that,

\[
2H^+ + e \rightarrow H^+_2(a), \quad H^+_2(a) + e \rightarrow H_2
\]

(3. a), (3. b)

the last step controlling the rate, where \(e\) is metal electron in the electrode, \(H(a)\) adsorbed hydrogen atom and \(H^+_2(a)\) adsorbed hydrogen-molecule-ion on the electrode surface; these mechanisms have been called by them the catalytic and the electrochemical mechanism\(^1\) respectively.

Number of evidences\(^3\) has been given for the mechanisms, some\(^8\) of them being based on the concept of the stoichiometric number \(\nu(r)\) introduced by Horiuti et al.\(^13\): \(\nu(r)\) of (2. a) is for instance 2, whereas that of (2. b), (3. a) or (3. b) is 1. The \(\nu(r)\) will hereafter be referred particularly to the rate-determining step, if not otherwise stated.

\(^{1)}\) According to the original statement of the mechanism, it was the act of formation of hydrogen molecule from a chemisorbed hydrogen atom, a proton, and a metal electron, which governed the rate of the electrode process. The present expression of the mechanism was adopted, since it has later turned out by an actual calculation that the electronic state of \(H\) and \(H^+\) before the neutralization was such as adequately covered by words "hydrogen-molecule-ion adsorbed on the electrode" [cf. ref. 8].
The experimental determination of $\nu(r)$ was based on the general equation$^{(5,7)}$:

$$V_s = \Phi \left[ 1 - \exp \left( \frac{\Delta F}{\nu(r)RT} \right) \right]$$

(4)

for the steady rate $V_s$ of the overall reaction, its forward rate $\Phi$ and free energy increase $\Delta F^\star$ of the whole assembly associated with the overall reaction, where $R$ and $T$ are the gas constant and absolute temperature respectively.

Eq. (2) is written particularly for the hydrogen electrode process as$^{(5,7)}$

$$i_s = \bar{i} \left[ 1 - \exp \left( \frac{2F\eta}{\nu(r)RT} \right) \right]$$

(5)

where $i_s$ and $\bar{i}$ are currents respectively corresponding to $V_s$ and $\Phi$, and $2F\eta$ is the expression of $\Delta F$ in terms of Faraday $F$ and overpotential $-\eta$. Deriving limiting value $\bar{i}_o$ of $\bar{i}$, i.e.

$$\bar{i}_o = \lim_{\eta \to 0} \bar{i}$$

from (5), we have

$$\nu(r) = -2\bar{i}_o F \left[ RT \left( \frac{d\bar{i}}{d\eta} \right) \right]$$

(6)

Reaction (1) on nickel was now shown to proceed through the catalytic mechanism$^{(5,7)}$, which requires $\nu(r)=1$, in accordance with the experimental results of Horiuti and Okamoto$^{(5,7,***)}$ obtained by using deuterium for labelling the forward current $\bar{i}$.

Bockris and Potter$^{(5)}$ report recently that $\nu(r)=2$ for the same reaction, analysing observed $\bar{i}$ using (6) without, however, measuring $\bar{i}_o$ directly. Below will be discussed the validity of their procedure and the conclusion arrived at in contradiction to our result mentioned above.

$^\star$ The $\Delta F$ is for instance,

$$\Delta F = \mu^{H_2} - 2\mu^{H^+} - 2\mu^e$$

for reaction (1), where $\mu^{H_2}$, etc. are chemical potentials of $H_2$, etc. respectively.

$^{**}$ The same notations are employed as those used by Bockris and Potter (ref. 1) except $\nu(r)$ for the sake of comparison.

$^{***}$ The $\bar{i}_o$ observed by deuterium agrees with that derived from $\left( \frac{d\bar{i}}{d\eta} \right)_{\eta \to 0}$ putting $\nu(r)=1$ in (6) as shown in ref. (7); $n$ in ref. (7) equals $2\nu(r)$ according to its definition.
§ 2. Consistency of The Procedure

Bockris and Potter\(^b\) determine \(i_0\) by extrapolating observed \(\log i_0\) at higher overpotential \(-\eta\) linearly to \(\eta=0\). Determining \(\left(\frac{di_0}{d\eta}\right)_{\eta=0}\) directly from observation on the other hand, they arrive at the conclusion \(\nu(r)=2\) according to (6). However, sufficient data are not given in their paper\(^b\) to enable us exclusively to follow their calculation. We should rather proceed to examine the consistency between their conclusion, \(\nu(r)=2\) and their procedure of linear extrapolation of \(i_0\), admitting the reported typical result of observation of Fig. 7 in their paper\(^b\).

Putting \(\nu(r)=2\) according to them in (5), we obtain \(i\) directly from observed \(i_0\) and \(\eta\). The upper group of points in Figs. 1 and 2 shows the result by the plot of \(\log i\) against \(\eta\), the bigger black dot on the ordinate giving \(\log i_0\) derived from the observed value of \(\left(\frac{di_0}{d\eta}\right)_{\eta=0}\).

![Dependence of Forward Current i on Overpotential -\eta](image)

**Fig. 1.**

Dependence of Forward Current \(i\) on Overpotential \(-\eta\)
Derived from Bockris and Potter's Observation,
J. Chem. Phys. 20, 614 (1952), Fig. 7, 0.005 N NaOH at 3°C.
by (6) with $\nu(r)=2$ as indicated there. The cross $\times$ on the ordinate shows $\log i_e$ extrapolated by them at $\eta=0$ from higher overpotential region, which they identify with $\log i_0$.

It is required for the latter identification being valid, that $i_e$ practically equals $i$ at least over higher overpotential region and that $\log i$ runs linearly with $\eta$ up to $\eta=0$. The former requirement is fulfilled according to (5), whereas the latter is not as shown in Figures, the points derived from their conclusion and observation deviating badly from any straight line through the cross.

Lower points $o$'s show values of $i$ alternatively calculated from their observation according to (5) putting $\nu(r)=1$, the bigger circle on the ordinate giving $i_0$ derived similarly from the observed $\left(\frac{di}{d\eta}\right)_{\eta=0}$ by (6) with $\nu(r)=1$ as indicated there. The points now deviate downwards from the straight line of extrapolation through the cross showing that the linear relation at higher overpotential is not obeyed at lower overpotential in any way.
Their conclusion and the assumption underlying their procedure thus contradict each other, if any regard were paid to (5), from which (6) used by them was derived.

BOCKRIS and POTTER arrive at (6), disregarding (5), by transforming ungrounded rate expressions (5) and (6) in their paper inexact, because they tacitly assume the standard activation free energy constant independent of \( \gamma \); this is not at all assured, since it may in general vary with the variation of the interaction among adsorbed particles on the electrode along with that of \( \gamma \).

Eq. (6) used by them is correct in so far as (5) is correct but their result \( \nu(r) = 2 \) is incorrect, since then their observation defy the assumed linearity basic to their procedure.

§ 3. Review on the Theory of Stoichiometric Number

Eqs. (5) and (6) in BOCKRIS and POTTER's paper give now an impression, although not affirmative of course, their origin being not given explicitly, that they are specially referred to step (2.a), after the manner of EYRING, GLASSTONE and LAIDLIER; the former group of authors has given an expression of their transition state method to the concept of the rate-determining step of (2.a) originally put forward by Erdey-Grusz and Volmer and further worked out by HORIUTI and POLANYI.

An expression of \( \nu(r) \) should not of course imply any peculiarity of a particular step, if it be used experimentally to find out \( \nu(r) \) of an \textit{a priori} unknown rate-determining step.

Another impression is that the stoichiometric number were treated as if inherent to each step. That this is not true may be shown by a simple example below. The process (3.a) of formation of \( H^+_2(a) \) may be detailed as

\[
H^* + e^- \rightarrow H(a), \quad H^* + H(a) \rightarrow H^*_2(a)
\]  

We see immediately that the stoichiometric number of one and the same step (7.a) or (2.a) is either 1 or 2 depending upon the sequence to which it belongs.

These points as well as the below-quoted remark of BOCKRIS and POTTER on our paper leads the present authors to feel it worth while briefly to review the theory of the stoichiometric number with re-

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* The electrostatic part of the interaction is separately allowed for from the standard activation free energy but the non-electrostatic part not.
ference to the concept of the rate-determining step and of the partial
equilibrium in order to avoid misunderstanding and confusion: "Oka-
moto, Horiiuti and Hirota have applied the transition state theory to
the recombination of hydrogen atoms at a nickel cathode, but this
treatment assumes that Nernst emf equation applies to hydrogen atoms
in an irreversible reaction, and this has not been validly demonstrated."

Let there exist a rate-determining step \( r \) prevailing in a certain
steady reaction, the initial complex \( I(r) \) or the final one \(^*\) \( F(r) \) of \( r \)
being formed from or converted into the chemical species implied in
the chemical equation of the overall reaction by the respective sequence
of steps in general. If the backward rate \( \tilde{v}(r) \) of \( r \) is insignificant
compared with the forward one \( \bar{v}(r) \), the steps forming \( I(r) \) at least,
must be in partial equilibrium, since otherwise the activity of \( I(r) \)
and hence \( \bar{v}(r) \), equaling in this case \( v(r) \) times the steady rate \( V_s \)
of the overall reaction, should vary with the rates of these steps forming
\( I(r) \) in contradiction to the premise of \( r \) being the rate-determining
step.

If \( \bar{v}(r) \) is significant, it is similarly required that every step con-
verting \( F(r) \) into the resultant of the overall reaction is also in partial
equilibrium. It follows that \( V_s \) of the steady reaction rate in the
presence of the rate-determining step is adequately derived from such
an idealized state as all constituent steps but \( r \) are practically in
equilibrium; the errors, if any, introduced by the additional assumption
of the partial equilibrium of steps converting \( F(r) \), must also be insig-
nificant in the case of insignificant \( \bar{v}(r) \).

What was done by Okamoto, Horiiuti and Hirota\(^3\) with regard to
the adsorbed hydrogen atom, commented upon by Bockris and Potter\(^1\)
as the "assumption of Nernst emf equation" as quoted above, was to
equate its chemical potential to the sum of the chemical potentials of
hydrogen ion and of metal electron, as the inevitable consequence of
(2. b) being the rate-determining step; valid demonstration of the former
is synonymous with that of the latter.

With reference to the idealized state of the steady reaction, (4)
is derived below starting from a simple theorem\(^{11(1)}\)**\(*\),

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\(^*\) It is meant by the initial complex the set of chemical species involved in the step at
the state prior to it, whereas the final complex \( F \) that posterior to it; the reactant
or resultant, the usual term for the set, is reserved here for the left or the right of
the chemical equation of the overall reaction.

\(^{**}\) Eq. (8) is obtained by rewriting (26.4) of Ref. (11) according to (8.12) there.
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\[
\frac{\tilde{v}(r)}{\bar{v}(r)} = \exp\left(-\frac{\Delta F(r)}{RT}\right) \quad (8)
\]

valid, as follows from its derivation\(^{15}\), for any step \(r\) involved in a steady overall reaction proceeding at thermal equilibrium, homogeneous or heterogeneous in an assembly, gaseous or condensed, where \(\Delta F(r)\) is the free energy increase associated with \(r\) similarly as \(\Delta F'\) is associated with the overall reaction.

The steady rate \(V_s\) of the overall reaction is expressed as

\[
V_s = \frac{\tilde{v}(r) - \bar{v}(r)}{\nu(r)} \quad (9)
\]

for any \(r\) involved according to the definition of \(\nu(r)\).

Specializing \(r\) now again to the rate-determining step and referring to the idealized state, we have from (8) and (9)

\[
V_s = \frac{\tilde{v}(r) - \bar{v}(r)}{\nu(r)} \quad (10. V)
\]

and

\[
\Delta F'(r) = \Delta F'/\nu(r) \quad (10. F')
\]

where

\[
\bar{v} = \frac{\tilde{v}(r)}{\nu(r)}
\]

since no free energy change is associated with any step except \(r\) according to (8), the forward and the backward rate of the former being practically balanced at its partial equilibrium, whereas \(r\) brings about \(\nu(r)\Delta F'(r)\) free energy increase for every act of the overall reaction making the total increase \(\Delta F'\).

Substituting \(\Delta F'(r)\) from (10. \(F'\)) into (10. \(V\)), we have (4).

Summary

Bockris and Potter's result on the stoichiometric number \(\nu(r)\) of the rate-determining step (number of acts of the step associated with every act of the overall reaction) of hydrogen electrode process on nickel was discussed for elucidating the discrepancy between their, \(\nu(r)=2\) and our, \(\nu(r)=1\).

It was shown that their conclusion leads to the result contradicting the assumption underlying their procedure in working out \(\nu(r)\), that the logarithm of the forward current varies linearly with the overpotential.
Theory of stoichiometric number was briefly reviewed with reference to the concept of the rate-determining step and of the partial equilibrium.

References

3) OKAMOTO, HORIUTI and HIROTA, ibid. 29, 223 (1936).
4) HIROTA and HORIUTI, ibid. 30, 151 (1936).
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DISCUSSIONS

The foregoing comment (abbreviated to HST in what follows) of Horiiuti and Sugawara (HS) upon the paper of Bockris and Potter (BP) has been submitted for publication to "The Journal of Chemical Physics" in which the latter paper of BP has appeared. HST has thus received first a comment (RI) of an anonymous referee, HS's remark (HSI) with regard to RI, a further comment (RII) of the same referee, finally a comment of another anonymous referee and was rejected on the ground of these comments.

HS, concluding these comments of the referees being completely ungrounded but due to their fundamental fallacies in the theory of reaction rate as well as their wrong attitude, have decided to reproduce here RI, HSI and RII and HS's further remark (HSII) in the form of discussions in order to submit them to the world's judgement. The comments of the second referee is however left out, because he gives, simply agreeing with the first referee, no new substantial point. Besides are excluded quotations from private communications and associated arguments, and several minor points inclusive of criticisms of the referees on HS's usage of English phrases and logics.

The points included fall thus into three groups respectively under topics i.e.

A. Validity of the catalytic mechanism.
B. Linearity of \( \log i \) to \( \gamma \).
C. Procedure of evaluating \( \nu(r) \).

Below will be given under each heading of the topics, RI, HSI, RII and HSII in succession.

A. Validity of the catalytic mechanism.

Referee (RI):—

I do not agree with the authors' claims in paragraph 3, page 2 or the detailed validity of his statements in the footnote,***. His earlier work, upon which these statements are essentially based, has been criticized by well-known workers in the field (e.g., Frumkin2).

The well-known worker criticizes in the paper 6, which the referee refers to, a mistake in the calculation by HIROTA and Horiuti, which has no bearing upon the catalytic mechanism. As to the latter, Frumkin states only his belief, without showing any ground, in the invalidity of Horiuti's argument, that the apparent variation of the observed current on the hydrogen electrode at constant overpotential, which was maintained by Frumkin as disproving the catalytic mechanism is due to the variation of conductivity of electrolyte, brought about by the experimental procedure of varying pH.

(The quotation here from private communication and associated discussions are omitted).

Referee (RII):

The authors cannot escape from the fact that their reasoning and conclusions concerning the catalytic mechanism has not been accepted by authors in other countries, in particular authors who have considerable international reputation in the field of hydrogen electrode kinetics, among whom Frumkin (ref. see RI) would surely occupy a high place. Other authors who have concluded that the catalytic mechanism has not the cogence ascribed to it by Horiuti are: Kimball, Glasstone and Glassner, Weiss, Lukowzew, de Bethune, Audubert and Bonnemay, Parsons and Bockris, Parsons, Hillson, Bockris. (Two following sentences relevant to the omitted sentences at the end of HSI are left out).

The principal evidence against the remarks of HST, p. 2 (par. 3) is

4) Lukowzew, Levina and Frumkin, ibid. 11, 21 (1939).

*) The calculation on the electrochemical mechanism on mercury cathode:— added at the conclusion.
that the mechanism of catalytic combination has now been definitely established as being associated with a TAFEL slope of approximately 0.029 at 25°C, whereas the experimental value is about 0.1 both in acid and most alkaline solutions.

**HORIUTI and SUGAWARA (HSII):**

The referee repeats in RII his point in RI precisely but with a pronounced gravity taking no notice of the reply in HSI. HS are interested in reason and nature rather than in reputation or majority, so that they can not escape from an utter contradiction against his new point in RII i.e. "The principal evidence against the remarks of HST".

It is shown by HORIUTI that what is called by the referee "the principal evidence" is essentially based on the erroneous expression for the rate \( \tilde{v} \) of a step, i.e.

\[
\tilde{v} = k_v a^t
\]  

(1)

where \( k_v \) is the rate constant or the specific rate and \( a^t \) the activity product of the initial complex \( I \), whereas the correct expression must include the activity coefficient \( f^* \) of the activated complex as

\[
\tilde{v} = k_v a^t / f^*
\]  

(2)

Eq. (2) gives the Tafel's constant \( \alpha \) at the condition where the reverse rate \( \tilde{v} \) is practically negligible according to (8), HST, as

\[
\alpha = - \frac{RT}{F} \frac{\partial \log \tilde{v}}{\partial \gamma} = - \frac{RT}{F} \frac{\partial \log k_v a^t}{\partial \gamma} + \frac{R \eta}{F} \frac{\partial \log f^*}{\partial \gamma}
\]

whereas (1) gives \( \alpha \) by the first term \(- \frac{RT}{F} \frac{\partial \log k_v a^t}{\partial \gamma}\) alone; (1) leads through the latter invariably to the conclusion \( \alpha = 2 \) for the catalytic mechanism given by TAFEL, however one details \( k_v \) and clothe it with modern words of kinetics, or to TAFEL's slope, \( b = - \frac{F}{RT} \frac{\partial \eta}{\partial \log i_c} = 0.029 \), with which, according to the referee, "the catalytic mechanism has now been definitely established as being associated" just as would

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2. HORIUTI, this volume, page 55.
have been said in the days of Tafel half a century ago, whereas \( f^* \) in Eq. (2) amends, through the second term \( \frac{RT}{F} \frac{\partial \log f^*}{\partial \eta} \), which amounts to ca. \(-1.5\), the classical value 2 of \( a \) to ca. 0.5 or the classical value 0.029 of \( b \) to ca. 0.1 over ca. 0.4 volt range of \( \eta \) in accordance with experiments.

The equivalent of Eq. (2) has been explicitly arrived at and the consequent behavior of \( a \) or \( b \) stated above actually elucidated before twenty years by Okamoto, Horiuti and Hirota\(^1\) through the generalization of the theory of reaction rate. Later have warned Glasstone, Laidler and Eyring in the footnote on page 576 of their book, “The Theory of Rate Process” New York 1941 that the result (of multiplication of \( k_v \) by \( a^\prime \)) should be divided by \( f^* \), although they have neither given \( f^* \) explicitly for the electrode phenomena, to which the above footnote is specially referred to, nor taken it into account in their practical treatment of this heterogeneous reaction. They deduced\(^2\), practically ignoring \( f^* \), the equivalent of the Tafel’s conclusion and the inference involved entered their book side by side with the above important note on \( f^* \).

This state of affairs might have led the followers of them to the persistence to the inexact equation (1) and to the associated “principal evidence” against the catalytic mechanism. As a matter of fact the point of the old paper of Okamoto, Horiuti and Hirota\(^1\) was correctly recognized just at that time by Frumkin\(^3\) to whom the referee attributed a high place, whereas confidentially ignored by recent authors especially Parsons\(^4\) and Bockris et al.\(^5\) and by the referee as well. Further, the number of authors, Kimball, Glasstone and Glassner\(^6\), Weiss\(^7\), de Bethune\(^8\), Audubert and Bonnemay\(^9\) among those enumerated by the referee in RII simply follow the above conclusion of Eyring, Glasstone

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and Laidler whereas none of them all gives any conclusion substantially independent of it against the catalytic mechanism. This state of affairs obliged Horiiuti to interpret and to develop the points of the old paper, with some revisions incorporating recent data, first in the terminology of the standard book of the majority of authors inclusive of the referee and then, after having shown the limit of applicability of the method of the latter work to the heterogeneous reaction, in the light of the generalized theory initiated in the old paper and developed later.

Conclusion:—Referee's claim against the catalytic mechanism is simply based on his fallacies of ignoring the activity coefficient of the activated complex necessarily to be implied in the rate expression.

B. Linearity of log \( i \) to \( \eta \)

Referee (RI):—

The criticism of BP's evaluation of \( \nu(r) \) is given here and will be explained because it is not expressed very clearly in the Japanese paper.

HS agree that BP's use of Eq. (6) (p. 2) is correct. However, they consider that BP's method of evaluating \( i_o \) (the exchange current, i.e., the velocity of both forward and reversible reactions of the hydrogen evolution reaction at the reversible potential) is invalid.

BP's method was to extrapolate overpotential values at high negative \( \eta \)'s (when the linearity of the plot of log \( i_e \) against \( \eta \) indicates that the back reaction \( H_2 \rightarrow 2H^+ + 2e^- \) contributes negligibly to \( i_e \)) and to take the intercept of log \( i_e \) at \( \eta = 0 \) as \( i_o \). (It may be noted that this method of evaluating \( i_o \) is the one which has been accepted since about 1930 and utilized by all workers who have hitherto evaluated \( i_o \). The first papers in which the method was used were by Bowden and Rideal.)

2) Horiiuti, this volume, p. 55
The method has not been previously questioned.

HS maintain that the method is invalid (p. 7, last par., line 3) because the assumption underlying it, i.e., that the velocity of the forward reaction depends logarithmically upon the overpotential, is invalid. It is certainly true that this assumption must be correct for the standard method of evaluating \( \dot{i}_o \) to be correct. However, this may be regarded as established upon the following grounds.

i) Its theoretical deduction is perfectly valid and has been given by a number of authors independently by different methods with the same result (cf. Volmer and Erdey-Gruez; Eyring, Glasstone and Laidler; Parsons). It is not correct to state (HST, p. 5, par. 2, line 5) that the standard free energy of activation varies with the overpotential. It is the electrochemical standard free energy (e.g., of activation) which varies with potential \( (\Delta \varphi) \), according to

\[
\Delta G_0 = \Delta G_0 + \alpha \Delta \varphi F \quad (\alpha = \text{const})
\]

but the standard free energy of a state depends only upon the properties of the constituent of the system in the standard state independently of the electric potential of this state*. Any other assumption denies the definition of electrochemical potential or free energy. If the atoms on the surface were close enough for their repulsive interactions to become important, the resultant energy change would be expressed in the potential term of (1).

ii) If the assumption made by BP were not correct, no linear relation of overpotential to \( \log \dot{i}_o \) would be observed, as is always the case when the overpotential is sufficiently negative to make the back reaction negligible in rate (cf. Reviews, e.g., Wirtz, Frumkin, Bockris). Thus, consider Eq. (5). It is

\[
i_o = \dot{i} \left(1 - \exp \left[ \frac{-2F\varphi}{v(r)RT} \right] \right)
\]

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or, for \( \eta \) large \(-ve\) (in practice \(< -50 \text{mv}\)),

\[
i_n = i
\]

But experimentally,

\[
\ln i_o \propto \eta
\]

\[
\therefore \quad i = \text{const.} \exp(-k\eta)
\]

where \( k \) is a constant.

Hence, the term \( i \), which BP assumed to have the form

\[
i = i_o \exp\left(-\frac{2\beta \eta F}{\nu(r)RT}\right) \quad (\beta = \text{const})
\]

is in fact the form made necessary by the experimental results, not only of BP's investigations but also those of all other workers who have found a linear relation between \( \eta \) and \( \log i_c \) in hydrogen evolution (see references above).

(Note that HS's Eq. (5) is identical in form with BP's Eq. (9).

The latter is

\[
i = i_o \exp\left[-\frac{2\beta \eta F}{\nu(r)RT}\right] \cdot \exp\left[\frac{2(1-\beta) \eta F}{\nu(r)RT}\right]
\]

or,

\[
i_c = i_o \exp\left[-\frac{2\beta \eta F}{\nu(r)RT}\right] \left[1 - \exp\left[-\frac{2\eta F}{\nu(r)RT}\right]\right]
\]

Hence BP's Eq. (9) is equivalent to HS's Eq. (5), if

\[
i = i_o \exp\left[-\frac{2\beta \eta F}{\nu(r)RT}\right]
\]

i.e., the rate of the forward reaction is indeed an exponential function of overpotential and it can only be of this latter form if the logarithmic dependence of \( \eta \) upon \( i_c \) (identical with \( i \) under the conditions of BP's extrapolation), observed experimentally, is to be obtained).

iii) (Not a ground but an indication here of a lack of specification in Figs. 1 and 2 of HST accepted gratefully by HS is omitted.)

Horituti and Sugawara (HST) --

Authors neither affirm nor deny \( a \) priori the validity of the linear dependence of the logarithm of the forward rate on the overpotential.
What they point out is the contradiction (p. 4, par. 2) between BP's conclusion, $v(r) = 2$ and the assumption of the linearity.

The referee's statement (p. 14, par. 2) "HS maintain that the method is invalid because the assumption underlying it, i.e. $\ldots$, is invalid" is hence wrong. HS do not maintain that the assumption itself or the conclusion itself is invalid individually but that they contradict each other. The grounds i) and ii) given by the referee for the "general validity" of the linear relation are hence rather unimportant in this respect but HS will offer remarks on them following the referee's heading.

i) Any natural law cannot be assured valid, if it be theoretically deduced from some particular picture. How could the referee guarantee for instance that $V$ in VOLMER and ERDEY-GRuz's paper$^1$ is a constant independent of $E$, which is essential for the linearity in question? EYRING, GLASSTONE and LAIDLER's deduction$^2$ and Parsons$^3$ also, which the referee refers to as "independent" are similar in this respect: they simply assume the activation free energy (electrochemical)$^4$ to vary linearly to the electrode potential, from which they derive the linearity in question. To maintain the general validity of the linearity because of these theoretical deductions is not so very different from insisting upon the idea that it is valid because it is assumed by these workers.

Authors should like to draw attention of the referee to the explanation of the linearity proposed by Horiuti and Polanyi$^4$. They do not assume the constants of linearity simply constant, but derive them from the potential curves of hydride and the hydroxonium ion. The linearity is valid, however, according to this more fundamental deduction only in the limited region of $\eta$.

With regard to the standard free energy, the authors wish to ask the referee the following questions.

If both the activated complex as well as the initial complex of the rate-determining step were neutral, when the potential term in (5) of BP vanished (we don't know precisely how the expression then should appear, since the origin of the equation is not shown at all),

1) VOLMER and ERDEY-GRuz, Z. physik. Chem. 150, 203 (1930).
$^*)$ Added at the composition.
where should the “repulsive interactions” (p. 14 par. 3, last sentence) be included? Would he assert in that case that the rate is proportional to \( a \) in BP’s (5) or the product of the activities of the initial complex of the rate-determining step? Would he then write the rate constant as being proportional to the product \( f_i \) of the activity coefficient of the initial complex of the rate-determining step? Does he admit on the other hand the correctness of the conclusion of the Bro"nsted’s theory of neutral salt effect which states that the rate constant is proportional to \( f_i \) and inversely proportioned to the activity coefficient \( f^* \) of the activated complex? If so, why is \( f^* \) absent in BP’s (5)? If the latter is claimed to be an expression of general validity not based on a particular assumption, why should \( \Delta G_0 \) in the expression not include \( RT \log f^* \), which causes \( \Delta G_0 \) to vary in general?

ii) It is not true that the linear relation of overpotential to \( \log i_\alpha \) is generally the case, when \( \gamma \) is sufficiently negative to make the back reaction negligible in rate (p. 14, last paragraph). Authors should admit with Bowden and Agar\(^1\) that for many reactions Tafel’s \( \alpha \) is constant\(^*)\) i.e. that the linear relation holds; but they request the referee not to overlook the remark of Bowden and Agar in another place\(**) that “high and variable value of \( \alpha \) of the overpotential on metals of this class supports the above view”.

Horiiuti and Mituya\(^3\) have actually observed the increase of \( \alpha \) from a proper fraction by unity with decreasing overpotential \( -\gamma \) of a mercury hydrogen electrode in accordance with the prediction derived from the electrochemical mechanism\(^4\).

If the referee realizes that the linear relation of \( \log i_\alpha \) to overpotential is an empirical rule of only limited validity both theoretically and experimentally, he would withdraw his note on page 15, par. 3 (the contents of parentheses), since an empirical equation of limited validity and an equation based on a general principle, which is valid irrespective of the validity of the rule, could hardly be identical or equivalent.

\(^1\) Bowden and Agar, Annual Report 35, 90 (1939).
\(^*)\) Ref. (1), p. 90, par. 3.
Referee (RII):—

i)*) The most thermodynamically rigid deduction of the relation of \( i \) to \( \gamma \) is given by PARSONS\(^1\). This deduction indicates that the relation between \( i \) and \( \gamma \) will be of the form,

\[
\log i = K \exp \left[ - \frac{\beta F \gamma}{RT} \right] \quad (***)
\]

(that assumed by BP) so long as \( \frac{\partial \phi_a}{\partial \phi} \rightarrow 0 \), where \( \phi_a \) is the potential of the nuclei of ions adsorbed in the Helmholtz layer at the electrode with respect to the solution and \( \phi \) is the Galvani p.d. between metal and solution. If this condition holds (and \( \frac{\partial \phi_a}{\partial \phi} \) is negligible except near to the electrocapillary maximum according to Stern’s theory of the diffuse double layer), then it does appear that (3) is the generally valid form of the relation between \( i \) and \( \gamma \) for hydrogen evolution in pure solutions. The deduction involves the usual separation of the electrochemical potential (here, of activation) into two parts, i. e.

\[
\Delta \mu_a = \Delta \mu_o + 2F\phi (****)
\]

Because the deduction as given by PARSONS\(^1\) does not involve any other assumptions apart from that mentioned (and the applicability of a Maxwellian distribution of particles near to the electrode) the difficulty experienced HST and by HSI in accepting (3) is not appreciated by the referee. The Japanese authors seem to be troubled by the effect of repulsive interactions on the (chemical) free energy of activation. However, the free energy of activation implicit in the derivation of (1) ****) is a standard free energy change. Any change in the ideality of a system (arising, e. g., from repulsive interactions among its components) affects the free energy of the system, but through the activity coefficient of logarithmic term in the relation between free energy and

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*) Attached at the compilation indicating the reference to ii, HSI; similar is ii, p. 19.

**) The \( i \) or \( a \) in the manuscript of the referee is replaced by \( i \) or \( \beta \) used by himself respectively with the same meaning in RL.


*****) Equation denoted by (1) is absent in RII except in its abstract not reproduced here, which has however its own Eq.(3) as RII does; (1) in the text refers most probably to (3) as judged from implication.
Stoichiometric Number of the Hydrogen Electrode Process on Nickel:

The standard free energy change remains, by definition, a constant, independent of concentration. This is the answer to the main question of HSI (p. 16, last sentence).

The other questions of p. 16 and 17 all refer to matters which are well elucidated in the Theory of Rate Process by GLASSTONE, LAIDLER and EYRING, New York, 1941, 403-405, where, in the referee's opinion, the discussion supercedes the original discussion of activated complex theory by BRÖNSTED*.

ii) The referee differs sharply from HSI in their contention that the linearity of log $i_0$ with $\gamma$ for hydrogen evolution is not generally the case, assuming that by "generally" they mean "usually". The following is the state of affairs indicated by the available results: log $i_0$ is linear with $\gamma$ (at $i_0$ high enough so that the reaction of dissolution of $H_2$ is negligible) over long c.d. ranges for all systems in which electrode and solution have been prepared in a pure state (i.e., no side reactions occur at low c.d.'s due to the effect of trace impurities) and where the evolution of $H_2$ is the sole reaction occurring at the electrode (e.g., no dissolution of the metal). This seems to have been clearly established for the following systems.

1) Hg in acid solutions.
2) Hg in alkaline solutions.
3) Pb in acid solutions.
4) Pt in acid and alkaline solutions.
5) Ni in acid and alkaline solutions.
6) Ag in acid solution.
7) Cu in acid and alkaline solutions.

Conversely, no examination has hitherto been reported where pure

---

7) BOCKRIS and PENTLAND, ibid. 48, 833 (1952).
* Cf. BELL, Acid-Base Catalysis, Oxford, 1941.
conditions obtained and any other experimental law (but log $i_c = K' - K'' \eta$) was observed. The work of 1928–1934, the most recent referred to by HSI (p. 17), which seems to indicate otherwise, is invalid because of impurity effects*). The efficacy of a high degree of purification in removing deviations from the linear relation of log $i_c$ to $\eta$ has been described in detail by Azzam, Bockris, Conway and Rosenberg\(^1\) and was noted as early as 1937 in one system by Levina and Sarinsky\(^2\).

The experimental results in pure systems thus appear fully to confirm the relation log $i_c = K' - K'' \eta$ in the region of overpotential where it is expected to apply. This being so, (3) can also be regarded as experimentally confirmed because there seems no reason to suspect that a relation which has been demonstrated to be valid over wide ranges of c.d.'s (where $i = i_c$; cf. above references) should break down (the supposition necessary if HS's criticism of BP is accepted) within 30 mv's of the reversible potential (the range where experiment cannot be used directly to verify (3), owing to the affect of the velocity of dissolution of $H_2$).

Re HSI p. 17, third paragraph, where a claim is made to have observed experimentally some deviation from (3), I have studied the publications concerned and the experimental work there reported appears to me to be identical with that of Mituya\(^3\), criticized by Frumkin\(^4\) as invalid because of the presence of Pt in the solution and the resulting contamination of the mercury electrode.

Finally if there is still any doubt concerning the validity of log $i_c = K' - K'' \eta$ as the equation usually describing the relation between the net c.d. during $H_2$ evolution and the overpotential, it is certainly experimentally true for Ni in acid and alkaline \(^2\) and this is the system for which it has been taken as true by BP in their calculation of log $i_o$ and thence of $\nu(\tau)$ by their Eq. (2).

**Horiuti and Sugawara (HSII):**

HS pointed out in HST the inconsistency involved in BP's procedure

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6. Cf. Lukowzew, Levina and Frumkin, loc. cit., and others under references for Ni above.
i.e. that between $\nu(r)$-value concluded and their process of $i_0$-estimation but not claimed necessarily the deficiency of the process itself of $i_0$-estimation; the inconsistency would persist even if the $i_0$-estimation process were somehow confidentially established, in which case the $\nu(r)$-value must be questioned. The experimental data of Figs. 1 and 2 of HST fits in for instance very well with the linearity for the $\nu(r)$-value of 1.5 as shown in Fig. 1 rather than for that of 1 or 2.

The $\nu(r)$ is not necessarily an integer; $\nu(r)=1.5$, if the rate-determining step,

$$
H^+ + e^- \rightarrow H(a)
$$

is followed by rapid ones,

$$
2H(a) + H^+ \rightarrow H_2(a), \quad H_2(a) + H(a) + e^- \rightarrow 2H,
$$

which complete the hydrogen electrode reaction,

$$
2H^+ + 2e^- = H_2
$$

where (a) indicates the adsorbed state. Such a mechanism, if it seem rather extraordinary, could not be a priori excluded of course.

![Graph](image)

Fig. 1.

log $i, \eta$-points calculated by HS's Eq. (5) from BP's $i, \eta$-observation, 0.005 N NaOH at 3°C, BP's Fig. 7

The question remains thus open, if the linear law were effectively established; one might in consequence, on the part of the referee, duly question the significance of the intrinsic correlation between the
v(r)-value and the γ-dependence of $i_0$ pointed out by HS, on BP's procedure, but on behalf of BP, defend the linear law indispensable for the validity of the BP's procedure. The attitude taken by the referee is of the latter sort.

He first kindly explains in RI (p.13, par. 3) the original point of HST, as being not very clearly stated in the Japanese paper, but incorrectly substituting it for the criticism against the linear law. HSI emphasized the due discrimination of the above two standpoints, but in vain after all as RII revealed. He thus defends the linear law with all his might first noting in RI (p. 13, par. 5, sentences in parentheses) that the method of evaluating $i_0$ used by BP is the standard one accepted since 1930, which has not been previously questioned, and then raising two points i) and ii) as grounds for it.

HS should agree with the referee that the method has ever been a standard one, in the sense, that none else was known until 1933 when the direct method of observing it by the exchange reaction of hydrogen isotope was found,$^1)$ as impressed in the usual term “exchange current” of $i_0$, and that the method has not been previously questioned too, in the sense, if it would give anything more than the order of magnitude of $i_0$, as indicated in the statement of WIRTZ,$^2)$ upon whose work the referee tries to base (P. 14, par. 4) his linear law, that *) “Trotzdem können die so bestimmten $i_0$ einen Anhalt dafür geben, bei welcher Grössenordnung der Stromstärke man etwa in der Nähe des reversiblen Potentials kommen könnte”.

The Anhalt dafür is moreover of such a sort as indicated by data given below of $i_0$ derived from observations of various workers for the hydrogen electrode of mercury, which is distinguished, as well known, in the reproducibility and the linearity of log $i_0$ to γ among hydrogen electrodes of different metals.

As shown in the Table, $i_0$-value in 0.1 N HCl at 20~22°C ranges from $0.5 \times 10^{-12}$ to $3 \times 10^{-12}$ amp cm$^{-2}$ according to different authors. Nobody could ever conceive that $i_0$-extrapolation of such an accuracy, even in this most favorable case, would be capable of discriminating between $v(r)$ values, 1, 2 and 1.5, which is proportional to $i_0$ according to (6), HST.

2) WIRTZ, Z. Elektrochem. 44, 303 (1938).
*) Ref. [2], p. 306, 1st column, line 14-18.
Stoichiometric Number of the Hydrogen Electrode Process on Nickel:

The controversies developed under items i) and ii) throughout RI, HSI and RII will now be briefly sketched and their points further discussed below respectively under the headings i) and ii).

i) The referee maintains in RI (p. 14, par. 3) that the linear law is established because it is theoretically independently derived by VOLMER and ERDEY-GRUZ, EYRING, GLASSTONE and LAIDLER and PARSONS and that $\Delta G$ remains unchanged by definition, whereas the energy change caused by the repulsive interactions of $H(a)'s$ be included in the (electrostatical) potential term in (1) (p. 14, par. 3, last sentence). The latter contention of

<table>
<thead>
<tr>
<th>$i_0$ (amp cm$^{-2}$ x 10$^{-12}$)</th>
<th>Aqueous Electrolyte</th>
<th>Temperature °C</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.5 N H$_2$SO$_4$</td>
<td>15</td>
<td>BOWDEN and RIDEAL, Proc. Roy. Soc. A 120, 59, 80 (1928)</td>
</tr>
<tr>
<td>6</td>
<td>0.2 N H$_2$SO$_4$</td>
<td>25</td>
<td>BOWDEN and KENYON, Nature 135, 105 (1935)</td>
</tr>
<tr>
<td>0.5</td>
<td>0.001 N, 0.1N HCl</td>
<td>22</td>
<td>LEVINA and SARINSKY, Acta Physicochim. 6, 491 (1937)</td>
</tr>
<tr>
<td>1.0</td>
<td>0.1 N HCl</td>
<td>20</td>
<td>JOFA, Acta Physicochim. 16, 908 (1939)</td>
</tr>
<tr>
<td>1.8</td>
<td>0.1 N HCl, 1 N H$_2$SO$_4$</td>
<td>20</td>
<td>JOFA, KABANOV, KUCHINSKY and CHISCHIAKOV, Acta Physicochim. 10, 317 (1939)</td>
</tr>
<tr>
<td>30</td>
<td>1 N HCl</td>
<td>—</td>
<td>JOFA, KALYCHEV and SHTIFMAN, Acta Physicochim. 12, 251 (1940)</td>
</tr>
<tr>
<td>1.5</td>
<td>0.25 N H$_2$SO$_4$</td>
<td>20</td>
<td>JOFA and MIKULIN, J. Phys. Chem. Russ. 18, 137 (1944)</td>
</tr>
<tr>
<td>40</td>
<td>0.25 N H$_2$SO$_4$, 3.4 N H$_3$PO$_4$</td>
<td>25</td>
<td>DE BETHUNE and KIMBALL, J. Chem. Phys. 13, 53 (1945)</td>
</tr>
<tr>
<td>3</td>
<td>0.1 N HCl</td>
<td>20</td>
<td>BOCKRIS and PARSONS, Trans. Faraday Soc. 45, 916 (1949)</td>
</tr>
<tr>
<td>0.6</td>
<td>0.1 N HCl</td>
<td>20</td>
<td>POST and HISKEY, J. Am. Chem. Soc. 72, 4203 (1950)</td>
</tr>
</tbody>
</table>

1) VOLMER and ERDEY-GRUZ, Z. physik. Chem. 150, 203 (1930).

*) This Table was compiled by Mr. Michio EN’YO of this laboratory, some of $i_0$-values not directly given by the author being worked out from the experimental data by himself, to whom HS's thanks are due.
him is put against the point held in HST (p. 5, par. 2) that $\Delta G_o$ in BP's rate expression varies with $\gamma$; it is essential for these "theoretical derivation" of the linearity, that $\Delta G_o$ remain constant independent of $\gamma$, in so far as they express the rate, ignoring $f^*$, as (1) on p. 11, $k_v$ there included as $\frac{kT}{h} \exp\left(-\frac{\Delta G_o}{RT}\right)$ and $\overline{\Delta G}$ in turn as $\Delta G_o = \Delta G_o + aF\Delta \phi$ (cf. (1) on p. 14), where $\Delta \phi$ varies by definition linearly with $\gamma$, since otherwise the contrived linearity of $\overline{\Delta G}$ with $\gamma$ would not transcribed into that of log $i$.

HSI points out now that the theoretical derivations of the linear law as referred to by the referee is but a transcription of an assumed linearity of the electrochemical standard free energy of activation on one hand and advanced several questions (p. 16, par. 6) which might induce the referee to reflect on the necessary inclusion of $f^*$ into the rate expression on the other hand; the questions include the whereabouts of the effect of the repulsive interactions in the case of the catalytic mechanism, when the potential term in (1) on p. 14, i.e. the refuge for the effect suggested by the referee is closed.

The referee now gives up in RII, with regard to the linear law, the reference to VOLMER and ERDEY-GRÜZ and to EYRING, GLASSTONE and LAIDLIER as evidences without any comment, and holds to the last to "the most thermodynamically rigid deduction" of PARSONS, whereas he seems never to have come upon the necessary inclusion of $f^*$ and associated change of the dependence of $i$ on $\gamma$. So much are the controversies developed up to RII under i). Below will be discussed the referee's last hold of "the most thermodynamically rigid deduction" and his contension on $f^*$ with reference to the repulsive interactions.

The referee's statement in RII (p. 18, middle) that the deduction as given by PARSONS of (3) on p. 18 does not involve any other assumptions apart from a few ones described there, is undisputably disproved by 2nd paragraph on page 1334 of the PARSONS' paper that "We assume that the electrical contribution to the standard free energy of the activated state ($A^*$) lies between that to the standard free energy of state $P$ and that to the standard free energy of state $Q$ i.e.,

$$\beta'[(\mu_a^0 - \mu_a^*) - (\mu_p^0 - \mu_p^*)]$$

1) VOLMER and ERDEY-GRÜZ, Z. physik. Chem. 150, 203 (1930).
where $\beta'$ is, important to note, assumed a constant proper fraction independent of $\gamma$ throughout his deduction. The constancy of $K$ in (3) in RII is to thank to the erroneous negligence of $f^*$, whereas the linear dependence of $\log i$ on $\gamma$ implied in the exponential factor to the above assumption; “the most thermodynamically rigid deduction” has hence after all no point more than that of deducing the linearity from the assumed linearity similarly as in the case of VOLMER and ERDEY-GRUZ and EYRING, GLASSTONE and LAIDLER no more maintained by him as evidence, except that the procedure of the former is more or less involved compared with that of the latters. The referee’s last hold of the “theoretical ground” comes hence after all to nothing.

We now turn to the problem of $f^*$ with reference to the repulsive interactions. HS should appreciate that the referee has developed from his random statement in RI of the repulsive interactions to be expressed in the potential term (p. 14, par. 3, last sentence) to that in RII of the repulsive interactions to affect through the activity coefficient (p. 18, last sentence). He does not state however in which activity coefficient should the effect of the repulsive interactions be included; $f^*$ could not be the shelter according to him, since “the other questions all refer to matters which are well elucidated in The Theory of Rate Process by GLASSTONE LAIDLER and EYRING, 403–405, where, in the referee’s opinion, the discussion supercedes the original discussion of activated complex theory of BRÖNSTED” (p.19, par.2), whereas $f^*$, successfully taken into account in the rate expression (cf. p. 17, 4th sentence) by the latter author, was not practically allowed for (cf. p. 12, par. 2) with regard to the heterogeneous reaction by GLE who “supprecede” the latter. He must have thus deserted the repulsive interactions and taken himself shelter in the latter standard book of him, so as not to be troubled by the deserted as the Japanese authors are (p. 18, 3rd last sentence). His last step of realizing that the repulsive interactions modulate the rate through $f^*$ correctly included in its expression, as stated in HSII, A. (p. 11–13), might hopefully be accomplished by explaining it as below, using preferably the terminology of “The Theory of Rate Process” in which “matters are well elucidated” as for him.

1) VOLMER and ERDEY-GRUZ, Z. physik. Chem. 150, 203 (1930).
*) Notation $\beta$ in the original paper is primed here for discriminating it from $\beta$ in Eq. 3 of RII.
The first thing to do would be to refer him once again to the foot-note \( ^\dagger \) on page 576 of his standard book\(^*\). In the next place HS might deduce the necessary inclusion of \( f^* \) in the rate expression along the line of the latter book as below\(^**\).

The fundamental expression for the rate is given by Eq. (131) on page 187 of the original book as

\[
\text{Rate of reaction} = c_+ \left( \frac{kT}{2\pi m^*} \right)^{\frac{1}{2}} \frac{1}{\delta}
\]

Defining now the concentration \( c'_+ \) referred to a different scale as

\[
c_+ = \frac{(2\pi m^*kT)^{\frac{1}{2}}}{h} c'_+ \delta
\]

in accordance with p.188 and p.189 of the original book, we have

\[
k_v = \frac{c'_+}{a_A a_B \cdots} \frac{kT}{h}
\]

It is of course at our disposal to write the above equation in the form,

\[
k_v = \frac{kT}{h} \exp \left( -\frac{\Delta G_0}{RT} \right)
\]

in terms of the standard free energy of activation \( \Delta G_0 \)\(^***\), as did by Parsons and Bockris\(^1\) but in that case, the standard state of the activated complex implied in \( \Delta G_0 \) must be that of unit concentration and in consequence \( \Delta G_0 \) should vary in general with the variable concentration of the assembly or with \( \eta \) in the present case as pointed out in HST (p.5, par. 2, line 5). If one choose alternatively the standard state of the activated complex that of the unit activity, so that \( \Delta G_0 \) is invariant, by definition, as declared by the referee, so have we to divide the result by \( f^* \) as footnoted on page 576 of his standard book.

It is not to wonder but essential that the concentration \( c'_+ \) appears in the expression of \( k_v \) instead of the corresponding activity, in so far as we are counting by rate the number of activated complex passing into the final complex\(^****\) per unit time which is given by the product

\(^1\) Parsons and Bockris, Trans. Faraday Soc. 47, 914 (1951).

\(^*\) Cf. p. 12, par. 2.

\(^**\) Exact account on the basis of the general theory is given by Horiuti (this volume, p. 56).

\(^***\) For the sake of simplicity we will restrict ourselves to the case when the potential term in \( \Delta G_0 \) is absent as in the catalytic mechanism, although it is not essential for the present argument.

\(^****\) Cf. footnote \( \# \) on p. 6.
of the universal frequency $\frac{kT}{h}$ and the concentration rather than the activity itself. When the referee has thus completed his last step of his development in this direction, he would be so much troubled by the repulsive interactions modulating the rate through $f^*$, just as these Japanese authors are.

ii) In RI the referee replaces his maintenance on the linearity of $\log i$ to $\eta$ by that of the $\log i_\circ$ observed at the condition where $\log i_\circ$ practically equals $\log i$ and tries to ground the linearity of $\log i_\circ$ on experimental data summarised in a few reviews of WIRTZ and others. WIRTZ states there however on the contrary that “In vielen Fällen ist $b$ nicht völlig konstant, sondern steigt etwas mit wachsendem Strom (z. B. BAARS$^2$). Die Stromspannungskurven sind nach unten konvex. Dies wird gelegentlich auf ungünstige Versuchsbedingungen geschoben. Die Erscheinung tritt jedoch so regelmässig auf, dass diese Erklärung nicht ausreicht”. In the two other references given by the referee, BOCKRIS$^3$ describes also a number of examples of deviation from the linear law without shifting it however to the “ungünstige Versuchsbedingungen”, although FRUMKIN$^4$ gives a few examples of validity (Pt, Ag, Hg). The exclusive linearity of $\log i$ to $\eta$ is hence not verified but ruthlessly denied by “grounds” themselves referred to by the referee as such. Neither could the content of parentheses closing the item ii) of RI ground the expression of $i$,

$$i = i_0 \exp \left[-\frac{2\beta\gamma F}{\nu r(\tau) kT} \right]$$

even if the ungrounded BP’s Eq. (9) or (A) on p. 15 be brought identical in form with HS’s Eq. (5), since the equation of the form of (A) follows, whatever be the functional form of $i$, from the existence of the rate-determining step and the thermodynamical requirement that the difference of the activation free energies of the forward and backward steps should equal the free energy difference of the final and the initial states which are just the content of HS’s Eq. (5). The description of RI under ii) is of no content except the above absurdities.

With regard to the observed deviations from the linearity pointed
out in HSI (p. 17, par. 2), RII states now that "Conversely, no examination has hitherto been reported where pure conditions obtained and any other experimental law (but log $\log \tau = K' - K'' \gamma$) was observed. The work of 1928–1934, the most recent referred to by HSI*), which seem to indicate otherwise, is invalid because of impurity effects**) (p. 20, 2nd sentence)". "The work of 1928–1934" includes now those of BAARS1) and of BOWDEN and RIDEAL2) on which principally are based the conclusions on the Stromspannungskurven of WIRTZ3), just referred to by the referee (p. 14, 2nd last line) as support. The referee thus changes his attitude of maintaining the latter set of works as evidence to that of declaring the same as invalid on the reason now of the impure experimental condition without any comment on its part as evidence before.

The referee tries in RII finally to defend the exclusive linear law referring to numerous works to such an extent that (p. 20, par. 4) finally if there is still any doubt with the linearity, it is certainly experimentally true for Ni for which BP has taken it true in their calculation of $\log \tau$. It would suffice to disprove his latter statement to refer to the BOCKRIS and AZZAM's observation® of $\log \tau$ of Ni electrode in 5N HCl, which badly deviates from the linearity to $\gamma$ revealing at $10^1$ amp cm$^{-2}$ the tendency to approach a finite value; this result obtained at the pure conditions recommended by the referee is carelessly or carefully omitted from Clause (5), RII for Ni, while the result on Hg of the same paper satisfying the linear law is included in Clause (1), RII for Hg.

It is moreover a distinct example of the deviation from the linear law, what is given by the referee under the Clause (6) as evidence; BOCKRIS and CONWAY state in the cited paper that the dependence of $-\gamma$ on $\log \tau$ at higher $\log \tau$, breaks into two pieces of straight lines, thus reserving the linear law by words but, as a matter of fact, the result may equally well or even better expressed by a smooth curve through the scatter of points.

It might further be pointed out in the very work of the BOCKRIS

3) WIRTZ, Z. Elektrochem. 44, 303 (1938).
5) Nowhere have HS referred to it most recent.

— 28 —
and Potter* defended by the referee, that $-\gamma$ bends upwards against log $i_e$ at its higher value and this deviation from the linearity is not eliminated, if one allows for the ohmic resistance of the electrolyte as reported by the latter authors*). The log $i_e$ extrapolated at $-\gamma$ value of 30 mv above that of the highest point of linear fit of Fig. 9 in BP's paper is about 0.14 greater than that observed at the same $-\gamma$, which magnitude is sufficient, as seen in Fig 1 and 2 of HST to change the conclusion from one of $\nu(r)=1$ and $\nu(r)=2$ to the other. There is hence a sufficient reason to expect that the linear law would break down within 30 mv's of the lowest linear fit i.e. at the reversible potential (cf. p. 20, par. 2) to disfigure the conclusion altogether. It is the BP's procedure of $i_e$-estimation associated with such an uncertainty, which would hardly be useful for the $\nu(r)$-determination more accurate than by order of magnitude.

The referee cannot now escape from taking back his statement of the last line on page 19 that “Conversely no examination has hitherto been reported, where pure conditions obtained and any other experimental law (but log $i_e=K'-K''\gamma$) was observed”, all these works providing disproofs having been referred to by him as obtained with electrodes and solutions prepared in a pure state or defended by him as being completely valid. His statement in the third sentence of page 20 of RII that “The efficacy of a high degree of purification in removing deviations from the linear relation of log $i_e$ to $\gamma$ has been described in detail by Azzam, Bockris, Conway and Rosenberg*) is also not true as it is, since, as described in the paper of these authors, their high degree of purification attained is not efficacious enough exclusively to remove the deviation from the linearity in the case of nickel and silver electrode.

One might persist wishfully in that the linear relation holds in the extreme case of perfect purification but this, if admitted at all, does not alter the conclusion, since the experiment of BP has been conducted under “the high degree of purification” actually realized rather than in an imaginary perfect condition beyond our experience.

It may be added with regard to the referee's comment (page 20, par. 3) on the work of Horiuti and Mituya* that the criticism of

*) Cf. ref. (1), p. 618, 1st column, last sentence and p. 622, 1st col. par. 1, last sent.
BOCKRIS, raising the point of FRUMKIN referred to by the referee has been disproved by HORIUTI, KEII and MITUYA, further comment of BOCKRIS being not obtained.

Conclusion:— The referee has assumed the defence of the exclusive validity of the linear law underlying the BP's procedure of \( i_0 \)-estimation, without however grounding it neither theoretically nor experimentally after all; the referee's claims are shown theoretically of no content, whereas badly defied by experimental results upheld by himself as evidences.

C. Procedure of Evaluating \( \nu(r) \).

Referee (RT):—

Fig. 1 and 2 of HST are perfectly consistent with BP's results for the following reasons:

(a) Only the upper lines (black dots) would be expected to yield a line passing through the value of \( \log i_0 \) used by BP because only for this line has it been assumed by HS that \( \nu(r) = 2 \). The best fit to the points shown does in fact pass within the 95% probability limits on \( \log i_0 \) (±0.2–0.5 given by BP).

(b) The scatter of points in the regions of very low \( -\eta \) is expected because of the inaccuracies inherent in current (i.e., \( i_0 \)) measurement in this range (\( 10^{-7} \) amp cm\(^{-2} \)) and the well-known difficulties connected with competing reactions when the current density is so low. Such deviations are shown, for example, in Fig. 7 of BP's paper. Taking into account this scatter at very low current densities, Figs. 1 and 2 would appear to provide a convincing proof of BP's assumption that

\[
i = \text{const.} e^{-\varepsilon\nu} \quad \text{or} \quad i = i_0 \exp \left(-\frac{2\beta F}{\nu(r) RT} \right),
\]

instead of the converse as maintained by HS.

HORIUTI and SUGAWARA (HST):—

We discuss now the reasons given by the referee (a) and (b) for

2) FRUMKIN, Acta Physicochim. 18, 23 (1943).

\( \ast \) The \( -\eta \) was inserted at the compilation presumably missing by misprint in the referee's manuscript.
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his important statement that "Figs. 1 and 2 would appear to provide a convincing proof of BP's assumption" (RI last sentence).

The referee maintains in stating reason (b) that the points of lower overpotential are of less weight because of the "inaccuracies inherent in current measurement". If now he constructs the best fit, stated in reason (a), consistently with his reason stated as (b), the passage of the fit through \( \log i_0 \) is a matter of course, since the procedure is just the repetition of that of determining \( \log i_0 \) by BP at the passage of the best fit to the point at higher overpotential, where \( i \) and \( i_0 \) are practically identical.

Now if such inaccuracies are inherent to the \( i_0 \)-measurement at lower overpotential as both systematic and amounting more than twice**

"the correct value" on BP's or the referee's best fit, what is the meaning at all in attempting to determine \( \left( \frac{di_0}{d\eta} \right)_{\eta=0} \) from such measurements or to calculate \( \nu(r) \) according to the equation,

\[
\nu(r) = -2i_0 F / \left[ RT \left( \frac{di_0}{d\eta} \right)_{\eta=0} \right]
\]

and to argue that \( \nu(r) \) be 1 or 2?

One might conceive it possible to construct \( i_0 \) at lower overpotential trusting to the linearity from the accurate measurement at higher overpotential by virtue of (5) of HST. In order to do so, it is required to put into (5) of HST the value of \( \nu(r) \), which is of course regained after carrying through the procedure of \( \nu(r) \)-determination using \( \left( \frac{di_0}{d\eta} \right)_{\eta=0} \) thus constructed. We obtain what we choose for the value of \( \nu(r) \). To inquire something more than a human arbitrariness into the Nature, the \( i_0 \)-measurement at lower overpotential is essential, to which however the inaccuracies are inherent according to the referee. If inaccurate, it is of no use to attempt to determine \( \nu(r) \).

Referee (RII):

The essential point of this controversy is here reached in HSI i.e. it is now discussed whether a more accurate value of \( \nu(r) \) can be ob-

*) Denoted by a cross in Fig. 1 or 2, BST:— added at the compilation.

**) The deviation of black dots from the best fit gives, according to (5) of BST, the logarithm of the ratio of \( i_0 \), observed over the "correct value" appropriate to the "best fit":—added at the compilation.
tained by HS's method, using Eq. (4), HST** or by BP’s method, using BP’s Eq. (2).

1. (Minor points here of arguments on misprints omitted)

2. p. 31 par. 3: The inaccuracies in measurements at very low c.d’s are in the overpotential rather than the c.d. No justification exists for the attitude taken by HS (p. 31, par. 3) that if the experiments at very low c.d’s become less accurate than those at high ones, there is no point in attempting to evaluate \( \nu(\gamma) \) by the use of BP’s Eq. (2). Every experimentally measured quantity involves some error. The question is: how much does a given uncertainty or bias in the measured value of \( \gamma \) affect the resultant value of \( \nu(\gamma) \), when this is calculated using HS’s Eq. (4)* or when it is calculated using BP’s Eq. (2)? The most important part of this report will therefore consist in an examination of the effect on \( \nu(\gamma) \), calculated by the two methods, of a certain error or bias in measurements of \( \gamma \).

(p.31, par.4: this appears obvious and is agreed).

Examination of the effect of a bias or error in overpotential measurements on the determination of \( \nu(\gamma) \).

Let us choose numerically convenient hypothetical parameters, of the same order as those observed experimentally by BP. Let: ... 

\[
\begin{align*}
\gamma &= 10^{-7.000} \text{amp cm}^{-2} & R &= 8.3141 \text{ joules (°C mol)}^{-1} \\
\beta &= 0.50 & T &= 293.15 \text{ °K (20 °C)} \\
F &= 96,000 \text{ conlombs g. equiv}^{-1} & \log_{e}10 &= 2.3026 \\
\nu(\gamma) &= 2.00 & 2.3026 \frac{RT}{F} &= 0.05816
\end{align*}
\]

If we now substitute these parameters the BP’s Eq. (9), i.e.

\[
i_{c} = i_{0} \left[ \exp \left( \frac{2\beta \gamma F}{\nu(\gamma)RT} \right) - \exp \left( \frac{2(1-\beta)\gamma F}{\nu(\gamma)RT} \right) \right]
\]

we obtain the values of \( i_{c} \) as a function of \( \gamma \) corresponding to the parameters quoted. This relation has been plotted in the referee’s Fig.1. The inset in Fig.1 gives the relation of \( \gamma \) to \( i_{c} \) at overpotential near to zero.

We now use Eq.(1)** to calculate \( i \), utilizing the value of \( i_{c} \) calcu-

* Eq. (5), HST fits better in with the implication, with which the referee refers actually to Eq. (5), HST in the later part of this R II.

** Eqs. (1) and (2) are not indicated in RII except in its abstract not reproduced here; Eq. (1) must be Eq. (5) of HST according to the note attached to the heading “Numerical effect etc” on p. 35, although it is not compatible with the description “... the derivation of (1) ...” on p. 18, 5th last line by which Eq. (3) there is presumably meant; cf. footnote **** on the same page:—added at the compilation.
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lated from (4). The result will be a known relation of \( \log i \) as a function of \( \gamma \), passing through \( \gamma = 0 \) at \( \log i = -7.000 \), because \( \log i = \frac{K'}{K''} \gamma \) is implicit in the deduction of (4). The actual line obtained is shown in Fig. 2 as the middle straight line.

Let it now be assumed that all the \( \gamma \) values traced as a function of \( \tilde{i} \) and \( \log \tilde{i} \) in Fig. 1 are subject to a bias of one \( \text{mv} \) (+ve or -ve), i.e. a constant error of one millivolt is superposed in the entire Tafel line (this is the order of bias which can be reasonably expected in overpotential work where the maximum reproducibility between individual workers is about \( \pm 5 \text{mv} \) and among the results of one worker on the same system \( \pm 3 \text{mv} \). It may arise from the liquid junction potentials between reference and working electrodes, or from thermo e.m.f.'s, etc.).

![Graph showing Tafel lines](image_url)

**Fig. 1.**

Calculated Tafel Line, Using \( \tilde{i} = \tilde{i}_0 \{ \exp[-2\beta \tilde{\nu} F/\nu(r)RT] - \exp[2(1-\beta \tilde{\nu} F/\nu(r)RT)] \}, \)

Where \( \log_{10} \tilde{i}_0 = -7.0000 \), \( \beta = 0.50 \) and \( \nu(r) = 2.00 \)

The resultant relation of \( \log i \) to \( \gamma \), calculated from (1)*, are shown by curves \( \times \times \times \) (−ve bias 1 mv) and the curves \( \circ \circ \circ \) (+ve bias 1 mv),

* Cf. footnote ***) on p. 32:— added at the composition.
Effect of Bias in Measured Overpotential on Calculated Values of log $i$.

Calculated from HORIUTI's Equation

$$i_0 = i(1 - \exp\left[\frac{2\pi F\nu(r)RT}{\eta}\right])$$

with $\nu(r) = 2.00$ and $T = 293.15^\circ$K.

of Fig. 2.

Numerical Effect of bias of $+1$ mv on the calculation of $\nu(r)$ from BP's equation.

The effect of numerically lowering all $\eta$ values of Fig. 1 by $1$ mv is to lower $i_0$ from $10^{-7.000}$ to $10^{-7.0014}$, (but note that $\left(\frac{\eta}{i_0}\right)_{\tau=0}$ remains unchanged).

If the value of $i_0$ is now calculated using this new (and erroneous) value of $i_0$ by means of BP's Eq. (2), the value for $\nu(r)$ changes from $2.00$ to $2.04$. Conversely, if the $\eta$ values of Fig. 1 are numerically raised $1$ mv, $i_0$ is changed to $10^{-7.0036}$ and using this (erroneous) value of $i_0$ in BP's Eq. (2), the value of $\nu(r)$ changes from $2.00$ to $1.96$.

Conclusion: If it is assumed that a series of overpotential values is subject to a bias of $+1$ mv or $-1$ mv, the values of $\nu(r)$ calculated from BP's Eq. (2) using the $i_0$'s resulting from $\eta$ values containing these biases (and for the order of parameters used in this examination), are

---

*) The referee writes this quantity as $(\frac{\eta}{i_0})_\tau$ or as $(\frac{\eta}{i_0})_{\tau=0}$:—added at the composition.

***) Presumably the misprint of $\nu(r):$—added at the composition.
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±2% of the values resulting from an ideal “correct” value of \( i_0 \). As we only have to distinguish whether \( \nu(r) \) is 1 or 2 to be able to use it as a diagnostic criterion, it is concluded that biases as stated do not sensibly effect the value of \( \nu(r) \) as calculated from BP’s Eq. (2).

Numerical effect of a bias +1 mv on the course of the log \( i-\gamma \) relation as estimated for HS’s Eq. (5) (RII Eq. (1)).

It is seen from RII, Fig. 2 that the effect of the biases of +1 mv and −1 mv on the log \( i-\gamma \) relation, calculated from HS’s Eq. (5) is very large for \( \gamma \) less than 10 mv. It follows, therefore, that a markedly non-linear relation between log \( i \) and \( \gamma \) occurs at low values of \( i_0 \), from the substitution of practical values in HS’s Eq. (5), even if log \( i \) is indeed linear with \( \gamma \) (as has been assumed in these calculations) when the values of \( \gamma \) substituted are biased by about +1 mv. Hence, such non-linear relations at low values of \( \gamma \) obtained similarly from HS’s Eq. (5) in HS’s Figs. 1 and 2 do not indicate the lack of applicability of log \( i=K_i-K_i^\gamma \). Comparison between HS’s Figs. 1 and 2 and RII’s Fig. 2 makes clear that HS’s Figs. 1 and 2 do indicate that a +ve bias of somewhat less than 1 mv existed in BP’s measurements.

Conclusion concerning merits of BP’s Eq. (2) and HS’s Eq. (5) as methods of calculating \( \nu(r) \).

The effect of biases of the order of 1 mv on the values of \( \nu(r) \) calculated from BP’s Eq. (2) has been shown to be negligible. The use of HS’s Eq. (5) to calculation \( \nu(r) \), however, involves the experimental evaluation of \( i \) by the use of deuterium and matching of this \( i \) through HS’s Eq. (5) with a certain value of \( \nu(r) \) thus to be determined. However, it has here been shown that it is just this HS’s Eq. (5) which, in the vital region very near to the reversible potential, is sensitive to small errors in measurement of \( \nu(r) \) and the shape of the relation of \( i \) to \( \gamma \) thus obtained from it, and hence the value of \( \nu(r) \) calculated, is therefore unreliable (RII, Fig. 2). The essential physical reason for this is that in the HS Eq. (5) the value of \( i \) depends on absolute values of \( \gamma \), whereas in this BP’s Eq. (2) the value of \( \nu(r) \) depends on the slope \( \left( \frac{\partial \gamma}{\partial i} \right)_{\gamma=0} \) (which is not effected by constant errors) and the value of log \( i_0 \), which is effected to a negligible extent as numerically illustrated above.

*) Here was inserted at the compilation \( i_0 \) presumably missing by misprint in RII.

**) Presumably −1 \( \gamma \) is meant instead; − added at the compilation.

*** Inserted at the compilation, missing presumably by misprint.
Horiiuti and Sugawara (HSII):

Here will be first summarised before discussing RII, fundamental facts and principles underlying \( \nu(r) \) and the procedure of its determination.

§ 1. Fundamentals of \( \nu(r) \)

I) A general theorem i.e. Eq. (4) of HST on the stoichiometric number \( \nu(r) \) of the rate-determining step \( * \) i.e.,

\[
V_s = \frac{\mathcal{F}}{\nu(r)} \left[ 1 - \exp \left( -\frac{\Delta F}{\nu(r) RT} \right) \right]^{**}
\]

(1. V)

has been advanced by Horiiuti et al.\(^1\) developing their previous treatises\(^2\); the theorem holds for any thermal reaction having a rate-determining step, homogeneous or heterogeneous\(^3\). Eq. (1.V) assumes the form of Eq. (5), HST, i.e.

\[
i = i \left[ 1 - \exp \left( -\frac{2F_r \gamma}{\nu(r) RT} \right) \right]
\]

(1. \( i \))

for the hydrogen electrode reaction,

\[
2H^+ + 2e^- = H_2
\]

(2)

for which \( \Delta F = 2F_r \gamma \) and \( i_e \) or \( i \) is respectively proportional to \( V_s \) or \( \mathcal{F} \).

II) It is the fundamental thermodynamical condition underlying

---


* The \( n = 2/\nu(r) \) was defined in the earlier papers (ref. 2) with special reference to the hydrogen electrode reaction as the number of hydrogen nuclei transposed from the state prior to the overall reaction to that posterior to it by one act of the rate-determining step and later (ref. 1) \( \nu(r) \) was defined as the number of forward acts of the rate-determining step required to transfer one reactant completely to a resultant [cf. footnote * on p. 6], which was thence called the stoichiometric number (ref. 1), as recently quoted by Parsons (Trans. Faraday Soc. 47, 1332 (1951)) and Bockris and Potter (J. Chem. Phys. 20, 614 (1952)).

** Eq. (26.5) of the original paper of Horiiuti (J. Res. Inst. Catalysis, Hokkaido Univ. 1, 8 (1948)) expressed by notations of the present use.
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(1. V) or (1. i) that $V_s=0$ at $\Delta F=0$ or $i_e=0$ at $\eta=0$ respectively.

III) $\bar{\Phi}_s$ ($i_e$) is the limiting value of $\Phi$ ($i$) at $\Delta F=0$ (or $\eta=0$) derived from (1) as,

$$\bar{\Phi}_0 = \lim_{\Delta F \to 0} \Phi = \lim_{\Delta F \to 0} \frac{V_s}{1 - \exp \left( \frac{\Delta F}{\nu(r) RT} \right)}$$

i.e.

$$\bar{\Phi}_0 = -\nu(r) RT \left( \frac{\partial V_s}{\partial \Delta F} \right)_{\Delta F = 0}$$

or

$$i_0 = \lim_{\eta \to 0} \frac{i_0}{i} = \lim_{\eta \to 0} \frac{1 - \exp \left( \frac{2F\eta}{\nu(r) RT} \right)}{1 - \exp \left( \frac{\Delta F}{\nu(r) RT} \right)}$$

i.e.

$$i_0 = -\frac{\nu(r) RT}{2F} \left( \frac{\partial i_0}{\partial \eta} \right)_{\eta = 0}$$

by differentiating as usual both the numerator and the denominator of $\bar{\Phi}$ ($i$) with respect to $\Delta F$ ($\eta$) at $\Delta F=0$ (or $\eta=0$) respectively. The \( \left( \frac{\partial V_s}{\partial \Delta F} \right)_{\Delta F = 0} \) (or \( \left( \frac{\partial i_0}{\partial \eta} \right)_{\eta = 0} \)) of (3. V. b) (or (3. i. b)) is in consequence the differential coefficient at the origin, where $V_s$ ($i_e$) vanishes according to II simultaneously with $\Delta F$ ($\eta$); Eq. (3. V. b) (or (3. i. b)) is Eq. (26.8) (or (27.5)) \(^*\) of HORIUTI \(^1\) expressed by notations of the present use \(^**\).

It is important to note that (3. V. b) or (3. i. b) is the differential form or the corollary of theorem (1. V) or (1. i) but not a separate equation independent of the latter \(^***\); this is illustrated geometrically by plotting $V_s$ or $i_e$ against $1 - \exp \left( \frac{\Delta F}{\nu(r) RT} \right)$ or $1 - \exp \left( \frac{2F\eta}{\nu(r) RT} \right)$ respectively,

\(^1\) HORIUTI, J. Res. Inst. Catalysis, Hokkaido Univ. 1, 8 (1948).

\(^*\) $F$ is missing by misprint in the denominator.

\(^**\) PARSONS (Trans. Faraday Soc. 47, 1382 (1951)) has deduced the equivalent of (3. i. b), similarly as BOCKRIS and POTTER (J. Chem. Phys. 20, 614 (1952)) have, from an incorrect rate equation, where $f*$ is ignored as referred to in A. and B. and the linearity of the electric part of the standard electrochemical free energy (cf. p. 16) assumed. PARSONS (loc. cit.) remarks with regard to the latter equivalent that an equation similar to it has been obtained by HORIUTI (J. Res. Inst. Catalysis, Hokkaido Univ. 1, 8 (1948)) for the special case of the hydrogen electrode reaction but in fact (3. V. b) and (3. i. b) have been derived quite generally as stated in I) without any restriction to the electrode reaction.

It will be shown in §3 with special reference to the paper of BP, how the correct equation (3. i. b) has been arrived at by them starting from an incorrect rate expression.

\(^***\) Eq. (1. i) is further a particular form of (1. V).
which is proportional to $\Delta F$ or $\eta$, when the latter is sufficiently near to zero; it is now an elementary principle of the differential calculus that slope $\delta$ or $i$ of the secant through the origin and a point on the curve at $\gamma$ tends to the slope $\delta_0$ or $i_0$ of the tangent at the origin as $\gamma$ approaches zero.

§ 2. $\nu(r)$-Evaluation of Horiuti et al.

Horiuti and Ikusima observed $i$ of a platinum hydrogen electrode by means of deuterium and simultaneously $i_\circ$ and $\eta$ as usual; from the latter two observations they have constructed $i$, $i_\circ$-curves according to (1.1) for $\nu(r)=1$ or 2 respectively and shown that the isotopically observed points of $i$ have fallen distinctly on the curve for $\nu(r)=1$ preferentially to the other for $\nu(r)=2^*$. It is important to note that the intercept of each $i$, $i_\circ$-curve at $i_\circ=0$ has been necessarily determined by (3.1.b) from the observed $\left(\frac{\partial i_c}{\partial \eta}\right)_{\eta=0}$ and that an independent proof for $\nu(r)=1$ is provided by the isotopically observed $i_0$ falling on the latter intercept for $\nu(r)=1$ as seen from Fig. 1 of their paper, as well as individually by each isotopic $i$ at different $\gamma\approx 0$ falling within experimental errors preferentially on the curve for $\nu(r)=1$. Horiuti and Ikusima preferred, in their first attempt of $\nu(r)$-determination, this careful procedure of providing a number of unanimous proofs at different values of $\gamma$ to the single determination at $\gamma=0$.

They have derived the isotopic $i$ by multiplying the current $i'$ associated with the directly observed rate of electrolytic evolution of deuterium by a constant factor $\kappa = S \frac{H}{D} + 1$, as $i = \kappa i'$, $\kappa$ being determined as the ratio of $i_\circ$ over $i'$ simultaneously observed at sufficiently large $-\eta$, where $i_\circ$ practically equals $i$; $S$ is the separation factor i.e. the ratio of the specific rate of evolution of protium to that of deuterium and $H$ or $D$ the amount of protium or deuterium contained in the solution which is kept practically constant at their experimental condition. Although it is not a priori assured, strictly speaking, that $S$ as well as $\nu(r)$ itself would not change along with the variation of $\gamma$, their individual constancy and hence the reliability of the conclusion is amply verified by the detailed coincidence of isotopic $i$ with that derived


*) The $n$ in the original paper equals $2/\nu(r)$ here.
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from i.e., γ-observation at every γ, provided that the effect of S-change, if any, on the former did not happen to be quantitatively identical with that of ν(τ)-change on the latter in every detail throughout the range of γ-variation.

The ν(τ) of the hydrogen electrode reaction on nickel was later evaluated at 11Hν from experimental data 2) at γ = 0 alone i.e. from those of \( \frac{\partial \mu}{\partial \gamma} \) and \( \gamma \) observed by means of deuterium according to (3.i.b), no data at γ ≠ 0 being available. The ν(τ) was similarly determined according to (3.V.b) corresponding to (3.i.b) 3) for the catalysed ammonia synthesis reaction in the presence of commercial ammonia synthesis catalyst using N\(^{15}\) shifted ammonia, where the isotopic difference in rates is hardly expected.

Throughout these ν(τ)-determination of Horiiuti et al., (3.V.b) or (3.i.b) plays an important part as the differential form or the corollary of (1) as necessarily it should.

§ 3. “BP’s Eq. (2)”

What is called by the referee “BP’s Eq. (2)” i.e.

\[
ν(τ) = -\frac{F\gamma_0}{RT} \left( \frac{∂\gamma}{∂\mu} \right)_{γ=0}
\]

is that obtained by a simple mathematical operation of inverting \( \left( \frac{∂\mu}{∂\gamma} \right)_{γ=0} \) into \( \left( \frac{∂\gamma}{∂\mu} \right)_{γ=0} \) and rearranging factors of (3.i.b) or Eq. (27.5) of Horiiuti 4), which is referred to by BP themselves. The attitude of the Board of Editors of the “Journal of Chemical Physics” represented by the anonymous referee would be to call as justified the original equation after the name of the “mathematical operator”.

BP expresses the forward and backward rates \( ν_1 \) and \( ν_2 \) of the hydrogen electrode reaction, in the course of their rediscovery or “derivation” of (3.i.b), as

\[
ν_i = k a_i (kT/h) \exp \left[ -\frac{\Delta G_i - \beta(\Delta \phi - \zeta)2Fv(τ)}{RT} \right]
\]


* The \( n \) in the paper equals 2ν(τ) as in the case of Horiiuti and Ikusima (vide supra).
and

\[ v_2 = \kappa a_2 (kT/h) \exp \left[ \frac{-\Delta G^* + (1-\beta)(\Delta \phi_e - \zeta)2F/\nu(r)}{RT} \right] \]  

(5. b)

where, as stated by BP, \( \kappa \) is the transmission coefficient, \( a_1 \) or \( a_2 \) the product of activities of the initial or final complex\(^*\) of the rate-determining step, \( \Delta G^* \) or \( \Delta G_c^* \) the standard free energy of activation for the forward or the backward step, \( \Delta \phi_e \) the inner potential of the electrode minus the inner potential of the solution, \( \zeta \) that part of \( \Delta \phi_e \) in the diffuse double layer and \( \beta \) a fraction \(<1\) of \( \Delta \phi_e - \zeta \) operating to facilitate the forward direction of the rate-determining step\(^**\).

These equations are, besides erroneous as stated in HSII, A., because of the negligence of \( f^* \), associated with ambiguities of including terms \( \beta(\Delta \phi_e - \zeta)2F/\nu(r) \) or \( (1-\beta)(\Delta \phi_e - \zeta)2F/\nu(r) \) in the exponential factor without any comment whatever; what is clear is that they are essential for arriving at the target (3.i. b) of the rediscovery as shown below.

If \( \beta \) has been introduced after the manner of EYRING, GLASSTONE and LAIDLER\(^1\), the coefficient \( 2F/\nu(r) \) of \( \beta(\Delta \phi_e - \zeta) \) or of \( (1-\beta)(\Delta \phi_e - \zeta) \) must be the charge of the initial complex\(^*\) of the rate-determining step, whose value \( 2F \) at \( \nu(r) = 1 \) conflicts with both the catalytic and the electrochemical mechanism, the charge\(***\) of the initial complex of the appropriate rate-determining step being 0 or \( F \) respectively; the possibility of the experimental determination of \( \nu(r) \) would be moreover a priori excluded for the catalytic mechanism, which secures no term including \( \nu(r) \) in (5). Only for the slow discharge followed by the rapid recombination of evolved hydrogen atoms, for which \( \nu(r) = 2 \), the appropriate value \( F \) accords with the mechanism.

TAFEL's constant \( 2\beta/\nu(r) \)\(****\) is given in agreement with exper-

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\*\) Original words "the reactant and product" of BP have been replaced as in the text because of the reason stated in footnote \* on p. 6.

\**) Plus sign of \( \beta \) in (5. a) in the original paper of BP is changed here, since Eq. (9) of BP and what follows it are not derived otherwise.

\***\) It is meant the charge of the initial complex apart from metal electron, if any.

\****\) It follows from (5. a) that TAFEL's constant \( -RT \frac{\partial \log \nu}{\partial F} \frac{\beta}{\nu(r)} \) is 2\(\beta/\nu(r) \) in accordance with the relation, \( \phi_e = \phi_r + \eta \), where \( \phi_r \) is the constant value of \( \phi_e \) of a reversible hydrogen electrode, provided that \( \zeta \) is constant as tacitly assumed by BP; 2\(\beta/\nu(r) \) is a proper fraction, according to BP's assumption, \( \beta < 1 \), necessarily when \( \nu(r) = 2 \), but not when \( \nu(r) = 1 \).
ments also in the last case only, but not in the former two cases, its value being 0 or 2β respectively. The "derivation" is hence only consistent for itself when it is prearranged specially for the slow discharge mechanism as actually concluded by BP, but after all inconsistent with BP's proclaimed attitude of applying the target (3.1.b) or (4) of rediscovery for diagnosing an unknown mechanism.

BP has thus managed to make $v_2/v_1$ proportional to the Boltzmann factor of $(\Delta \phi - \zeta) 2F/\nu(r)$ and further equal to $\exp \left( \frac{2F\gamma}{\nu(r)RT} \right)$, expressing $\Delta \phi$ as the sum of its constant value $\Delta \phi_r$ at equilibrium and $\gamma$, tacitly assuming $\zeta$ constant, and resorting to the thermodynamical condition, II), §1, that $\dot{i}_c = 0$ i.e. $v_1 = v_2$ at $\gamma = 0$. The latter relation,

$$v_2/v_1 = \exp \left( \frac{2F\gamma}{\nu(r)RT} \right)$$

incorporated with the other, $\dot{i}_c \propto v_1 - v_2$ is just the content of the theorem (1), from which their target (3.1.b) or (4) follows as shown in §2, irrespective of the function $v_1$ or $i$; this explains how they arrived at the target correctly starting from the incorrect rate expression (5), in which $1/\nu$ is ignored and ungrounded linear law included, the latter defects affecting the function $v_1$ and $v_2$ individually, but not their ratio $v_1/v_2$.

§ 4. Effect of "bias"

We study now the referee's elaborate work on the effect of "bias" or "constant error" in overpotential on the determination of $\nu(r)$. It might be noted at the outset, although very plain, that (i) the result of the observation of $\dot{i}_c$ as a function of $\gamma$, "biased" or not, must be unique, but not change its character according as $(\frac{\partial \gamma}{\partial \psi})_{\psi=0}$ be determined or $i$ evaluated according to (1. $\dot{i}$) from it and that (ii) the result of such unique character must be compatible, at least within experimental errors, with the condition II), §1 underlying (1. $\dot{i}$) and hence its corollary (3.1.b), that $\dot{i}_c$ vanishes at $\gamma = 0$.

Now according to (3.1.a), $\dot{i}_0$ is the limiting value of the slope $i$ of the secant through the origin to the curve of $\dot{i}_c$ plotted against $1 - \exp \left( \frac{2F\gamma}{\nu(r)RT} \right)$ i.e. the slope of the tangent to the curve at $\gamma = 0$. If $i$ tends to infinity as $\gamma$ approaches zero owing to the "bias", as drawn
in Fig. 2 of RII, so must $i_0$ as well as $\left(\frac{\partial i_c}{\partial \eta}\right)_{\eta=0}$ be necessarily infinity according to (3.1). It is hence quite absurd to state that $\left(\frac{\partial i_c}{\partial \eta}\right)_{\eta=0}$ be unaffected by the “bias” i.e. remains the same as in the “unbiased” case as read in RII “but note that $\left(\frac{\partial \eta}{\partial i_c}\right)_{\eta=0}$ remains unchanged” (p. 34, 5th line in parentheses) and “whereas in this BP’s Eq. (2) the value of $\nu(r)$ depends on the slope $\left(\frac{\partial \eta}{\partial i_c}\right)_{\eta=0}$ (which is not effected by constant errors) and the value of log $i_0$, which is effected to a negligible extent as numerically illustrated above” (last 4 lines of RII on p. 35).

Below will be illustrated how the above absurdities could come about. Let $OX$ in Fig. 1 be the plot of $i_c$ against the “unbiased” $-\eta$, which passes through the origin $O$ as in the upper figure of Fig. 1 of RII. The referee “biases” $\eta$ positively by shifting its origin toward its negative side. Let $R_1$ be the new origin, $R_2$ the intersection of the vertical through $R_1$ with $OX$, and $x$ a point on $R_2X$, whose coordinates referred to the new origin be $i_c$ and $\eta$. The $i$ appropriate to $x$ is related with the slope $i_c/\eta_1$ of the secant to the broken line $R_1R_2X$ through origin $R_1$ and $x$, in general, according to (1.1), as

![Diagram](image-url)
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\[ i = - \frac{\nu(r) RT}{2F \Sigma} \cdot \frac{i_c}{\gamma} \quad (6. \ i) \]

where

\[ \Sigma = \frac{1 - \exp\left(-\frac{2F\gamma}{\nu(r) RT}\right)}{2F\gamma/\nu(r) RT} = \frac{1}{1} + \frac{1}{2!} \left(\frac{2F\gamma}{\nu(r) RT}\right) + \frac{1}{n!} \left(\frac{2F\gamma}{\nu(r) RT}\right)^{n-1} \quad (n = 3, 4, \ldots, \infty) \quad (6. \ \Sigma) \]

approaches 1 as \( \gamma \) tends to zero, so that (6.\i) reduces to (3.\i.\b) at the extremity. As \( x \) nears \( R_i \), the slope \( -i_c/\gamma \), and hence \( i \) tends to infinity as drawn in Fig. 2 of RII; the limiting value, \(-\left(\frac{\partial i_c}{\partial \gamma}\right)_{\gamma=0}\) of \(-i_c/\gamma\), or the slope of \( R_iR_\gamma \) is necessarily infinity. That \( \left(\frac{\partial i_c}{\partial \gamma}\right)_{\gamma=0} \) is the limiting value of \( i_c/\gamma \) i.e. the differential coefficient at the origin in general, is implied even in the “derivation” of BP \(^*\), where \( \left(\frac{\partial \gamma}{\partial i_c}\right)_{i_c=0} \) is invariably defined as the limiting value of \( \frac{\gamma}{i_c} \) at \( \gamma = 0 \).

One would conclude \( \left(\frac{\partial i_c}{\partial \gamma}\right)_{\gamma=0} \) not affected by “bias” as the referee does, only when his perception of the experimental result is disrupted in contradiction to (i) in the manner that his origin jumps back, particularly in the case of \( \left(\frac{\partial i_c}{\partial \gamma}\right)_{\gamma=0} \)-determination, to the origin \( O \) of the “unbiased” state in Fig. 1, which should be hidden, even to the referee, behind the “biased” observation, or even jump up to \( R_i \), so that a finite value \( R_iR_\gamma \) of \( i_c \) suddenly vanishes at the moment of disruption. In other words the referee perceives the experimental result as given by \( OX \) with origin at \( O \) or by \( R_iR_\gamma X \) with origin at \( R_i \) according as he deals with \( \left(\frac{\partial i_c}{\partial \gamma}\right)_{i_c=0} \) or \( i_c/\gamma \).

We will now set aside the absurdity of the referee that the slope of the secant through the origin suffer from the “bias”, whilst that of its limiting value i.e. that of the tangent there remain proof against it, and proceed in the next section to the confirmation of the point raised in HST that the conclusion, \( \nu(r)=2 \) of BP and their procedure of the linear extrapolation contracticit each other, with a firm perception of the

\[^*\) Cf. Eq. (12) of BP.\]
§ 5. $\nu(r) = 2$ and the Linear Extrapolation

Let a sequence of $i_c, \gamma$-points be the result of observation with homogeneous uncertainties $\Delta i_c$ and $\Delta \gamma$. The $i_c/\gamma$ of any observed point gives approximately the slope of a secant through the origin and through a point $P$ representing virtual values of $i_c$ and $\gamma$, but less accurately as $P$ nears the origin. To the secant corresponds now $i$ according to (6. i) or (1. i), whereas to its limiting case i.e. the tangent at the origin does $i_c$ as shown in §4. The $i$ is now less and less accurate as $P$ nears the origin, since the same is the case with $i_c/\gamma$ and $\Sigma$ in (6. i) **). The most inaccurate in consequence is $i_c$ corresponding to the limiting value $(\frac{\partial i_c}{\partial \gamma})_{\gamma\rightarrow 0}$ of $i_c/\gamma$ i.e. the slope of the tangent at the origin, on the contrary to the conclusion from the disrupted perception detailed in the foregoing section.

As a matter of fact, however, one could not draw a tangent at the origin "mathematically" through coincident two points there which are individually more or less scattered; the "tangent" is actually a secant over a finite range of $\gamma$, where the practical linearity of $i_c$ to $\gamma$ within experimental errors is assumed. BP have thus proceeded to draw a straight line through the sequence of points just in the "vital region very near to the reversible potential" (RII, p. 35, last par., 3rd sentence) as in upper figures in their Fig. 7 and taken its slope for the value of the tangent.

In consistence with the above assumption of practical linearity underlying this procedure and to ii), §4, the origin of $\gamma$ ought to be taken at the point on the straight line, where $i_c$ vanishes; if $i_c$ were sufficiently accurate in accordance with the last proclamation of the referee***) that "The inaccuracies in measurement at very low c.d.'s are in the overpotential rather than the c.d." (RII, p. 32, par. 3, sentence 1) on the contrary to the first one (RI, p. 30, par. 5, sentence 1), the constant error in $\gamma$ or the "bias", if any, should thus be eliminated so much accurately as $i_c$ is***) or the true origin of $\gamma$ is determined on

***) The error of $\Sigma$ caused by a given amount of $\Delta \gamma$ increases steadily, although very slightly, as $-\gamma$ decreases, as shown by an actual calculation.

****) It is immaterial as regards the accuracy of $(\frac{\partial i_c}{\partial \gamma})_{\gamma\rightarrow 0}$ or of $i_c/\gamma$ as shown in a), §6, which of $i_c$ and $\gamma$ is less inaccurate. On this ground the referee's latest proclamation is literally admitted for the sake of a concrete presentation.
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the ground of the basic thermodynamical condition, ii), §4. With regard to Fig.1 the true origin should be located at O on the elongation of RX, if the latter is sure to give invariably the slope \( \left( \frac{\partial i_c}{\partial \eta} \right) \) of the tangent at the origin according to the above; the slope \( \frac{i_o}{\eta} \) of the secant and hence \( i \) is determined as referred to O even more accurately than \( \left( \frac{\partial i_c}{\partial \eta} \right) \) or \( i_o \) is.

This is the logical consequence of the referee's latest proclamation on the precision and of the principles underlying the BP's procedure of \( \left( \frac{\partial i_c}{\partial \eta} \right) \) -determination which is fully supported by him and hence must be admitted by him.

It is now the coordinate of the points thus determined from the upper figures of Fig. 7 of BP, from which \( i \) of crowded points at \( \gamma \) smaller than 0.015 Volt in Fig. 1 and 2 of HST has been worked out by (1.1); less crowded points at greater \( \gamma \) have been determined from those in the lower figure of BP's Fig. 7. The crowded points in the vital region are not suffering from the "bias", if the "tangent" are not, as incorrectly sanctioned by the referee but ultimately assured by the above logical consequence. It is hence absurd to attribute the deviation of the crowded points in Figs. 1 and 2 of HST from the straight line of the extrapolation to the "bias" and even to estimate the amount of the "bias" responsible for it plausibly (RII, p. 35, par. 3, last sentence). The inconsistency between the conclusion, \( \nu(r)=2 \) and the postulated linearity of log \( i \) to \( \gamma \) is now established by the systematic deviation in Figs. 1 and 2 of HST of points of \( \nu(r)=2 \) from the straight line of the linear extrapolation, if the "tangent" through the origin is correctly determined in upper figures of BP's Fig. 7.

To demonstrate the inconsistency further, although not essential, the "tangent" of the upper figure of BP's Fig. 7 determined from points × (for 0.005 N NaOH at 3°C) to which Fig. 1 of HST is appropriate, is represented in Fig. 2, (a) by the plot of log \( i \) against \( \gamma \). The \( i \) of the "tangent" being \( \left( \frac{\partial i_c}{\partial \eta} \right) \), \( \eta \), we have according to (1.1)

\[
i = \left( \frac{\partial i_c}{\partial \eta} \right) \eta \left[ 1 - \exp \left( \frac{2F\gamma}{\nu(r)RT} \right) \right]
\]

Substituting for \( \left( \frac{\partial i_c}{\partial \eta} \right) \) the reciprocal of \( \left( \frac{\partial \gamma}{\partial i_c} \right) \) \( \nu=0 \) i.e. \(- 24.8 \times 10^4 \) ohm cm\(^{-2} \).
in 5th line on the right of BP's Table V, we have the representation, "\( \nu(r)=1 \)" or "\( \nu(r)=2 \)" according as \( \nu(r) \) is 1 or 2 respectively. The big black dot or circle on the ordinate shows \( \dot{i}_0 \) calculated from the above value of \( \left( \frac{\partial \dot{i}_c}{\partial \eta} \right)_{\eta=0} \) according to (3.i.b) for \( \nu(r)=1 \) or 2 respectively, which lies on the curves "\( \nu(r)=1 \)" or "\( \nu(r)=2 \)" respectively as it should. Fig. 2,(b) is the reproduction of the upper figure of BP's Fig. 7 for 0.005 N NaOH at 3°C with the ordinate and absissa inverted, whose "tangent" is represented in (a).

The corresponding points in (a) and (b), Fig.2 deviate from the representation and the "tangent" respectively in the same direction, as they should according to (1.i) and (7), the deviation in (a) being \( \log_{10} \left( \frac{\dot{i}_c}{\left( \frac{\partial \dot{i}_c}{\partial \eta} \right)_{\eta=0}} \right) \) or the common logarithm of the ratio of the ordinate of
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the point in (b) to the ordinate of the "tangent" at the same γ. If the "tangent" in (b) runs probably amidst the scatter of points, its representation in (a) must of course do similarly; it is true that deviation is represented magnified in size in (a) at γ near zero but systematic upward or downward deviation of the sort shown in Fig. 2, RII can not be the case, if the "tangent" be properly drawn without corresponding systematic deviations. The deviation of points in Figs. 1 and 2 of HST from the straight line of extrapolation is now represented by that of the representation "ν(r)=2" from the latter, closely illustrating the inconsistency between the conclusion, ν(r)=2 and the linear extrapolation as initially pointed out in HST.

Let us assume for the moment that the linear relation between log i and γ is essentially correct and the discrepancy between the representation and the straight line of extrapolation is due to the fortuitous error of drawing the latter, resulting in the "negative" deviation ca. -0.1 of log, io as seen from Fig. 2, which lies adequately within the 95% probability limits*) 0.3−0.5 of log, io-extrapolation reported by BP. With equal right would one maintain however, in favour of the conclusion ν(r)=1, that the straight line of extrapolation runs above the appropriate representation "ν(r)=1", with the "positive" deviation ca. 0.2 of log, io which lies amply within the probability limit too. The situation is quite similar with the other example reproduced in Fig. 2 of BP i.e. the conclusion ν(r)=2 is almost equally probable to that ν(r)=1 with due regards to the 95% probability limit given by BP. These two being all those given in detail by BP accessible to the present analysis, the conclusion ν(r)=2 is not at all conclusive even apart from the case of ν(r)=1.5 pointed out on p.21, which is most favoured by the extrapolated log, io.

The assumed essential correctness of the linearity is, however, although bitterly defended by the referee, betrayed even by works which he himself advances as support as shown in B, HSII, ii) (pp.27–30). The BP's procedure of ν(r)-determination and their conclusion is hence unreliable.

§ 6. Discussion of Points of RII

On the basis of the above developments, the individual points

*) HS understand what is termed the 95% probability limits by BP as well as by the referee those covering 95% of errors, being not informed of its exact definition.
raised in RII will be discussed below.

a) RII, p. 32, par. 3 (with heading 2).

The referee changes his point in RI (p. 30, par. 5) that “…because of the inaccuracies inherent in current (i.e. \( i_c \)) measurement in this range (\( 10^{-7} \text{ amp cm}^{-2} \)) and the well-known difficulties connected with competing reactions when the current density is so low” and states here without any comment that “the inaccuracies in measurements at very low c.d.’s are in overpotential rather than in c.d.” In general it is of less meaning to compare the accuracies of two observed quantities of different dimensions; we require to do this some prescribed conversion for comparison e.g. that their relative errors be compared as usually almost unconsciously presupposed. We are interested here in the functional relation between \( i_c \) and \( \gamma \), and the individual magnitude of the error of the respective quantities is of less importance, the error e.g. \( \Delta f \) of their function \( f = i_c/\gamma \) being caused by the error \( \Delta \gamma \) of \( \gamma \) equivalently as by the error \( \Delta i_c \) of \( i_c \) of the magnitude \( f \Delta \gamma \), as it follows from the elementary theory of errors. The referee would not have needed at all to change his point in RI even without any comment for justification, except for the introduction of his elaboration on the “bias”.

b) RII, p. 32, par. 3, line 7.

The referee’s question here next to the statement of a) above is quite trivial, inasmuch as the “BP’s Eq. (2)” is nothing but a simple “mathematical” transformation of the corollary (3.i.b) of (1.i) i.e. “HS’s Eq. (4)” as shown in §1 and §3, in so far as one’s perception of the experimental result is not disrupted as detailed in §4, as he deals with “BP’s Eq. (2)” or “HS’s Eq. (4)”.

c) RII, p.32, par. 4 to p.35, par. 3.

One could no more attribute the inconsistency between the conclusion, \( \nu(\gamma) = 2 \) and the procedure of the linear extrapolation of \( i_o \) to the “bias”; referee’s estimation of the effect of “bias” on \( \nu(\gamma) \) is simply upset by the fact that \( \left( \frac{\partial i_c}{\partial \gamma} \right)_{\gamma = 0} \) tends necessarily to infinity, if \( i \) should, according to him, with decreasing \( -\gamma \) as detailed in §4. It is quite absurd to attribute to the “bias” (RII, p.35, par.3, last 3 lines), the deviation of points in HS’s Figs.1 and 2, which is instead, as shown in §5, the definite indication of the discrepancy between BP’s conclusion \( \nu(\gamma) = 2 \), BP’s observed \( i_o, \gamma \)-relation of the “tangent” and the
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BP's extrapolated $i, \eta$-relation just in the "vital" region (p. 35, last par., line 7) of the referee.

d) Last par., RII.

The first sentence is not true; the "bias" effects, if at all, as developed in detail in §4 and 5, the $\nu(r)$ determined by "BP's Eq.(2)" so much as or even more than that by HS's Eq.(5). Referee's statement in the second and third sentence is the confession of his ignorance in HORIUTI and IKUSIMA's procedure detailed in §2; the $\nu(r)$-determination there at different $\eta$ is individually independent so much as that by the particular form (3.i.b) restated in "BP's Eq.(2)" is, and accurate even the more than the latter. The essential mental reason leading to the referee's "essential physical reason" in the last sentence has been elucidated in §4.

Conclusion:—It is the ignorance of the referee to the fundamental fact that the slope $i$ of the secant through the origin to $i, 1 - \exp\left(\frac{2F\eta}{\nu(r)RT}\right)$-curve is determined from a given sequence of observed $i, \eta$-points not less accurate than its limiting value at $\eta = 0$, i.e. the slope $i_0$ of the tangent to the curve at the origin is, which has led him to his fallacies that the $i$-evaluation gets more and more inaccurate as $\eta$ nears zero even infinitely but suddenly restores its accuracy as $\eta$ just vanishes and that the claimed inconsistency in BP's procedure of $\nu(r)$-determination be on this reason deflectable. BP's procedure of evaluating $\nu(r)$ is unreliable because of the implied inexact method of the $i, \eta$-extrapolation.